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Beta transmutations in apatite with ferric iron as electron acceptor – implication for nuclear waste
form development

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Abstract: Apatite-structured materials have been considered for immobilization of a number of fission products from reprocessing nuclear fuel because of their chemical durability as well as compositional and structural flexibility. It is hypothesized that the effect of beta decay on the stability can be mitigated by introducing appropriate electron acceptor at the neighboring sites in the structure. Decay series $^{137}\text{Cs} \rightarrow ^{137}\text{Ba}$ and $^{90}\text{Sr} \rightarrow ^{90}\text{Y} \rightarrow ^{90}\text{Zr}$ were investigated using a spin-polarized DFT approach to test the hypothesis. Apatites with compositions of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and $\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6\text{F}_2$ were selected as model systems for radionuclides Cs and Sr incorporation respectively. Ferric iron was introduced in the structure as an electron acceptor. Electron density of states, crystal and defect structure, and energies before and after beta decay were calculated. Calculated electron density of states suggests that the extra electron is localized at the ferric iron, which changes its oxidation state and becomes ferrous iron. The crystal and defect structures were analyzed based on the volume, lattice parameters, radial distribution functions, metal cation to coordinating oxygen distances, and the metaprism twist angle of apatite crystal structure. The results show that there are minor changes in the crystal and defect structure of $\text{CsFeCa}_8(\text{PO}_4)_6\text{F}_2$ with Cs^+ and Fe^{3+} substitutions undergoing $\text{Cs} \rightarrow \text{Ba}$ transmutation, and of $\text{Ca}_3\text{SrY}_4\text{Fe}_2(\text{SiO}_4)_6\text{F}_2$ with Sr^{2+} and Fe^{3+} substitutions undergoing $\text{Sr} \rightarrow \text{Y} \rightarrow \text{Zr}$ transmutations. The last decay change, from $\text{Y}^{3+} \rightarrow \text{Zr}^{4+}$, causes relatively larger changes in the local defect structure around Zr involving the coordination environment. The results on calculated cohesive energy suggest that transmutations of $\text{Cs}^+ \rightarrow \text{Ba}^{2+}$ and $\text{Sr}^{2+} \rightarrow \text{Y}^{3+} \rightarrow \text{Zr}^{4+}$ in both apatite compositions are energetically favorable, which are consistent with the minor structure distortions. The results confirm the structural and compositional adaptability of apatites upon beta transmutations. The study suggests that apatite-structured materials could be promising nuclear waste forms to mitigate the beta decay induced instability, by incorporating variable valence cations such as ferric iron in the structure. The study demonstrates a methodology which evaluates the structural stability of waste forms incorporating fission products undergoing beta decay.

1. Introduction

Sustainable nuclear energy requires radioactive nuclear wastes to be safely disposed. Currently, the long-term solution to high-level radioactive waste is to permanently place the waste in geological setting for over hundred thousand years. During past decades, to immobilize the radionuclides, various nuclear waste forms have been developed to incorporate radionuclides from reprocessing of the used nuclear fuel and from defense programs. For actinides, the primary focus has been oriented toward host materials that can withstand the substantial damage caused by alpha-decay.¹⁻⁷ For radioactive fission products from reprocessing of used nuclear fuel, since most of them (e.g., ^{135,137}Cs, ⁹⁰Sr, ¹²⁹I, ⁹⁹Tc) are beta-emitters, the radiation damage often is not a concern, while compositional change and chemical degradation are the focus. The most problematic ones among the radionuclides are those with low loading capacity, weak chemical binding in waste forms, and low affinity to engineering barriers and rocks in disposal environment, including Cs, Sr, Tc, and I. Borosilicate glass has been developed and produced at industrial scale to immobilize high-level waste by vitrification process.^{8,9} This is largely due to the chemical flexibility of the glass to incorporate a range of nuclear waste elements and the existing melting technology to produce the glass. In order to improve the durability, increase waste loading, and reduce waste volume and overall cost, glass-ceramic waste forms¹⁰⁻¹² and ceramic waste forms^{4,5,13-17} have been developed. Multiphase ceramics, such as the synthetic rock (SYNROC) targeting an assemblage of durable crystalline phases, have been demonstrated to incorporate various radioactive waste elements.^{15,18} The concept of SYNROC is based on the knowledge that naturally occurring minerals containing radioactive species are similar to the radionuclides in nuclear waste. Those mineral analogues have desirable characteristics that demonstrate their long-term durability in natural environment over geological timescales. Both glass-ceramic and ceramic waste forms are desired to incorporate radionuclides by targeting certain crystalline phases, such as zirconolite ($\text{CaZrTi}_2\text{O}_7$), perovskite (CaTiO_3), and hollandites ($\text{Ba}(\text{Al,Ti})_2\text{Ti}_6\text{O}_{16}$) in titanate-based ceramic nuclear wastes, and powellite (XMoO_4 , X= alkali, alkaline earths, lanthanides) and oxyapatite ($\text{Ca}_2\text{Ln}_8(\text{SiO}_4)_6\text{O}_2$) in borosilicate-based glass-ceramic waste form.^{8,10,15,18,19}

The crystalline phases incorporate radioactive fission products such as ^{137}Cs and ^{90}Sr at their lattice sites. However, ^{137}Cs has a half-life of about 30 years and is transmuted to ^{137}Ba (stable). ^{90}Sr has a half-life of about 29 years, which is first transmuted to ^{90}Y (half-life 64.2 hours) and then to ^{90}Zr (stable). In a beta decay, a nucleus is converted into another nucleus with the same mass and the atomic number increased by one while emitting an electron and electron antineutrino. The energy release includes the kinetic energies of the emitted electron, neutrino, and recoiling nucleus. Beta electron has kinetic energy in MeV range, which mainly causes electron excitations in the range of micrometers to millimeters in ceramics.²⁰ The kinetic energy of the recoil is in eV range, which is often lower than the threshold displacement energy of ceramic materials to cause damages. For apatite, threshold displacement energy is in the range of tens of eV.²¹ Thus, both the recoil and the beta electron often cause short-term changes that will dissipate with minor or no damages to the host as previous studies suggested,²²⁻²⁴ and will not be considered in this study. The sudden increase in the nuclear charge and the extra electron from the beta decay, which causes long lasting modifications of the host phase chemistry and changes of the thermodynamic and mechanical properties, is the focus of this study. These changes can produce thermodynamic instability of those phases and microstructure changes, which may fundamentally impair the performance of nuclear waste forms incorporating those radionuclides.^{25, 26}

The effect of a beta decay to the host phase largely depends on the nature of the decay and the host material.²³⁻³¹ Relatively short-lived radionuclide ^{134}Cs (~2 years) generated from ^{133}Cs (stable) through neutron irradiation was used to investigate transmutation effect on a number of nuclear waste glasses, pollucite, and supercalcine.²⁶ The results suggest that, with 6% of the total Cs had undergone transmutations, there were no significant changes that would be of any consequence of a waste management concern.²⁶ Based a chemical mitigation approach, crystalline phases that could accommodate the parent and daughter nuclides in the same crystalline phase were experimentally investigated using sol-gel method for ceramics including pollucite, perovskite, anorthite, and garnet.²⁵ Among the phases studied, perovskite was found to be able to incorporate both Ba and Cs in its structure.²⁵ These early studies suggested certain deleterious

effects on solid nuclear waste form.^{25, 26} Recent density functional theory studies of the effect of beta decay of ^{137}Cs ²⁹ and ^{90}Sr ^{23, 27, 29} in crystalline phases suggest important chemical and structural modifications of the host phases, which is characterized by the radioparagenesis process^{23, 29, 30, 32}, a structural and chemical transformation process over time resulting from beta decay of radionuclides in a solid phase. These studies proposed a strategy of "backward design", where the chemical evolution of the waste form is explicitly considered with the goal of achieving a defined end state, thus opening an avenue for long-term nuclear waste management. However, it is also necessary to consider strategies to reduce the impact from the chemical and valence changes of the constitute elements (e.g., $^{137}\text{Cs}^+$ to $^{137}\text{Ba}^{2+}$) and to prevent potential phase transition or decomposition. Such changes can also lead to volume change and unusual properties of the crystalline waste form,^{23, 32} resulting in dramatic changes in its durability. Compared to alpha decay damages to materials (mainly irradiation effect, i.e., defect formation and amorphization) that can be annealed upon increase of temperature and time, the beta-decay effect (mainly compositional effect) is permanent. Thus, the effect of chemical changes on the integrity of the waste forms needs to be evaluated for the design of advanced waste forms. In this regard, it is constructive to develop a strategy to evaluate and potentially mitigate the beta decay induced instability.

It would be desirable that both the extra electron and increased nuclear charge from beta decay are locally compensated within the phase without causing dramatic changes in the structure. First, this requires charge balance to be maintained, which can be achieved by chemical substitutions of variable valence ions to compensate the extra electron and increased nuclear charge. In addition, the structure must be flexible enough to accommodate the changes in the valence and size of the nuclides.^{25, 26, 33, 34} For instance, when a monovalent cation (e.g., $^{137}\text{Cs}^+$) is transmuted to a divalent cation (e.g., $^{137}\text{Ba}^{2+}$), the transmutation could be coupled to a substitution with an electron acceptor (i.e., a nuclide with its valence state to be reduced) to retain the charge neutrality of the host phase. The lattice sites must be of suitable size and similar bonding coordination environment for both parent and daughter nuclides, in order to accommodate the transmutation and to trap the electron. Although it is theoretically possible for a daughter nuclide to have the same valence

state as the parent nuclide, it leads to exotic rare oxidation state that may not be stable at normal conditions (e.g., $^{137}\text{Cs}^+$ to $^{137}\text{Ba}^{1+}$). These requirements point to materials having chemical and structural flexibility with a range of chemical substitutions. While the composition of nuclear glass is known to be flexible and bonding ordering in glass is considered short-ranged, the structural accommodability upon beta transmutation is unknown. Since glasses are formed from melts upon cooling in a 3-D network of interconnected structural blocks with a fractal structural geometry, beta transmutation can cause disruptions of the 3-D interconnected structural blocks, potentially resulting in instability of the glass. Many natural minerals with potential interests to nuclear waste forms have structural and compositional flexibility such as apatite $\text{A}_5(\text{XO}_4)_3\text{Z}$ ($\text{A} = \text{Na}^+, \text{K}^+, \text{Cs}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Cd}^{2+}, \text{Pb}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{REE}^{3+}, \text{and Ac}^{4+}$, $\text{X} = \text{P}^{5+}, \text{Si}^{4+}, \text{S}^{6+}, \text{V}^{5+}, \text{Cr}^{5+}, \text{As}^{5+}, \text{Mn}^{5+}, \text{Ge}^{4+}$, $\text{Z} = \text{OH}^-, \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{O}^{2-}, \text{CO}_3^{2-}, \text{and IO}_3^-$), powellite related minerals – scheelite and fergusonite ABO_4 ($\text{A} = \text{Ca}, \text{Pb}, \text{Ba}, \text{Y}, \text{La}, \text{Ce}, \text{Nd}, \text{B} = \text{Mo}, \text{W}, \text{Nb}, \text{Ti}$), hollandite AB_8O_{16} ($\text{A} = \text{Cs}, \text{Sr}, \text{Ba}, \text{Rb}, \text{B} = \text{Al}, \text{Ti}, \text{Fe}, \text{Mn}$), crichtonite $(\text{Ca}, \text{Sr}, \text{La}, \text{Ce}, \text{Y})(\text{Ti}, \text{Fe}, \text{Mn})_{21}\text{O}_{38}$, murataite $(\text{Y}, \text{Na})_6(\text{Zn}, \text{Fe})_5(\text{Ti}, \text{Nb})_{12}\text{O}_{29}(\text{O}, \text{F})_{14}$. Among these minerals, apatite shows great structural and compositional flexibility, which is demonstrated by the fact that the apatite structure can deviate from hexagonal symmetry while still maintaining the topology of the crystal structure.³⁵⁻³⁷

In apatite ($\text{A}_5(\text{XO}_4)_3\text{Z}$), A cation occupies two crystallographic sites (two at site-I and three at site-II), X often forms tetrahedron with oxygen, and Z occupies the structural channel.^{35, 36} Because its multiple crystallographic sites can be occupied by elements with different charges, changes associated with the valence and identity of radioactive elements resulting from radioactive decay of those beta emitters, e.g., ^{137}Cs and ^{90}Sr , could be potentially offset by a charge transfer between the sites and structural distortions within the phase. This charge transfer and structural distortion, preferably but not necessarily local within a couple of bond distance, would prevent possible phase transition or decomposition caused by the decay without compromising the integrity of the phase. The emitted electron could be trapped by a variable valence metal ion in the structure, and the transmuted element (e.g., ^{137}Ba , $^{90}\text{Y}/^{90}\text{Zr}$) remains in the structure. Thus, apatite-structured phases may be tolerant against or can potentially mitigate the aging effect of

radionuclides from radioparagenesis.

The purpose of this study is to test the above hypothesis that apatite-structured phases can tolerate structure and energetic instability caused by beta decay of fission products ^{137}Cs and ^{90}Sr by introducing ferric iron as electron acceptor in the neighboring sites of the crystal structure. Electron density of states, crystal and defect structure, and cohesive energies of before and after beta decay were calculated using a spin-polarized DFT approach. The results are expected to shed light on nuclear waste form design and evaluation of the structural instability caused by incorporated fission products undergoing beta decay.

2. Methods

Density functional theory with generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional³⁸ as implemented in the Vienna ab initio simulation package (VASP)^{39, 40} was employed for the structural optimization and total energy calculation. In the calculations, only iron, which is introduced as an electron acceptor, has open shell. As the first row transition metal, the spin-orbit coupling of iron is less important than other terms in the Hamiltonian for structure and energetic calculations and can be neglected as discussed recently for metal complexes and oxides.⁴¹⁻⁴³ Therefore, a spin-polarized DFT approach was used in the calculations. Total energy $E_{TOT}[\rho_\alpha, \rho_\beta]$ is expressed in terms of $\rho_\alpha(\vec{r})$ and $\rho_\beta(\vec{r})$, which are the spin-up and spin-down electron densities, corresponding to the diagonal elements in spin space. Calculations were done with PAW formalism,^{44, 45} which was developed using concept of pseudopotentials⁴⁶ in the plane-wave basis. A self-consistency cycle with a Pulay mixer and an iterative matrix diagonalization scheme was used to calculate the Kohn Sham (KS) state until the difference of the total energy less than 0.0001 eV. All atoms were allowed to move, and system volume was allowed to change. The k-meshes were generated in the Brillouin zone with a $2 \times 2 \times 3$ Monkhorst-Pack grid. The energy cutoff was set as 520 eV. Both Brillouin zone sampling and energy cutoff were fully tested for convergence, and produced satisfactory results.

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ was selected as a model system for Cs incorporation. Both Cs and Ba can substitute Ca in the $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$.^{47, 48} Ferric iron, Fe^{3+} , is introduced at the neighboring site of Cs^+ to maintain the

charge neutrality for the coupled-substituted ($\text{Cs}^+ + \text{Fe}^{3+} \rightarrow 2 \text{Ca}^{2+}$) in $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$; it also serves as an electron acceptor. For Sr^{2+} incorporation, $\text{Y}_4\text{Ca}_2(\text{SiO}_4)_6\text{F}_2$ was selected as a model.⁴⁹ Since ^{90}Sr undergoes a two-step decay to ^{90}Y and then ^{90}Zr , each Sr^{2+} needs two Fe^{3+} . In this case, Sr^{2+} substitutes Ca^{2+} ($\text{Sr}^{2+} \rightarrow \text{Ca}^{2+}$) and Fe^{3+} substitutes Y^{3+} ($\text{Fe}^{3+} \rightarrow \text{Y}^{3+}$). Apatite has been shown to be capable of incorporating quadrivalent ions such as Th and U by coupled substitution.⁵⁰⁻⁵² It is expected Zr^{4+} to be able to be incorporated in the apatite structure. All the substitutions are treated as defect in the structure. After the transmutations, the lowest energy configurations for the reduced iron (Fe^{2+}) and transmuted ions (Ba^{2+} , Y^{3+} , Zr^{4+}) may be different from the initial configurations. In this study, Fe^{2+} , Ba^{2+} , Y^{3+} , and Zr^{4+} are kept at the same positions of the Fe^{3+} , Cs^+ , and Sr^{2+} respectively. The calculated results are expected to provide an upper bound in terms of the total energy.

The chemical changes involving the beta decay of ^{137}Cs can be represented as a reaction: $^{137}\text{Cs} \rightarrow ^{137}\text{Ba} + e^-$. In order to evaluate energetics of this reaction, the equation needs to be chemically balanced if the reaction is to be treated as a regular substitution reaction. However, the reaction is a nuclear reaction with an atomic number change of the nucleus, and an appropriate way to evaluate the energetics associated with the change is to compare their cohesive energies, which was previously employed to compare the energetics of the phases with the transmutation product and its parent.^{23, 53, 54} The cohesive energy (E_c) is defined as the energy difference between a material and isolated atoms, The difference in the cohesive energy (ΔE_c) before and after transmutation ($A \rightarrow B$) was calculated as:

$$\Delta E_c = (\sum E_{B_{\text{atom}}} - E_{B_{\text{apatite}}}) - (\sum E_{A_{\text{atom}}} - E_{A_{\text{apatite}}}) \quad (1)$$

Where $E_{B_{\text{apatite}}}$ and $\sum E_{B_{\text{atom}}}$ denote for the total energy of the system and summation of all the isolated atoms after beta decay respectively, and $E_{A_{\text{apatite}}}$ and $\sum E_{A_{\text{atom}}}$ denote those before the decay. Equation (1) can be simplified as

$$\Delta E_c = (E_{B_{\text{atom}}} - E_{B_{\text{apatite}}}) - (E_{A_{\text{atom}}} - E_{A_{\text{apatite}}}) \quad (2)$$

Where E_{Atom} and E_{Atom} represent the energy of the isolated radionuclide before and after the decay. Based on the above definition, the higher the ΔE_c is, the more energetically favorable the transmutation product is than its parent.

Radial distribution functions (RDF) were calculated to evaluate the local structural changes involving the substituted sites using the Interactive Structure Analysis of Amorphous and Crystalline Systems (ISAACS).⁵⁵ The number of δr steps and the smoothing factor were set as 500 and 0.02 respectively.

3. Results and discussion

3.1 $^{137}\text{Cs} \rightarrow ^{137}\text{Ba}$ beta decay

Multiple configurations are possible for Cs^+ and Fe^{3+} coupled substitution ($\text{Cs}^+ + \text{Fe}^{3+} \rightarrow 2 \text{Ca}^{2+}$) in $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ because there are two Ca sites (site-I and site-II). The cation at site-I is coordinated with nine O^{2-} , while cation at site-II is coordinated to seven O^{2-} and one F.³⁶ Together with PO_4 groups, the Site-I cations with O form a framework structure. The Site-II cations are next to the channel site, which is occupied by anion F⁻. There are four possible configurations for the coupled substitution: Cs^+ at Site-I with Fe^{3+} at Site-I or Site-II, denoted as $\text{Cs}^+(\text{I}) - \text{Fe}^{3+}(\text{I})$ or $\text{Cs}^+(\text{I}) - \text{Fe}^{3+}(\text{II})$ respectively, and Cs^+ at Site-II with Fe^{3+} at Site-I or Site-II denoted as $\text{Cs}^+(\text{II}) - \text{Fe}^{3+}(\text{I})$ or $\text{Cs}^+(\text{II}) - \text{Fe}^{3+}(\text{II})$ respectively. Only neighboring sites were considered for substitutions for simplicity (Figure 1). The computational supercell has $\text{Ca}_8\text{Fe}_1\text{Cs}_1(\text{PO}_4)_6\text{F}_2$ composition (denoted as $\text{Cs}^+-\text{Fe}^{3+}$), resulting in Cs ~12 wt% concentration. After beta decay, the composition becomes $\text{Ca}_8\text{Fe}_1\text{Ba}_1(\text{PO}_4)_6\text{F}_2$ (denoted as $\text{Ba}^{2+}-\text{Fe}^{2+}$), where Ba^{2+} is at the position of Cs^+ .

Electronic structure: The results from the electronic structure calculations suggest that, after $^{137}\text{Cs} \rightarrow ^{137}\text{Ba}$ transmutation, the extra electron is localized at the iron site, and the iron, initially ferric Fe^{3+} , is reduced to ferrous iron, Fe^{2+} . Spin-polarized density of states (DOS) for $\text{Cs}^+-\text{Fe}^{3+}$ and $\text{Ba}^{2+}-\text{Fe}^{2+}$ apatites in four configurations are shown in Figure 2. In all cases, the DOSs show a “sandwich-like” feature with the Fe 3d orbitals between the valence bands and the conduction bands. For $\text{Cs}^+-\text{Fe}^{3+}$ in all four configurations,

a high spin state of Fe^{3+} (d^5) is observed. The occupied spin α components of Fe^{3+} are delocalized with O 2d orbitals in the valence bands, while five unoccupied spin β components are localized between the valence and the conduction bands. For $\text{Ba}^{2+}\text{-Fe}^{2+}$, the iron remains high spin. Some spin α 3d orbitals are localized, and all spin beta 3d orbitals remain localized. One occupied 3d orbital appears in spin β projection, which is not occupied in $\text{Cs}^+\text{-Fe}^{3+}$ configurations. The result suggests that the extra electron from beta decay has been “trapped” locally at the iron site, leading to a reduction of the iron, $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$. Similar results were obtained in all configurations (Figure 2), showing that the electron trapping by the ferric iron is robust. This is in contrast to ^{137}Cs in CsCl without a variable valence atom in the crystal structure to trap the extra electron.³² Based on the DFT studies, the extra electron is delocalized and occupies the conduction band in BaCl, resulting in the metallic nature of BaCl phase with a complex mixture of ionic, metallic, and covalent bonding characters.^{29, 32} The Ba atom in such phase would have a formal +1 charge, an unusual oxidation state of the atom. The results for the ^{137}Cs incorporated in the apatite demonstrate that the variable valence iron cation is effective to trap the electron from the ^{137}Cs beta decay and to maintain the charge neutrality in apatite structure, without leading to unusual valence state of the transmuted nucleus.

Cohesive energy: The cohesive energy calculations suggest that the $\text{Ba}^{2+}\text{-Fe}^{2+}$ apatite is energetically favorable with respect to $\text{Cs}^+\text{-Fe}^{3+}$ apatite in all configurations considered. Calculated total energies for different configurations of the optimized structures and isolated Ba and Cs atoms are listed in Table 1. For $\text{Cs}^+\text{-Fe}^{3+}$ apatite, the configuration with Fe^{3+} at Site-I and Cs^+ at Site-II, i.e., $\text{Cs}^+(\text{II})\text{-Fe}^{3+}(\text{I})$, has the lowest total energy among all four configurations, suggesting a site preference of Fe^{3+} at Site-I site and Cs^+ at Site-II. For $\text{Ba}^{2+}\text{-Fe}^{2+}$ apatite, Fe^{2+} located at site (I) and Ba^{2+} at site (II), i.e., $\text{Ba}^{2+}(\text{II})\text{-Fe}^{2+}(\text{I})$, has the lowest energy. Considering the order of the Shannon-Prewitt Crystal Radius is $\text{Cs}^+ > \text{Ba}^{2+} > \text{Ca}^{2+} > \text{Fe}^{3+}$,⁵⁶ the site preference based on the calculations is consistent with the understanding that larger cations with lower charge preferentially enters the Site-II site next to the structural channel rather than the Site-I site in the framework site.⁵⁷ The difference between cohesive energies of $\text{Cs}^+\text{-Fe}^{3+}$ and $\text{Ba}^{2+}\text{-Fe}^{2+}$ (ΔE_c) were calculated according to equation (2). The calculated cohesive energy changes from the $\text{Cs}^+\text{-Fe}^{3+}$ to $\text{Ba}^{2+}\text{-}$

Fe^{2+} apatite are positive in all configurations (Table 1), suggesting the energetic stability of the $\text{Ba}^{2+}\text{-Fe}^{2+}$ apatite with respect to the $\text{Cs}^+\text{-Fe}^{3+}$ apatite. Similar results have been obtained from $^{137}\text{CsCl}$ to $^{137}\text{BaCl}$. Although an exotic oxidation state of Ba was calculated, the BaCl phase may have mechanical stability based on an examination of its elastic constant and phonon dispersive relations.³²

Crystal and defect structure: The calculated results suggest there are only minor changes in the crystal and defect structure of substituted sites. The volume and lattice parameters for the $\text{Cs}^+\text{-Fe}^{3+}$ apatite and $\text{Ba}^{2+}\text{-Fe}^{2+}$ apatite with different configurations are listed in Table 2. The volumes are decreased by 1.4 – 3.1%, which is a combined result of a cation size decrease ($\sim 18.4\%$) from Cs^+ (1.74 Å) to Ba^{2+} (1.42 Å) and increase ($\sim 17.9\%$) from Fe^{3+} (0.78 Å) to Fe^{2+} (0.92 Å). In all configurations, the volume shrinking accompanies with the reducing of lattice constants in almost all dimensions. The lattice constants and volume are predominantly determined by the cation to anion bond distances.^{58, 59} There are also minor distortions of the hexagonal lattice as measured by the angles of the lattice constants ($\leq 0.7\%$), consistent with minor changes in the volume and lattice dimensions.

The calculated radial distribution functions (RDFs) are plotted in Figure 3. Between $\text{Cs}^+\text{-Fe}^{3+}$ and $\text{Ba}^{2+}\text{-Fe}^{2+}$ apatites in all configurations, the P-O bond distance for all configurations (first peak) remains unchanged, suggesting the (PO_4) units are rigid and intact in the apatite structure. The changes of the Ca-O bond distances are small for a given configuration between $\text{Cs}^+\text{-Fe}^{3+}$ and $\text{Ba}^{2+}\text{-Fe}^{2+}$ apatites and among different configurations. Figure 4 shows the average and standard deviation Cs/Ba-O bond distances of $\text{Cs}^+\text{-Fe}^{3+}$ and $\text{Ba}^{2+}\text{-Fe}^{2+}$ apatite for the four configurations. A decrease in the bond distance from Cs-O to Ba-O is observed for all four configurations with a similar standard deviation for each configuration, which suggests a volume contraction as a result of the transmutation without leading to increased local structure distortions. The location of iron has less influence on the average and deviation of Cs-O or Ba-O bond distances than the influence of Cs/Ba location because the average and standard deviation are similar Fig. 4A and 4C, and between Fig. 4B and 4D (Figure 4), which is mainly due to a small increase of ionic radius from Fe^{3+} to Fe^{2+} with respect to a larger reduction of ionic radius from Cs^+ to Ba^{2+} . Figure 5 illustrates the

bond distance change of one of the Ba-O bonds after Ba substitution for Cs in $\text{Cs}^+\text{-Fe}^{3+}$ apatite during each step of the energy optimization. The result shows a decreasing bond distance while the structure being optimized, accompanying with reduced total system energy (Figure 5).

The metaprism twist angle ϕ of apatite structure is a quantitative measure of framework structure and the shape of the Site-I polyhedron of apatite structure, which is variable and dependent on apatite composition. The value is often between 0° (trigonal prism) and 60° (octahedron).³⁶ This variability reflects the structural flexibility and allows its structure to accommodate a wide range of substitutions at different sites. Because ϕ value arises from the interplay between several atoms, this single parameter is proved to be highly sensitive to crystallochemical variations and structural changes, especially the site-I and site-II cations.⁵⁷ In this study, the angle is used to measure flexibility of the structure and the local lattice distortion from its host structure. The metaprism twist angle ϕ was calculated for individual metaprisms from the coordinates of substituted cation at site-I, O(1) and O(2).³⁶ Figure 6 shows the average and range of metaprism twist angle for $\text{Cs}^+/\text{Fe}^{3+}$ and $\text{Ba}^{2+}/\text{Fe}^{2+}$ apatites with different configurations. The twist angle (24.3°) of $\text{Ca}_{10}(\text{PO})_6\text{F}_2$ is provided as a reference. The angle varies in a wide range, from 37.3° to 5.6° , reflecting great flexibility of the structure to accommodate different cations with different charge. The changes of the averaged twist angles before and after the transmutation, however, are small (about 2 degree), except in $\text{Cs}^+(\text{II}) - \text{Fe}^{3+}(\text{I})$, which has a change of approximately 7 degree. The result suggests that the twist angle varies as a result of incorporation, but only minor distortions because of the beta decay.

Collectively, the localization of the extra electron, positive cohesive energy, and minor structural distortions as suggested by the density of states, energetics, and the structural characterization provide a consistent evidence that the $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ could be a candidate for ^{137}Cs incorporation by a coupled substitution $\text{Cs}^+ + \text{Fe}^{3+}$ for Ca^{2+} to mitigate the beta decay induced structure instability, without leading to unusual properties of the new phase with the transmuted nucleus.

3.2 $^{90}\text{Sr} \rightarrow ^{90}\text{Y} \rightarrow ^{90}\text{Zr}$ beta decay

Apatite $\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6\text{F}_2$ was selected as a model system for Sr^{2+} incorporation because it has both trivalent cation (Y^{3+}) and divalent cation (Ca^{2+}). In $\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6\text{F}_2$ structure, Ca^{2+} is at Site-I site and Y^{3+} is at Site-II site.⁶⁰ In order to accommodate the two-steps beta decay of ^{90}Sr involved higher charged species (Y^{3+} and Zr^{4+}), a coupled substitution was proposed - $\text{Ca}_3\text{Sr}_1\text{Y}_4\text{Fe}_2(\text{SiO}_4)_6\text{F}_2$, donated as $(\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+})$, where one Ca^{2+} and two Y^{3+} substituted by Sr^{2+} and Fe^{3+} respectively. For a given Sr^{2+} substitution, there are two possible configurations for $\text{Ca}_3\text{Sr}_1\text{Y}_4\text{Fe}_2(\text{SiO}_4)_6\text{F}_2$: two Fe^{3+} ions substituted for Y^{3+} at the same or different z coordinates (at Site-II, next to the channel). Unlike the four configurations of Cs^+ and Fe^{3+} coupled substitution, discussed in the previous section where different configurations have similar total energies, the configuration with both Fe^{3+} ions with different z coordinates in neighboring site of the substituted Sr^{2+} ion has a significant lower in total energy (2.15 eV lower) than the other configurations, suggesting the former configuration is the preferred configuration for the Fe^{3+} and Sr^{2+} substitution. Therefore, only configuration with one Sr^{2+} and two Fe^{3+} substitutions at different z coordinates ($\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+}$) was considered for the further discussion (Figure 7). The two-step decay leads to apatites with compositions of $\text{Ca}_3\text{Y}_5\text{Fe}_2(\text{SiO}_4)_6\text{F}_2$ (donated as $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$) and $\text{Ca}_3\text{Zr}_1\text{Y}_4\text{Fe}_2(\text{SiO}_4)_6\text{F}_2$ (donated as $\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$).

Electronic structure: Figure 8 shows the DOSs for the systems of $\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+}$, $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$, and $\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$ apatites. For the $\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+}$ apatite, the two Fe^{3+} ions are in the high-spin state, and they have a ferromagnetic order. The DOS exhibits ten occupied spin-up (partially delocalized with d orbitals of oxygen) and ten empty spin-down (localized) d-like orbitals (Figure 8-A). For $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$ (Figure 8-B) and $\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$ (Figure 8-C), the magnetic order does not change, and the Fe^{2+} and Fe^{3+} maintain high-spin. Comparing with $\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+}$, one electron fills in d-like spin beta orbital of $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$, and two electrons in d-like spin beta orbitals of $\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$. The results suggest that the extra electrons from beta decay from $\text{Sr} \rightarrow \text{Y} \rightarrow \text{Zr}$ are trapped locally at the iron sites, leading to a reduction of the ferric iron, $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$, similar to the $\text{Cs} \rightarrow \text{Ba}$ decay discussed in the previous section ($^{137}\text{Cs} \rightarrow ^{137}\text{Ba}$ beta decay). This is in contrast to transmutation studies^{23, 27} of $^{90}\text{SrTiO}_3$ to $^{90}\text{ZrTiO}_3$, $^{90}\text{SrH}_2$ to $^{90}\text{ZrH}_2$,

$^{177}\text{Lu}_2\text{O}_3$ to $^{177}\text{Hf}_2\text{O}_3$, ^{109}CdS to ^{109}AgS , and ^{90}Sr to ^{90}Zr in C-S-H (calcium-silicate-hydrate, a cement phase), where in those cases a variable valence atom is not present to trap the extra electron, resulting in an unusual electronic state of the phases based on DFT studies.^{23, 27} In the case of C-S-H phase, the electronic structure was not presented in the study but an unusual oxidation state of Y and Zr is expected.²⁷

Cohesive energy: The calculated differences in the cohesive energies (ΔE_c) between $\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+}$ and $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$ apatites and between $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$ and $\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$ apatites in the two-step beta decay are 4.43 eV and 1.39 eV for $\text{Sr} \rightarrow \text{Y}$ and $\text{Y} \rightarrow \text{Zr}$ respectively. The positive values suggest that both decay steps lead to energetically stable apatites, similar to the $\text{Cs} \rightarrow \text{Ba}$ decay as discussed in the previous section. In the cases without a variable valence atom to trap the extra electron,^{23, 24, 30} the new phase with the transmuted nucleus is expected to be unstable or metastable, and possibly undergoes phase transition or phase separation because of the unusual nature of the electronic state of the phase. For instance, from ^{109}CdS to ^{109}AgS , the wurtzite structure becomes rocksalt structure.²⁴ From $^{90}\text{SrTiO}_3$ to $^{90}\text{ZrTiO}_3$, the $^{90}\text{ZrTiO}_3$ is expected to decompose to ZrO_2 , TiO_2 , and Ti metal.^{23, 30} In the case with a variable valence atom to trap the extra electron in apatite presented in this study, the phase could be stabilized with the beta electron trapped locally in the structure.

Crystal and defect structure: The calculated lattice parameters and cell volume are listed in Table 3. Unlike the volume decrease from Cs^+ to Ba^{2+} apatite, which is due to decreases of all three lattice dimensions, the $\text{Sr} \rightarrow \text{Y}$ and $\text{Y} \rightarrow \text{Zr}$ series cause the lattice constant a and b to increase and c to decrease. The volume is decreased by 1.4% and 0.1% for the apatite with Sr (ionic radius: 1.26 Å) $\rightarrow$ Y (1.02 Å) and Y (1.02 Å) $\rightarrow$ Zr (0.84 Å) respectively, corresponding to ionic radius decrease of 19.1 % and 17.6 % respectively, and increase (~17.9 %) from Fe^{3+} (0.78 Å) to Fe^{2+} (0.92 Å). Again, smaller cation sizes of Y^{3+} and Zr^{4+} than Sr^{2+} contribute the volume shrink that is only partially offset by the size increase from Fe^{3+} to Fe^{2+} . There are only minor lattice distortions of the hexagonal lattice as measured by the metaprisim twist angle ϕ . The calculated RDFs are plotted in Figure 9. The Si-O peak doesn't change from $\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+}$ to $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$ apatites or from $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$ to $\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$ apatites, suggesting the ridged SiO_4 units are

intact, similar to the PO_4 units in the ^{137}Cs to ^{137}Ba decay case. However, both Fe-O and Ca/Sr/Y/Zr-O peaks change notably, with Fe-O distances increasing and Ca/Sr/Y/Zr-O distances decreasing from $\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+}$ to $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$ and from $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$ to $\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$ apatite. The Sr^{2+} and its transmuted products (Y^{3+} , Zr^{4+}) are located at Site-I site, which is expected to have a coordination number of nine. Figure 10 shows the Sr/Y/Zr-O bond distances of nine nearest neighbors of the cation with oxygen. Comparing $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$ apatite to $\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+}$ apatite, all nine bond distances decreased nearly uniformly. Comparing $\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$ apatite to $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$ apatite, the bond distances with its first seven neighbors decrease consistently, but the eighth and ninth bond distances increase instead. The result suggests a change of the coordination environment from Y^{3+} to Zr^{4+} apatite.

Using the Grubbs' test in one-sided (minimum) form, the coordination environment was quantitatively evaluated according to the relative contributions of the ligands to the total crystal field terms.^{61, 62} The crystal-field Hamiltonian has R^{-3} , R^{-5} ..., dependence, where R is the distance between metal cation to ligand. Mathematically, the R^{-3} dependence offers a convenient criterion to estimate the contribution to the crystal field from each ligand, in other words, the coordinating ligands to the central metal ion. The tested range was chosen from the top contributor down to include the proposed coordination number found plus one. The G value was calculated for lowest contributor, as a suspected outlier, and compared to the Grubbs' critical value to determine the confidence interval.⁶² For the $\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$ system, the test result suggests that the $\text{Zr}^{4+}\text{-O}$ coordination number is changed from 9 to 7 for Y^{3+} decay to Zr^{4+} at 99% confident interval, which is consistent with visual inspection of Figure 10, as a result of the high charged species Zr^{4+} with a smaller ionic radius.

Above analysis suggests that $\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6\text{F}_2$ could be a candidate for ^{90}Sr incorporation with coupled substitutions of Sr^{2+} for Ca^{2+} and Fe^{3+} for Y^{3+} at the site-I and site-II respectively to mitigate structure instability induced by beta decay. Although structure distortions are larger than in the $\text{Cs} \rightarrow \text{Ba}$ case, each of the beta decay steps ($\text{Sr} \rightarrow \text{Y}$ and $\text{Y} \rightarrow \text{Zr}$) is energetically favorable with overall small structure distortions.

4. Implication to nuclear waste development

Long-term safe nuclear waste disposal is essential for an integrated solution in nuclear fuel cycle for a sustainable nuclear energy future. For waste form development of the fission products from reprocessing of used nuclear fuel, the main focus has been on long term chemical degradation and durability of the waste forms in disposal environment. The compositional changes of those radionuclides caused by beta decay present an additional challenge and complicate the waste form design. A successful demonstration of a waste form that resists and mitigates the induced instability by beta decay would provide a path to address the challenge. A strategy has long been proposed for crystalline ceramic waste forms to mitigate such instability of a host material that incorporates those fission products without inducing phase decomposition or exotic electronic state of the host. In the light of principles of crystal structure and chemical composition, the following may be considered in selecting such a host material: (1) the extra beta electron and increased nuclear charge from beta decay are locally compensated within the phase; (2) variable valence elements and radionuclides are incorporated to the phase by coupled substitution; (3) both the composition and crystal structure of the host phase need to be flexible enough to accommodate the changes; (4) the best candidate structures may be phases with great compositional and structural flexibility and have demonstrated a wide range of chemical substitutions in the structure. Apatite-structured materials meet all these criteria and the results presented here suggest that apatite could be a promising waste form to mitigate the beta decay induced instability. Studies on other potential host structures are expected to provide more information on whether these criteria are sufficient and generally applicable to select viable waste form host structures. The methodology presented here could be applied to candidate nuclear waste form materials for incorporating fission products undergoing beta decay. Experimental methods capable of examining chemical and structural changes induced by beta decay are necessary to verify the results of the present study. Such an experimental method may be made possible by using short-lived radionuclides undergoing beta decay.

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Figure captions

Figure 1. The structure of $\text{Cs}^+\text{-Fe}^{3+}$ substituted apatite – $\text{Cs}_1\text{Fe}_1\text{Ca}_8(\text{PO}_4)_6\text{F}_2$ after energy optimization. Fe^{3+} and Cs^+ substitute two Ca^{2+} in $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, where Fe^{3+} is on top of Cs^+ . Blue, gold, green, pink, red, and silver balls represent Ca^{2+} , Fe^{3+} , Cs^+ , P^{3+} , O^{2-} , and F^- respectively.

Figure 2. Density of states (DOS) of $\text{Cs}^+\text{-Fe}^{3+}$ (left panel) and $\text{Ba}^{2+}\text{-Fe}^{2+}$ (right panel) with different $\text{Cs}^+/\text{Ba}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ configurations. (A): $\text{Cs}^+(\text{I})\text{-Fe}^{3+}(\text{I})$; (E): $\text{Cs}^+(\text{I})\text{-Fe}^{3+}(\text{II})$; (C): $\text{Cs}^+(\text{II}) - \text{Fe}^{3+}(\text{I})$; (G): $\text{Cs}^+(\text{II}) - \text{Fe}^{3+}(\text{II})$; and (B), (D), (F) and (H) for corresponding $\text{Ba}^{2+}\text{-Fe}^{2+}$ apatite. Curves above and below the central line in each panel represent partial DOS for spin (α) (red) and spin (β) (blue) components. Fermi level is the thin dashed lines.

Figure 3. The calculated total radial distribution functions for $\text{Cs}^+ - \text{Fe}^{3+}$ apatite (solid blue lines) and $\text{Ba}^{2+} - \text{Fe}^{2+}$ apatite (dashed red lines). (A): $\text{Cs}^+(\text{I})\text{-Fe}^{3+}(\text{I})$; (B): $\text{Cs}^+(\text{II})\text{-Fe}^{3+}(\text{I})$; (C): $\text{Cs}^+(\text{I})\text{-Fe}^{3+}(\text{II})$, and (D): $\text{Cs}^+(\text{II})\text{-Fe}^{3+}(\text{II})$.

Figure 4. The average and standard deviation Cs-O and Ba-O bond distances for (A): Cs⁺(I) - Fe³⁺(I); (B): Cs⁺(II) - Fe³⁺(I); (C): Cs⁺(I) - Fe³⁺(II); and (D): Cs⁺(II) - Fe³⁺(II) configurations. The symbols (filled) are the average and upper/lower bars mark one standard deviation of the average. Circles are Cs⁺-Fe³⁺ apatite, and triangles are Ba²⁺-Fe²⁺ apatite.

Figure 5. Change of Ba-O band distance (blue) and total energy (red) during geometry optimization.

Figure 6. The average and range of metaprism twist angle for Cs⁺ contained species (black bars) and the decay product Ba²⁺ contained species (red bars). (A): Cs⁺(I) - Fe³⁺(I); (B): Cs⁺(II) - Fe³⁺(I); (C): Cs⁺(I) - Fe³⁺(II); and (D): Cs⁺(II) - Fe³⁺(II) apatite. For Cs⁺(II)-Fe³⁺(I) in (B) and Ba²⁺(I)-Fe²⁺(II), the range is within the symbols. The horizontal dashed line donates the twist angle of Ca₁₀(PO)₆F₂ of 24.3°.

Figure 7. The optimized structure of (Fe³⁺-Sr²⁺-Fe³⁺), where Sr²⁺ replaces Ca²⁺ at site-I and two Fe³⁺ replace two Y³⁺ at site-II. Green, golden, pink, grey, blue, red, and silver balls represent Sr²⁺, Fe³⁺, Ca²⁺, Y³⁺, Si⁴⁺, O²⁻, and F⁻ respectively.

Figure 8. Density of states (DOS) of Fe³⁺-Sr²⁺-Fe³⁺ (A), Fe²⁺-Y³⁺-Fe³⁺ (B), and Fe²⁺-Zr⁴⁺-Fe²⁺ (C). Curves above and below the central line in each panel represent partial DOS for spin (α) (red) and spin (β) (blue) components. Fermi level is the thin dashed lines.

Figure 9. Total radial distribution functions for Fe³⁺-Sr²⁺-Fe³⁺ (black solid line) → Fe²⁺-Y³⁺-Fe³⁺ (blue solid line) → Fe²⁺-Zr⁴⁺-Fe²⁺ (red solid line) apatites.

Figure 10. The bond distances of nine nearest neighbors of the cation Sr (black filled circles), Y (blue filled triangles), and Zr (red filled squares). The dashed lines are eye-guides.

Table.1 Total energies and the cohesive energy change for four different configurations of $\text{Cs}^+/\text{Ba}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ are at different sites (unit: eV).

	$\text{Cs}^+(\text{I}) - \text{Fe}^{3+}(\text{I})$	$\text{Cs}^+(\text{II}) - \text{Fe}^{3+}(\text{I})$	$\text{Cs}^+(\text{I}) - \text{Fe}^{3+}(\text{II})$	$\text{Cs}^+(\text{II}) - \text{Fe}^{3+}(\text{II})$
Total energy	-295.61	-295.76	-295.47	-295.49
	$\text{Ba}^{2+}(\text{I}) - \text{Fe}^{2+}(\text{I})$	$\text{Ba}^{2+}(\text{II}) - \text{Fe}^{2+}(\text{I})$	$\text{Ba}^{2+}(\text{I}) - \text{Fe}^{2+}(\text{II})$	$\text{Ba}^{2+}(\text{II}) - \text{Fe}^{2+}(\text{II})$
Total energy	-299.38	-300.94	-300.71	-300.79
	Cs	Cs	Cs	Cs
Total energy	-2.41	-2.41	-2.41	-2.41
	Ba	Ba	Ba	Ba
Total energy	-1.23	-1.23	-1.23	-1.23
$\Delta \text{Ec}(\text{Ba-Cs})$	4.95	6.36	6.42	6.48

Table 2. The comparison of the volume and lattice parameters in $\text{Cs}^+ - \text{Fe}^{3+} \rightarrow \text{Ba}^{2+} - \text{Fe}^{2+}$

	volume	a	b	c	α	β	γ
$\text{Cs}^+(\text{I}) - \text{Fe}^{3+}(\text{I})$	550.2	9.497	9.497	7.043	90.0	90.0	120.0
$\text{Ba}^{2+}(\text{I}) - \text{Fe}^{2+}(\text{I})$	542.4	9.486	9.486	6.961	90.0	90.0	120.0
Changing	-1.4%	-0.1%	-0.1%	-1.2%	0.0%	0.0%	0.0%
$\text{Cs}^+(\text{II}) - \text{Fe}^{3+}(\text{I})$	559.7	9.796	9.656	6.827	90.7	90.1	119.9
$\text{Ba}^{2+}(\text{II}) - \text{Fe}^{2+}(\text{I})$	550.6	9.656	9.550	6.896	90.2	89.4	120.0
Changing	-1.6%	-1.4%	-1.1%	1.0%	-0.6%	-0.7%	0.1%
$\text{Cs}^+(\text{I}) - \text{Fe}^{3+}(\text{II})$	565.3	9.588	9.613	7.167	90.3	90.2	121.2
$\text{Ba}^{2+}(\text{I}) - \text{Fe}^{2+}(\text{II})$	554.8	9.532	9.546	7.075	90.0	90.5	120.5
Changing	-1.9%	-0.6%	-0.7%	-1.3%	-0.4%	0.3%	-0.6%
$\text{Cs}^+(\text{II}) - \text{Fe}^{3+}(\text{II})$	573.3	10.059	9.751	6.752	90.0	90.0	120.0
$\text{Ba}^{2+}(\text{II}) - \text{Fe}^{2+}(\text{II})$	555.7	9.719	9.629	6.861	90.0	90.0	120.1
Changing	-3.1%	-3.4%	-1.2%	1.6%	0.0%	0.0%	0.0%

Table 3. The comparison of the volume and lattice parameters in $\text{Ca}_3\text{Sr}_1\text{Y}_6\text{Fe}_2(\text{SiO}_4)_6\text{F}_2 \rightarrow$

$\text{Ca}_3\text{Y}_7\text{Fe}_2(\text{SiO}_4)_6\text{F}_2 \rightarrow \text{Ca}_3\text{Zr}_1\text{Y}_6\text{Fe}_2(\text{SiO}_4)_6\text{F}_2$ transmutation.

	Volume	a	b	c	α	β	γ
$\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+}$	538.4	9.257	9.333	7.040	89.8	90.7	117.7
$\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$	531.0	9.370	9.443	6.860	89.7	89.7	119.0
change	-1.4%	1.2%	1.2%	-2.6%	-0.1%	-1.1%	1.1%
$\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$	530.5	9.548	9.464	6.683	89.3	90.1	118.6
Change	-0.1%	1.9%	0.2%	-2.6%	-0.5%	0.5%	-0.3%

Table 4. The comparison of the volume and lattice parameters in $\text{AgFePb}_8(\text{VO}_4)_6\text{I}_2 \rightarrow \text{AgFePb}_8(\text{VO}_4)_6\text{IXe}$
 $\rightarrow \text{AgFePb}_8(\text{VO}_4)_6\text{I}$ process.

	volume	a	b	c	α	β	γ
I-Fe^{3+}	742.9	10.726	10.938	7.443	93.5	90.7	121.4
Xe-Fe^{3+}	742.6	10.718	11.143	7.321	93.2	89.5	121.7
change	0.0%	-0.1%	1.9%	-1.6%	-0.3%	-1.3%	0.2%
vac- Fe^{3+}	705.0	10.572	10.863	7.314	93.2	88.7	122.8
change	-5.1%	-1.4%	-2.5%	-0.1%	0.0%	-0.9%	0.9%

Figure 1. The structure of $\text{Cs}^+\text{-Fe}^{3+}$ substituted apatite

Figure 2. Density of states (DOS) of $\text{Cs}^+ - \text{Fe}^{3+}$ (left panel) and $\text{Ba}^{2+} - \text{Fe}^{2+}$ (right panel)

Figure 3. The calculated total radial distribution functions for $\text{Cs}^+ - \text{Fe}^{3+}$ apatite

Figure 4. The average and standard deviation Cs-O and Ba-O bond distances

Figure 5. The evaluation of Ba-O band distance (Blue solid) and total energy (black dots)

Figure 6. The metaprism twist angle for Cs^+ contained species

Figure 7. The optimized structure of (Fe^{3+} - Sr^{2+} - Fe^{3+})

Figure 8. Density of states (DOS) of $\text{Fe}^{3+}\text{-Sr}^{2+}\text{-Fe}^{3+}$ (A), $\text{Fe}^{2+}\text{-Y}^{3+}\text{-Fe}^{3+}$ (B), and $\text{Fe}^{2+}\text{-Zr}^{4+}\text{-Fe}^{2+}$ (C).

Figure 9. Total radial distribution functions

Figure 10. The bond distances of nine nearest neighbors

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