1998

Synthesis and Physical Characterization of Solid-State Materials.

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SYNTHESIS AND PHYSICAL CHARACTERIZATION
OF
SOLID STATE MATERIALS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Patrick Allen Kolniak
B. S. Louisiana State University at Shreveport, 1989, 1990
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ABSTRACT

Two quantitative X-ray powder diffraction methods were used to analyze phosphogypsum, a currently underutilized solid by-product of phosphoric acid production. Three kinds of synthetic mixtures were prepared to reflect the variable composition of phosphogypsum: AG (anhydrite and gypsum), QCD (quartz, calcite, and dolomite), and AGQCD.

Compositions derived from the Whole Pattern fitting method for the binary and ternary mixtures agreed reasonably well with known values, with residuals $<R^2> = 0.10$ for eleven AG samples, and $<R^2> = 0.018$ for thirteen QCD samples. However, in the five-component mixtures, overlap of anhydrite, dolomite and gypsum peaks prevented quantitation.

Compositions derived from the Matrix Flushing method were generally superior, with $<R^2> = 0.009$ for eleven AG mixtures, $<R^2> = 0.0004$ for thirteen QCD mixtures, and $<R^2> = 0.0197$ for nine AGQCD mixtures. The most notable exception is the determination of AG mixtures with 0-10% gypsum. The measured compositions were distorted in favor of gypsum, apparently due to the affinity of gypsum for water.

Two single crystal structures, one organometallic and the other inorganic, were determined. $(\text{phen})_2\text{Cu}^+\text{(hfacac)}^-$ crystallizes in triclinic space group P 1 with: $a = 10.284(0)$ Å, $b = 11.685(0)$ Å, $c = 12.519(0)$ Å and $\alpha = 114.97(0)$°, $\beta = 90.77(0)$°, $\gamma = 105.78(0)$°. $\text{Ba}_4\text{K}_9\text{BiO}_3$, $x = 0.419(0)$, a superconductor with $T_c = 29.5$°K. It crystallizes in cubic space group with $Pm\bar{3}m$ symmetry and a cell constant of $a = 4.2948(0)$Å.
The diffraction-quality crystal of $\text{Ba}_{1.4}\text{K}_{0.6}\text{BiO}_3$ was synthesized by electrosynthesis in a molten KOH flux at 225°C. The synthesis required ultra-pure KOH (99.99%). $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ (99.8%), $\text{Bi}_2\text{O}_3$ (99.9998%), and a cover gas of water-saturated ultra-pure Ar. The melt composition was based on weight ratios $\text{K}/\text{Ba} = 17.2$ and $\text{K}/\text{Bi}=12.5$. The electrode deposition potential was 0.677 volts, starting current $I \equiv 20\, \mu\text{A}$. Every attempt was made to maintain a current density of less than $0.5\, \text{mA/cm}^2$, to ensure slow crystal growth.
CHAPTER 1
INTRODUCTION

1.1 Introduction

This dissertation and thesis consists of three research phases. The first part involved the application of Whole Pattern Fitting and Matrix Flushing techniques for quantitative analysis of X-ray powder diffraction patterns. The goal was to evaluate which method could best determine the components of cement mixtures, and its incorporation to determine the effects of phosphogypsum in cement mixtures. The second part involved determining the structure of a single crystal of Bis-1.10 phenanthroline copper(I) hexafluoroacetylacetone by single crystal X-ray diffraction. The third part consisted of the electrocrystallization of a single phase of $\text{Ba}_{1.5} \text{K}_x \text{BiO}_3$ in molten KOH, and an single crystal X-ray analysis of a superconducting phase $\text{Ba}_{0.58} \text{K}_{0.41} \text{BiO}_3$ with a transition temperature of 29.5°K.

1.2 Historical

In 1895 Wilhelm Conrad Röntgen assembled equipment\(^1\), such as a large induction coil and a suitable discharge tube, for taking up work on the subject of Cathode rays. It was known previously from Lenard’s work, a student of Hertz, that these rays are absorbed by air, gases, and thin metal foils, and this absorption increases proportionally to the thickness of material and decreases if a higher voltage is used. Röntgen was interested in an additional discovery by Lenard, and that was the intensity of the fluorescence excited in different crystals varies with the voltage used. When Röntgen began his experiments he noticed a barium platino cyanide screen lying on a
table at a considerable distance from the tube showed a flash of fluorescence every time a
discharge of the induction coil went through the tube. This flash could not be due to
cathode rays because these would have been fully absorbed by the glass wall of the tube,
the thin aluminum foil or 'window' in front of the tube, and the air. He concluded that
the fluorescence was caused by something unknown, the unknown X, that traveled in a
straight path from the spot where the cathode ray in the tube hit the glass wall; that the
unknown agent was absorbed by metals and that these cast a shadow in the fluorescent
area of the screen. He therefore spoke of X-rays: he showed that these rays were
exponentially absorbed in matter with an exponent roughly proportional to the mass
traversed. He made use of the photographic action of X-rays and took the first photo of
the bones in a living hand. Although Röntgen did not understand how these X-rays are
produced, he developed the first technical X-ray tube by letting the cathode rays impinge
on a heavy metal anode, instead of the glass wall, to increase the output of X-rays. To
generate X-rays, electrons are accelerated by an electric field and directed against a
metal target, these rapidly moving electrons are very quickly decelerated, converting
their energy of motion into a quantum of radiation. Röntgen's discovery of X-rays gave
the world a new method of observation beyond the visual; that is, to observe and
interpret an inner universe that was previously hidden from view. From the structure of
the bones in a living hand to the complex superlattice of the highest temperature
superconductor, X-rays have proven to be an invaluable tool to the entire scientific
community.

The discovery of X-rays affected all areas of science, but none more than
crystallography. In 1912, von Laue, Friedrich, and Knipping used X-rays to prove the
internal periodicity of atoms existed inside a crystal of copper sulfate. A photographic plate was placed behind the crystal. When the X-rays emitted by the Röntgen tube struck crystal, the photographic plate revealed the diffracted X-rays in the form of fuzzy spots. This discovery by von Laue proved that X-rays behaved like waves as it propagated through structured solid matter, rather than particles. He showed that the phenomenon could be described in terms of diffraction by a three dimensional grating.

Based on van Laue's work, W.L. Bragg noted the similarity of diffraction to ordinary reflection and deduced a simple equation treating diffraction as "reflection" from planes in a lattice. This equation became known as Bragg's Law.

\[ 2d \sin \theta = n \lambda. \]

The process of reflection is described by the above equation in terms of incident and reflected rays making an angle, \( \theta \), with a fixed crystal plane and interplanar spacing, \( d \), for an integral number of wavelengths, \( n \lambda \). In 1913, W.L. Bragg published the first crystal structures based on Laue diagrams of diffraction patterns from various minerals and crystalline compounds.

With the foundation in place, crystallography began to develop rapidly, but early research required single or one phased crystals to observe well ordered diffraction patterns. This was necessary to further the development of X-ray crystallography analysis. Other scientist's investigations required the use X-ray crystallography to understand the structure and composition of our own planet and the geologic process it entails. The problem that most geologic materials are not found as single crystals was an obstacle. In 1921, Hadding made the first attempt to systematically study the effect of absorption on the lattice constants as computed from powder photographs. To analyze a
sample of mixed composition, by X-ray powder diffraction, required the development of methods to minimize errors in determining lattice constants of each component. These errors are a result of the sample mixture containing randomly oriented lattice planes. Improvements in sample preparation, X-ray camera design, and the procedure of performing powder diffraction analysis, have been successful. The application of Quantitative X-ray Diffraction (QXRD), by powder methods, has proven to be an invaluable analytical tool in the area of geology and other areas of science.

The growing knowledge of the internal structure of materials furthered a fundamental question about the relationship between composition and structure, and the chemical and physical property's exhibited. The question about the effect the internal lattice would have on the motion of electrons, as exhibited in insulators, semiconductors, conductive metals, and superconductors, would take a giant step forward with the development of Bloch's function (1928). A solid may be idealized into a completely regular arrangement of atoms, and the motions of electrons in such a system may be investigated ab initio. In this method, an electron belongs not to one atom, but to the whole crystal. This approach is named after Felix Bloch, and the band theory of solids is its important outcome. Bloch proved, by an elegant application of group theory, that the motion of the electrons are contained in the solutions of the form

\[ \psi = u(x) e^{i k \cdot r} \]

which are called Bloch functions. \( u(x) \) is a function of \( x \) which has the same periodicity of the lattice, i.e.

\[ u(x + R) = u(x) \].
In general, there will be a different \( u_e(r) \) for each \( E \). \( \psi_e \) may be referred to as a wave propagated in the direction of \( \mathbf{k} \), the wave vector, having an amplitude that is modulated by the periodicity of the lattice. It is interesting to note that X-rays and Bloch waves are both subject to the Bragg reflection condition and this emphasizes the idea that it is the crystal lattice of a solid that determines its Brillouin zone shape. Each zone corresponding to an allowed energy band.

Presently, much is understood about the electronic, magnetic, and optical properties of materials. Methods of analysis and synthesis have advanced considerably over the past century, and predictability in the synthesis of such materials and the properties they will exhibit have become more reliable. There is one exception, superconductivity. The mechanism of this type of conductivity has generated a great deal of theoretical work that is plausible but uncertain, and the predictability of the synthesis of a new superconductor seems like random chance. Superconductivity was discovered in 1911 by Heike Kamerlingh Onnes, when studying mercury metal that had been cooled to 4K by liquid helium. Until 1986, the highest \( T_c \) remained at only 23K for Nb₃Ge, discovered by researchers at Westinghouse in 1973. A breakthrough was made in 1986 by K. A. Mueller and G. Bednorz. They reported an onset of superconductivity near 30K for a mixed metal oxide. The composition of this ceramic superconductor was determined to be \( \text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4 \) by Shoji Tanaka and his co-workers. The superconductivity of this compound contained a copper atom with an average oxidation state greater than 2. The presence of an unstable copper(III) seemed significant. In an attempt to maintain this copper(II):copper(III) ratio, without disrupting the crystal structure, site substitutions were made. First, substitution was made with group II-A, the
alkaline earth elements, strontium for barium. Superconductivity increased from 30K to 40K$^8$. In 1987 the next step, a III-B substitution, yttrium for lanthanum, dramatically raised the transition temperature from 40K to 93K$^9$. Scientists were now able to research and demonstrate superconductivity using liquid nitrogen cooling. The question as to why the substitution of these particular elements caused such a dramatic change in the transition temperature still remains unanswered. The presence of mixed valence and an central atom with an unstable high oxidation state, for example the copper(III) atom, seemed central to the escalation of the transition temperature beyond 23K. When a plausible theory to explain superconductivity in one compound is submitted and certain concepts excepted, an exception is found in the synthesis of a new type of superconductor. In 1988, superconductivity was discovered in transition metal free compound that exceeded 23K. This compound, Ba$_{1-x}$K$_x$BiO$_3$, had a transition temperature of 30K$^{10}$. The discovery of a new bismuth based superconducting compound has provided an interesting contrast to the copper oxide system. The Ba$_{1-x}$K$_x$BiO$_3$ compound is believed to have a structure related to the perovskite, ABO$_3$, with octahedral coordination around the A and B sites. The copper oxide system is based on a superlattice, where coordination around the Cu ions are linear or square planar. In contrast to the copper oxide system, the mixed valence is achieved by a doping of the A site with barium and potassium, where superconductivity occurs over a narrow range of x. Copper oxide superconductors do not contain any group I-A elements. The two superconducting oxide system share the concept of mixed valence. The bismuth ion has an average oxidation state greater than 4 and the copper ion has an average oxidation state greater than 2. Although the Bi(V) species is a more stable ion than Cu(III), higher
oxygen coordination around an central atom with an unstable higher oxidation state is interesting. In the copper oxide system, superconductivity disappears when the average oxidation state of the copper ion is less than or equal to 2.

Successful synthesis of superconductive materials in the copper oxide system is achieved primarily by the ceramic method\textsuperscript{11}, where all constituent reagents are stable at extreme temperatures and pressures. The Ba\textsubscript{1-x}K\textsubscript{x}BiO\textsubscript{3} compounds have been synthesized primarily by electrosynthesis in a molten potassium hydroxide flux. The lack of stability of the potassium component, at the extreme temperatures used in the ceramic method, limits its usefulness in that method of synthesis. The electrosynthesis method has gained much attention with the synthesis of the bismuth based superconductor and has provided an effective alternative to more widely accepted techniques.

The search for new high T\textsubscript{c} superconductors has focused on families of metals, classes of compounds and has helped to extend or extrapolate our understanding of various structure-property relationships. This fallout has not only generated materials with varying electronic, magnetic, and optical properties, but has helped enhance our knowledge and understanding of methods of synthesis, analysis, and application.

Technological advances have enabled research scientists to utilize a variety of strategies to refine older and more widely used methods used to develop newer materials and to grow crystals. In many cases, it is the synthesis of a novel compound that has triggered a new line of research. The goal is to produce single phases of known superconducting compounds or to create new compounds.
CHAPTER 2

QUANTITATIVE X-RAY POWDER DIFFRACTION ANALYSIS
OF PORTLAND CEMENT RELATED MIXTURES

2.1 Literature Review

2.1.1 Production and Disposal of Phosphogypsum

Phosphogypsum (PG) is a solid by-product of phosphoric acid ($\text{P}_2\text{O}_5$) production from phosphate rock. Phosphoric acid ($\text{P}_2\text{O}_5$) is a major constituent of many agricultural fertilizers. The "wet process" is most frequently used\textsuperscript{12} for phosphoric acid production. In the United States, the wet process is the primary choice due to its cost efficiency and flexibility in processing varying grades of phosphate containing rock. However, the greatest disadvantage is the high production rate of the by-product phosphogypsum.

Phosphate rock and sulfuric acid ($\text{H}_2\text{SO}_4$) are the primary raw materials needed for the phosphoric acid production by the wet process. Simplified chemical equations of the overall reaction can be given as:

\[
\text{Phosphate rock} + \text{Sulfuric acid} \rightarrow \text{Phosphoric acid} + \text{Phosphogypsum}
\]

\[
\text{Ca}_{10}\text{F}_2\text{(PO}_4\text{)}_6 + 10\text{H}_2\text{SO}_4 + 20\text{H}_2\text{O} \rightarrow 10\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 6\text{H}_3\text{PO}_4 + \text{HF}
\]

The resulting filter cake containing calcium sulfate($\text{CaSO}_4$) is called Phosphogypsum. The filter cake and wash solution are piped into large stock piles and allowed to settle. In phosphogypsum, calcium sulfate exists in at least three forms: anhydrate ($\text{CaSO}_4$), hemihydrate ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), and di-hydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), also called gypsum.

Percentages of each crystal type in a given sample influence, both directly and indirectly, the properties of phosphogypsum.
As a general rule, 4.5 to 5.5 tons of phosphogypsum are produced for every ton of phosphoric acid produced\textsuperscript{13}, resulting in 150 to 200 million metric tons of annual phosphogypsum production worldwide. The phosphogypsum generation rate for the United States is estimated to be 40 million metric tons per year. According to Chang and Mantell\textsuperscript{14}, the annual worldwide production of phosphogypsum is managed as depicted in Figure 2-1. The demand for phosphoric acid further magnifies the problem of efficiently and economically dealing with the growing phosphogypsum supplies. Phosphogypsum must compete with natural gypsum in the production of building products and cements. In the U.S., it is more economical to use natural gypsum rather than phosphogypsum\textsuperscript{15}, because phosphogypsum is viewed as a waste product with varying degrees of purity and not as a quality by-product. In the United States, more restrictive regulations were applied to the management of phosphogypsum. As a result, the percentage of phosphogypsum that is stockpiled annually is higher in the United States than in other countries. As of 1989, there were over 95 million tons of

Figure 2-1 Annual worldwide management of phosphogypsum.
phosphogypsum disposed of in the state of Louisiana. It is estimated that about 650 million tons of phosphogypsum are stockpiled in the state of Florida.

2.1.2 Chemical and Mineralogical Properties of Phosphogypsum

As previously mentioned, phosphogypsum consists of various forms of crystalline sulfate (CaSO₄ · xH₂O, where x = 0, \( \frac{1}{2} \), 2). In phosphate production, sulfuric acid (H₂SO₄) reacts with phosphate rock. This "phosphate rock" is not a pure crystalline mineral. Calcium fluorapatite (Ca₅₀F₂(PO₄)₆) is the primary reactant in the phosphate rock. It is quarried from large phosphate deposits, derived primarily from fossilized bones and shells.

![Content by Weight (%)](image)

Figure 2-2 Results of bulk chemical analysis of phosphogypsum. * not measured as a percent.

It occurs as an accessory mineral in igneous, metamorphic and sedimentary rocks. Therefore, the composition of the phosphate rock varies with the geology of the quarry site. This leads to a diversity in the composition of phosphogypsum stockpiled around
the world. Bulk chemical compositions of phosphogypsum produced in states of Texas, Florida, and Louisiana\textsuperscript{16} are shown in Figure 2-2.

2.1.3 Toxicity and Radiological Aspects of Phosphogypsum

Concentrations of various trace elements found in phosphogypsum produced in Louisiana and Florida\textsuperscript{17} are presented in Figure 2-3. These elements include: selenium, arsenic, barium, lead, and mercury. The presence of these elements in large stockpiles of phosphogypsum have a potential for leaching into the groundwater. Possible ground and surface water contamination is a primary environmental concern. Additionally, phosphogypsum may also contain a number of radionuclides such as radium-226, thorium-228 and 230, lead-210, uranium-234 and 238, and polonium-210. Researchers have investigated the typical radiological content of phosphogypsum produced in

![Trace Elements Concentration (mg/kg)](image-url)

Figure 2-3 Trace element concentrations in phosphogypsum.
Florida, Table 2-1. Therefore, an extensive effort must be given to the toxic and radiological characterization of phosphogypsum to assess its environmental impact at various storage facilities, and its use as a recyclable material.

Table 2-1 Radioactivity found in Phosphogypsum produced in Florida.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Concentration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium-238 and 234</td>
<td>4–6 pCi/g</td>
<td>18, 19</td>
</tr>
<tr>
<td>Radium-226</td>
<td>8–38 pCi/g</td>
<td>18, 19, 20</td>
</tr>
<tr>
<td>Lead-210</td>
<td>low but increases with decay of Radium-226</td>
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</tr>
<tr>
<td>Thorium-228</td>
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<td>Thorium-230</td>
<td>&lt;13 pCi/g</td>
<td></td>
</tr>
<tr>
<td>Polonium-210</td>
<td>40 pCi/g</td>
<td>21</td>
</tr>
</tbody>
</table>

2.1.4 Utilization of Phosphogypsum in low grade construction materials

It is generally believed\cite{22} that the tri-calcium aluminate \((\text{CaO})_3\text{Al}_2\text{O}_3\) phase of portland cement is the source of aluminate ions, which can react with sulfate ions by the dissolution of gypsum to form tri-calcium aluminate tri-sulfate hydrate

\[
(\text{CaO})_3\text{Al}_2\text{O}_3^{(aq)} + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}^{(aq)} \rightarrow (\text{CaO})_3\text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}
\]

commonly called ettringite. It is the formation of ettringite in hardened concrete over time that is generally believed to be the common cause to disruptive expansion. It has
been considered, whether the addition of certain amounts of phosphogypsum into the portland cement mixture, would help form a stable cement product for use in low grade construction and building materials.

2.2 Objective for using Quantitative X-ray Powder Diffraction (QXRD)

The goal of this project is to develop a quantitative and reliable X-ray powder diffraction method for the analysis for minerals in Phosphogypsum and some products of its reaction with portland cement. In X-ray powder diffraction, the basic assumption underlying all quantitative interpretations is that the intensity of a diffraction peak produced by a mineral is directly dependent on the weight fraction present. The standard approach to quantitative analysis has been to construct calibration curves based on the measurement of peak intensities from carefully prepared mixtures of minerals. These studies have also revealed a variety of matrix effects, which implies that the intensity is also dependent on the types and quantities of the minerals present in the mixture.

Matrix Flushing theory (Chung, 1974a;b) offers alternatives for the derivation of simple intensity-concentration equations free from matrix effects. The Matrix Flushing method establishes that the intensity-concentration relationship between each and every pair of components in a multi-component system is not perturbed by the presence or absence of other components explained below. The concept such as "matrix-flushing" established by (Chung, 1974a:b) utilize Reference Intensity Ratios (RIR) in the notation that has been developed in recent years (Hubbard and Synder, 1983, 1988).
2.3 Basics of Quantitative X-ray Powder Diffraction

In material science, it is important to know the mineralogical composition of solids in order to predict their chemical reactions with other substances, or their response to changing environmental conditions. The mineral content, in many cases, provides clues to the compressive strength, durability, and other physical properties of single phases and aggregates. Most investigations in this area of science and technology begin by determining the qualitative and quantitative mineralogical composition of the materials being studied. X-ray powder diffraction, (XRD), is one of the most common analytical tools used in the basic characterization of crystalline materials. In some cases, poorly ordered or amorphous substances may also be analyzed by XRD. The basic utility of this method is derived from the dependence of diffraction phenomena on the varieties of atoms present and the orderliness of their spatial distribution. The basic aspects of these substances are unique for each mineral. XRD methods can reveal which minerals are present and estimate their chemical composition and weight percent abundance from the locations and intensities of peaks in the XRD pattern. In recent years, advances in our basic understanding of diffraction phenomena have enabled materials scientists to decode the information contained in the XRD pattern and to develop better methods for their quantitative interpretation. X-ray diffraction analysts have been motivated since the discovery X-rays to decode this information buried within the X-ray diffraction pattern without resorting to such methods as calibration curves or internal standards. The most widely used method for quantitative analysis include Whole Pattern Fitting and Matrix Flushing. The Matrix Flushing method requires the use of Reference Intensity Ratios or RIR’s as developed by Chung (1974a;b).
2.3.1 The Internal Standard Method

The internal-standard method\textsuperscript{27} is the most general of any of the methods for quantitative X-ray powder diffraction analysis. This method lends itself most easily to the generalization into the RIR or Matrix Flushing method. The intensity of the \( i \)-th diffraction line, from a pure phase \( \alpha \) in the form of a flat plate on a powder diffractometer is given by Bragg-Bretano geometry:

\[
I_{\alpha} = \frac{KcK_{\alpha}}{\mu} \quad (2.1)
\]

The intensity of a diffraction line \( i \) from phase \( \alpha \) in a mixture of phases is given by (Klugh and Alexander, 1974):

\[
I_{i,\alpha} = \frac{KcK_{\alpha}X_{\alpha}}{\rho_{\alpha}\left(\frac{\mu}{\rho}\right)^{m}} \quad (2.2)
\]

\( X_{\alpha} \) = weight fraction of phase \( \alpha \)

\( \rho_{\alpha} \) = density of phase \( \alpha \)

The mass absorption or mass attenuation coefficient of a mixture with \( m \) phases is described by:

\[
\left(\frac{\mu}{\rho}\right)_{m} = \sum_{j=1}^{\#\text{phases}} X_{j}\left(\frac{\mu}{\rho}\right)_{j} \quad (2.3)
\]

\( \mu \) = linear absorption coefficient of each mineral

\( Kc \) is a constant for a particular experimental system

\[
Kc = \frac{1.5}{64\pi} \cos^{2}2\theta_{m}\left(\frac{e^{2}}{m_{e}c^{2}}\right)^{\circ} \quad (2.4)
\]

where
$I_0 =$ incident beam intensity

$r =$ radius of the diffractometer

$\lambda =$ wavelength of X-ray radiation

$\left| \frac{e^2}{m_e c^2} \right|^2 =$ an electromagnetic radiation term required for X-rays and omitted for neutrons

$c =$ speed of light

$e$ and $m_e =$ charge and mass of electron

$2\theta_r =$ diffraction angle for monochrometer

$K_{i\alpha} =$ is a constant for a given crystal structure $\alpha$, diffraction line $i$ and set of experimental conditions. The constant is modeled exactly as:

$$K_{i\alpha} = \frac{M_i}{V_\alpha} \left| F_{i\alpha} \right| \left( \frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta} \right) \tag{2.5}$$

where

$M_i =$ multiplicity for reflection $i$.

$V_\alpha =$ volume of unit cell of phase $\alpha$.

$\left( \frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta} \right) =$ Lorentz and polarization corrections for diffractometer $(L_p)$.

$F_{i\alpha} =$ the structure factor for reflection $i$, which relates the intensity to the crystal structure parameters

$$F_{hkl} = \sum_{j = 1}^{\# \text{of atoms in cell}} f_j \exp 2\pi i (hx_j + ky_j + lz_j), \tag{2.6}$$

where

$h,k,l =$ miller indices of line $i$ of phase $\alpha$
x, y, z = fractional co-ordinates for atom j

\[ f_j = \text{atomic scattering factor for atom } j = f_{\text{corr}} \exp - \frac{B_j \sin^2 \theta}{\lambda} \]

where

- \( f_{\text{corr}} = \) the atomic scattering factor corrected for anomalous dispersion

  namely:

  \[ |f_{\text{corr}}|^2 = (f_0 + \Delta f)^2 + (\Delta f')^2 \]

- \( B_j = \) Debye-Waller temperature factor for atom i in phase \( \alpha \)

- \( \theta = \) Bragg diffraction angle

The fundamental problem in QXRD analysis arises from the \( \left( \frac{\mu}{\rho} \right)_m \) term in equation (2.3). To solve for the weight fraction of phase \( \alpha \) we must be able to compute \( \left( \frac{\mu}{\rho} \right)_m \) and this requires knowledge of the weight fractions of each phase. The internal-standard method is based on the elimination of the absorption factor \( \left( \frac{\mu}{\rho} \right)_m \) by computing the ratio

\[ \frac{I_{\alpha}}{I_{i_s}}, \]

the intensity for line \( i \) of phase \( \alpha \) divided by the intensity for line \( j \) of the internal standard \( s \). This ratio of intensities comes from dividing two intensities and gives following relationship, linear in weight fraction of phase \( \alpha \):

\[ \frac{I_{\alpha}}{I_{i_s}} = K' \frac{X_\alpha}{X_s}. \]  

(2.7)
This relationship permits the analysis with the addition of a known amount of internal standard. To establish a calibration curve a plot of \( \frac{X_s I_{sa}}{I_{js}} \) is plotted versus \( X_a \). The slope of this straight is \( K' \). In such cases when \( X_s \) is a known weight fraction from a standard this relationship can be simplified to

\[
\frac{I_{sa}}{I_{js}} = K'' X_a.
\]

(2.8)

2.3.2 Generalized Reference Intensity Ratio’s (RIR)

The use of multiple lines from each phase can be accommodated by independently determining \( K' \)'s for each analyte line-internal standard line pair. A more general approach, which avoids introduction of multiple calibration constants, is to use relative intensities \( I_{\text{rel}} \) and the Reference Intensity Ratio, RIR. This more general equation was developed by Hubbard

\[
\frac{I_{sa}}{I_{js}} \frac{I_{rel}^s}{I_{rel}^s} X_s = K = \text{RIR}_{\alpha,s}.
\]

(2.9)

and Synder, 1988. The \( I_{\text{rel}} \) term, relative intensities of the standard and the phase \( \alpha \) as found in the Powder Diffraction File (PDF), are seldom accurate. The user should accurately determine the relative intensities in question. Once the calibration constant \( K \) is determined, it need not be redetermined before each analysis since variations in the incident-beam intensity cancel in the \( \frac{I_{sa}}{I_{js}} \) ratio just as \( \left( \frac{\mu}{\rho} \right)_{in} \) is eliminated.

A particularly important case is when corundum is used as the reference material and the integrated intensities are used. Corundum, \( \alpha-\text{Al}_2\text{O}_3 \), has been chosen for the
determination of RIR's by Powder Diffraction Files (PDF) for its purity, stability, and availability. In this case the RIR is referred to as $\frac{I}{I_c}$. The definition of $\frac{I}{I_c}$ was first proposed by Visser and de Wolff (1964). The PDF contains $\frac{I}{I_c}$ values for over 2500 phases of minerals, which are published in search manuals and on CD ROM. The use of $\left(\frac{I}{I_c}\right)_a$ value from the PDF allows us to avoid preparing our own standards to determine the calibration constant and simplify our determination of $X_a$. The equation 2.9 becomes

$$X_a = \frac{I_{a/c}}{I_{jc}} \frac{I_{rel}^{a/c}}{I_{rel}^{jc}} \frac{X_c}{RIR_{a,c}} = \frac{I_{a/c}}{I_{jc}} \frac{I_{rel}^{a/c}}{I_{rel}^{jc}} \left(\frac{I}{I_c}\right)_a . \quad (2.10)$$

Further simplification arises from the addition of an known amount of an internal standard. From the equation, 2.10, it can be shown that

$$RIR_{a,s} = \frac{RIR_{a,c}}{RIR_{s,c}} = \frac{\left(\frac{I}{I_c}\right)_a}{\left(\frac{I}{I_c}\right)_s} . \quad (2.11)$$

Hence, we can combine $\frac{I}{I_c}$ values for phases $a$ and $s$ to obtain the Reference Intensity Ratio for phase $a$ relative to phase $s$. Taking $s$ to be the internal standard and substituting equation 2.11 into equation 2.10 and rearranging.

$$X_a = \frac{I_{a/c}}{I_{jc}} \frac{I_{rel}^{a/c}}{I_{rel}^{jc}} \frac{RIR_{s,c}}{RIR_{a,c}} X_s . \quad (2.12)$$
2.3.3 The Reference Intensity Ratio or Matrix Flushing Method

The RIR or Matrix Flushing Method involves the analysis of a mixture of identified phases without the addition of an internal standard, and requires only a few of the most intense reflections. Chung (1974a:b) was the first to point out that if all the phases in a mixture are identified and the RIR value known for each phase, then an additional equation holds:

\[ \sum_{k=1}^{n} x_k = 1, \]  

(2.13)

where \( n \) is the number of phases in the mixture. This equation permits analysis without adding any standard to the unknown specimen. This is seen by arbitrarily choosing one of the phases as \( s \) and then using equation 2.12 to solve for the ratio of the weight fraction of each phase to the weight fraction of \( s \) namely

\[ \frac{X_\alpha}{X_s}, \frac{X_\beta}{X_s}, \text{ etc.} \]

For \( n \) phases in a mixture this produces \( n-1 \) ratios. The relationship given in equation 2.13 allows the writing of the \( n^{th} \) equation. The system of \( n \) linear equations can be solved to produce the weight fractions of \( n \) unknown phases from the following equation:

\[ X_\alpha = \frac{I_{i\alpha}}{RIR_{i\alpha}} \left[ \sum_{i}^{n} \frac{1}{RIR_i I_{j\alpha}^{ref}} \right]. \]  

(2.14)
It is important to note that any sample containing unidentifiable phases invalidates the use of the Chung Method. When using the RIR values from another source, for example published $\sqrt{I}$ values or the Ir on the PDF card, the Chung or RIR method can only be considered semi-quantitative. For reasonable accuracy it is recommended to obtain pure specimens of the phases to be determined and an internal standard added to them. These samples should be carefully measured to determine accurate values for $\sqrt{I}$s and RIR's and only these values should be used in the analysis.

2.3.4 QXRD by Whole Pattern Fitting

With the availability of automated X-ray powder diffractometers, digital diffraction data are now routinely available on computers. Complete diffraction patterns provide the opportunity to perform quantitative phase analysis using all the data in a given pattern rather than considering only a few of the strongest reflections. As the name implies, Whole Pattern methods involve fitting the entire diffraction pattern, often including the background, with a synthetic diffraction pattern or a pattern produced from a combination of observed standard diffraction patterns. It is recommended to utilize patterns produced experimentally for the known combinations of minerals. A computer program uses the 100% fractions of each component in the mixture, and each is treated as a standard. These standards are then used as a comparison against each component in the mixture. The whole pattern fitting approach is one that is facilitated by the use of personal computers to collect and store the intensities at each preset step in the entire diffraction pattern. The comparison is achieved by matching the intensities at each point in the unknown pattern with those in a standard. Standard mineral intensities are reduced
by a fractional multiplier until they match the unknown. The fractional multiplier represents the weight fraction of the pure mineral in the mixture. The actual calculation uses all of the points and employs a least squares approach to obtain the multiplier that produces the best agreement among the standard and unknown data points. The minimal value of $R^2$ (residual) is used to select the combination of standard mineral patterns and multipliers that best matches the unknown pattern.

$$R^2 = \frac{\sum (I_{\text{obs}}(2\theta) - I_{\text{calc}}(2\theta))^2}{\sum (I_{\text{obs}}(2\theta))^2}$$

2.4 Materials and Sample Mixtures Used in the Investigation

Chemically pure materials were utilized to prepare mixtures to test various X-ray powder diffraction methods. This was necessary in order to determine which analytical method provided the best agreement between known and observed intensities. The methods of interest, Whole Pattern Fitting and Matrix Flushing, were compared. Each material was scanned to check for mineral purity before use. Dr. Amitava Roy of the LSU Institute for Recyclable Materials provided a sample of ettringite. The ettringite proved to be impure and the XRD intensities were so low that its incorporation in the general analytical program was abandoned.

Mixtures of the selected materials were prepared in three groups with varying percentages by weight of the constituents. Table 2-1, Anhydrite and Gypsum (AG), Quartz, Calcite, and Dolomite (QCD), and all five (AGQCD) mixtures used as standards. Anhydrite (CaSO$_4$) and gypsum (CaSO$_4$·2H$_2$O) were used in one.
Anhydrite\textsuperscript{29} crystallizes in the orthorhombic group \textit{Amma} with the cell parameters $a = 6.991$, $b = 6.996$, $c = 6.238$ Å. Gypsum\textsuperscript{30} crystallizes in the monoclinic system \textit{I2/a} with the cell parameters $a = 5.670$, $b = 15.201$, $c = 6.533$ Å and $\beta = 118^\circ$. Calcite (CaCO$_3$), dolomite (CaMg(CO$_3$)$_2$), and quartz (SiO$_2$) were used in the second group. Calcite\textsuperscript{31} crystallizes in the hexagonal system \textit{R\bar{3}c} with the cell parameters $a = 4.9896$ and $c = 17.061$ Å. Dolomite\textsuperscript{31} crystallizes in the hexagonal system \textit{R\bar{3}} with cell parameters $a = 4.8033$ and $c = 15.9840$ Å. Quartz\textsuperscript{32} crystallizes in the hexagonal system \textit{P3$_2$1} with cell parameters $a = 4.9133$ and $c = 5.4048$ Å. A mixture of all five minerals constituted the third group. This allowed us to evaluate the interaction effects in the sulfates and their most commonly associated minerals separately, and in the five component mixture. All mixtures were duplicated and some were analyzed in duplicate. The mixtures were prepared by drying each mineral powder at 60°C overnight before weighing. After preparation, the powders were homogenized and reduced to a material with an average particle diameter below 5mm by grinding with ethyl alcohol in a Micronizer mill. The alcohol was removed by drying as above. Higher drying temperatures were avoided in order to minimize the dehydration of the gypsum. All powder diffraction patterns for sample mixtures can be found in the Appendix A.

2.5 Methods of Investigation

2.5.1 Part I- Semi-quantitative Approach Using Computer Generated Diffraction Profiles of Minerals

This investigation was conducted in four parts. In part I, reference mineral powder patterns were calculated to produce model structures derived from previously published papers. The minerals of particular interest were those involved in the analysis.
of phosphogypsum, portland cement, and the products of their reactions. These samples included: gypsum, anhydrite, quartz, calcite, dolomite, and ettringite. The necessary information produced in these published papers was utilized to obtain the atomic positions of known or hypothesized crystal structures, space groups, cell volume, etc.

This information was fed into a computer program called MICRO-POWD. The MICRO-POWD package consists of five programs: SET UP, POWD, DINT, GRAPH, and COMB. The SETUPPWD routine allows the user to input data required for the POWD and DINT routines; for instance, the name and chemical formula, set up the appropriate diffractometer trace and peak shape, input space group, atomic coordinates, cell volume, temperature factors, etc. POWD will calculate the integrated intensities for a theoretical powdered sample in random orientation placed in an X-ray beam. This routine then uses these data to simulate a diffractometer trace from which it extracts the peak intensities. At the end of the routine it compares the inputted mineral density to an calculated mineral density to see how successful the routine worked based on the stored data. DINT calculates the interatomic distances and angles for the crystal structure using the same data as stored for POWD. This calculation also provides a check on the stored data, primarily the position coordinates of the atoms which are some times incorrect in the original paper describing the structure. The GRAPH routine creates an intensity map of the sample base on the d-I data produced in the POWD routine. COMBIN allows the user to combining numerous diffraction patterns, previously created, and select a desired weight fraction for each mineral. COMBIN will simulate the effects of combing them in their weighted proportions along with background effects and statistical noise. The routine produces a single-valued intensity
<table>
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<th>Sample No.</th>
<th>Anhydrite</th>
<th>Calcite</th>
<th>Dolomite</th>
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</table>
versus two theta trace which would be very close to that which is obtained from experimental patterns.

2.5.2 Part II- Application of the Matrix Flushing Method

As these theoretical patterns are produced in part I, part II will utilize a quantitative XRD procedure utilizing a matrix flushing approach to be applied to real samples. The matrix flushing routine was produced by Philips, Inc. To utilize this program, a minerals database was created which contains the peak positions and intensities obtained JCPDS-IUDD card files. The identification of the materials in the compound was accomplished with a search/match program supplied by Philips, Inc. It incorporates "fuzzy" mathematical logic to compute a match score for each mineral in the database with the peaks in the XRD program. The higher the match score, the greater the probability that the phase is present in the sample. The score, the amount of peak shift, and the relative intensities of the peaks are then used by the investigator to select the most likely identifications for the peaks in the observed pattern. The Matrix Flushing approach to quantitative analysis is one that utilizes reference intensity ratios, \textbf{RIR}'s, to correct the measured intensities obtained during the collection of an X-ray diffraction pattern. It provides quantitative estimates of mineral abundance from external standards thus avoiding the problem of peak overlap, dilution, and increased sample handling associated with the use of an internal standard. Hence, the basic equation for the determination of the $X_{\text{exp}}$ by the Matrix Flushing Method, in a mixture of quartz, anhydrite, calcite, and dolomite follows from equation 2.14, where
The quantitative analysis software provided by Philips, Inc. has a subroutine to calculate the RIR’s and to compute the weight fractions for the mixtures of standard materials. The program is based on the measurement of the integrated intensities of pre-selected peaks.

### 2.5.3 Part III- Comparing Theoretical to Experimental Diffraction Patterns

Part III, ran in parallel to parts I and II, involved the method of curve fitting. In part III, it was necessary to collect the patterns, then employ a spread sheet program called KALEIDAGRAPH, which is a graphics application for the personal computer.

The intensities of pure minerals both experimentally and theoretically derived were loaded into Kaleidagraph, as well as the combined mixtures of quartz/calcite/dolomite and gypsum/anhydrite in varying weight proportions of each combination. The data on the mixtures were produced theoretically and experimentally, and the same weight proportions in the experimental set was used for the production of the theoretical patterns. Comparison was made between the two. A peak fitting routine produced by Philips, Inc. was used to smooth out the peaks and subtract out the background. The area under the peak (c.p.s) was also determined by this program.

\[
X_{\text{GYP}} = \left[ \frac{1}{1 + \frac{\text{RIR}_{\text{GYP}}}{\text{I}^{\text{obs}}_{\text{GYP}}}} \right] \left( \frac{\text{I}^{\text{obs}}_{\text{QTZ}} + \text{I}^{\text{obs}}_{\text{ANH}} + \text{I}^{\text{obs}}_{\text{CAL}} + \text{I}^{\text{obs}}_{\text{DOL}}}{\text{RIR}_{\text{QTZ}} + \text{RIR}_{\text{ANH}} + \text{RIR}_{\text{CAL}} + \text{RIR}_{\text{DOL}}} \right) \tag{2.15}
\]

and \( \text{RIR}_{\text{mineral}} = (\text{I}^{\text{cal}}_{\text{mineral}}/\text{I}^{\text{cordium}})_{50:50} \).
2.5.4. Part IV- Whole Pattern Fitting

To fulfill the objective, another method of quantitative analysis was employed to contrast the Matrix Flushing Method. The Whole Pattern Fitting routine offered an interesting comparison by requiring the entire diffraction profile to resolve the fractional components of the mixtures. This was the purpose for using the MICRO-POWD computer program. It was intended to use a synthetic diffraction profile for the fitting routine. To avoid a semi-quantitative analysis, the 100% fraction of each component used in the mixtures were treated as a standard. These standards are then used for a comparison against each mixture.

2.6 Results and Discussion

2.6.1 QXRD using Matrix Flushing

In the Matrix Flushing approach, pre-selected peaks, Figure 2-4, that are the strongest in intensity were used to “finger print” each mineral, Table 2-2. A typical analysis of five minerals requires about 5 minutes. The minerals were combined for three different concentration ranges. Low quantities are those quantities below 10 weight percent. Intermediate is between 20 to 50 weight percent. The highest interval is for minerals more than 70 weight percent. The most complex mixture, AGQCD, had the most analytical determinations in the low weight percent range. This is because many of these mixtures were prepared to evaluate the ability to analyze small quantities of non-sulfate materials in a dominant matrix of gypsum or anhydrite. A general assessment of the total analytical error was obtained by calculating the residual $\langle R^2 \rangle$ for each observed and reference values, Table 2-4, 2-6.
Primary Peaks for Matrix Flushing

Figure 2-4 Primary peak profiles used in Matrix Flushing.
Table 2-3 Operating parameters for the Matrix Flushing Method.

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<th>Analytical Phase</th>
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### Table 2-4
Weight percent determined by Matrix Flushing for sample mixtures
Anhydrite/Gypsum and Quartz/Calcite/Dolomite

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<th>Quartz</th>
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### Table 2-5
Weight percent determined by Matrix Flushing for sample mixture
Anhydrite/Gypsum/Quartz/Calcite/Dolomite

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<th>Sample No.</th>
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<th>Dolomite</th>
<th>Gypsum</th>
<th>Quartz</th>
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2.6.2 QXRD by Whole Pattern Fitting

In the Whole Pattern fitting approach, samples were prepared with the same ratio's used in the Matrix Flushing method. The whole pattern of the samples were used to deduced the weight fraction in the sample. Figure 2-5. Comparison between known and observed weight fractions were used to deduce a minimized residual $<R^2>$. Table 2-8. These residual values were compared with those generated from the Matrix Flushing method for the purpose of evaluation.

The results from the anhydrite/gypsum mixtures, Figure 2-9, fit reasonably well with the measured quantities, where the residual $<R^2> = 0.10$ is based on 11 values. For mixtures containing calcite, dolomite, and quartz, the $R^2$ increased and the differences in the known and unknown observed values increased. Figure 2-10. In the complex mixtures of all five components, the similarities in dolomite, anhydrite, and gypsum patterns were such that the overlap could not be resolved. Figure 2-11. Powder diffraction patterns can be found in Appendix A.

2.7 Conclusions

Compositions derived from the Matrix Flushing method were generally superior, with $<R^2> = 0.009$ for eleven AG mixtures, Figure 2-6, $<R^2> = 0.0004$ for thirteen QCD mixtures, Figure 2-7, and $<R^2> = 0.0197$ for nine AGQCD mixtures. Figure 2-8. The most notable exception in the determination of AG mixtures with 0-10% gypsum. The measured compositions were distorted in favor of gypsum, apparently due to the affinity of gypsum for water. The Q/C/D mixtures produced superior results, which is a consequence of no peak overlap of the primary peaks, Figure 2-7. In the A/G/Q/C/D
Figure 2-5  Diffraction peak profiles used in Whole Pattern Fitting.
Table 2-6  Results from QXRD using Whole Pattern Fitting with minimized R$^2$ value.

<table>
<thead>
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<th>Sample No.</th>
<th>Anhydrite</th>
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<th>Gypsum</th>
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mixtures anhydrite was distorted in favor of gypsum and some peak overlap with anhydrite and dolomite (low\%) was distorted in favor of gypsum. Figure 2-8. The results of the weight percents determined by the Matrix Flushing method are indicated in Tables 2-3, 2-4.

Compositions derived from the Whole Pattern fitting method for the binary and ternary mixtures agreed reasonably well with known values, with residuals $<R^2>= 0.10$ for eleven AG samples, and $<R^2>= 0.018$ for thirteen QCD samples. In the Q/C/D mixtures, quartz with calcite and/or dolomite observed results favored calcite and dolomite. Figure 2-5, 2-10, resulting from peak overlap. In the A/G/Q/C/D mixtures, anhydrite was distorted in favor of gypsum and mixtures with quartz/calcite and/or dolomite, the observed results favored calcite and/or Dolomite. Figure 2-5. 2-11, a consequence of peak overlap.

Although based on only one peak area measurement for each mineral, the analysis by Matrix Flushing, were superior to those obtained by Whole Pattern Fitting. Improved analytical performance can be achieved by longer counting times to decrease the uncertainties in the X-ray peak measurements. Better sample preparation to help stabilize the water in gypsum. when a mixture includes both gypsum and anhydrite should be considered.
Figure 2-6  Comparison of known and observed quantities in anhydrite/gypsum mixtures using Matrix Flushing.
Figure 2-7  Comparison of known and observed quantities in quartz/calcite/dolomite mixtures used in Matrix Flushing.
Figure 2-8  Comparison of known and observed quantities in A/G/Q/C/D mixtures used in Matrix Flushing.
Figure 2-9  Comparison of known and observed quantities in anhydrite/gypsum mixtures used in Whole Pattern Fitting.
Figure 2-10  Comparisons of known and unknown quantities in quartz/calcite/dolomite mixtures used in Whole Pattern Fitting.
Figure 2-11 Comparison of known and observed quantities in A/G/Q/C/D mixtures used in Whole Pattern Fitting
CHAPTER 3

STRUCTURE OF BIS-1,10 PHENANTHROLINE COPPER(I) HEXAFLUOROACETYLACETONATE

The crystal structure of the title complex (3.1a), [Cu(C\textsubscript{12}H\textsubscript{8}N\textsubscript{2})\textsubscript{2}][HCF\textsubscript{6}] is presented. The structure is formed by discrete [Cu(phen)\textsubscript{2}]\textsuperscript{+} cations and hfac anions (phen = 1,10-phenanthroline, hfac = hexafluoroacetylacetonate). The Cu atom is coordinated by four donor N atoms with a distorted tetrahedral geometry in the presence of a weakly coordinated hfac anion.

![Figure 3-1a](image)

In 1985, Doyle, Eriksan & Van Engan\textsuperscript{13} noted that, in the presence of various alkenes and dien, Cu\textsubscript{2}O will react with certain partially fluorinated \(\beta\)-diketones to form complexes of the type [Cu(diket)\textsubscript{n}]\textsubscript{L\textsubscript{m}} where n and m are 1 or 2. Following the methods of synthesis of copper(I) \(\beta\)-diketone complexes, as reported by (Doyle et al., 1985), phenanthroline was used as a stabilizing ligand. A product of this reaction, prepared by Dr. Kumaravel at Louisiana State University, was a new compound (3.1a). The following ratio of 1 mole Cu\textsubscript{2}O to 2 moles of hexafluoroacetylacetonate and 2 moles of phenanthroline in the presence of THF was prepared. An orange-brown compound was isolated from the product mixture. A crystal having the dimensions 0.20x0.20x0.10 mm\textsuperscript{3}.
was selected and mounted on a thin glass fiber for structure identification. Data were collected on an Enraf-Nonius CAD-4 diffractometer within $1^\circ < \theta < 30^\circ$ using graphite monochromatic MoKα radiation at 294K. Crystal unit-cell parameters, obtained by centering 25 reflections having $\theta$ value between 2 and $12^\circ$, were determined to be triclinic with space group $P\bar{T}$. Data were corrected for background, Lorentz, polarization and absorption effects. The trial structure model obtained by MULTAN and Direct methods with successive interpretation of difference Fourier maps. 7551 independent reflections were measured and 4815 reflections with $I > 1\sigma(I)$ were used to refine 447 parameters by full-matrix least square refinement method. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. Convergence was achieved with $R=0.058$, $wR=0.055$, goodness-of-fit($S$)=1.037.

The $N_1$-$Cu$-$N_2$, $N_1$-$Cu$-$N_3$, $N_1$-$Cu$-$N_4$, and $N_2$-$Cu$-$N_4$ bonding angles for the title compound, illustrated by ORTEP plot Figure 3.1, are 82.3(1), 143.8(1), 119.5(1), and 117.5(1)$^\circ$, and the bonding distances for $Cu$-$N_1$, $Cu$-$N_2$, $Cu$-$N_3$, and $Cu$-$N_4$ are 2.012(3), 2.073(3), 2.013(3), and 2.070(3)$\AA$, respectively. The dihedral angle between the least-squares plane of $N_1$, $C_{12}$, $C_{11}$, $N_2$ and $N_3$, $C_{24}$, $C_{23}$, $N_4$ is 82.99$^\circ$.

Structures of the type $[Cu(phen)_2]^+[A^-]$, where $A$=[$ClO_4]^-$ or [$CuBr_2]^-$, were reported by Healy, Englehardt, Patrick, and White\textsuperscript{44} in 1985. These compounds provided interesting comparisons to the title compound. For $[Cu(phen)_2][CuBr_2]$ the bond angles and distances were similar to the title compound, where $N(A)$-$Cu$-$N(B)$, $N(A)$-$Cu$-$N(A')$, $N(A)$-$Cu$-$N(B')$, and $N(B)$-$Cu$-$N(B')$ are 82.2(3), 146.0(3), 115.8(3), and 118.5(2)$^\circ$, with $Cu$-$N(A)$, $Cu$-$N(B)$ distances of 2.006(8) and 2.071(5)$\AA$, with a dihedral angle between the ligands of 76.8$^\circ$. In contrast, $[Cu(phen)_2][ClO_4]$ had bond angles and
distances for N(A)-Cu-N(A'), N(B)-Cu-N(B'), N(A)-Cu-N(B), and N(A)-Cu-N(B') of 81.4(3), 80.9(3), 109.7(3), and 144.7(2)°, with Cu-N(A), Cu-N(B) bonding distances of 2.045(8) and 2.053(9)Å, and a dihedral angle between the ligands of 49.9°. The minimum bonding distance between the Cu atom and an atom of the hfac anion was 3.7652(3)Å for Cu...F4. The minimum bonding distance between an atom of the [Cu(phen)2]+ molecule and the hfac anion was 3.0658(5)Å for N4...F4. Experimental details are listed in Table 3.1: atomic coordinates, bond distances, angles, anisotropic thermal parameters are given in Tables 3-2 to 3-4.

Figure 3-1  Molecular structure of bis-1,10 phenanthroline copper(I) hexafluoroacetylacetonate (3.1a) with displacement ellipsoids drawn at the 40% probability level.

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Table 3-1 Experimental details of Bis-1,10 Phenanthroline Copper(I) hexafluoroacetylacetonate (3.1a).

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**Cell constants**

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*table con’d*
Decay of standards < 1%

Reflections measured 7942

Independent reflections 7551

2θ range, deg 2 < θ < 12

Range of h,k,l (min/max) (0/14), (-16/15), (±17)

Reflections observed 4815

Criterion for observed I > 1σ(I)

Computer programs MULTAN

No. of parameters varied 447

Weights $w = 4F_o / \left[ \sigma^2(I) + (0.02F_o^2)^2 \right]$

$GOF = \sqrt{\frac{\sum w * |F_o| - |F_c|}{\text{degrees of freedom}}} = 1.037$

$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} = 0.058$

$R_w = \sqrt{\frac{\sum w * |F_o| - |F_c|}{\sum w * |F_o|}} = 0.055$

Largest feature final diff. Map 0.3990(eÅ³)
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Table con’d
H1  0.222(3)  0.298(3)  0.101(3)  0.05(1)*  
H2  0.104(4)  0.249(4) -0.076(3)  0.07(1)*  
H3  -0.129(4)  0.126(4) -0.125(4)  0.08(1)*  
H5  -0.332(4)  0.008(3) -0.062(3)  0.06(1)*  
H6  -0.422(5) -0.077(4)  0.071(4)  0.09(2)*  
H8  -0.376(5) -0.111(4)  0.249(4)  0.09(2)*  
H9  -0.234(4) -0.060(4)  0.422(4)  0.08(2)*  
H10  0.108(4)  0.507(3)  0.427(3)  0.05(1)*  
H13  0.335(4)  0.041(3)  0.304(3)  0.05(1)*  
H14  0.504(4)  0.043(3)  0.421(3)  0.06(1)*  
H15  0.601(4)  0.235(3)  0.599(3)  0.06(1)*  
H17  0.613(4)  0.457(4)  0.741(3)  0.08(1)*  
H18  0.520(4)  0.629(4)  0.784(3)  0.07(1)*  
H21  0.183(4)  0.081(3)  0.449(3)  0.06(1)*  
H22  -0.004(4)  0.434(3)  0.870(3)  0.05(1)*  

Starred atoms were refined isotropically (B_{iso}).

B_{eq} = \left( \frac{3}{8\pi^2} \right) \sum_i \sum_j U_i a_i^* a_j^* a_i a_j

<p>| Table 3-3 Bond distances (A), angles(°), and torsion angles(°) of 3.1a. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| F6 C29 1.309(5) | O1 C26 1.242(4) | O2 C28 1.224(5) | N1 C1 1.328(6)  | N1 C12 1.365(4) |
| N2 C10 1.324(6) | N2 C11 1.357(5) | N3 C13 1.326(5) | N3 C24 1.359(3) | N4 C22 1.322(6) |
| N4 C23 1.357(5) | C1 C2 1.395(6)  | C2 C3 1.360(6)  | C3 C4 1.402(6)  |                |
|                |                |                |                |                |</p>
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CHAPTER 4
THE ELECTROSYNTHESIS OF Ba_{1-x}K_xBiO_3 (X = 0.419) IN A KOH FLUX

4.1 Introduction

In 1988 a transition metal-free, high temperature, type II superconductor, Ba_{1-x}K_xBiO_3 (BKBO), with Tc = 30K was discovered\textsuperscript{35,36}. The discovery of this bismuth based compound offered an interesting contrast to the copper-oxide based superconductors. In 1989, Norton and Tang\textsuperscript{37} developed a low temperature electocrystallization technique, which incorporates a molten salt in a three electrode, one compartment cell. This molten salt consists of KOH pellets maintained at a temperature of 260°C. This low temperature technique, as opposed to high temperature sintering, offers a relatively simple and low cost method of experimentation. Since 1988, this method of synthesis has proven to be the best method for growing these crystals\textsuperscript{38-40}.

The kinetic and thermodynamic processes of electocrystallization of BKBO in a KOH flux is still not completely understood. This lack of understanding has led to the production of inhomogenous sample phases. Many researchers have made attempts to fine tune this process to produce a more homogeneous product. The method of analysis has been to use powder diffraction methods, some using neutron, but most using X-ray diffraction. No one has produced a definitive crystal structure based on single crystal X-ray diffraction. The goal of this research was to produce single crystals of a superconductive phase of this compound and to determine the structure of the desired phase by single crystal X-ray diffraction.
4.2 Methods of Preparation for the Electrocrystallization (EC) of BKBO

Ba$_{1-x}$K$_x$BiO$_3$ compounds were first synthesized by Cava et al.\textsuperscript{36} using the ceramic method. Stoichiometric amounts of barium, potassium and bismuth oxides were mixed and placed in sealed quartz tubes and heated to elevated temperatures. This method of synthesis produced mixed phases of BKBO, with a Tc $\approx$ 15K.

In 1988, another method was used to synthesize Ba$_{1-x}$K$_x$BiO$_3$ ($x \approx 0.4$). The method of synthesis, developed by Norton and Tang\textsuperscript{37}, utilized the electrochemical technique. A simple description of the electrochemical oxidation is shown in Figure 4-1.

The synthesis was carried out in a potassium hydroxide flux at 260 °C

\[ \text{Energy level of electrons} \]

\[ \text{Electrode} \quad \text{Solution} \quad \text{Electrode} \quad \text{Solution} \]

\[ \text{Vacant MO} \quad \text{Occupied MO} \]

\[ M - e^- \rightarrow M^+ \]

Figure 4-1 Representation of an oxidation process of a species M in a solution. The molecular orbitals (M.O.) of species M shown are the highest occupied M.O. and the lowest vacant M.O.

and demonstrated its utility for growing a better quality of BMBO (M=K,Rb), M-doped barium bismuthates. In comparison to the ceramic method\textsuperscript{36}, electrosynthesis in a molten...
salt produced crystalline materials with improved \( T_c \) (15K compared to 30K) and magnetic susceptibility. The following reaction typifies the overall process:

\[
9 \text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O} + 11\text{Bi}_2\text{O}_3 + 6\text{KOH} \rightarrow 15\text{Ba}_{1.6}\text{K}_{0.4}\text{BiO}_3 + 7\text{Bi}(\text{metal}) + 84\text{H}_2\text{O}
\]

The synthesis time is limited by the depletion of \( \text{Bi}_2\text{O}_3 \) from the melt through deposition of Bi metal on the counter (cathodic) electrode and the mixed-valent bismuthate on the working (anodic) electrode. The superconductive properties of BKBO depend on the percentages of barium and potassium present. The transition to a superconductive phase, with a \( T_c \approx 32\text{K} \), begins at around 38\% potassium and peaks around 39\%. The transition temperature slowly declines until a 50\%:50\% ratio of K:Ba is obtained. The BKBO compound becomes a semiconductor for K\% > 50\%. In the compound \( \text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3 \), the percentage of Bi\(^{3+}\) is 30\% and Bi\(^{5+}\) 70\%. Increasing the Bi\(^{5+}\) percentage in BKBO drives the \( \text{K}_2\text{O} \) component upward, \( \text{BaBiO}_3 \) to \( \text{KBiO}_3 \).

Norton and Tang laid the foundation for the successful electrosynthesis of \( \text{Ba}_{1.8}\text{K}_3\text{BiO}_3 \), BKBO. Yet, crystal structure analysis has been relegated to that of powder diffraction, as a result of poor sample quality that is unsuitable for single crystal diffraction. As reported by Norton and Tang, the process has supplied a product containing mixed phases of BKBO. Upon considering the work done by Norton and Tang, it was decided that the electrosynthesis process of BKBO could be improved. A necessary starting point was the cell and experimental design. This was followed by careful modification of experimental procedures based on results by Norton and Tang and other researchers. The final acceptable procedure was a result of careful analysis of subsequent experiments performed as part of this dissertation.
4.2.1 Designing a Cell

Norton and Tang's cell design included a low cost Teflon (PTFE) reaction cell and a quartz holder for the three electrodes. Potentiostatic deposition was performed using a three electrode, one-compartment cell geometry. The working electrode (positive or biased anodically) can be silver or platinum. The counter electrode (negative or biased cathodically) was typically platinum. The reference electrode, which was placed in close proximity to the working electrode, was a rod of bismuth 1 cm. in diameter which was relatively stable. It was important that all materials used were of the highest purity to minimize contamination of the melt. The Teflon reaction cell was an excellent container for the aggressive molten KOH flux, but Teflon begins to soften and melt when heated beyond 290°C. The quartz holder contains a placement for the three electrodes, working (WE), reference (RE), and counter (CE), and in/out ports for the water saturated cover gas. The quartz holder was not in intimate contact with the reaction cell, but covers the cell sufficiently to maintain an inert atmosphere for the molten salt.

In designing the cell, a low cost Teflon reaction cell seemed more than adequate for the electrocrystallization (EC) process. A quartz holder for the three electrodes was unavailable, and its fabrication was costly. It was decided to design a lid that would maintain intimate contact with the reaction cell. The reaction cell was a 100ml Teflon PTFE beaker. The top of the beaker, containing the lip for pouring, was cut off. A block of Teflon, 0.51 inches thick, was used to construct the lid. The lid was made circular with a diameter equal to the reaction cell diameter, 2.15 in. So the lid would fit securely onto the reaction cell, the lid was cut inward from the circumference 0.24 inches, equal to the thickness of the reaction cell, (diagram 4-2, side view). The depth the lid would
set into the reaction cell, 0.27 inches, was greater than the thickness above, to enhance thermal stability. The lid had to be thick to hold the electrodes securely, especially at elevated temperatures of 260 to 280°C.

![Diagram of lid design](image)

Figure 4-2 A diagram of the lid design used in the electrocrystallization process of BKBO. CE= counter electrode, WE= working electrode, RF= reference electrode, IN/OUT refers to ports for cover gas. l and d refer to length and diameter.

The next consideration was designing the placement of the three electrodes and the in/out ports for the cover gas. The three electrodes were placed along the diameter of the lid. The in/out ports for the cover gas were placed ±90° from the alignment of the electrodes. (diagram 4-2, top view). The diameter of the holes drilled into the Teflon lid were determined by the diameter of the electrodes including the in/out ports for the cover gas. The placement of the reference electrode, between the working and counter
electrodes, was necessary to minimize polarization on the working electrode. The proximity of the reference and working electrode increases the impedance between them. The increase in impedance helps maintain a stable potential on the working electrode.

4.2.2 Experimental Arrangement

Once the design of the cell was completed and manufactured to specifications, the next step was to incorporate the required equipment into the experiment. A high current potentiostat was required to maintain a positive potential on the working electrode. A heating mantle, temperature controller, and voltage regulator (STACO) were necessary to heat the KOH flux to the required temperature and maintain that temperature. Figure 4-3. A magnetic stirrer was used to mix the components in the KOH flux prior to electrocrystallization. A water trap was used to bubble N\textsubscript{2} or Ar gas. The presence of the N\textsubscript{2} or Ar gas maintains an inert atmosphere within the cell. The presence of water vapor keeps the KOH flux hydrated at elevated temperatures. A change in the hydration of the flux affects mass transport of the desired reactants.

4.2.3 Containment of the Teflon (PTFE) Reaction Cell

Containment of the reaction is extremely important when working with molten salts. When the temperature of the flux ranges from 200 to 300°C, the melt is extremely corrosive and dangerous. Precautions were taken to provide a stable support for the reaction cell, and the area around the cell was kept organized to prevent accidents. The gas tank was placed in front of the bench and to the right to help shield the reaction area as in Figure 4-3. The magnetic stirrer was placed in a large metal tray. The stirrer provided support for the heating mantle that contained the Teflon reaction cell. The
heating mantle was considerably larger than the 100ml reaction cell. A 600ml Pyrex beaker was placed inside the heating mantle described in Figure 4-4.

![Diagram of experimental set-up for electrocrystallization process.](image)

Figure 4-3 Experimental set-up for electrocrystallization process.

Because of its excellent thermal conductivity, aluminum foil was used to line the gap between the Pyrex beaker and the reaction cell. Enough foil was used to secure a tight fit for the Teflon cell. With the foil in place, the thermocouple was put between the sheets of aluminum. The thermocouple, which detects a change in the temperature of the heating mantle, was connected to a temperature controller. The aluminum foil was not to be higher than the lip of the reaction cell, such that the cell could be easily removed to dispose of the melt.
4.2.4 Disposal of Molten Alkali Flux

The materials used in this synthesis, $\text{Bi}_2\text{O}_3$, $\text{Ba(OH)}_2\cdot8\text{H}_2\text{O}$, and KOH, are stable compounds, which are toxic if inhaled or swallowed. In the process of electrocrystallization, some of the $\text{Bi}^{3+}$ ions are partly subjected to reduction and some are oxidized. Synthesis was complete upon depletion of $\text{Bi}^{3+}$ from the melt. Corrosion of the Bi reference electrode in the KOH flux is uncertain.

After the electrocrystallization process had ended, the lid containing the three electrodes was removed and the melt exposed. The heating mantle was turned off and magnetic stirrer turned on. Stirring helps cool the melt more quickly, and dislodges sediment from the bottom of the reaction cell. When the melt had almost solidified, the reaction cell was less dangerous to handle, and the cell could be removed from the heating mantle wearing asbestos gloves. It was placed in a large Pyrex beaker under the
fume hood, and the strongly basic melt, almost solidified, was slowly redissolved with the addition of deionized water. The melt can still be reactive and may pop or sputter when the deionized water were added. The fume hood window was pulled down, and about 2ml of deionized water was slowly added by dropper. The basic solution was slowly neutralized by adding HCl or HNO₃ solutions.

4.2.5 Calibration of the Cell Temperature

In the process of electrosynthesis, the reaction temperature is extremely important and must remain stable. The temperature affects the solubility of the reactants and viscosity of the molten salt. Temperature drives the mass transport of the components to the nucleation sites on the working electrode. The mechanism of mass transport affects the morphology of the crystals. Since the thermocouple would corrode, it was placed in the foil outside the reaction cell and not in the melt. Therefore, calibration between the internal cell temperature and the temperature controller was needed.

The cell was half-filled with NaCl. A thermometer was placed through a hole in the lid into the salt. With the lid firmly in place, the temperature controller was compared to the readings on the thermometer, from 200 to 280°C, the range for possible experimental conditions. The temperature on the controller was selected, and the temperature in the reaction cell was allowed to stabilize for an hour before increasing the temperature on the controller. It was expected that there would be a temperature drop through the cell wall. Figure 4-5, shows that the variation in temperature between the
cell and the controller averaged 29°C. Therefore, the temperature controller was adjusted 29°C higher to obtain the proper reaction temperature.

Figure 4-5  A graph depicting the variation between the temperature reading on the controller versus the internal cell temperature.

4.3 Investigating Norton and Tang's work

In a typical experiment, performed by Norton and Tang, weight ratios of reactants are considered. Weight ratios $\text{KOH/ Ba(OH)₂ \cdot 8H₂O = 12.5}$ and $\text{KOH/Bi₂O₃ = 8.43}$ were used. First, KOH pellets are melted in the crucible at 180 to 200 °C, then Ba(OH)$_{2}$ \cdot 8H$_{2}$O, white crystal flakes, were added to the clear melt. Once the Ba(OH)$_{2}$ \cdot 8H$_{2}$O dissolved, Bi$_{2}$O$_{3}$, a fine yellow powder, was added to the melt. A white hydrate, Ba(OH)$_{2}$ \cdot 8H$_{2}$O, forms. Bi$_{2}$O$_{3}$ is only partially soluble in this melt and stirring is used to enhance dissolution. The electrocrystallization process is performed under an inert atmosphere of H$_{2}$O saturated Ar/N$_{2}$ gas and every attempt was made to keep the system isothermal.
Electrolysis of the melt was begun at an applied potential between 0.6 and 0.9 volts vs. reference electrode. Deposition begins immediately and is terminated by withdrawing the crystal-laden electrode from the melt. The BKBO crystals tend to be blue to black in color and cubic in form. These crystals can be air cooled and rinsed with distilled water to dissolve the attached melt.

One reason for successful synthesis of BKBO using a molten salt matrix is that:

1. all constituent reagents are soluble in the KOH flux, and the product phases are relatively insoluble. (2) The potassium oxide, K₂O, component of BKBO was not stable in the normal high temperature solid state synthesis. This material can only be produced by the electrochemical deposition process (ECP). (3) The ECP synthesis is more easily controlled by electric current in contrast to the conventional ceramic crystal growth techniques, which are driven by thermal energy. (4) In the solid state, chemical oxidation requires the diffusion of oxygen across the ambient gas/condensed phase interface: since a solid polycrystalline surface barrier film of the oxidized product phase may form, which impedes oxygen transport. In the electrochemical system, the oxidative power is delivered directly to the desired crystal interface.

4.3.1 Melt Oxidizes

Initially, it was necessary to reproduce Norton and Tang’s procedure to synthesize the Ba₁₋ₓKₓBiO compound. The purity of the components of the melt was not a primary concern at this point. Since that cell design and experimental set-up differed from Norton and Tang’s, it was of interest to produce a product. The materials used in the cell and the arrangement of electrodes were similar to Norton and Tang’s. The counter electrode was a silver wire, the reference electrode was bismuth rod (dia. =
Icm.), and the working electrode was platinum wire. Figure 4-6. The reactant components in the cell were KOH pellets (89%+), Ba(OH)$_2$·8H$_2$O (99.8%), and Bi$_2$O$_3$.

![Cell & lid (side view)](image1.png) ![lid (top view)](image2.png)

Figure 4-6 Diagram indicating cell design and electrode placement.

(99.9%). The cover gas consisted of water saturated N$_2$ or Ar. The in house N$_2$ is easily accessible through connections in the lab and was used in this experiment.

The cell and the electrodes were cleaned with 5M HCl followed by 5M HNO$_3$ solution to remove any impurities. They were then rinsed thoroughly with deionized water. The Teflon cell was placed in the oven to dry. The electrodes were each rotated in the oxidizing flame of a Bunsen burner for 10 minutes, then placed in concentrated nitric acid, HNO$_3$. This procedure for final cleaning of the electrodes was repeated 3 times prior to each experiment.

The dry Teflon cell was placed in the heating mantle, Figure 4-4, and heated to a temperature of 200°C and 45.0 grams of KOH pellets were added to the cell and allowed...
to melt under flowing \( \text{N}_2 \) gas bubbled through the water trap. When the melt formed, 3.60 grams of a flaky white, \( \text{Ba(OH}_2 \cdot 8\text{H}_2\text{O} \), were added to the melt. Stirring was used to enhance dissolution. Then 5.33 grams of \( \text{Bi}_2\text{O}_3 \), yellow powder, were added to the melt. Immediately a gray precipitate formed, probably \( \text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O} \). The temperature of the cell was increased to 260°C and the ingredients were stirred for an hour. A potentiostat was used to maintain a positive potential on the working electrode.

*Potentiostat* controls the voltage across the working-counter electrode pair, and it adjusts this voltage to maintain the potential difference between the working and reference electrodes. It is the job of the potentiostat to force through the working electrode whatever current is required to achieve the desired potential at any time. Since the current and the potential are related functionally, that current is unique. Thus, the potentiostat’s response (the current) actually is the experimental observable.

Once a potential is applied across the electrodes, the electrocrystallization process is initiated. A potential of \( \text{E} = \pm 0.7 \) volts vs. Bi ref. was placed on the working electrode. As the crystals grew, at the nucleation sites on the working electrode, the current passing through the cell increased as a function of an increase in surface area on the working electrode. After 24 hours, the melt was inspected; it had turned black indicating, air oxidation had occurred.

### 4.3.2 Melt Solidifies Around Reference Electrode

The experiment was repeated a second time under the same conditions as above except that exposure of the melt to air was minimized. The flow rate of the cover gas was increased slightly to ensure a more inert atmosphere. The lid was removed briefly.
when adding the reagents to the melt, and secured for the electrosynthesis process. The next day, upon inspection, it was noticed that the melt had solidified around the reference electrode. Heat was convecting through the electrodes, primarily the large bismuth rod reference electrode, which was cooler due to exposure to ambient temperature.

4.3.3 Dendritic Crystal Growth

Sample preparation was the same as the first experiment. The concern was to keep the electrodes at a temperature close to the temperature in the reaction cell. To minimize the temperature gradient, glass wool was wrapped around the electrodes, and the space in-between the electrodes was packed with glass wool. Since the electrodes are elevated above the heating mantle, heating cables were connected to the voltage regulator and wrapped around the perimeter of the beaker. Figure 4-3. The cables helped maintain an elevated temperature around the electrodes, and additional glass wool was packed within the area of the heating cables and between the electrodes. Then the heating mantle and heating cables were covered with a sheet of glass wool.

The amount of current passing through the cell depends on the depth the working electrode is inserted into the melt. With the starting potential $E = +0.7$ volts, the current was $I = -1.0$ mA. After 15 minutes, the current had increased to $I = -1.2$ mA. This indicated crystallization could be taking place. After 21 hours, the current through the cell had decreased to $I = -0.1$ mA. The electrosynthesis process was halted and the working electrode inspected. The working electrode contained a large mass of black crystals. The crystals were dendritic in shape, long and thin, but no solidification of the
melt was noticed. The cause of the dendritic growth could be due to elevated starting current, I = -1.0 mA, and an elevated temperature. This resulted in a rapid mass transport to the nucleation sites.

It was discovered the N\textsubscript{2} gas system had a number of leaks allowing air into the system. Since, the in-house N\textsubscript{2} was unreliable for future experiments, and was probably the root cause of the previous failed attempts, it was replaced with a tank of Ar gas.

### 4.4 Evaluating Current Research on the Electrocrystallization of BKBO.

Although the molten hydroxides may provide a suitable reaction environment, there are technical difficulties associated with this type of ionic liquid. Due to the high chemical aggressiveness associated with these melts, there was little knowledge of suitable experimental conditions. This has led to poorly reproducible results for many investigations\textsuperscript{36}.

Molten hydroxides are autoprotolytic: thus, hydroxide ions in the melt dissociate into water and oxide ions, which are, respectfully the conjugate acid and conjugate base of the solvent:

\[ 2\text{OH}^- \leftrightarrow \text{H}_2\text{O} + \text{O}^{2-} \]

Water was the strongest acid stable in the molten hydroxides and the oxide ion was the strongest base that can be found in this media. Since water was a proton solvated hydroxide ion, the “pH” in these liquids was defined by

\[ \text{pH}_2\text{O} = -\log[\text{H}_2\text{O}] \]

[\text{H}_2\text{O}] affects the solubility of the reactants as well. Roberts \textit{et al.}\textsuperscript{18} noted this in the electrosynthesis of BKBO in a KOH flux. When yellow Bi\textsubscript{2}O\textsubscript{3} were added to the melt.
the melt retained most of the undissolved yellow Bi$_2$O$_3$. Upon the addition of 
Ba(OH)$_2$·8H$_2$O, the solubility of Bi$_2$O$_3$ was believed to be enhanced by the formation of a white precipitate Bi$_2$O$_3$·2H$_2$O. The [H$_2$O] was a variable that was extremely difficult to control. One can attempt to minimize a wide variation in [H$_2$O] by trying to maintain an isothermal system and slow consistent flow rate of the water saturated cover gas.

Other researchers have studied the variable conditions of electrosynthesis in KOH flux. There was an underlying trend found by these researchers. A slow growth based on low current density (0.5mA/cm$^2$) at the working electrode yields a more homogeneous phase, but optimum growth time and current density remain uncertain.

Some disparity was found between the procedural details implemented by Norton and Tang and those of current researchers. Disparity was found in these key areas: temperature, deposition potential (volts), and weight ratio’s used to synthesize BKBO compounds. Both K$^+$/Ba$^{2+}$ and K$^+$/Bi$^{3+}$ were found to be significant factors which influence the production of a homogeneous phase of BKBO.

The deposition potential affects the ratio of Bi$^{5+}$/Bi$^{3+}$ produced, which in turn determines the degree of K$^+$ doping. Also, a positive potential placed on the WE affects the degree of oxidation at the WE, which in turn affects the rate of crystal growth at the WE. A typical range of deposition potential for the production of superconducting phase appears to be from 0.68 to 0.75 volts vs. Bi ref..

Temperature affects the solubility and rate of mass transfer (the rate at which reactants are carried to reacting surface of the working electrode (WE) by convection).
A lower temperature than required for optimum growth can lead to what is called **Hopper Growth.** Hopper growth develops when the rate of mass transfer is too slow to bring the reactants to the face of the growing crystal, where current density is lower, as opposed to the edges and corners, where current density is higher.

The description of the process by Norton and Tang was vague. The electrode potential recommended, 0.6 to 0.8 volts, is appropriate for the oxidation of Bi$^{+3}$ to Bi$^{+5}$, but an association of specific potentials to crystal morphology, composition, and homogeneity was not discussed. The weight ratios $\text{KOH/Ba(OH)}_2 \cdot 8\text{H}_2\text{O} = 12.5$ and $\text{KOH/Bi}_2\text{O}_3 = 8.43$ provided a general starting point, but emphasis on the variation of these ratios, and how these ratios affect crystal morphology, composition, and homogeneity were not discussed. The reaction temperature of the melt at 260°C, used by Norton and Tang in these recent articles, was not found to produce a BKBO product with a measurable transition temperature. Synthesis, at the above reaction temperature, Rosamillia et al.$^{40}$ was found to produce a dendritic product. This correlates with the results found in experiment III above.

Finally, Norton and Tang did not discuss the effect at the nucleation site of current density on the working electrode. This has been found to have a pronounced affect on the BKBO transition temperature, crystal morphology, cell lattice parameters, and sample homogeneity.

These articles independently focused on critical procedural parameters in the electrocrystallization process: weight ratios of the components, cell temperature, potential at the working electrode, and current density. Considering the information from the recently published articles, the approach in this work was to consolidate these
published results, and to optimize the results by maximizing these trends for successful
electrocrystallization of the desired $\text{Ba}_{1-x}\text{K}_x\text{Bi}_3$ phase.

The next phase of experiments incorporated modifications in experimental
procedure. These changes included: (1) Argon, replaced the in-house nitrogen as a cover
gas. Argon is heavier than nitrogen and provides a better cover gas. Ar forms an
excellent clathrate with water. This was necessary, since the viscosity of the melt, mass
transport of its components, and pH all depend on $[\text{H}_2\text{O}]$. (2) A cell temperature range
of 220°C to 230°C was explored. (3) Weight ratio of $\text{KOH/}\text{Ba(OH)}_2\cdot8\text{H}_2\text{O} = 17.2$ and
$\text{KOH/}\text{Bi}_2\text{O}_3 = 12.5$, were found to give optimal results. (4) A cell potential range of $E = 
+0.670$ to $+0.68$volts was explored. (5) While maintaining a stable cell, the starting
current was kept as low as possible by minimizing the depth of the working electrode
into the molten salt. To grow the crystals slowly, maximize size and homogeneity, it
was necessary to maintain a low current density, less than $0.5\text{mA/cm}^2$, at the nucleation
site on the working electrode.

4.4.1 Brief Description of the Electrical Double Layer

The behavior of the electrical double layer is well documented in aqueous
solutions. The solution side of the electrode surface is thought to be made of several
"layers." The layer closest to the electrode, the inner layer, contains solvent molecules
and sometimes other species (ions or molecules) that are considered to be specifically
absorbed. Figure 4-8. In the inner layer, the electrical centers of the specifically adsorbed
ions is called the inner Helmholtz plane (IHP), which is at a distance $x_1$. The total charge
density from the specifically adsorbed ions in this inner layer is $p'$. Solvated ions only
approach the metal to a distance \( x_2 \); the locus of centers of these nearest solvated ions is called the *outer Helmholtz plane* (OHP). The interaction of the solvated ions with the charged metal involves only long range electrostatic forces, so that their interaction is essentially independent of the chemical properties of the ions. These ions are said to be *nonspecifically adsorbed*. Because of thermal agitation in the solution, the nonspecifically adsorbed ions are distributed in a three dimensional region, called the *diffuse layer*, which extends from the OHP into the bulk solution. The excess charge density in the diffuse layer, \( \rho^d \), so that the total excess of the charge density on the solution side of the double layer, \( \rho^s \), is given by

\[
\rho^s = \rho^f + \rho^d
\]

The thickness of the diffuse layer depends on the total ionic concentration in the solution.

Due to the low solubility of \( \text{Bi}_2\text{O}_3 \) in a molten KOH flux, a similar behavior may result during and towards the end of the electrocrystallization process (ECP). This could explain some of the unusual fluctuations in the current during ECP, which is depicted graphically later in the dissertation. These fluctuations may result from a shift in equilibrium caused by some of the inert \( \text{Bi}_2\text{O}_3 \) becoming soluble by an unknown mechanism.

### 4.4.2 New Modifications

Taking into consideration the above modifications, a new melt was prepared. 68.87 grams of KOH (87+%, purity) was placed in the Teflon cell and melted at 200°C.
4.01 grams of Ba(OH)$_2$·8H$_2$O (98+%) were added with stirring to the molten KOH, followed by the addition of 5.51 grams Bi$_2$O$_3$ (99.99%). Stirring continued for 24 hours at a temperature of 220°C. The potentiostat was then set to $E_{ap}=0.677$ volts, and the depth of the working electrode, in the molten salt, was minimized to lower the starting current. The cell was stable with $I=-30\mu$A. Throughout the electrocrystallization process there was a steady increase in the current at the working electrode. This resulted from an increase in surface area on the working electrode through nucleation of the crystalline product, Figure 4-7. The drop in current signals the end of the electrocrystallization process. This is attributed to a decreasing concentration of the species being oxidized, in this case Bi$^{3+}$ ions, during the electrosynthesis process. This

Figure 4-7 Proposed model of the electrode/solution double layer

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current, increase and decrease over time, are a result of the availability of the electroactive species at the electrode surface.

Figure 4-8 Observed change in current with time on the working electrode (WE).

4.4.3 Results

The crystals obtained were similar to those described by Norton and Tang, cubic in shape and black-blue in color. Evaluation of these applied procedures will be based primarily on the quality of the crystals, the data collection, and refined model of a single crystal. A specimen suitable for single crystal X-ray analysis was difficult to find. Some of the crystals grew from each other making them difficult to separate. The large crystals broke into many pieces. A small fragment of a larger crystal was mounted for single crystal diffraction. Analysis generated a cubic type cell with lattice constant $a = 4.2839\text{Å}$. The agreement based on average of all reflections was poor and refinement of the model in a cubic space group yielded negative thermal parameters around the central bismuth atom. A source of the disorder was probably a result of impurities present in the melt. It
was decided to grow crystals smaller in size, 0.1 to 0.2 mm, attempting to minimize sample inhomogeneities and approach the dimensions desired for single crystal analysis.

### 4.4.4 Annealing the Crystals with Oxygen Gas

Annealing is a method used to eliminate lattice defects in various types of semi- and superconductors, especially compounds that are doped to enhance magnetic and electronic properties. Some common defects include *point* defects, namely, vacant lattice sites and interstitial atoms (extra atoms not at lattice sites). Although the concentration of such defects can be small, they nevertheless have a profound impact on the properties of crystals.

The simplest type of defect is a lattice vacancy. Such a missing atom or ion is known as a *Schottky defect*. A Schottky defect can be created by transferring an atom or ion from the body of the crystal to the surface. Energy is required for this process and there is an increase in entropy. The other common type of defect is the *Frenkel defect*, in which an atom is displaced from a lattice position to an interstitial position.

Annealing depends on the rate of diffusion in solids, and diffusion can be affected by defects. As an atom diffuses through a crystal, it must surmount a series of energy barriers presented by its neighbors as it moves from lattice site to lattice site or from interstitial position to interstitial position. Let us consider the interstitial diffusion of impurities. If this barrier height is $\varepsilon$, then $\exp(-\varepsilon/kT)$ can be thought of as the fraction of time that the atom will have energy exceeding $\varepsilon$. If $\mu$ is the frequency with which the diffusing atom vibrates around its interstitial position, then the probability per unit time
that the atom will be able to pass over the barrier is

\[ p \lambda \mu e^{\sigma T} \]

The temperature for the annealing process is critical for minimizing entropy and maximizing atom or ion mobility. Annealing treatments involve sufficiently slow cooling rates that the material approaches the equilibrium situation at any temperature, including the final temperature. Using the ceramic method for crystal synthesis, Hinks et al. noted the mobility of the potassium ions at temperatures below 450°C. The volatility of the K\(^+\) ions would make the growth of single-phase crystals through high temperature sintering impossible.

An attempt was made to improve the quality of the BKBO crystals, by annealing in an oxygen gas environment to fill any oxygen vacancies. It is assumed that oxygen vacancies are a primary source of the disorder. Caution must be exercised when an oxygen tank is used in an experiment, because oxygen is a strong oxidizer and extremely flammable. A tube furnace containing a quartz tube, stoppered at both ends and rubber tubing attached, was used to contain the flow of oxygen gas. The crystals were placed in a small quartz boat. A thermocouple and digital multimeter were utilized to monitor the temperature of the furnace, Figure 4-9. An oil trap was required to prevent a backdraft of ambient air after the annealing procedure was concluded. Taking into consideration the volatility of potassium ions, the annealing temperature ranged from 350 to 400°C at a duration of two hours. The crystals were slowly heated up to the desired range for two hours, then cooled slowly for two hours. The total annealing time was six hours.
4.4.5 Results of X-ray Analysis on Annealed Crystals

No noticeable improvement in the quality of the data collected by single crystal X-ray diffraction was noted for the oxygen-annealed material. The crystals seemed to be a darker color, which could be a result of surface defect removal. The crystals remain disordered. Lack of a successful annealing treatment probably is a result of: (1) the temperature range (limited by the volatility of the potassium ions). The annealing temperature for the BKBO crystals was not sufficiently high to allow for ion mobility. (2) A high concentration of impurities creating irreversible disorder. (3) Variation of different phases of BKBO present in the crystal. (4) All the above.

Although improvement in the electocrystallization process is warranted, it is possible that the volatility of the potassium ions prevents attainment of appropriate annealing conditions.
4.5 Electrosynthesis while Stirring

After the previous ECP, it was noticed that there was some sediment in the bottom of the Teflon cell. Considering the low solubility of Bi$_2$O$_3$ in the molten salt, the remaining sediment was suspected to contain Bi$_2$O$_3$ and Ba(OH)$_2$·8H$_2$O. Therefore, it was decided to stir the solution during the electrocrystallization process. The stirring process made use of a magnetic stirrer and a 1.0 in. x 0.25 in. stir bar.

Taking into consideration the above modifications, the new melt was prepared. 68.99 grams of KOH (87+% purity) were placed in the Teflon cell and melted at 200°C. 4.01 grams of Ba(OH)$_2$·8H$_2$O (98+% purity) were added with stirring to the molten KOH, followed by the addition of 5.52 grams Bi$_2$O$_3$ (99.99%). Stirring was allowed to proceed for 1 hour at a temperature of 220°C. The potentiostat was then set to $E_{\text{app}}$ 0.677 volts vs. Bi ref., and the working electrode adjusted to minimize the current. The cell was difficult to stabilize while stirring, because the action of the stir bar caused a slight motion of the electrodes. As a result, the current fluctuated, but the electrocrystallization began with a starting current of $I= -70\mu\text{A}$. After 24 hours, the current had increased to $I= -2.43\text{mA}$, which indicated the surface area around the working electrode had increased as a result of crystal growth. Electrocrystallization was halted and the working electrode inspected. The working electrode contained a large disordered mass of small black-blue crystals. Stirring disordered the nucleation sites and accelerated the mass transport of the reactants to the working electrode contributing to the small sized crystals. A single crystal of suitable size for X-ray diffraction analysis could not be found.
4.6 Growing Smaller Crystals for X-ray Diffraction

The rapid growth of the crystals in the previous experiment is a result of ineffective stirring overwhelming mass transport of the reactants to the nucleation sites on the working electrode. The goal in this experiment was to generate a large number of small crystals with appropriate dimensions for single crystal X-ray diffraction, while at the same time keeping the current density as low as possible. Without stirring, crystals were grown at a higher starting current by increasing the depth of the working electrode in the melt. A greater exposure of the metal surface increases the number of nucleation sites (which speeds up the crystal growth) and should result in smaller crystals.

The new melt was prepared with 68.94 grams of KOH (87+%, purity) placed in a Teflon cell and melted at 200°C. With stirring, 4.01 grams of Ba(OH)$_2$·8H$_2$O (98+%) were added to the molten KOH, and followed by the addition of 5.51 grams Bi$_2$O$_3$ (99.99%). Stirring was allowed to proceed for 1 hour at a temperature of 215°C. The potentiostat was set to $E_{\text{app}}$ 0.677 volts vs. Bi ref., and the depth of the working electrode was adjusted until $I = -70\mu A$, the rate of nucleation increased. The higher starting current is a result of greater surface area exposure on the working electrode.

The temperature was decreased to slow down mass transport in an attempt to compensate for the increased growth rate. The cell remained stable, and the electrocrystallization process was over in less than 48 hours. Figure 4-10 depicts the changes of the cell current over time for the electrocrystallization process.
Figure 4-10  Current change through the reaction cell over time as a result of increasing the number of nucleation sites on the working electrode.

4.6.1 Results

The crystals produced in the above experiment were black-blue and much smaller as expected, about (0.15 to 0.1mm)x 0.075mm x 0.05mm. The crystals covered the entire surface of the electrode exposed to the melt and without the disordered mass observed previously. There were fewer overlapping layers of growth. When the crystals grew, nucleation predominated at the corners of the cubes from the previous layer.

Figure 4-11. Separating these crystals for single crystal diffraction was not possible.

Figure 4-11  A depiction of the predominate growth pattern of the BKBO crystals in this experiment.
Samples, to be synthesized next, needed to be much larger with the emphasis on decreasing the number of nucleation sites. For single crystal diffraction analysis, a corner from a large cube shaped crystals would be a more homogeneous phase of BKBO.

4.7 Electrocrystallization with a Galvanostat

It had been noted from previous experiments, the crystals are smaller the greater the distance from the center of the working electrode. Crystals that nucleate early on the working electrode are larger, where there exist the fewest number of surfaces and the current density is more homogeneous. As the crystals nucleate, the current density looses its homogeneity around the working electrode and crystalline mass. The current density at the corners of each cubic crystal is the greatest and must be rapidly increasing with increasing surface area. This leads to massive nucleation at the corners of the growing crystals which in turn leads to disordered growth. Figure 4-11. What is of primary concern is to restrict nucleation from the corners of the cubic shaped crystal.

The first step towards crystallizing larger crystals was minimizing the number of nucleation sites on the metal surface of the working electrode. Additional steps were included for preparing the electrodes discussed in 4.3.1. After the electrodes were cleaned, they were polished with a fine powder of Alumina, Al₂O₃. Inspection of the platinum, Pt, working electrode under a light microscope revealed numerous deep pits. These pits could have formed from removal of the crystals and cleaning. These cavities seemed too deep, and polishing would not completely generate an ideal smooth surface. The working electrode was again placed in the oxidizing flame of the Bunsen burner, for a duration of 1 hour. The electrode was rotated 90° every 15 minutes. It was intended
that the platinum surface would be heated to the point of melting to fill in the pitted surface. Inspection under the light microscope indicated an improved surface, but with minimal change to the deep cavities.

previous crystals were grown at a fixed applied potential, \( E_{\text{app}} \), allowing the current to vary. in this experiment, the crystals grown were galvanically, that is, with a fixed applied current, \( I_{\text{app}} \). A galvanostat applies a controlled current between the working and counter electrodes and the potential between the working and reference electrode becomes the dependent variable. in the potentiostat mode, the starting current was determined by the depth of the working electrode in the KOH flux. in the galvanostat mode, the potential was determined by the depth of the working electrode in the melt. The experiment must be monitored carefully because the applied potential determines the percentage of Bi(III) oxidized to Bi(V), which establishes the ratio of Ba:K. It was the intention in this experiment to force nucleation to a slower rate with

Figure 4-12 A general diagram outlining the use of a jack to adjust the depth of the working electrode.
increasing surface area, the opposite of previous experiments. The purity of the melt was enhanced to improve the quality of the crystals.

The new melt was prepared with 38.695 grams of KOH (87+%) and 29.605 grams of KOH (99.99%, Alpha Aesar). The 68.30 grams of KOH (93%) were placed in the Teflon cell and melted at 200°C. With stirring, 3.97 grams of Ba(OH)$_2$ · 8H$_2$O (98+%) were added to the molten KOH, and followed with the addition 5.47 grams Bi$_2$O$_3$ (99.9998%, Alpha Aesar). Stirring was allowed to proceed for 1 hour at a temperature of 225°C. The Galvanostat was set to $I_{\text{app}} = -49.95\mu$A, and the working electrode adjusted to $E_{\text{APP}} = 0.681$ volts vs. Bi ref. To adjust the potential, the depth of the working electrode was changed. The reaction cell and heating mantle were placed on a small jack with the working electrode clamped to a ring stand. Figure 4-12. Adjusting the height of the jack changed the depth of the working electrode. In a typical experiment, using a potentiostat, the potential fluctuates ± 0.001 volts. An attempt was made to restrict the voltage variation to ±0.002 volts.

With the current held constant, the potential on the working electrode decreased steadily as the surface area increased. The experiment was stopped periodically to decrease the depth of the working electrode in the melt to obtain the appropriate potential on the working electrode.

In the Galvanostat mode, it was expected the current density would decrease with increasing surface area, driving the rate of nucleation slower resulting in a more homogeneous phase. The following graph, see Figure 4-13, depicts the change in potential over time.
Figure 4-13 Each break indicates where ECP was halted to raise the working electrode. This was necessary to increase the applied potential to the appropriate range for oxidation.

The experiment required 26.7 hours for completion. The crystals on the working electrode increased in size the longer they were exposed to the melt. Figure 4-14. As a result of raising the working electrode to maintain the appropriate potential, it was noticeable that the time intervals between adjustments, Figure 4-13, increase in duration over the course of the experiment. The slowing growth rate forced nucleation away from the corners of the cubes and onto the faces.

Figure 4-14 A depiction of crystal growth on the surface of the working electrode resulting from ECP in the Galvanostat mode.
4.7.1 Results

The crystals obtained were blue-black and cubic shaped, and well ordered along the surface of the Pt working electrode. The amount of nucleation on corners of the cubes was minimized and the overall quality greatly improved. Analysis, based on single crystal x-ray diffraction, revealed considerable disorder. This could be a result of electrosynthesis at constant current allowing the potential to fluctuate. The potential placed on the working electrode determines the ratio of Bi$^{3+}$ to Bi$^{5+}$, which affects the ratio of K$^+$ to Ba$^{2+}$. Allowing the potential to fluctuate resulted in a fluctuation of these ratio’s. Therefore a constant potential must be maintained to produce single phased crystals containing the appropriate ratio of K$^+$ to Ba$^{2+}$.

To help eliminate fluctuations in the cell potential, it would be necessary to have the potential monitored by a computer. Any change outside the defined boundaries prescribed for the electrocrystallization process would result in feedback to mechanical device attached to the working electrode. This mechanical device would carefully adjust the working electrode, by raising or lowering, and maintaining the appropriate potential.

4.8 Electrocrystallization with Ultra-pure Reagents I

In potassium hydroxide, KOH, pellets are 87%+ pure as a standard. The remaining 13% of impurities contains about 6% Na$^+$ cations. Footnote noted that the presence of sodium ion in a molten salt has a strong affinity with the Bi(V) site in the crystal. The presence of sodium and other impurities has resulted in a decrease in superconductivity. The sodium impurity, a +1 ion in a +5 ion site, causes Schottky
cation site be balanced in some way. In this case, the balance would be achieved by another Schottky defect, a missing anion. Therefore, to improve the quality of the crystals and minimize lattice imperfections; the purity of the melt was improved for this experiment.

The new melt was prepared with 90.01 grams of KOH (99.99%. Alpha Aesar) placed in the Teflon cell and melted at 200°C. With stirring, 5.85 grams of Ba(OH)$_2$·8H$_2$O (98+%) were added to the molten KOH, and followed with the addition of 6.54 grams Bi$_2$O$_3$ (99.9998%, Alpha Aesar). Stirring was allowed to proceed for 1 hour at a temperature of 225°C. The potentiostat was set to $E_{\text{app}} = 0.680$ volts vs. Bi ref., and the working electrode adjusted to establish a starting current of $I_{\text{app}} = -30.5 \mu A$.

With the exception of using a potentiostat, the set up from the previous experiment was utilized. Consideration must be given to control the rate and orientation of nucleation. This requires minimizing the number of nucleation sites, and in this case to prevent the cell current from increasing rapidly. Therefore, the cell current was monitored, Figure 4-15. The working electrode was adjusted as in the previous experiment.

The only question prior to the beginning of the experiment was how much variation in the current should be allowed. The problem with the answer is that the extent of the current fluctuations are unknown. Since the actual depth of the working electrode in the melt is unknown, the true current density is unknown. It was decided to let the current vary about 250$\mu$A, before raising the working electrode to lower the current in the cell.
4.8.1 Results

The cell current increased slowly and gradually accelerated. Figure 4-15. The working electrode was raised sufficiently to begin electrocrystallization at a lower cell current. After electrocrystallization was halted, the crystal laden working electrode was placed in a beaker of deionized water to elute the melt. The crystals were removed from the working electrode and placed on a piece of filter paper to dry. The crystals were inspected through a stereo microscope. The crystals were black in color and cubic in shape. Allowing the current to increase towards the end produced a considerable number of satellites around the perimeter of the crystalline mass. It was decided that the current in the next experiment would be contained within I= -0.5mA. A setting of the potentiostat to $E_{\text{app}} = 0.677$ volts vs. Bi ref., would lower the current density to slow the growth rate.
4.9 Electrocrystallization with Ultra-pure Regents II

The new melt was prepared with 95.2 grams of KOH (99.999%, Alpha Aesar) placed in the Teflon cell and melted at 200°C. With stirring, 5.91 grams of Ba(OH)$_2$·8H$_2$O (98+%) were added to the molten KOH, followed by the addition of 6.65 grams Bi$_2$O$_3$ (99.9998%, Alpha Aesar). Stirring was allowed to proceed for 1 hour at a temperature of 225°C. The potentiostat was set to $E_{\text{app}}$ = 0.677 volts vs. Bi ref., and the working electrode was adjusted to establish a starting current of $I_{\text{app}}$ = -20.0 $\mu$A. Again, the rate and orientation of nucleation must be controlled. This requires minimizing the number of nucleation sites by preventing a rapid rise in the cell current. Therefore, the cell current was monitored. Figure 4-16. From results in the previous experiment, the working electrode was adjusted accordingly such that the cell current would not exceed -0.5mA.
4.9.1 Results

The cell current increased slowly and gradually accelerated. Figure 4-16. The working electrode was raised sufficiently to begin electrocrystallization at a lower cell current and to prevent the cell current from exceeding -0.5mA. After electrocrystallization was halted the crystal laden working electrode was placed in a beaker of deionized water to elute the melt. The crystals were removed from the working electrode and placed on a piece of filter paper to dry. The crystals were inspected through a stereo microscope. The crystals were black in color and cubic in shape. The crystals were large and well defined. Crystals were analyzed by single crystal X-ray diffraction, and were determined to be Ba$_{0.158}$K$_{0.42}$BiO$_3$ with Pm$ar{3}$m symmetry. A transition of Tc$\approx$ 29.5K was determined by the Department of Physics at Louisiana State University.
CHAPTER 5

SINGLE CRYSTAL STRUCTURE OF Ba$_{0.58}$K$_{0.42}$BiO$_3$

5.1 Introduction

The crystal structure of the title complex Ba$_{0.58}$K$_{0.42}$BiO$_3$, BKBO, is presented. The compound is a perovskite type structure of the form ABO$_3$. The A site is shared by barium and potassium. The B site is mixed valent and occupied by the bismuth species: Bi$^{+3}$ and Bi$^{+4}$. This phase of BKBO was determined to have a transition temperature, Tc, of 29.5K by the Department of Physics at Louisiana State University.

5.2 Background

In 1988 a transition metal-free high type II superconductor, Ba$_{1-x}$K$_x$BiO$_3$, with Tc $=\ 30$K was discovered$^{35,36}$. The discovery of this bismuth based compound offered an interesting contrast to the copper-oxide based superconductors. The predominate method for synthesis of high quality BKBO crystals makes use of a low temperature electocrystallization technique in an molten alkali hydroxide flux, developed by Norton and Tang in 1988.

Single crystals of Ba$_{1-x}$K$_x$BiO$_3$ were synthesized by this author using the technique of electrosynthesis in a molten KOH flux. The experimental conditions to achieve these results required ultra-pure KOH (99.99%), Ba(OH)$_2$·8H$_2$O (99.8%), and Bi$_2$O$_3$ (99.9998%). The cover gas consisted of water saturated ultra-pure Ar gas. The reaction temperature was 225°C. The melt components were based on weight ratios of K/Ba = 17.2 and K/Bi=12.5. The electrode deposition potential was chosen to be 0.677
volts vs. Bi ref., and starting current I = 20 μA. Every attempt was made to keep the starting current as low as possible. This was necessary to minimize the number of nucleation sites for growing large crystals slowly.

5.2.1 Determining the Ratio of Bi$^{3+}$:Bi$^{5+}$

Defect chemistry can be defined as charge compensation reactions that occur in non-stoichiometric material to preserve charge neutrality. In the electrosynthesis of BKBO compounds, altervalent substitutions of ions in different oxidation states ensure the overall charge on the solid is zero. In the oxidation of Bi$^{3+}$ to Bi$^{5+}$, a redox potential is chosen such that only some of the Bi$^{3+}$ species are oxidized to Bi$^{5+}$. This incomplete oxidation determines the ratio of K$^{+1}$:Ba$^{+2}$ at the A site of the ABO$_3$ compound. The ratio of Bi$^{3+}$:Bi$^{5+}$ can be determined from K$^{+1}$:Ba$^{+2}$ ratios as follows:

1). Determine the total charge contribution for each type of anion.

Let $A_T$ represent the total charge contribution from the anions. $n =$ number of atoms, $a =$ oxidation state of anion, and $C_T =$ charge contribution from the cations.

$$A_T = \sum_{i} n_i a_i$$

$A_T = 3(-2) = -6$  $\longrightarrow$  $C_T = +6$

2). Determine the total charge contribution from the counter cations. Ba$^{+2}$ and K$^{+1}$.

Let $Q$ represent the total charge from the counter cations. $f =$ that fraction of atoms sharing the same position in the crystal. $c =$ oxidation state of counter cations, and $Z =$ charge contribution from the bismuth atoms.
\[ Q = \sum_i f_i c_i \]

\[ Q = 0.42(1) + 0.58(2) = 1.58 \quad \rightarrow \quad Z = 6 - 1.58 = 4.42 \]

3). Determine the ratio of \( \text{Bi}^{+5}:\text{Bi}^{+3} \).

i). Let \( \text{Bi}' = \text{Bi}^{+5} \) and \( \text{Bi}'' = \text{Bi}^{+3} \), where the Bi primes represent that fraction of atoms sharing the same position in the crystal. In parenthesis is the corresponding oxidation number.

\[ \text{Bi}'(5) + \text{Bi}''(3) = Z = 4.42 \]

ii). Consider that the bismuth atoms share a whole site.

\[ \text{Bi}' + \text{Bi}'' = 1, \text{ solve for } \text{Bi}'' \]

\[ \text{Bi}'' = 1 - \text{Bi}' \]

iii). Substitute for \( \text{Bi}'' \)

\[ \text{Bi}'(5) + (1-\text{Bi}')(3) = 4.42 \]

\[ 5\text{Bi}' + 3 - 3\text{Bi}' = 4.42 \]

\[ 5\text{Bi}' - 3\text{Bi}' = 4.42 - 3 \]

\[ 2\text{Bi}' = 1.42 \]

\[ \text{Bi}' = 0.71, \text{ therefore } \text{Bi}'' = 1 - 0.71 = 0.29 \]

\[ \Delta \text{Bi}^{+5} = 0.71 \text{ and } \text{Bi}^{+3} = 0.39, \text{ hence } \Delta \text{Bi}^{+3}:\text{Bi}^{+5} = 0.39:0.71 \]

5.2.2 Structural and Electrical Properties in \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \)

The electrical and structural properties of \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \) depend directly on the value of \( x \). BKBO undergoes various phase transitions that correlate to its electronic properties. Table 5-1 correlates the variation in \( x, K^{+1} \), with corresponding structural and electronic properties in \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \). The structure and electronic properties of
Ba$_2$Bi$^3$Bi$^5$O$_6$ were determined by Cox and Sleight$^{11}$. Norton and Tang$^{17}$ were the first to synthesize a superconducting cubic phase for $x \approx 0.38$ and $T_c \approx 32$ K. Pei et al.$^{2}$ elucidated a detailed phase diagram of varying K content, $0.1 \leq x \leq 0.5$, and structure determined by neutron powder diffraction. Tang et al.$^{13}$ synthesized an 8 K superconductor with $x \approx 0.56$ and a semi-conductor for $x \approx 0.62$. Kodialam et al.$^{44}$ synthesized an $x = 1.0$, KBiO$_3$ (red, transparent). The red color may be due to the band gap resulting from a charge transfer transition: O $2p$ to Bi $6s$. Some of these crystals were found to be darker in color and appear opaque, which may result from mixed valency of bismuth.

The parent compound, BaBiO$_6$, adopts a monoclinic structure and contains tilted corner sharing BiO$_6$ octahedra with alternating short and long Bi-O bonds (2.12 and 2.28 Å). Upon potassium doping, Ba$_{1-x}$K$_x$BiO$_3$ shows two structural phase transitions with increasing $x$. At $x \approx 0.1$, the breathing mode distortion disappears, leading to an orthorhombic structure, and identical Bi-O bonds. Then at $x \approx 0.375$, the octahedral tilt distortion is suppressed resulting in the cubic perovskite system.

<table>
<thead>
<tr>
<th>$x = K$</th>
<th>cell symmetry</th>
<th>electronic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0 &lt; x \leq 0.1$</td>
<td>monoclinic</td>
<td>insulator</td>
</tr>
<tr>
<td>$0.1 &lt; x \leq 0.35$</td>
<td>orthorhombic</td>
<td>semi-conductor</td>
</tr>
<tr>
<td>$0.35 &lt; x \leq 0.62$</td>
<td>cubic</td>
<td>superconductor</td>
</tr>
<tr>
<td>$0.5 &lt; x \leq 1$</td>
<td>cubic</td>
<td>semiconductor</td>
</tr>
</tbody>
</table>
It is interesting to note that the change in the amount of K⁺ in \( \text{Ba}_{1.5} \text{K}_x \text{BiO}_3 \) does not vary linearly with increasing transition temperature. Instead the peak transition temperature is around \( x \approx 0.38 \) and decreases slowly until \( x = 0.56 \) then superconductivity ceases and the cell structure remains cubic. Figure 5-1.

![Graph](image)

**Figure 5-1** Variation in K⁺ content with transition temperature within the superconducting cubic phase.

### 5.3 Superconductivity and \( \text{Ba}_{0.58} \text{K}_{0.42} \text{BiO}_3 \)

#### 5.3.1 Historical

In 1911 the Dutch physicist Heike Kamerlingh Onnes, curious about the behavior of matter at low temperatures, accomplished the task of liquefying helium, the last of the inert gases to be condensed. Liquid helium enabled Onnes to cool down materials to temperatures near one kelvin of absolute zero. Onnes, on the verge of an apocryphal discovery, asked a student to measure the electrical resistance of mercury, an unusual
element in its own right. The student reported that the resistance disappeared when the
temperature of the sample fell below 4.2 K. Onnes sent him back to the laboratory to
find what Onnes thought was an “error” producing an experimental artifact. After several
attempts, the error could not be found, and the workers realized they had made an
historic discovery. Onnes won the 1913 Nobel prize for this and many other discoveries
in low temperature physics.

To discern the cause of superconductivity, effects of a materials transition to a
superconductive state needed to be determined, defined, and characterized. Zero
resistance to current flow was not the only reason for amazement. The behavior of
superconductors in a magnetic field proved equally astonishing. In 1933 two German
physicists, Walter Meissner and Robert Ochsenfeld, found that a superconductor can
expel magnetic fields when cooled below its transition temperature. The complete
expulsion of a magnetic field is known as the Meissner effect. Zero resistance and
expulsion of a magnetic field propelled a tremendous amount of intellectual energy to
research this enigmatic electromagnetic behavior. At this point, observation had far
surpassed theory. Quantum models in the 1930’s could explain conductivity in “normal”
metals, but behavior of superconductors proved to be the exception.

In 1957 John Bardeen, Leon N. Cooper, and J. Robert Schrieffer developed a
theory that helped provide a basis of a quantum theory of superconductivity, known as
the BCS theory. This theory states that the conduction of electrons travel without
meeting resistance because they move in pairs, termed Cooper pairs. Electrons form
these Cooper pairs because they interact with phonons, mechanical vibration in the
crystalline lattice that resemble sound waves. The movement of the atoms in the lattice
tend to neutralize the repulsion that electrons normally have for one another, and actually produce a small attractive force between electrons. The effectiveness of this interaction depends sharply on temperature. The transition temperature is that point on the thermal scale where superconductivity occurs. At temperatures above this critical point, thermal fluctuations destroy the Cooper pairs, hence the superconducting state of the material.

It is the pairing interaction that determines two microscopic distance scales in a superconductor. The first is the spatial separation of the electrons in a Cooper pair. This distance is referred to as the coherence length. The coherence length is the smallest length in a superconductor over which electronic properties, such as local resistivity, can change. In the 1950s the coherence length was best introduced into theory through the Landau-Ginzburg equations. In typical superconductors the coherence length ranges from hundreds to thousands of angstroms.

The second microscopic characteristic is related to the strength of the Meissner effect. The effect occurs when a small magnetic field is applied to a superconductor, creating currents that flow near the surface of the material. These induced currents create a magnetic field that precisely cancels the applied field in the rest of the material. The magnitude of these induced currents falls off exponentially with increasing distance from the surface of the superconductor. The length over which this decay occurs is called the magnetic or London penetration depth. This depth is a fundamental length that characterizes a superconductor. In typical superconductors, this length can vary from hundreds up to tens of thousands of angstroms.

The coherence length and magnetic penetration depth emerge as consequences of the BCS theory, and define two broadly different categories of superconductors. Type
Type I superconductors, or soft superconductors exhibit a magnetization curve in the form of Figure 5-1a. They have a coherence length longer than the penetration depth. Pure elements tend to exhibit this behavior. These materials tend to be low temperature, low field superconductors. If the field reaches a critical strength \( H_c \), which varies from substance to substance, it enters the material destroying superconductivity.

![Type I and Type II Superconductors](image)

**Figure 5-2** Magnetization curves for type I and type II superconductors. (a) Magnetization versus applied magnetic field for a bulk superconductor exhibiting a complete Meissner effect (perfect diamagnetism). A superconductor with this behavior is called a type I. Note the minus 4\( \pi \)M is plotted on the vertical scale: the negative value of M corresponds to diamagnetism. (b) Superconducting magnetization curve of a type II superconductor. The flux starts to penetrate the specimen at a field \( H_{c1} \) lower than the thermodynamic critical field \( H_c \). Below \( H_{c1} \) the specimen is a normal superconductor. \( a \). The specimen is in a vortex state. \( b \), between \( H_{c1} \) and \( H_{c2} \), and it has superconducting properties up to \( H_{c2} \). Above \( H_{c2} \) the specimen is a normal conductor \( c \) except for possible surface effects.

Above the critical field \( H_c \) the specimen is a normal conductor. Because their lack of resistance disappears at low fields, type I superconductors have little potential for interesting technological applications.
Other materials, that exhibit a magnetization curve of the form of Figure 5-1b and are known as type II superconductors, are much more useful. These materials tend to be alloys, ceramics (mixed-valent oxides), or transition metals with high values of electrical resistivity in the normal state. The penetration depth of these superconductors is longer than the coherence length. As a result, they remain superconducting even after the magnetic field enters. Type II superconductors can withstand high fields up to what is called the upper critical field, and thus carry the largest currents.

Since the unexpected discovery of superconductivity in 1911 by Heike Onnes, predicting this phenomenon, for any arbitrary combination of atoms has remained elusive. Breakthroughs in the direction of understanding, "What is superconductivity?", have absolutely depended on happenstance beginning with the discovery itself.

5.3.2 Determination of Superconductivity in \(\text{Ba}_{0.58}\text{K}_{0.42}\text{BiO}_3\)

Characterization of superconductors involves the measurement of \(T_c\) and the determination of the chemical composition, crystal structure, and impurity phases. The use of AC magnetic susceptibility for \(T_c\) determination is based on the Meissner effect. A sample of \(\text{Ba}_{0.58}\text{K}_{0.42}\text{BiO}_3\) was submitted to Dr. Goodrich at the LSU department of Physics for \(T_c\) determination. Figure 5-3 illustrates a magnetization plot in an applied field of 50 Gauss. A \(T_c = 29.5\text{K}\) was determined. The magnetic susceptibility, \(\chi\) (EMU, \(\text{m}^3/\text{Kg}\)), was plotted against \(T(\text{K})\).
Figure 5-3  Magnetization plot for Ba$_{0.58}$K$_{0.42}$BiO$_3$ at a Tc = 29.5K.

5.4 Crystal Structure Details of Ba$_{0.58}$K$_{0.42}$BiO$_3$

The electrocrystallization product contained single crystals of Ba$_{1-x}$K$_x$BiO$_3$. The value of $x=0.419$, as derived from single crystal analysis, implies a possible superconducting phase, as confirmed by the result in section 5.3.2. The crystal chosen for single crystal X-ray diffraction was 0.05mm x 0.075mm x 0.1mm. A hemisphere of data, 3458 reflections, was collected and averaged to 212 unique reflections. The agreement value for all reflections was $R = 0.088$. The cubic cell has $a=4.2948$ Å and Pm$\bar{3}$m space group symmetry, Figure 5-4. A combination of Direct methods and Fourier analysis was used in the structural analysis. The atomic coordinates and thermal parameters are described in the following Table 5-3. Full-matrix least-squares refinement with 7 variables converged to final $R$ values of $R=0.028$ and $R_w=0.038$ based on 212 reflections. The Bi to Ba/K distance is 3.7194Å, and the Bi-O distance is 2.1474 Å. Figure 5-4.
Figure 5-4  Molecular structure of Ba$_{0.58}$K$_{0.42}$BiO$_3$ with displacement ellipsoids drawn at the 60% probability level.
Table 5-2  Experimental details of Ba_{0.58}K_{0.42}BiO_{3}.

**Compound**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Color/shape</th>
<th>Formula weight</th>
<th>Space group</th>
<th>Temp., °C</th>
<th>Cell constants</th>
<th>Dcalc, g cm^{-1}</th>
<th>Radiation, graphite monochr.</th>
<th>Max. crystal dimensions, mm</th>
<th>Decay of standards</th>
<th>Reflections measured</th>
<th>Independent reflections</th>
<th>2θ range, deg</th>
<th>Range of h,k,l(min/max)</th>
<th>Reflections observed</th>
<th>Criterion for observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba_{0.58}K_{0.42}BiO_{3}</td>
<td>Black-blue</td>
<td>433.42</td>
<td>Pm3m</td>
<td>294K</td>
<td>4.2948(2)</td>
<td>79.22(6)</td>
<td>Mo Ka</td>
<td>0.1x0.08x0.05</td>
<td>&lt; -0.1%</td>
<td>3458</td>
<td>212</td>
<td>10° &lt; θ &lt; 22</td>
<td>(±11), (0/11), (±11)</td>
<td>212</td>
<td>I &gt; 1σ(I)</td>
</tr>
</tbody>
</table>

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Computer programs

No. of parameters varied

Weights

Direct Methods

\[ w = 4 \frac{F_o}{\sigma^2(I) + (0.02F_o^2)^2} \]

\[ \text{GOF} = \sqrt{\sum w \cdot |F_o| - |F_c|} \]

\[ \text{degrees of freedom} \]

\[ R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \]

\[ 0.78 \]

\[ Rw = \sqrt{\sum w \cdot |F_o| - |F_c|} \]

\[ \sum w \cdot |F_o| \]

\[ 0.028 \]

\[ 0.032 \]

largest feature final diff. Map

\[ 9.1655 (e \text{ Å}^3) \]

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Table 5-3 Atomic coordinates and thermal parameters of Ba$_{0.58}$K$_{0.42}$BiO$_3$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>(B_{eq}(\AA))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.212(3)*</td>
</tr>
<tr>
<td>Ba</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.59(1)*</td>
</tr>
<tr>
<td>K</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.6(1)*</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>1.54(7)</td>
</tr>
</tbody>
</table>

Starred atoms were refined isotropically (\(B_{iso}\)).

\[B_{eq} = \frac{8\sigma^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j\]

Table 5-4 Bond distances (\(\AA\)), angles (°), and torsion angles (°) of Ba$_{0.58}$K$_{0.42}$BiO$_3$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance ((\AA))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-Ba</td>
<td>3.719(0)</td>
</tr>
<tr>
<td>Bi-K</td>
<td>3.719(0)</td>
</tr>
<tr>
<td>Bi-O</td>
<td>2.147(0)</td>
</tr>
<tr>
<td>Ba-O</td>
<td>3.036(0)</td>
</tr>
<tr>
<td>K-O</td>
<td>3.036(0)</td>
</tr>
<tr>
<td>Ba-Bi-Ba</td>
<td>180.(0)</td>
</tr>
<tr>
<td>Ba-Bi-O</td>
<td>125.(0)</td>
</tr>
<tr>
<td>O-Bi-O</td>
<td>180.(0)</td>
</tr>
<tr>
<td>O-Bi-O</td>
<td>180.(0)</td>
</tr>
<tr>
<td>Bi-Ba-Bi</td>
<td>180.(0)</td>
</tr>
<tr>
<td>Bi-K-Bi</td>
<td>180.(0)</td>
</tr>
<tr>
<td>Bi-K-O</td>
<td>144.(0)</td>
</tr>
<tr>
<td>Bi-K-Bi</td>
<td>180.(0)</td>
</tr>
<tr>
<td>O-K-O</td>
<td>180.(0)</td>
</tr>
<tr>
<td>Bi-O-Bi</td>
<td>180.(0)</td>
</tr>
<tr>
<td>Ba-O-Ba</td>
<td>180.(0)</td>
</tr>
<tr>
<td>Bi-Ba-O</td>
<td>90.00 (0.00)</td>
</tr>
<tr>
<td>K-Ba-O</td>
<td>90.00 (0.00)</td>
</tr>
<tr>
<td>Bi-K-O</td>
<td>90.00 (0.00)</td>
</tr>
<tr>
<td>Ba-K-O</td>
<td>90.00 (0.00)</td>
</tr>
</tbody>
</table>

Table 5-5 Anisotropic Thermal Parameters of Ba$_{0.58}$K$_{0.42}$BiO$_3$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(U_{11})</th>
<th>(U_{22})</th>
<th>(U_{33})</th>
<th>(U_{12})</th>
<th>(U_{13})</th>
<th>(U_{23})</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.026(2)</td>
<td>0.006(2)</td>
<td>0.026(2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The form of the anisotropic displacement factor is:

\[\exp \left\{-2\sigma^2\left\{h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2(hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})\right\}\right\}

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CHAPTER 6

CONCLUSIONS, CONCEPTS, AND PERSPECTIVES

6.1 Introduction

The search to understand various solid state materials by synthesis or physical characterization is a powerful driving force in all areas of the sciences, whether it be to determine a use for a low hazard waste product such as Phosphogypsum, or the synthesis and characterization of exotic new semi- and superconducting materials. Technological advances have enabled research scientists to utilize a variety of strategies to refine older and more widely used methods required to develop and characterize newer materials. In many cases, it is the synthesis of a novel compound that has triggered a new line of research.

6.2 Perspectives on Some Electronic Aspects of Solid State Materials

The characteristic properties of solids depend directly on the behavior of the electrons in them. Among these properties are the following: (1) magnetic (ferro and antiferro-magnetic ordering; paramagnetism) (2) optical (the emission and absorption of light, and photochemical reactions) (3) surface (transfer of electrons to another phase, such as in electrochemistry) (4) electrical conduction (properties of metals, semi-, and superconductors). Therefore, it is the electronic properties of the solid that forms the basis for its application. This wide diversity of electronic properties of solids reflects an equally wide range of chemical-bonding interactions.
6.2.1 Intrinsic Properties of Solid State Materials

Consider a hydrogen atom and the existence of discrete energy levels around the hydrogen nucleus, which may be occupied by electrons. If two identical nuclei are placed close together, their energy levels are perturbed. An electron situated between the nuclei is attracted to both and, therefore, experiences a lower potential energy. The energy level associated with the unperturbed electron splits. The lowered energy level corresponds to an electron having a high probability of residing between the nuclei. Two electrons may occupy this bonding level, which results in a net lowering of the electron energy of the system. If this energy reduction exceeds the gain in potential energy as a result of coulombic repulsion between the two nuclei, a covalent chemical bond forms.

As more nuclei are added to this system, additional energy-level splitting occurs. For a large atomic array, many closely spaced levels form bands of allowed electron energies. For example, the silicon atom contains two electrons in the 3s orbital and two in the 3p orbital. As the silicon atoms are brought closer together into the diamond configuration, the 3s and 3p orbitals begin to broaden and the gap between them decreases. Eventually, the gap disappears, and the electron states take on mixed s and p character, i.e., hybridization. Further decrease in atomic spacing results in the appearance of two new energy bands separated by a gap \( E_g \). Figure 6-1. The lower valence band consists of four states per atom associated with the four bonds to the nearest neighbor atoms. Since four electrons per atom occupy these states, a significant lowering of the total electronic energy results from the formation of covalent bonds. Electrons in the valence band have bonding character and reside in regions of low potential energy, whereas electrons in the upper conduction band have anti-bonding character. Further
decrease of atomic spacing, which may be induced by applied pressure, increases the energy gap, whereas thermal expansion of the lattice decreases the energy gap. This is a characteristic of semiconductors.

![Diagram showing band structure of metals, semiconductors, and insulators]

Figure 6-1 Idealized band structure of metals, semiconductors, and insulators. The shaded band is filled with valence electrons and the open band is empty. Metals have a partially filled valence band.

The density of states, or the number of states available for occupation within a given energy increment, is important to understanding material properties. Energy levels or bands contain a fixed number of electron states in direct proportion to the number of atoms in the crystal. Narrow lower lying energy bands, which correspond to atomic like states, have electrons localized near the nuclei. The density of states at these energies is large. The broad valence and conduction bands have relatively low densities. The density of states is low near the band edges, where the electrons have small kinetic energy.
The probability that an energy state is occupied by an electron is governed by Fermi-Dirac statistics. According to the Pauli principle, no more than two electrons may occupy a single energy state. It is useful to define a reference level, called the Fermi

![Fermi-Dirac distribution in a semiconductor](image)

Figure 6-2 Fermi-Dirac distribution in a semiconductor. (a) Pure solid; (b) n-type; and (c) p-type semiconductors. Shading represents occupied levels.

energy $E_F$, Figure 6-2, at which states have a 50% probability of being occupied. At a
temperature of absolute zero, the total electronic energy is minimal. All states below the
Fermi level are occupied and all above are empty. As the temperature increases,
electrons are excited above the Fermi level. The probability of occupation is given by the
following formula:

\[ P(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)} \]

where \( k \) is Boltzmann's constant. When the energy \( E \) is distant from \( E_f \) (\( |E - E_f| \gg kT \)),
this function decays in simple exponential fashion.

For each electron in the conduction band, there is a corresponding electron
vacancy or hole in the valence band. The Fermi level in this case is located at the
midpoint of the band. The conductivity of a semiconductor depends on the number of
conduction electrons and holes. At absolute zero, the Pauli principle dictates that no
current can flow because there are no empty states in the valence band into which an
electron can move. As the temperature increases, conduction electrons are released into
a sea of empty states.

Similarly, because holes are empty states, they have freedom of movement in the
valence band. The conductivity of semiconductors increases with increasing temperature
because of the creation of additional charge carriers. Figure 6-3. From Fermi-Dirac
statistics, the concentration of conduction electrons or holes \( n_i \) varies as \( \exp(-E_g/2kT) \).

In an insulator, \( E_g > 3 \) volts and \( n_i \) is very small. A metal displays a large low
temperature conductivity, which decreases as temperature rises. The metal is
characterized by a partially filled energy band. Electrons near the Fermi level may move
into unoccupied states that are also located near the Fermi level. As the temperature
increases, thermal agitation of the lattice inhibits the flow of electrons. Superconductors share this same trend towards a decrease in resistance with decreasing temperature, yet contradict the behavior of semiconductors.

The energy band theory helps explain optical properties of materials. Photons with energy $h\nu$ greater than the semiconductor gap energy, $E_g$, may excite electrons from the valence to the conduction band. Lower energy photons cannot excite electrons into the forbidden gap, i.e., the region in which electrons cannot exist; therefore, they pass through the material. Visible photon energies are in the red to blue range, 1-3 volts. Insulators are frequently transparent ($E_g > 3$ volts) and metals ($E_g = 0$) are opaque.

Coloration of semiconducting and insulating crystals is generally caused by the presence of energy levels within the gap.
6.2.2 Extrinsic Properties

Many device materials contain defects or purposely introduced impurities. These nonidealities tend to introduce energy states into the band gap and may alter the number of available charge carriers. The most common impurities introduced into the silicon crystal are the group V elements: phosphorous (P), arsenic (As), and antimony (Sb), and the group III element boron (B). These impurities are substitutional, i.e., they occupy normal Si atom positions in the crystal lattice. The group V elements have five valence electrons, four of which participate in covalent bonding with the surrounding Si atoms. The fifth electron weakly bound to the impurity and, at higher temperatures, is excited into the conduction band. For this reason, the group V impurities are called electron donors. When silicon is doped predominately with electron donors, it is called $n$-type.

The group III element boron contains three valence electrons that participate in covalent bonding. At 0K, the fourth bond is half filled, leaving the boron atom in a neutral charge state. Little energy is required to excite a valence electron into this fourth bond, creating a hole in the valence band. Boron is an electron acceptor. The acceptor doped material is termed $p$-type.

Impurities give rise to shallow levels. These shallow levels are located within 0.1 volts of the band edge, so that the majority of impurity atoms contribute charge carriers to the conduction or valence bands. Other impurities give rise to deep levels located throughout the energy gap. Gold, for example, gives rise to four energy levels in the band gap of germanium, corresponding to four possible charge states. The gold atom can act as a multiple acceptor or as a donor by giving up its lone valence electron to the conduction band. An empty lattice site or vacancy also give rise to deep levels. The
energy levels associated with the atoms surrounding the vacant site become atom-like and move into the gap. Associated with each atom is a dangling bond directed towards the empty lattice position. These atoms undergo a Jahn-Teller spatial distortion and cause the filled electron levels to drop lower in the gap. The magnitude of the distortion depends on the charge state of the vacancy.

6.3 Correlation between Superconductors and the Intrinsic/Extrinsic Properties of Solid State Materials

Attempts to determine the type of compounds that might become superconductive begin with trying to understand the parameters which influence the superconductivity in materials (Debye frequency, density of electron states at the Fermi surface, Coulomb interaction, and electron-phonon interaction, etc.). Establishment of empirical rules and correlations between superconductivity and various crystallochemical and physical properties within a series of materials can produce only an incomplete picture.

6.3.1 Generalizations about Superconductivity in Superlattices

The high temperature superconductors (YBa$_2$Cu$_3$O$_y$ $T_c \approx 97$K, Tl$_2$Ba$_2$Ca$_2$Cu$_2$O$_{10}$, $T_c \approx 125$K, etc.) contain the complex architecture of a superlattice. The superlattice is a manipulation of the various intrinsic and extrinsic properties discussed in the previous sections. Certain structural, chemical, and electronic generalizations can be made about these copper oxide based systems$^{45}$:

1. All the presently known high-$T_c$ superconductors have orthorhombic or tetragonal symmetry, except Ba$_{1-x}$K$_x$BiO$_3$ which is cubic.
2. Superconductivity occurs within two-dimensional copper-oxygen arrays (CuO₂ planes) and in compounds exhibiting mixed valent copper. An average formal oxidation state of copper greater than +2 is achieved by cation substitutions (e.g. La⁺³: Sr⁺² or Ba⁺²:K⁺⁺), by introducing vacancies (Sr site in Bi₂SrₓCaCuxO₈), or by introducing excess oxygen. The Y-Ba-Cu-O exhibit mixed valence compounds with N/(N-1) electrons for the planes and N/(N-2) electrons for the chains.

3. Superconducting CuO₂ planes are separated by a charge reservoir layers (e.g. CuO chains for YBaCuO).

4. The electronic band at the Fermi level is strongly hybridized due to similarity in energy between Cu:3d and O:2p states.

5. Superconductivity appears in all cases at the doping level for which the antiferromagnetic insulating state looses its local moment to become metallic.

6. Charge transport occurs via electron holes belonging to the copper:3d and O:2p bands, and probably originates in the CuO₂ layers. In (NdₓCeₓ)CuO₄ electrons are only found as charge carriers.

Theses generalizations about the high-Tc copper based superconductors evolved from an intersection of experimental data from a plethora of copper oxide superlattices. Attempts are made to maximize these points of intersection to discover an underlying trend. One method is to specifically design defect chemistry superlattices layer by layer, and some as thin as 6.7 nm. The idea is to produce layered material that have the high carrier density and low electronic dimensionality, which is characteristic of high-Tc superconductors. This type of superconductor is made by alternating nanometer thick
layers of high carrier concentration ("charge reservoir layers") with nanometer thick layers of high carrier mobility. Some of these compounds have been produced via electrosynthesis. These compounds are electrodeposited on an electrode by pulsing the overpotential, between 90 and 300 mV for the Pb-Tl-O system.

6.3.2 The Irony of Superconductivity

Superconductivity is an enigma. A majority of the elements in the periodic table are superconducting. Most of the transition metals become superconductive at low temperatures. Most of the non-transition elements (Si, P, Ge, As, Se, Sb, Tl, Bi) and metals (Y, Cs, Br, V, Ce) only become superconducting under pressure. Several elements are superconducting when prepared as thin films (Li, Cr, Si, Eu), or irradiated by α-particles (Pd). Under normal conditions, the highest Tc’s among the pure elements are observed for Pb (Tc = 7.19K) and Nb (Tc = 9.25K).

The discovery of new superconductors is similar to the California gold rush from the 19th century. Modern scientist’s have attempted to leave no stone unturned in their synthesis of more exotic compounds. Compounds typically are designed around the profile of a previous discovery, but superconductivity seems to be discovered in compounds that are not expected to be superconductive. Until 1985, alloys were the focus for generating superconductive materials with the highest Tc = 26K for Nb₃Ge. Mixed valent metal oxides (ceramics) were considered to be insulators until the discovery of the YBa₂Cu₃O₇ superconductor in 1986. In 1989, the discovery of cubic Ba₄₋ₓKₓBiO₃ (Tc ≈ 32K for x ≈ 0.38), a doped semiconductor. In 1991, the alkali doped C₆₀ compounds were found with a Tc up to 33K.
The connection between structure and superconductivity is at present not very well defined, especially since the physical mechanisms for the phenomenon are unresolved for many systems, and particularly for the high temperature superconducting cuprates.

6.3.2.1 Doped Oxide Semiconductors: Low Symmetry vs. High Symmetry

Some oxide semiconductors exhibit superconductivity after they have been rendered metallic by doping. The Ba$_{1-x}$K$_x$BiO$_3$ compound is an exceptional case. In this compound, the two dimensional structures (CuO$_2$ planes) typical of the high-Tc superconductors are absent. Superconductivity was found to be phonon mediated through the three dimensional network of the BiO$_6$ octahedra. The oxygen isotope was utilized to establish the nature of the superconducting pairing mechanism. A coupling constant$^{46}$, $\alpha_{\text{ox}} = 0.4 \pm 0.1$ was obtained for Ba$_{0.625}$K$_{0.375}$BiO$_3$. Comparing this to YBa$_2$Cu$_3$O$_7$ with a much lower value of $\alpha_{\text{ox}} = 0.05$, indicates that the phonon-phonon coupling is negligible in the pair mechanism of these High-Tc materials. In comparison to the coupling constants measured for other superconductive materials, it would seem that a decreasing coupling constant follows increasing transition temperatures.

It is important to note that bonding in the Bi-O system$^{46}$ is quite different from the Cu-O materials. The Cu-O bonding is strongly $d$ in character, while the Bi $d$-orbitals are filled and are far below the Fermi surface. For the Bi-O superconductors, bands formed from the Bi(6s)-O(2p) orbitals are located at the Fermi surface, whereas the Cu(3d)-O(2p) are at the Fermi surface of the Cu-O superconductors.
6.3.2.2 Alkali Doped Buckminster Fullerenes

In 1991 superconductivity was discovered in alkali doped fullerene crystals of composition \( A_3C_{60} \) (\( A = K, \text{Rb}, \text{Cs} \))\(^{17,48} \). These compounds have high transition temperatures (18K for \( \text{K}_3C_{60} \), 28K for \( \text{Rb}_3C_{60} \), and 33K for \( \text{Cs}_2\text{RbC}_{60} \)). These compounds are cubic and alkali doped similar to BKBO. \( A_3C_{60} \) exhibits metallic behavior and hence superconductivity only when the alkali metal atoms donate valence electrons to the narrow conduction band, which then becomes half filled. The high \( T_c \) values seem to be accounted for within the BCS theory on the basis of electron-phonon coupling. This results from a high Debye temperature (due to the small size of the C atoms) combined with a relatively high electron-state density (narrow conduction band).

6.4 Correlation of Electronegativity and Transition Temperature

The connection between structure and superconductivity is an important step forward in understanding this phenomenon. An interesting paper by Nepela and McKay\(^{49} \) involves the correlation between electronegativity and transition temperature in high temperature superconductors. Their assumption was if pairing in high temperature superconductors is mediated by charge fluctuations, then critical temperature should scale with the difference in electronegativities between anions and cations (\( \Delta \chi \)).

Electronegativities for gaseous elements are taken from Pauling's work. For other elements, \( \chi \) is derived from the relation \( \chi = 0.44\varphi - 0.15 \), where \( \varphi \) is the work function. The average cation or anion electronegativity for each compound refers to the simple weighted average of its constituents:
\[
\left(\frac{1}{N_{A,C}}\right) \sum_{i} n_{A,C}^{i} \chi_{A,C}^{i}
\]

where

\[
N_{A,C} = \sum_{i} n_{A,C}^{i}.
\]

The electronegativity difference is \(\Delta \chi = (\chi_{A} - \chi_{B})\). The values for \(T_{c}\) and \(\Delta \chi\) are plotted in Figure 6-5. A best fit to the Cu and Ti based compounds yields:

\[
T_{c} = 646.2(\Delta \chi - 1.9) \text{K}.
\]

This equation can be used to predict the characteristic \(T_{c}\) as one isovalent cation or anion is substituted for another. Bismuth (Bi) and tungsten (W) based superconducting compounds are also included in Figure 6-5. The transition temperature for these compounds is less than the transition temperature of the Cu compounds at the same \(\Delta \chi\). However, the electronic specific heat, \(\zeta\), is an order of magnitude smaller. Thus, if \(T_{c}\) is normalized by \(1/\zeta\), these compounds would fit roughly on the Cu line. The significance

Figure 6-4  Graph depicting correlation between the transition temperature (\(T_{c}\)) and \(\Delta \chi\)(delta chi) for various superconducting metal oxides.

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of fluorine(F) substitution for oxygen(O) is truly intriguing. It would be interesting to substitute a fluorine(F) for an oxygen(O) in Ba$_{1-x}$K$_x$BiO$_3$ to make a Ba$_{1-x}$K$_x$BiO$_2$F compound.

6.5 Electrosynthesis of PdO$_2$ and AgO Compounds

Considering the intrinsic and extrinsic properties of semi and superconductors discussed in previous sections, PdO$_2$ and AgO are semiconductors that would be interesting to dope with various alkali and alkaline earth elements. Both Pd and Ag can produce unstable high oxidation states, Pd$^{4+}$ and Ag$^{3+}$, which should result in mixed valent compounds. The goal is to alter the electronic properties of these metal oxides by increasing average oxidation state of these elements, Pd $>^{+2}$ and Ag $>^{+2}$, to force a Jahn-Tellur distortion in an ABO$_3$ type compound.

6.5.1 Electrosynthesis of KBaPdO$_2$ in a PTFE Cell

PdCl$_2$ was reacted with HNO$_3$ to make soluble the Pd$^{2+}$ in an acidic solution. The red solution was then neutralized with KOH pellets. As the pH of the solution turned basic, a tan colored PdO$\cdot$H$_2$O compound began to precipitate out. The solution was separated from the precipitate by gravimetric filtration. The precipitate was washed three times with 500ml of boiling deionized water to removed the salts: K$^+$, Cl$^-$, NO$_3^-$). The PdO$\cdot$H$_2$O was placed in an oven to dry at a temperature of 150°C.

The setup for this electrosynthesis process is the same as the BKBO. 60 grams of KOH was placed in a Teflon cell and the pellets were melted at a temperature of 200°C. With stirring, 4.0 grams of Ba(OH)$_2$$\cdot$8H$_2$O were added to the melt followed by 2.0 grams of PdO$\cdot$H$_2$O. Stirring continued for an hour. A strip of palladium metal was used.
as the reference electrode. The temperature of the melt was increased to 225 °C. Under the Ar(H2O) cover gas the potentiostat was set at Ep=1.0 volts vs. Pd ref. The starting current was minimized to I= -80μA. The cell seemed stable for two hours and was allowed to proceed overnight. Upon inspection the following morning, it was found that the Teflon cell had completely corroded.

The process was repeated but very closely watched. 60 grams of KOH were placed in a Teflon cell and the pellets were melted at a temperature of 200 °C. With stirring, 4.0 grams of Ba(OH)2 · 8H2O were added to the melt followed by 2.0 grams of PdO · H2O. Stirring continued for an hour. The temperature of the melt was increased to 225 °C. Under the Ar(H2O) cover gas the potentiostat was set at Ep=1.0 volts vs. Pd ref. The starting current was minimized to I= -83μA. The cell was stable for 6 hours, when the electrocrystallization process (ECP) was halted. The following day the ECP was initiated and the temperature on the thermostat was stable. After 6 hours ECP was halted and melt and electrodes were inspected. Upon inspection, it was observed that the melt appeared like a molten plastic. Upon closer inspection, the inner walls of the Teflon cell were eroded close to the surface of the melt. It appears that the PdO had oxidized the Teflon polymer. The Teflon cell was salvaged and the search for an inert reaction cell was initiated.

6.5.2 Electrosynthesis of KBaPdO2 in Vitreous Carbon Cell

A cell made out of vitreous carbon was selected to replace the Teflon cell. The electrode holder fitted perfectly on the new cell. The process was repeated as before. 40 grams of KOH were placed in a Teflon cell and the pellets were melted at a temperature
of 200 °C. With stirring, 3.0 grams of Ba(OH)$_2$·8H$_2$O were added to the melt followed by 1.5 grams of PdO·H$_2$O. Stirring continued for an hour. Upon removal of the Teflon stir bar, prior to initiating the electrocrystallization process, a ring of palladium metal was observed around the surface of the melt. Apparently the palladium was reduced by the carbon in the cell.

6.5.3 Electrosynthesis I of KBaPdO$_2$ in a Nickel Crucible

The solution to the materials problem was to utilize all material that could not be oxidized by palladium. The best choice was platinum, but the price would be extremely high. The most available and affordable was nickel. The 30ml nickel crucible was placed inside the 100ml Teflon cell. The Teflon cell was used to support the lid containing the electrodes. 25 grams of KOH pellets were placed to the nickel crucible, and melted at a temperature of 200 °C. Stirring with a silver spatula, 2.0 grams of Ba(OH)$_2$·8H$_2$O were added to the melt followed by 1.5 grams of PdO·H$_2$O. Stirring lasted about a minute. The temperature of the melt was increased to 230 °C. Under the Ar(H$_2$O) cover gas the potentiostat was set at $E_p=1.0$ volts vs. Pd ref. The starting current was minimized to $I=-325\mu A$. The high current is a result of the conductivity of the nickel crucible. ECP was closely monitored. The cell current had increased $20\mu A$ after twenty minutes. ECP was stopped for ten minutes to disrupt the equilibrium of rapid nucleation. This is, in effect, pulsing the potential except the pulse lasted twenty minutes. This was continued twice an hour for six hours. The final current was $I=-0.585mA$. The next day the working electrode was adjusted to minimized the starting current at $I=-0.467mA$. The same procedure was continued with a pulse of twenty minutes and break for ten minutes, for
six hours. The final current was I = -0.85mA. The electrodes were inspected for crystals. The counter electrode contained a small amount of metal, and the working electrode contained a small dark blue mass of crystals. The working electrode was placed in a beaker of deionized water for thirty minutes then the crystals were placed on a piece of filter paper and inspected under the microscope. The largest crystals were of the dimensions of 0.075mm x 0.05mm x 0.025mm. Several of the crystals were mounted for single crystal X-ray diffraction. The crystals revealed considerable disorder with extremely broad and irregular peaks. A unit cell could not be indexed.

Figure 6-5 The morphology of the crystals recovered from electrosynthesis in a nickel crucible.

6.5.4 Electrosynthesis of KYPdO$_3$ in a Nickel Crucible

The procedure is similar to the previous experiment. The 30ml nickel crucible was placed inside the 100ml Teflon cell and to it were added 25 grams of KOH pellets. The KOH pellets were melted at a temperature of 200°C. Stirring with a silver spatula, 2.0 grams of Y$_2$O$_3$ were added to the melt followed by 1.5 grams of PdO·H$_2$O. Stirring lasted about a minute. The temperature of the melt was increased to 230°C. Under the Ar(H$_2$O) cover gas the potentiostat was set at Ep=1.0 volts vs. Pd ref. The starting current was minimized to I = -310μA and ECP was closely monitored. The cell current had increased 15μA after twenty minutes. ECP was stopped for ten minutes to disrupt the equilibrium of rapid nucleation. This was continued three times an hour for six hours.
The final current was \( I = -0.475 \text{mA} \). The next day the working electrode was adjusted to minimize the starting current to \( I = -0.420 \text{mA} \). The same procedure was continued with a pulse of twenty minutes and break for ten minutes, for six hours. The final current was \( I = -0.785 \text{mA} \). The electrodes were inspected for crystals. The counter electrode contained a small amount of metal (Pd or Ni?), and the working electrode contained a small blue-purple mass or crystals. The working electrode was placed in a beaker of deionized water for thirty minutes then the crystals were placed on a piece of filter paper and inspected under the microscope. The crystals did not have a regular shape and were somewhat curved. They seemed amorphous and glassy. The product yield was considerably less than the previous experiment. The reason could be the lack of solubility of the \( \text{Y}_2\text{O}_3 \) for which a considerable amount was recovered after the melt was neutralized. Better results probably could be achieved with \( \text{Y}_2\text{O}_3 \cdot \text{H}_2\text{O} \) or \( \text{Y(OH)}_3 \).

### 6.5.5 Electrosynthesis of KUPdO$_3$ in a Nickel Crucible

The procedure is similar to the previous experiment. The 30ml nickel crucible was placed inside the 100ml Teflon cell and to it were added 25 grams of KOH pellets. The KOH pellets were melted at a temperature of 200 °C. Stirring with a silver spatula, 2.0 grams of \( \text{UO}_2 \) were added to the melt followed by 1.5 grams of PdO \( \cdot \text{H}_2\text{O} \). Stirring lasted about a minute. The temperature of the melt was increased to 230 °C. Under the \( \text{Ar(H}_2\text{O)} \) cover gas the potentiostat was set at \( E_p = 1.0 \) volts vs. Pd ref. The starting current was minimized to \( I = -285 \mu\text{A} \) and the ECP was closely monitored. The cell current had increased 18\( \mu\text{A} \) after twenty minutes. ECP was stopped for ten minutes to disrupt the equilibrium of rapid nucleation. This was continued three times an hour for
six hours. The final current was $I = -0.430 mA$. The next day the working electrode was adjusted to minimized the starting current to $I = -0.405 mA$. The same procedure was continued with a pulse of twenty minutes and break for ten minutes, for six hours. The final current was $I = -0.745 mA$. The electrodes were inspected for crystals. The counter electrode contained a small amount of metal (Pd or Ni?), and the working electrode contained a large brown black mass of crystals. The working electrode was placed in a beaker of deionized water for thirty minutes then the crystals were placed on a piece of filter paper and inspected under the microscope. The crystals were hexagonal in shape with a slight curved in the center of the crystal and extremely thin. The product yield was the most by far. The reason could be the relative solubility of $\text{UO}_2 > \text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O} > \text{Y}_2\text{O}_3$. The dimensions of these crystals were about $0.07 \text{mm} \times 0.05 \text{mm} \times 0.015 \text{mm}$.

Figure 6-6 The morphology of the crystals resulting from an introduction of $\text{UO}_2$ into the melt.

Several of the crystals were mounted for single crystal X-ray diffraction. The crystals revealed considerable disorder with extremely broad and irregular peaks. A unit cell could not be indexed.

6.5.6 Electrosynthesis II of $\text{KBaPdO}_2$ in a Nickel Crucible

A 100ml nickel, straight walled crucible was obtained and replaced the use of the smaller crucible and the Teflon cell. This was necessary to scale up the reactants to
generate larger crystals. The Teflon lid containing the electrodes fitted perfectly onto the crucible. 50 grams of KOH pellets were placed in the nickel crucible, which were melted at a temperature of 200°C. Stirring with a silver spatula, 4.0 grams of Ba(OH)$_2$$\cdot$8H$_2$O were added to the melt followed by 2.0 grams of PdO. In this experiment, anhydrous PdO was used to increase the Pd content in the melt. Stirring lasted about a minute. The temperature of the melt was increased to 230°C. Under the Ar(H$_2$O) cover gas the potentiostat was set at $E_p$=1.0 volts vs. Pd ref. The starting current was minimized to $I$=-425μA. The high current is a result of the conductivity of the larger nickel crucible. The ECP process was closely monitored. The cell current did not increase much after several hours up to $I$=-435μA. ECP and stopped after six hours. The final current was $I$=-0.445mA.

The next day the working electrode was adjusted to minimized the starting current. Beginning ECP at $I$=-0.440mA. After six hours ECP was halted, the current reading was $I$=-0.450mA. The next day the working electrode was adjusted to minimize the starting current to $I$=-0.445mA. After six hours, ECP was halted at the current reading $I$=-0.4650mA. On the fourth day, ECP was begun at a starting current of $I$=-0.455mA. After six hours ECP was halted at the current reading was $I$=-0.4650mA. After very little change in the current of the cell, the electrodes were inspected. No metal was found on the counter electrode nor were any crystals recovered. Instead, after neutralization of the melt, almost all of the anhydrous PdO was recovered. The problem resembled that of the Y$_2$O$_3$. PdO must be hydrated in order for the Pd species to be solvated and undergo oxidation.
Considering the expense of sufficient amounts of PdO·H₂O for electrosynthesis, further investigations were suspended. My attention turned to a cheaper, more readily available compound, Ag₂O.

6.5.7 Electrosynthesis of KBaAgO₂ in a Teflon Cell

In AgO, the Ag²⁺ is a result of the disproportionation of Ag²⁺ to Ag⁺ and Ag³⁺, which is an interesting mixed valent case. AgO, a semiconductor, would be an interesting candidate to dope with potassium (K) and other elements. In particular, it would be interesting to increase the valency to greater than 2. The setup for this electrosynthesis process is the same as that for BKBO. Since the redox couple Ag⁺ → Ag⁺², with E₀ = 0.65 volts(SHE), is not as strong an oxidizer as Pd⁺² → Pd⁺⁴, with E₀ = 0.95 volts(SHE), the 100ml Teflon cell was utilized. AgO might be a preferred starting material, but none was available.

60 grams of KOH were placed in a Teflon cell and the pellets were melted at a temperature of 200 °C. With stirring, 4.0 grams of Ba(OH)₂·8H₂O were added to the melt followed by 4.0 grams of Ag₂O. Stirring continued for an hour. A strip of silver metal was used as the reference electrode. The temperature of the melt was increased to 225 °C. Under the Ar(H₂O) cover gas the potentiostat was set at E₀ = 0.8 volts vs. Ag ref. This potential was chosen to generate an overpotential. This should be necessary to increase the concentration of Ag⁺³ in the lattice, but what the appropriate overpotential should be is uncertain.

The starting current was set at I = -44μA. The cell seemed stable for two hours and was allowed to proceed overnight. Upon inspection the following morning the
current reading had increased to $I = -1.5\, mA$. Electrocryrstallization was halted and the electrodes inspected. It was discovered that the melt contained an enormous amount of silver metal. Apparently, any products formed were completely soluble in this aggressive molten salt environment. The next experiment included an aqueous basic environment.

### 6.5.8 Electrosynthesis I of $\text{KBaAgO}_2$ in $2\text{M KOH}$

A $2\text{M KOH}$ solution was prepared with semiconductor grade pellets (99.998\%). A 500ml Pyrex beaker was chosen for the reaction vessel. A Teflon support was also incorporated to hold the three electrodes.

250mls of $2\text{M KOH}$ solution was placed in a 500ml Pyrex beaker. With stirring, 2.0 grams of $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ were added followed by 2.0 grams of $\text{Ag}_2\text{O}$. While stirring, it was noticed that a considerable amount of $\text{Ag}_2\text{O}$ remained undissolved. The speed of the stir bar was reduced as much as possible. The potentiostat was set at $E_p = 0.8$ volts vs. Ag ref. The starting current was minimized to $I = -25\mu\text{A}$. The cell was stable for 6 hours with minimal change in the current and no crystal formation was noticed on the working electrodes. The reaction was allowed to proceed overnight. Upon inspection the following morning, no crystal formation was noticed on the electrodes, but black specks, possibly crystals, were swirling around in solution. Some of the solution was pipetted out and inspected under the microscope. The specks turned out to be a black powder. The electrocrystallization process was halted.

A literature search was then performed on the crystallization of $\text{Ag}_2\text{O}$. It was discovered that prior to 1969, $\text{Ag}_2\text{O}$ was synthesized electrochemically and the resulting product was a black powder. The synthesis of large single crystals of $\text{Ag}_2\text{O}$ was a
problem during the 1960's until Nanis and Kim\textsuperscript{50} electrolytically grew 1cm sized crystals in a 2M AgNO\textsubscript{3} solution. The potential was $E_p = 0.64$ volts vs. Ag ref.

### 6.5.9 Electrosynthesis II of KBaAg\textsubscript{2} in 2M KOH

A 2M AgNO\textsubscript{3} solution was prepared with the addition of grams to 250mIs of a 2M KOH solution was placed in 500ml Pyrex beaker. After dissolution of AgNO\textsubscript{3}, 2.0 grams of Ba(OH)\textsubscript{2} \cdot 8H\textsubscript{2}O were added. The speed of the stir bar was lowered as much as possible. The potentiostat was set at $E_p = 0.8$ volts vs. Ag ref. The starting current was minimized to $I = -28\mu$A. The cell was stable for 6 hours with minimal change in the current and no crystal formation was noticed on the working electrodes. The reaction was allowed to proceed overnight. Upon inspection the following morning, there was some gray precipitate in the solution, possibly Ag\textsubscript{2}O and a few black crystals on the working electrode (anode). The electrocrystallization process was continued for another 24 hours. On the second day, there was no noticeable increase in crystal growth, but more black powder had formed in solution. Apparently, a basic solution favors the black powder of AgO irregardless of the addition of AgNO\textsubscript{3}.

The few crystals that remained on the anode were dark black and orthorhombic in shape as opposed to the cubic black crystals of AgO. The crystals were somewhat intergrown making isolation difficult. The largest was about $0.05\text{mm} \times 0.05\text{mm} \times 0.025\text{mm}$ The largest crystal broke while trying to isolate the crystals. It probably would be necessary to incorporate Ba(NO\textsubscript{3})\textsubscript{2}, or any nitrated form of an element, also into the 2M AgNO\textsubscript{3} solution for a future experiment with this system.
6.6 Conclusions

The investigation of (AB)PdO\textsubscript{2}, (AB)AgO\textsubscript{2} or \textsubscript{3}, and various other mixed/valent compounds would be an interesting research direction to follow. Interesting superconducting properties might be a result of mixed valency; in particular if one of the valences is a strong oxidizing agent, Pd\textsuperscript{4+}, Ag\textsuperscript{+3}, Cu\textsuperscript{+3}, etc.. Electrosynthesis is an excellent method for doping and incorporating unstable high oxidation states into a crystalline lattice. Additionally, the electrosynthesis aids in increasing oxygen coordination around the central atom. Possibly, the electrosynthesis of a double mixed valent compound should be considered. Careful attention of the redox potentials would be necessary to synthesize a double mixed valent compound. The redox potentials should be close together. The overpotential of the cell would have to be greater than the potential for the strongest oxidizing agent. The introduction of fluorine(F) for an oxygen(O) in Ba\textsubscript{1-x}K\textsubscript{x}BiO\textsubscript{3} to make a mono-fluorine substituted Ba\textsubscript{1-x}K\textsubscript{x}BiO\textsubscript{3}F or other fluorine substituted mixed valent compounds would be intriguing.
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APPENDIX A

POWDER DIFFRACTION PATTERNS FOR ANHYDRITE/GYPSUM, QUARTZ/CALCITE/DOLOMITE, AND ANHYDRITE/GYPSUM/QUARTZ/CALCITE/DOLOMITE MIXTURES

XRD LAB GEOLOGY & GEOPHYSICS DEPT.

Diffraction software: PC-APD

Sample Identification: AG001BB
Data measured at: 3/23/93 1:22 P.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochrometer used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 1376.41
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Anhydrite 100%, Gypsum 0%
XRD LAB GEOLOGY & GEOPHYSICS DEPT.

Diffraction software: PC-APD

Sample Identification: AG002BB
Data measured at: 3/23/93 14:39

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha 1 [\(\lambda\)]: 1.5406
Wavelength Alpha 2 [\(\lambda\)]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle \(2^\circ \theta\): 2
End angle \(2^\circ \theta\): 50
Step size \(2^\circ \theta\): 0.04
Maximum intensity: 1303.21
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 17
Anhydrite 99%, Gypsum 1%
XRD LAB GEOLOGY & GEOPHYSICS DEPT.

Diffraction software: PC-APD

Sample Identification: AG003BB
Data measured at: 3/24/93 7:33

Diffractometer type: PW1710 BASED
  Tube anode: Cu
  Generator tension [kV]: 40
  Generator current [mA]: 21
  Wavelength Alpha1 [Å]: 1.5406
  Wavelength Alpha2 [Å]: 1.54439
  Intensity ratio (alpha1/alpha2): 0.5
  Divergence slit: AUTOMATIC
  Irradiated length [mm]: 12
  Receiving slit: 0.2
  Monochromator used: YES

Start angle [° θ]: 2
End angle [° θ]: 50
Step size [° θ]: 0.04
Maximum intensity: 1383.84
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 18
Anhydrite 95%, Gypsum 5%
Diffraction software: PC-APD

Sample Identification: AG004BB
Data measured at: 3/24/1993 8:06:00 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [\(\lambda\)]: 1.5406
Wavelength Alpha2 [\(\lambda\)]: 1.54439
Intensity ratio (\(\alpha_1/\alpha_2\)): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [\(2^\circ \theta\)]: 2
End angle [\(2^\circ \theta\)]: 50
Step size [\(2^\circ \theta\)]: 0.04
Maximum intensity: 1204.09
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 22
Anhydrite 90%, Gypsum 10%
Sample Identification: AG005BB
Data measured at: 3/24/93 8:45 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 1036.84
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 20
Anhydrite 70\%. Gypsum 30\%
Diffraction software: PC-APD

Sample Identification: AG006BB
Data measured at: 3/24/1993 9:13 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 852.64
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 27
Anhydrite 50%, Gypsum 50%
XRD LAB GEOLOGY & GEOPHYSICS DEPT.

Diffraction software: PC-APD

Sample Identification: AG007BB
Data measured at: 3/24/1993 9:45 A.M.

Diffractometer type: PW1710 BASED
 Tube anode: Cu
 Generator tension [kV]: 40
 Generator current [mA]: 21
 Wavelength Alpha1 [\(\lambda\)]: 1.5406
 Wavelength Alpha2 [\(\lambda\)]: 1.54439
 Intensity ratio (alpha1/alpha2): 0.5
 Divergence slit: AUTOMATIC
 Irradiated length [mm]: 12
 Receiving slit: 0.2
 Monochromator used: YES

Start angle \([2^\circ \theta]\): 2
End angle \([2^\circ \theta]\): 50
Step size \([2^\circ \theta]\): 0.04
Maximum intensity: 1339.56
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 26
Anhydrite 30%, Gypsum 70%
XRD LAB GEOLOGY & GEOPHYSICS DEPT.

Diffraction software: PC-APD

Sample Identification: AG008BB
Data measured at: 3/24/1993 12:31 P.M.

Diffractometer type: PW1710 BASED
  Tube anode: Cu
  Generator tension [kV]: 40
  Generator current [mA]: 21
  Wavelength Alpha1 [Å]: 1.5406
  Wavelength Alpha2 [Å]: 1.54439
  Intensity ratio (alpha1/alpha2): 0.5
  Divergence slit: AUTOMATIC
  Irradiated length [mm]: 12
  Receiving slit: 0.2
  Monochromator used: YES

  Start angle [2° Θ]: 2
  End angle [2° Θ]: 50
  Step size [2° Θ]: 0.04
  Maximum intensity: 1892.25
  Time per step [s]: 1
  Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
  Peak base width: 2
Minimum significance: 0.75
Number of peaks: 25
Anhydrite 10%, Gypsum 90%
Diffraction software: PC-APD

Sample Identification: AG009BB
Data measured at: 3/24/1993 1:14 P.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochrometer used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 2106.81
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 25
Anhydrite 5%. Gypsum 95%
Diffraction software: PC-APD

Sample Identification: AG010BB
Data measured at: 3/25/1993 7:59 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [° θ]: 2
End angle [° θ]: 50
Step size [° θ]: 0.04
Maximum intensity: 2034.01
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 27
Anhydrite 1%, Gypsum 99%
XRD LAB GEOLOGY & GEOPHYSICS DEPT.

Diffraction software: PC-APD

Sample Identification: AG011BB
Data measured at: 3/25/1993 9:14 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [\(\lambda\)]: 1.5406
Wavelength Alpha2 [\(\lambda\)]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochrometer used: YES

Start angle [\(2^\circ \Theta\)]: 2
End angle [\(2^\circ \Theta\)]: 50
Step size [\(2^\circ \Theta\)]: 0.04
Maximum intensity: 1980.25
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 23
Anhydrite 0%. Gypsum 100%
Diffraction software: PC-APD

Sample Identification: QCDO1BB
Data measured at: 3/22/1993 1:07:00 P.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 5198.41
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 9
Quartz 100%
Diffraction software: PC-APD

Sample Identification: QCD02BB
Data measured at: 3/22/1993 1:31 P.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 1608.01
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 11
Diffraction software: PC-APD

Sample Identification: QCD03BB
Data measured at: 3/22/1993 1:58 P.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [\(\lambda\)]: 1.5406
Wavelength Alpha2 [\(\lambda\)]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochrometer used: YES

Start angle [2\(^\text{o}\) \(\theta\)]: 2
End angle [2\(^\text{o}\) \(\theta\)]: 50
Step size [2\(^\text{o}\) \(\theta\)]: 0.04
Maximum intensity: 2116
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 12
Dolomite 100%
Diffraction software: PC-APD

Sample Identification: QCD04BB
Data measured at: 3/22/1993 7:20 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochrometer used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 1274.49
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 16

157
Calcite 75%, Quartz 25%
Diffraction software: PC-APD

Sample Identification: QCD05BB
Data measured at: 3/23/1993 7:43 A.M

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochrometer used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 3069.16
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 17
Calcite 25%, Quartz 75%
Diffraction software: PC-APD

Sample Identification: QCD06BB
   Data measured at: 3/23/1993  8:12 A.M

Diffractometer type: PW1710 BASED
   Tube anode: Cu
   Generator tension [kV]: 40
   Generator current [mA]: 21
   Wavelength Alpha1 [\(\lambda\)]: 1.5406
   Wavelength Alpha2 [\(\lambda\)]: 1.54439
   Intensity ratio (alpha1/alpha2): 0.5
   Divergence slit: AUTOMATIC
   Irradiated length [mm]: 12
   Receiving slit: 0.2
   Monochrometer used: YES

   Start angle \([2^\circ \theta]\): 2
   End angle \([2^\circ \theta]\): 50
   Step size \([2^\circ \theta]\): 0.04
   Maximum intensity: 1738.89
   Time per step [s]: 1
   Type of scan: STEP

   Minimum peak tip width: 0
   Maximum peak tip width: 1
   Peak base width: 2
   Minimum significance: 0.75
   Number of peaks: 19
Dolomite 75%. Quartz 25%
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Diffraction software: PC-APD

Sample Identification: QCD07BB
Data measured at: 3/23/1993 8:38 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha 1 [\(\lambda\)]: 1.5406
Wavelength Alpha 2 [\(\lambda\)]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [\(2^\circ \Theta\)]: 2
End angle [\(2^\circ \Theta\)]: 50
Step size [\(2^\circ \Theta\)]: 0.04
Maximum intensity: 3696.64
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 20
Diffraction software: PC-APD

Sample Identification: QCD08BB
Data measured at: 3/23/1993 9:11 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [\(\lambda\)]: 1.5406
Wavelength Alpha2 [\(\lambda\)]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochrometer used: YES

Start angle \([2^\circ \theta]\): 2
End angle \([2^\circ \theta]\): 50
Step size \([2^\circ \theta]\): 0.04
Maximum intensity: 1451.61
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 20
Calcite 25%, Dolomite 75%

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Diffraction software: PC-APD

Sample Identification: QCD09BB
Data measured at: 3/23/1993 9:40 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochrometer used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 1451.61
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 18
Calcite 75%, Dolomite 25%
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Diffraction software: PC-APD

Sample Identification: QCD010BB
Data measured at: 3/23/1993 10:42 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 1918.44
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 21
Calcite 40%, Dolomite 10%, Quartz 50%
Diffraction software: PC-APD

Sample Identification: QCD011BB
Data measured at: 3/23/1993 11:10 A.M.

Diffractometer type: PW 1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 1806.25
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 25
Calcite 10%, Dolomite 80%, Quartz 10%
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Diffraction software: PC-APD

Sample Identification: QCD012BB
Data measured at: 3/23/1993 11:50 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° θ]: 2
End angle [2° θ]: 50
Step size [2° θ]: 0.04
Maximum intensity: 1681
Time per step [s]: 1
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 14
Calcite 90%, Dolomite 5%, Quartz 5%
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Diffraction software: PC-APD

Sample Identification: AGQCD1BB
Data measured at: 6/04/1993 12:51 P.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° Θ]: 10
End angle [2° Θ]: 50
Step size [2° Θ]: 0.02
Maximum intensity: 2391.21
Time per step [s]: 2
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 22
Anh 90%, Cal 3.3%, Dol 3.3%, Qtz 3.4%
Diffraction software: PC-APD

Sample Identification: AGQCD2BB
Data measured at: 6/04/1993 3:23 P.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [\(\lambda\)]: 1.5406
Wavelength Alpha2 [\(\lambda\)]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [\(2^\circ \theta\)]: 10
End angle [\(2^\circ \theta\)]: 50
Step size [\(2^\circ \theta\)]: 0.02
Maximum intensity: 1260.25
Time per step [s]: 2
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 32
Anh 45%, Cal 3.3%, Dol 3.3%, Gyp 45%, Qtz 3.4%
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Diffraction software: PC-APD

Sample Identification: AGQCD3BB
Data measured at: 6/07/1993 8:20 P.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [Å]: 1.5406
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° θ]: 10
End angle [2° θ]: 50
Step size [2° θ]: 0.02
Maximum intensity: 1303.21
Time per step [s]: 2
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 27
Cal 3.3%. Dol 3.3%. Gyp 90%. Qtz 3.4%
Diffraction software: PC-APD

Sample Identification: AGQCD4BB
Data measured at: 6/07/1993 10:19 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [\(\lambda\)]: 1.5406
Wavelength Alpha2 [\(\lambda\)]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [\(2^\circ \theta\)]: 10
End angle [\(2^\circ \theta\)]: 50
Step size [\(2^\circ \theta\)]: 0.02
Maximum intensity: 2152.96
Time per step [s]: 2
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 26
Anh 80\%, Cal 6.6\%. Dol 6.6. Qtz 6.8\%
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Diffraction software: PC-APD

Sample Identification: AGQCD5BB
Data measured at: 6/07/1993 12:20 P.M.

Diffractometer type: PW1710 BASED
  Tube anode: Cu
  Generator tension [kV]: 40
  Generator current [mA]: 21
  Wavelength Alpha1 [Å]: 1.5406
  Wavelength Alpha2 [Å]: 1.54439
  Intensity ratio (alpha1/alpha2): 0.5
  Divergence slit: AUTOMATIC
  Irradiated length [mm]: 12
  Receiving slit: 0.2
  Monochrometer used: YES

  Start angle [2° θ]: 10
  End angle [2° θ]: 50
  Step size [2° θ]: 0.02
  Maximum intensity: 1253.16
  Time per step [s]: 2
  Type of scan: STEP

  Minimum peak tip width: 0
  Maximum peak tip width: 1
  Peak base width: 2
  Minimum significance: 0.75
  Number of peaks: 37
Anh 40%, Cal 6.6%, Dol 6.6%, Gyp 40%, Qtz 6.8%
Diffraction software: PC-APD

Sample Identification: AGQCD6BB
Data measured at: 6/07/1993 2:59 P.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [\(\lambda\)]: 1.5406
Wavelength Alpha2 [\(\lambda\)]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° \(\theta\)]: 10
End angle [2° \(\theta\)]: 50
Step size [2° \(\theta\)]: 0.02
Maximum intensity: 1204.09
Time per step [s]: 2
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 31
Cal 6.6%, Dol 6.6%, Gyp 80%, Qtz 6.8%
Diffraction software: PC-APD

Sample Identification: AGQCD7BB
Data measured at: 6/08/1993 8:22 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [: 1.5406
Wavelength Alpha2 [: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochromator used: YES

Start angle [2° θ]: 10
End angle [2° θ]: 50
Step size [2° θ]: 0.02
Maximum intensity: 1971.36
Time per step [s]: 2
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 27
Anh 70%, Cal 10%, Dol 10%, Qtz 10%
Diffraction software: PC-APD

Sample Identification: AGQCD8BB
Data measured at: 6/08/1993 9:56 A.M.

Diffractometer type: PW1710 BASED
   Tube anode: Cu
   Generator tension [kV]: 40
   Generator current [mA]: 21
   Wavelength Alpha1 [\(\lambda\)]: 1.5406
   Wavelength Alpha2 [\(\lambda\)]: 1.54439
   Intensity ratio (alpha1/alpha2): 0.5
   Divergence slit: AUTOMATIC
   Irradiated length [mm]: 12
   Receiving slit: 0.2
   Monochromator used: YES

   Start angle [\(2^\circ \theta\)]: 10
   End angle [\(2^\circ \theta\)]: 50
   Step size [\(2^\circ \theta\)]: 0.02
   Maximum intensity: 1024
   Time per step [s]: 2
   Type of scan: STEP

   Minimum peak tip width: 0
   Maximum peak tip width: 1
   Peak base width: 2
   Minimum significance: 0.75
   Number of peaks: 33

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Anh 35%, Cal 10%, Dol 10%, Gyp 35%, Qtz 10%
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Diffraction software: PC-APD

Sample Identification: AGQCD9BB
Data measured at: 6/08/1993 11:42 A.M.

Diffractometer type: PW1710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 21
Wavelength Alpha1 [\(\lambda\)]: 1.5406
Wavelength Alpha2 [\(\lambda\)]: 1.54439
Intensity ratio (alpha1/alpha2): 0.5
Divergence slit: AUTOMATIC
Irradiated length [mm]: 12
Receiving slit: 0.2
Monochrometer used: YES

Start angle [\(2^\circ \theta\)]: 10
End angle [\(2^\circ \theta\)]: 50
Step size [\(2^\circ \theta\)]: 0.02
Maximum intensity: 1062.76
Time per step [s]: 2
Type of scan: STEP

Minimum peak tip width: 0
Maximum peak tip width: 1
Peak base width: 2
Minimum significance: 0.75
Number of peaks: 33
VITA

Patrick Allen Kolniak was born September 25, 1964, in Shreveport, Louisiana, where he lived most of his life. High school education was completed through Loyola College Prep School in 1983. He began studies at Louisiana State University at Shreveport in August of 1983 as a Biology major. In the spring of 1989, he received his Bachelor of Science degree in Chemistry. Continuing his education at LSU-S, he earned his Bachelor of Science degree in physics and math in the spring of 1990. In August of the same year, he moved to Baton Rouge and enrolled as a graduate student at Louisiana State University. On May 17, 1991, he married Donna Marie Wilson and became stepfather to Hali Soderman. Then on August 8, 1995, he became a father again with the birth of Camille Marie Kolniak. He is currently a candidate for the degree of Doctor of Philosophy with a major in physical chemistry. He is a member of the following societies: Kappa Sigma alumnus, Phi Lambda Upsilon.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Patrick Allen Kolniak

Major Field: Chemistry

Title of Dissertation: Synthesis and Physical Characterization of Solid State Materials

Approved:

[Signatures of Major Professor and Chairman, Dean of the Graduate School]

EXAMINING COMMITTEE:

[Signatures of committee members]

Date of Examination: 11/5/97