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Project Title:	New Fission Product Waste Forms: Development and Characterization
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1. Executive Summary

Research performed on the program "New Fission Product Waste Forms: Development and Characterization," in the last three years has fulfilled the objectives of the proposal which were to 1) establish ceramic waste forms for disposing of Cs, Sr and minor actinides, 2) fully characterize the phase relationships, structures and thermodynamic and kinetic stabilities of promising waste forms, 3) establish a sound technical basis for understanding key waste form properties, such as melting temperatures and aqueous durability, based on an in-depth understanding of waste form structures and thermochemistry, and 4) establish synthesis, testing, scaleup and commercialization routes for wasteform implementation through out in-kind collaborations. In addition, since Cs and Sr form new elements by radioactive decay, the behavior and thermodynamics of waste forms containing different proportions of Cs, Sr and their decay products were discovered using non-radioactive analogues.

Collaborations among researchers from three institutions, UC Davis, Sandia National Laboratories, and Shott Inc., were formed to perform the primary work on the program. The unique expertise of each of the members in the areas of waste form development, structure/property relationships, hydrothermal and high temperature synthesis, crystal/glass production, and thermochemistry was critical to program success. In addition, collaborations with the Brigham Young Univeristy, Ben Gurion University, and Los Alamos National Laboratory, were established for standard entropies of ceramic waste forms, sol-gel synthesis, and high temperature synthesis.

This work has had a significant impact in a number of areas. First, the studies of the thermodynamic stability of the mineral analogues provided an important technical foundation for assessment the viability of multicomponent oxide phases for Cs and Sr removal. Moreover, the thermodynamic data discovered in this program established information on the reaction pathways for the potential reaction products. The phase equilibria and thermodynamics involving the intermediates in the decay process in this program will assist in selection of the best process for Cs or Sr immobilization. In addition, data from the study can be used to develop engineering solutions for potential process upsets. Second, the glass – crystal stability of

multicomponent oxide phases that were representative silicates on this program is highly distinguishable for mother compounds and decay products, thus providing a fundamental understanding on the separate effects from chemistry and from radiation. Finally, we have developed a foundation for understanding chemistry-structure-energetics relationships in titanosilicates that can be used to develop more effective materials.

2. A comparison of the actual accomplishments with the goals and objectivities of the project.

The project accomplished the proposed goals on schedule. In addition, work on the program lead to new discoveries not anticipated in the original proposal. Of particular importance was the discovery of the glass – crystal stability of multicomponent oxide phases that possess naturally occurring mineral phases. This further demonstrates the separate effects from chemistry and from radiation.

3. Summary of project activities for the entire period of funding, including original hypotheses, approaches used, problems encountered and departure from planned methodology, and an assessment of their impact on the project results.

I. Research Objectives

The objective of this program is to identify new fission product waste forms and disposal strategies specific to titanosilicate secondary waste generated from Cs, Sr, and minor actinides ion exchange processes. The goal of the program is to reduce the costs associated with guanidinium carbonate steam reforming waste process, to minimize the risk of contamination to the environment during waste processing, and to provide DOE with technical solutions to a variety of issues related to Cs, Sr, and minor actinide disposal. The technical objective of the proposed work is to fully characterize the phase relationships, structures and thermodynamic and kinetic stabilities of crystalline metal oxide based waste forms and to establish a sound technical basis for understanding key waste form properties, such as melting temperatures and aqueous durability, based on an in-depth understanding of waste form structures and thermochemistry. In addition, since Cs and Sr form new elements by radioactive decay, and this decay occurs almost completely over hundred years, we will study the behavior and thermodynamics of waste forms containing different proportions of Cs, Sr, and their decay products, using non-radioactive analogues.

II. Methods and Results

The methods and results section is organized to summarize progress in several major areas. In the first section the durability of waste forms possessing naturally occurring mineral phase is discussed. This is followed by structure – property relationship studies on potential beta decay products from three representative silicates. In this same section, glass – crystal stability studies are summarized and the properties of crystal structure studies and structure property relationships are summarized and the possibility of producing materials instability through amorphization from radiation damage and during vitrification is discussed. Finally results from high temperature reaction calorimetry to determine thermodynamic parameters are presented.

a. Aqueous Durability of Possible Oxide Forms for Immobilization of Short-lived Fission Products

In an effort to better understand the long term stability of titanosilicates (fresnoites) as potential waste forms for Cs^+ radiological cations (Cs^+ decays to Ba^{2+} via beta decay), aqueous durability studies modeled on modified Product Consistency Test – Procedure B (PCT-B) were undertaken. The test provides constraints on rates of aqueous dissolution of the fully loaded Ba- titanosilicate phases. The barium fraction released (FR%) can be expressed as follows: FR% = 100 × (mass of barium released / total mass of barium in the sample). This expression provides a correlation of barium release without considering the effect of the geometric surface area. To incorporate the surface area into the PCT test, the normalized Ba leaching rate (*NL*) can be calculated by the following equation: NL (g $(m^2d)^{-1}$) = CV / fAt, where C is the concentration of Ba in the leachate (g/ml); V, the leachate volume (ml); f, the initial fraction of Ba in fresnoite; A, the surface area of the test specimen (m^2); and t, the duration of test (days). Surface area was calculated by follows: A = (surface area per unit mass × original mass of the sample), where surface area per unit mass for spherical particles is calculated from the equation: $4\pi r^2 / ((4/3)\pi r^3 \cdot d)$. The radius ($r$) used was 5 μm determined by BSE images and the density (d) of fresnoite crystal and glass used was 4.44 g/cm^3 and 4.29 g/cm^3, respectively[1].

Table I. The modified Product Consistency Test – Procedure B (PCT-B) Results for Fresnoite Glass (A) and Crystal (E).

	3 days		10 days	
	FR% (Ba loss)	*NL* ($10^{-3}g\cdot(m^2d)^{-1}$)	FR% (Ba loss)	*NL* ($10^{-3}g\cdot(m^2d)^{-1}$)
A	0.42	10.1	0.33	2.34
E	0.33	8.26	0.43	3.20

Calculated fraction released (FR%) and normalized Ba leaching rate (*NL*) data of the product consistency test (PCT) conducted on fresnoite glass (A) and crystal (E), are shown in Table I. The normalized Ba leaching rate (*NL*) observed for both glass and crystal samples decreased as a function of time, comparable to other titanosilicates[2, 3]. The changes in *NL* values for glass (A) showed more severe drops than crystal (E). For example, the 10-d *NL* value of A was 23% of the 3-d *NL* value, while the 10-d *NL* value of E was 39% of the 3-d *NL* value. The greater changes in *NL* of A suggest that the glass released Ba more quickly than the crystal under hydrothermal conditions. Thus, the crystal phase of fresnoite showed better aqueous durability, especially for a short-term leaching test. For example, 3-d *NL*(A) / 3-d *NL*(E) was equal to 1.20 and 10-d *NL*(A) / 10-d *NL*(E) was 0.74. For crystal (E), 10-d *NL* value was 3.20×10^{-3} ($g\cdot(m^2d)^{-1}$), suggesting appreciable higher stability compared with other ceramics, such as borosilicates (10^{-2} ($g\cdot(m^2d)^{-1}$))[4, 5]. The tests suggest that both glassy and crystalline fresnoite exhibit favorable aqueous stability and should be explored further as radioactive waste forms for long-term storage.

b. Structure/Property Relationship Studies

Phase stability and crystal chemistry studies for compositions related to the mineral phases are vital to predicting long- and short-term performance of waste forms. Moreover, the relations among crystalline and amorphous or glassy states for oxide forms are important due to the possibility of producing materials instability through amorphization from radiation damage and during vitrification. Further challenges relate to the incorporation of the decay products (Ba, Y, Zr) into the waste forms initially designed to hold Cs and Sr. Through beta decay, cesium decays to barium, while strontium decays to yttrium, and then to zirconium. Therefore, not only the stability of Cs- or Sr-loaded waste forms (Cs-Ti-Si-O and/or Sr-Ti-Si-O systems), but also that of a potential decay product series (Cs-Ba-Ti-Si-O and/or Sr-Y-Ti-Si-O systems) in a naturally occurring mineral or a ceramic is of fundamental importance.

In this program, we have focused on three representative silicates that are possible ceramic forms for immobilization of short lived fission products in radioactive waste. Silicates are generally classified according to their SiO_4 groups. Orthosilicates (or neosilicates) contains only isolated SiO_4 tetrahedra; sorosilicates (or pyrosilicates) does Si_2O_7 group; and tectosilicates (or framework silicates) does SiO_4 tetrahedra linked in three dimensions. Figure 1 shows crystal structures of representative silicates groups, for example, (A) orthosilicates ($CaTiSiO_5$), (B) sorosilicates ($Ba_2TiSi_2O_8$), and (C) tectosilicates ($CsTiSi_2O_{6.5}$).

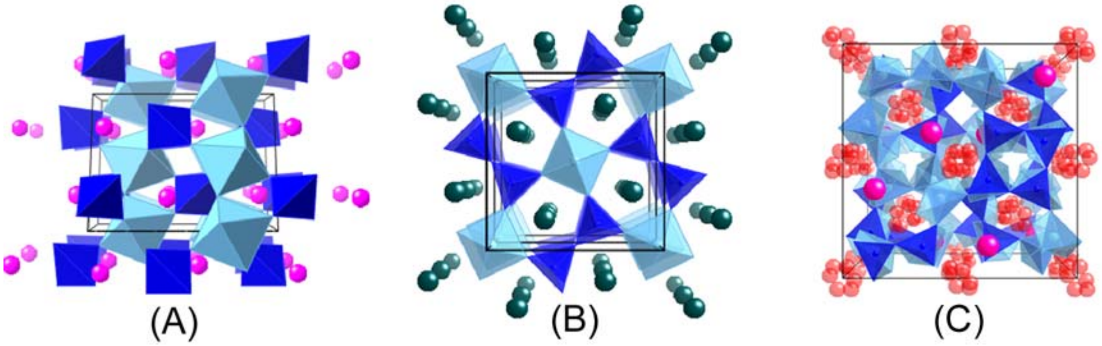

Figure 1. Crystal structures of (A) $CaTiSiO_5$ (orthosilicates), (B) $Sr_2TiSi_2O_8$ (sorosilicates) and (C) $CsTiSi_2O_{6.5}$ (framework silicates).

Cs-Ba-Ti-Si-O System

Cesium titanium silicate $CsTiSi_2O_{6.5}$ is a titanium analogue of pollucite ($CsAlSi_2O_6$). To understand the local environments in waste forms and to separate the effects of chemistry and radiation, it is appropriate to study the Ba substitution into $CsTiSi_2O_{6.5}$ in a non-radioactive setting. We focused on two decay product series: (1) with charge-balance in pollucite, and (2) with one to one replacement of Cs by Ba. Because ionic substitutions must occur by charge-balanced routes, the charge-coupled substitution ($2Cs^+ = Ba^{2+}$ + vacancy) in $CsTiSi_2O_{6.5}$ were considered. Alternatively, the series with a stoichiometric one to one replacement of Cs by Ba represent the decay process which would occur due to radioactive decay of Cs.

While the compound $BaTiSi_2O_7$ does exist,[5] it does not have a crystal structure similar to $CsTiSi_2O_{6.5}$ and no phase diagram in the $CsTiSi_2O_{6.5} - BaTiSi_2O_7$ has been found in the literature. Therefore, it was not known how much, if any, barium could be substituted into $CsTiSi_2O_{6.5}$ without leading to the formation of one or more additional phases. To obtain fully crystalline $CsTiSi_2O_{6.5}$ samples with Ba-substitutions, we developed a seed crystal approach to produce single phase Ba-substituted $CsTiSi_2O_{6.5}$ materials.[6] As shown in Figure 2, the XRD patterns of these materials were indeed closer to single phase pollucite, with only minor second phase material present (<10%).

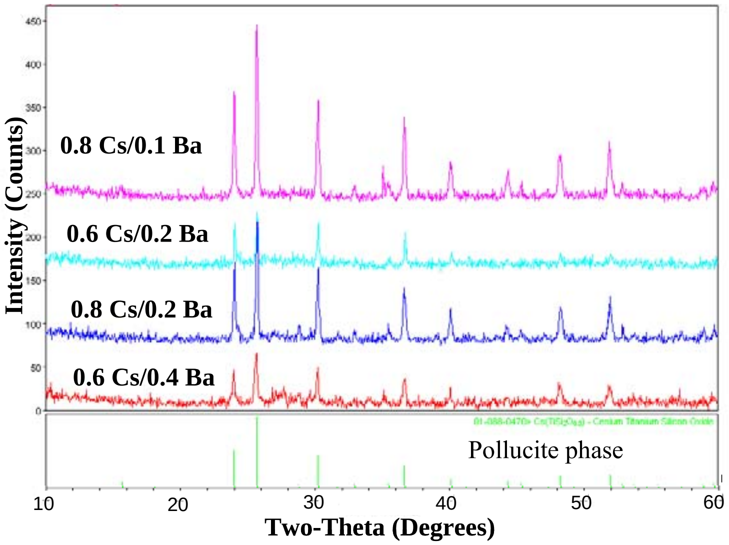

Figure 2. The powder X-ray diffraction patterns for materials with 10 wt% $CsTiSi_2O_{6.5}$ seed crystals that were heated to 750 °C for 20 h. In this figure, ‘‘1.0 Cs/0.0 Ba’’ refers to $CsTiSi_2O_{6.5}$, ‘‘0.8 Cs/0.1 Ba’’ to $Cs_{0.8}Ba_{0.1}TiSi_2O_{6.5}$, ‘‘0.6 Cs/0.2 Ba’’ to $Cs_{0.6}Ba_{0.2}TiSi_2O_{6.5}$, ‘‘0.8 Cs/0.2 Ba’’ to $Cs_{0.8}Ba_{0.2}TiSi_2O_{6.6}$ and ‘‘0.6 Cs/0.4 Ba’’ to $Cs_{0.6}Ba_{0.4}TiSi_2O_{6.7}$.

Microprobe analysis was performed on the $Cs_{0.6}Ba_{0.2}TiSi_2O_{6.5}$ material with 10% $CsTiSi_2O_{6.5}$ seeds crystallized at 750˚C for 20hr to verify that the barium was indeed incorporated into the pollucite phase as opposed to remaining in an amorphous phase. If the barium was not incorporated in the pollucite phase, most points analyzed would have essentially no barium, with the only exceptions being the secondary barium-rich phase. To the contrary, the microprobe results from 40 points indicated substantial barium content in approximately 90% of the points though always less than the corresponding cesium content (Figure 3). Those other points with no barium were presumably the remnants of the seed crystals. This result indicated that barium did not diffuse into the seed crystals for these heat treatment conditions. Thus, the microprobe results were consistent with the incorporation of the barium into the pollucite phase, as suggested by the XRD data.

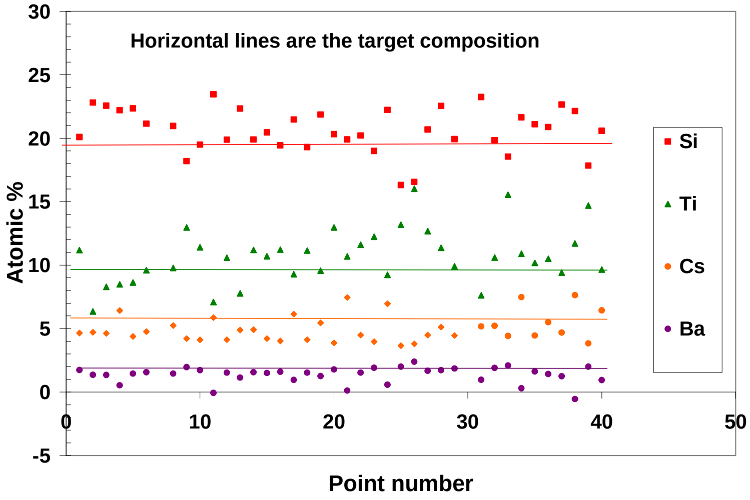

Figure 3. Microprobe results on $Cs_{0.6}Ba_{0.2}TiSi_2O_{6.5}$ with 10% $CsTiSi_2O_{6.5}$ seeds heated to 750˚C for 20 hr.

Sr-Y-Ti-Si-O System

Strontium titanosilicate ($Sr_2TiSi_2O_8$) is the Sr-analogue of fresnoite ($Ba_2TiSi_2O_8$). To incorporate the reaction $3Sr^{2+} = 2Y^{3+}$ + vacancy in the fresnoite composition, Y-substituted Sr-analogues of fresnoite, $(Sr_{2-x}Y_{2/3x})TiSi_2O_8$ ($x = 0, 0.5, 0.75, 1, 1.25, 1.5$) were prepared by high temperature synthesis and were found to form glass upon cooling. The Y-end-member ($Y_{1.33}TiSi_2O_8$, $x = 2$) crystallized to a mixture of Y_2TiSiO_7, TiO_2 and SiO_2 upon quenching in air. The Y-substituted Sr-fresnoite glass system can hold a realistic extent of substitution of Sr by Y up to at least 50% Sr in the charge-balanced fresnoite composition, making this system a useful waste form for ^{90}Sr and its beta decay products.

Figure 4 shows backscattered electron (BSE) images for the samples presenting no anomalous grains or secondary phases, and no heterogeneities in composition for glassy samples. For $Sr_{0.5}YTiSi_2O_8$ ($x = 1.5$), a Si-rich phase (likely glassy SiO_2) was exsolved as ~1 µm uniform dots embedded in the glass matrix. $Y_{1.33}TiSi_2O_8$ (G, $x = 2$) showed larger (~40 µm) grains of a Si-rich (cristobalite as confirmed by XRD) phase within the crystallized $Y_2Ti_2O_7$ phase.

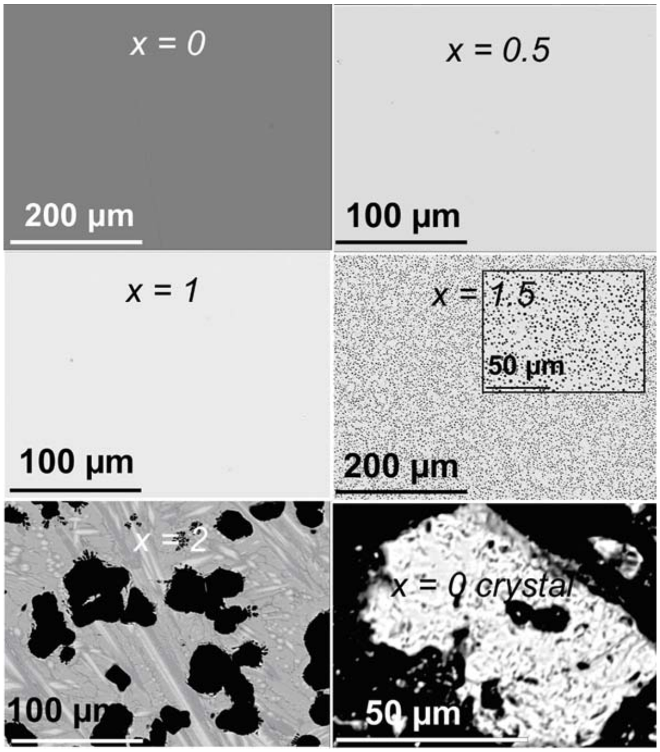

Figure 4. BSE images of as-prepared $Sr_{2-x}Y_{0.67x}TiSi_2O_8$ samples, with x values of 0, 0.5, 1, 1.5 and 2. BSE image of crystalline $Sr_2TiSi_2O_8$ is also shown.

With the discovery of a promising system as a waste form with high levels of loading, the crystallization behaviors of thermally treated Y-substituted $Sr_2TiSi_2O_8$ system were studied by the XRD (Figure 5). $Sr_2TiSi_2O_8$ composition crystallized to the Sr-analogue of fresnoite ($Sr_2TiSi_2O_8$) and structural transformation (tetragonal to cubic) became prominent in Y-rich samples. In the crystallized $Sr_{2-x}Y_{2/3x}TiSi_2O_8$ (x = 0, 0.5, 0.75, 1 and 1.25) samples, the Sr-analogue of fresnoite $Sr_2TiSi_2O_8$ (PDF#39-0228) was identified in sample A as the only phase; $Sr_2TiSi_2O_8$ and unknown phases (which we could not match with any known Y or Sr phases) were observed in sample B, C, D and E. Y-richer samples showed decreasing relative intensity of peaks at 27.80° to those at 29.85°. The peaks at 27.80° and 29.85° correspond to (201) and (211) planes of crystalline fresnoite, respectively. No peaks corresponding to (201) plane were observed when $x \geq 1$ (*e.g.*, $SrY_{0.67}TiSi_2O_8$, $Sr_{0.75}Y_{0.83}TiSi_2O_8$). When $x = 1.25$ ($Sr_{0.75}Y_{0.83}TiSi_2O_8$), we observed the (211) peak shifted to 29.99° from 29.85°. It is likely that the tetragonal to cubic structural transformation of $Sr_{2-x}Y_{0.67x}TiSi_2O_8$ occurs with increasing Y substitution. The peaks of Y-end-member ($Y_{1.33}TiSi_2O_8$), which crystallized to $Y_2Ti_2O_7$, rutile TiO_2, and cristobalite SiO_2 phase, are shown in Figure 4 for comparison. In the fresnoite structure (Figure 6), both of the (201) and (211) planes bisect the unit cell through the central TiO_5 square pyramid, but no Sr sites are located on the (211) planes. Thus, it is reasonable to assume that the (201) plane is more sensitive to any changes at the Sr sites than the (211) plane. It is likely that the decrease in the electron density of the (201) plane due to the substitution of Sr by Y + vacancy results in the decrease in the intensity of the (201) peaks. In addition, the smaller ionic radius[7] of Y (r(8) = 1.019 Å) than that of Sr (r(8) = 1.26 Å) may contribute to the structural transformation observed.

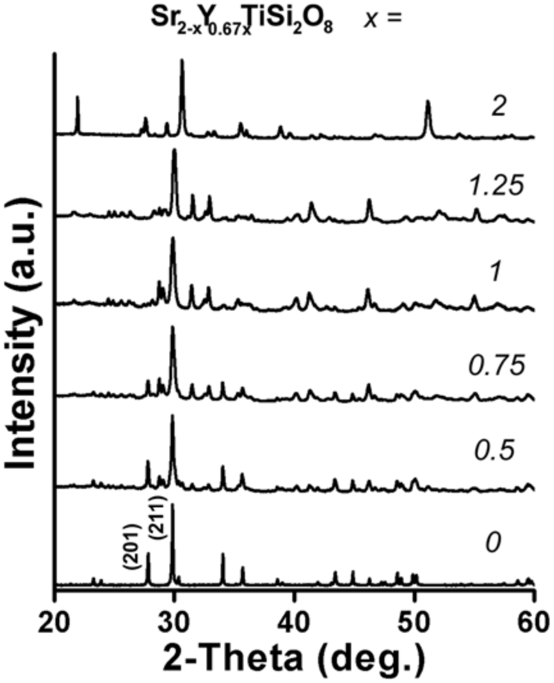

Figure 5. Powder X-ray diffraction (XRD) patterns of crystallized Y-substituted Sr-analogue of fresnoite ($Sr_{2-x}Y_{0.67x}TiSi_2O_8$, $x = 0, 0.5, 0.75, 1$ and 1.25). The peaks from $Y_{1.33}TiSi_2O_8$ ($x = 2$) are shown for comparison.

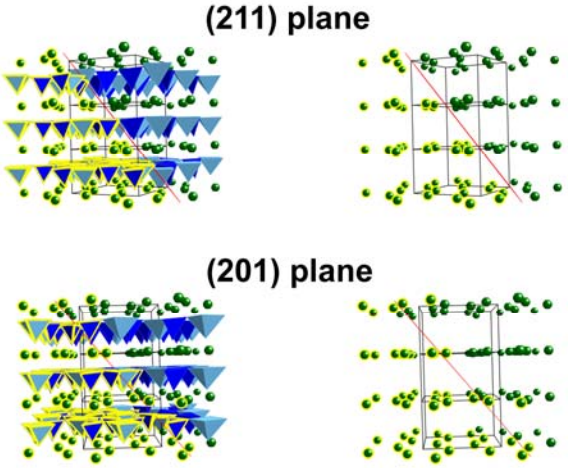

Figure 6. Crystal structure of fresnoite showing (201) and (211) lattice planes. Sphere represents a modifying cation. Tetrahedral and square pyramidal polyhedra represent SiO_4 and TiO_5 frameworks of fresnoite.

Strontium titanosilicate ($SrTiSiO_5$) is the Sr-analogue of titanite ($CaTiSiO_5$). A series of Sr-analogues of titanite glass waste form for radioactive Sr and its potential intermediates in beta decay product has been prepared between $SrTiSiO_5$ and $Y_{0.67}TiSiO_5$ by high temperature synthesis. The Y-substituted Sr-titanite glass system can hold an extent of substitution of Sr by Y up to at least 50% Sr in the charge-balanced titanite composition. Crystallization behavior of the $Sr_{1-x}Y_{0.67x}TiSiO_5$ glass system were examined by XRD (Figure 7) and could be summarized as follows: Sr-rich samples crystallize mainly to the Sr-analogue of fresnoite ($Sr_2TiSi_2O_8$) and Y-rich samples mainly to pyrochlore $Y_2Ti_2O_7$.

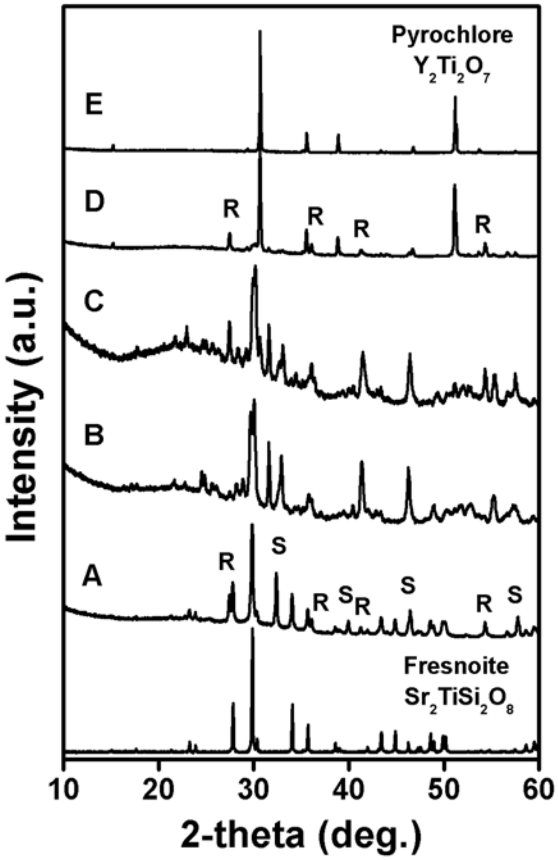

Figure 7. The powder X-ray diffraction (XRD) patterns of crystallized Y-substituted Sr-analogues of titanite ($Sr_{1-x}Y_{0.67x}TiSiO_5$, $x = 0, 0.25, 0.5, 0.75$ and 1). Peaks corresponding to the pyrochlore $Y_2Ti_2O_7$ phase, the rutile TiO_2, and the perovskite $SrTiO_3$ are marked with a "*P*", "*R*", "*S*".

c. The Glass – Crystal Stability of Sr-Y-Ti-Si-O system

The glass forming ability that relates to the materials instability through amorphization were characterized and summarized in Table II. The enthalpy of vitrification (ΔH_{vit}) of $Sr_2TiSi_2O_8$ was 17.1 ± 1.6 kJ/mol,[8] or about two times larger than that of SiO_2 cristobalite (9 kJ/mol) on a two-oxygen basis.[9] The higher ΔH_{vit} is consistent with the reluctant glass forming ability of the

Sr-fresnoite ($Sr_2TiSi_2O_8$) composition as compared with silica. ΔH_{vit} of fresnoite ($Ba_2TiSi_2O_8$) was 93.8 ± 3.0 kJ/mol.[10] Thus, $Sr_2TiSi_2O_8$ glass is less stable than $Ba_2TiSi_2O_8$ with respect to its oxides, reflecting the weaker basicity of SrO than of BaO. ΔH_{vit} of titanite ($CaTiSiO_5$) is 80.8 ± 3.6 kJ/mol (32.3 ± 1.4 kJ/mol on a 2-oxygen basis).[11] Thus, ΔH_{vit} on a 2-oxygen basis increases with increasing Ti / (Ti + Si). ΔH_{vit} of the aluminosilicate analogue anorthite ($CaAl_2Si_2O_8$) is 77.8 ± 0.8 kJ/mol (19.5 ± 0.2 kJ/mol on a 2-oxygen basis).[9] Thus Sr-analogue of fresnoite shows slightly better glass forming ability than anorthite and titanite. The glass forming ability is in the following order: $Sr_2TiSi_2O_8 > CaAl_2Si_2O_8 > Ba_2TiSi_2O_8 > CaTiSiO_5$. The ready glass formation of $Sr_2TiSi_2O_8$, even in the absence of radiation, suggests that amorphous phases may dominate as the Sr and Cs containing waste forms decay.

Table II. The enthalpies of vitrification (ΔH_{vit}) of silicates.

	ΔH_{vit} (kJ/mol)	
	reported	2-oxygen basis
SiO_2 (cristobalite)[9]	9	9
$CaAl_2Si_2O_8$ (anorthite)[9]	77.8	19.5
$Ba_2TiSi_2O_8$ (fresnoite)[10]	93.8	23.5
$CaTiSiO_5$ (titanite)[11]	80.8	32.3
$Sr_2TiSi_2O_8$ (fresnoite)[8]	68.5	17.1

The glass – crystal stability of the potential beta decay product (Y substitution product) from Sr-Ti-Si-O system were characterized by DSC (Figure 8). Crystallization includes both nucleation and crystal growth. Crystallization can happen fast (bulk crystallization) or slowly (surface crystallization). In the latter case, nucleation starts on the surface first, then the crystal growth continues into the bulk. ΔT (the difference between the onset glass transition temperature and the onset crystallization temperature) less than ~100 K is often used as the criterion for bulk crystallization for similar titanosilicate materials[1]. By this definition, the parent compounds (Sr-Ti-Si-O system) undergo bulk crystallization, whereas the beta decay products (Sr-Y-Ti-Si-O system) undergo surface crystallization. This suggests that the glass–crystal stability of the potential beta decay product (Y substitution product) from Sr-Ti-Si-O system is different from that of the Sr-end-members.

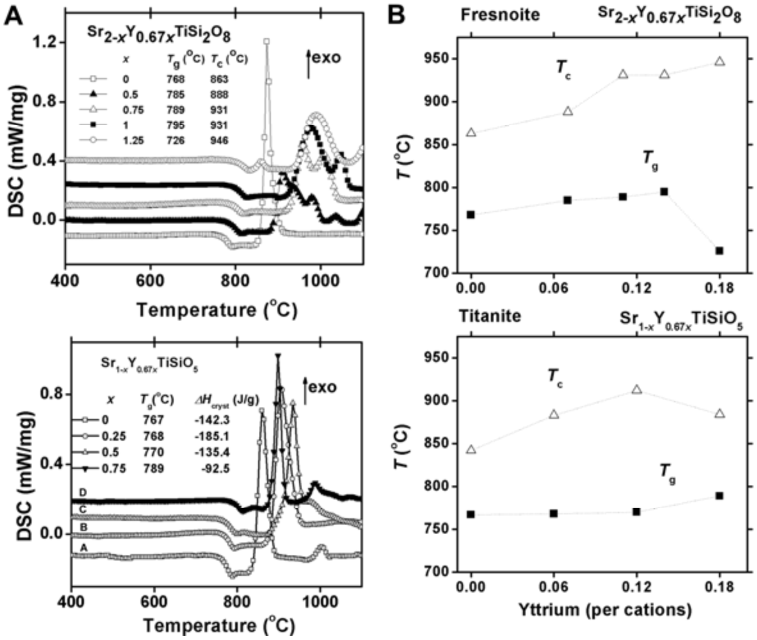

Figure 8. (A) Differential scanning calorimetry (DSC) traces showing the onset glass transition temperatures (T_g) and the onset crystallization (T_c) for Y-substituted Sr-analogue of fresnoite and titanite glass samples. (B) T_g and T_c are summarized as a function of yttrium to cations ratios (Y / (Sr + Y + Ti + Si)) of fresnoite $Sr_{2-x}Y_{2/3x}TiSi_2O_8$[8] and of titanite $Sr_{1-x}Y_{2/3x}TiSiO_5$[12].

For $SrTiSiO_5$, the major exothermic peak at 861 °C was due to crystallization to $Sr_2TiSi_2O_8$, confirmed by XRD. We could write the reaction: $SrTiSiO_5$ (glass) $\rightarrow \frac{1}{2}Sr_2TiSi_2O_8 + \frac{1}{2}TiO_2$. The ΔH_{cryst} calculated was −34.7 kJ/mol and this value was comparable to half of ΔH_{vit} of $Sr_2TiSi_2O_8$ (−68.5 ± 6.2 kJ/mol) determined from drop solution enthalpies for $Sr_2TiSi_2O_8$ glass and crystal[8]. This result indicated that there might be only a narrow window in temperature for the synthesis of the crystalline Sr-analogue of titanite ($SrTiSiO_5$), because the energetically more stable fresnoite phase would form and leave non-stoichiometric residues prior to the crystallization of $SrTiSiO_5$. This glass-crystal behavior was analogous to that of $BaTiSiO_5$ reported in previous study[10].

For $Sr_2TiSi_2O_8$, TG of all samples showed no significant weight change (less than 0.3%). The enthalpy of crystallization (ΔH_{cryst}) calculated from the sharp crystallization peak for $Sr_2TiSi_2O_8$ was −60.9 kJ/mol and this value was similar to that of $Sr_2TiSi_2O_8$ (−68.5 ± 6.2 kJ/mol). The crystallization behavior of Y-substituted $Sr_2TiSi_2O_8$ was different from that of $Sr_2TiSi_2O_8$. We could not obtain reasonable ΔH_{cryst} values for Y-substituted $Sr_2TiSi_2O_8$ because of broad and overlapping DSC peaks. The trend observed in T_c and T_g of Y-substituted $Sr_2TiSi_2O_8$ glasses as a function of yttrium per cations is shown in Figure 8. This trend was compared with that in Y-substituted $SrTiSiO_5$ in our previous study[12]. When Y / (Sr + Y + Ti + Si) reaches 0.18, both systems show different behavior in T_c and T_g from the trend. This difference may suggest a change in crystallization mechanism and/or the presence of crystallization nuclei or nanocrystals in the most Y-rich samples.

d. Thermodynamic Studies Using High-Temperature Reaction Calorimetry

Energetics of Ba-substituted $CsTiSi_2O_{6.5}$ Pollucite

The thermodynamic stability of a potential beta decay product series of two types, one with a replacement of one Ba for every two Cs to maintain charge balance ($Cs_{1-x}Ba_{0.5x}TiSi_2O_{6.5}$, $x = 0.1$), and the other with a stoichiometric one to one replacement of Cs by Ba, as would occur due to radioactive decay of Cs ($Cs_{1-x}Ba_xTiSi_2O_{6.5+0.5x}$, $x = 0.2$) was studied. The enthalpies of formation of Ba-substituted $CsTiSi_2O_{6.5}$ were obtained from drop solution calorimetry in a molten lead borate ($2PbO{\cdot}B_2O_3$) solvent at 702 °C. The enthalpies of formation from constituent oxides were exothermic and became less so with increasing Ba content. The effect of vacancy in the pollucite structure is more dominant factor than that of Ba replacement in thermochemical stability of the Ba-substituted $CsTiSi_2O_{6.5}$ phase (Figure 9).

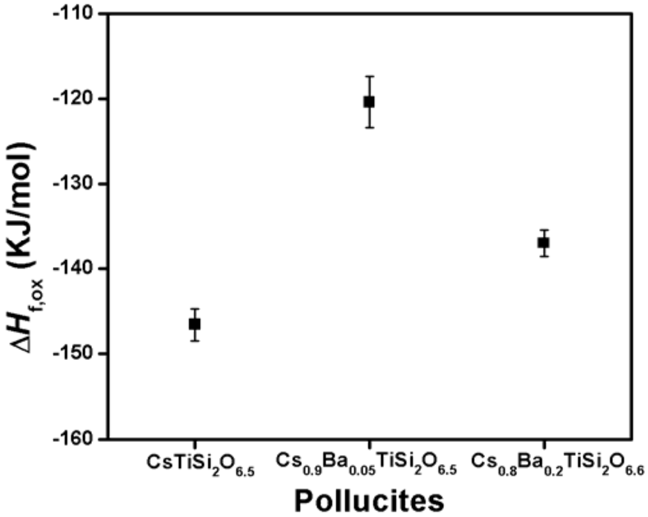

Figure 9. Enthalpies of formation from the oxides ($\Delta H^o_{f,ox}$) for pollucite samples. The average $\Delta H^o_{f,ox}$ for $CsTiSi_2O_{6.5}$, $Cs_{0.9}Ba_{0.05}TiSi_2O_{6.5}$ and $Cs_{0.8}Ba_{0.2}TiSi_2O_{6.6}$ samples are shown. $Cs_{0.8}Ba_{0.2}TiSi_2O_{6.6}$ and $Cs_{0.9}Ba_{0.05}TiSi_2O_{6.5}$ represent potential intermediates in beta decay products with one to one replacement of Cs by Ba and with charge-balance in pollucite structures, respectively.

Energetics of Y-substituted Sr-analogues of Fresnoite

The enthalpies of formation of Y-substituted Sr-fresnoite glasses were obtained from drop solution calorimetry in a molten lead borate ($2PbO{\cdot}B_2O_3$) solvent at 702 °C. The enthalpy of formation ($\Delta H^o_{f,ox}$) of $Sr_2TiSi_2O_8$ crystal was −396.4 ± 4.2 kJ/mol as compared with that of $Ba_2TiSi_2O_8$, −342.3 ± 4.6 kJ/mol. Measured drop solution enthalpies (ΔH_{ds}) of glassy $Sr_{2-x}Y_{2/3x}TiSi_2O_8$ ($x = 0, 0.5, 1$) and crystalline $Sr_2TiSi_2O_8$ samples as well as reference ΔH_{ds} values of binary oxides, SrO,[13] $YO_{1.5}$,[14] TiO_2[15] and SiO_2[16] (Table III), were used in a thermodynamic cycle to establish the enthalpy of formation ($\Delta H^{o}_{f,ox}$) of $Sr_{2-x}Y_{2/3x}TiSi_2O_8$ from the constituent oxides (Table IV). The standard enthalpies of formation of fresnoite from the elements ($\Delta H^{o}_{f,el}$) can be derived from the calculated $\Delta H^{o}_{f,ox}$ values and the $\Delta H^{o}_{f,el}$ values of the constituent oxides (Table III).[13, 14, 17] $\Delta H^{o}_{f,ox}$ for Y-substituted $Sr_2TiSi_2O_8$ from constituent oxides was exothermic but became less so with increasing Y content. The thermodynamic stability of the Y-substituted Sr-analogue of crystalline fresnoite may become marginal with increasing Y content.

Table III. Enthalpies of drop solution in lead borate at 702 °C (ΔH_{ds}) and enthalpies of formation from the oxides ($\Delta H^{o}_{f,ox}$) and from the elements ($\Delta H^{o}_{f,el}$) at 25 °C for glassy Y-substituted Sr-analogue of fresnoite $Sr_{2-x}Y_{0.67x}TiSi_2O_8$ ($x = 0, 0.5, 1$), crystalline $Sr_2TiSi_2O_8$ and reference values of binary oxides.

x	ΔH_{ds} (Jg^{-1})	ΔH_{ds} (kJmol^{-1})	$\Delta H^{o}_{f,ox}$ (kJmol^{-1})	$\Delta H^{o}_{f,el}$ (kJmol^{-1})
0	487.8 ± 5.3	198.7 ± 2.2	-327.9 ± 4.6	-4274.3 ± 5.4
0.5	478.2 ± 4.4	188.0 ± 1.8	-247.5 ± 3.6	-4216.2 ± 4.4
1	487.7 ± 3.3	184.8 ± 1.3	-139.8 ± 2.4	-4141.9 ± 3.4
SrO	-	-131.4 ± 1.9[13]	-	-590.5 ± 0.9[13]
$YO_{1.5}$	-	12.0 ± 0.6[14]	-	-952.7 ± 1.1[14]
TiO_2	-	55.4 ± 1.2[15]	-	-944.0 ± 0.8[17]
SiO_2	-	39.1 ± 0.3[16]	-	-910.7 ± 1.0[17]
$Sr_2TiSi_2O_8$ crystal	656.0 ± 3.3	267.2 ± 1.4	-396.4 ± 4.2	-4342.8 ± 5.1

Uncertainty is two standard deviations of the mean.

Table IV. Thermochemical cycle used to calculate the enthalpies of formation of Y-substituted Sr-analogue of fresnoite samples $Sr_{2-x}Y_{0.67x}TiSi_2O_8$ from the constituent oxides.

	Reaction	Enthalpy
1	$Sr_{2-x}Y_{0.67x}TiSi_2O_8$ (solid, 25°C) → $(2-x)$SrO (dissolved, 702°C) + $0.67x YO_{1.5}$ (dissolved, 702°C) + TiO_2 (dissolved, 702°C) + $2SiO_2$ (dissolved, 702°C)	$\Delta H_1 = \Delta H_{ds}$ (sample)
2	SrO (solid, 25°C) → SrO (dissolved, 702°C)	$\Delta H_2 = \Delta H_{ds}$ (SrO)[13]
3	$YO_{1.5}$ (solid, 25°C) → $YO_{1.5}$ (dissolved, 702°C)	$\Delta H_3 = \Delta H_{ds}$ ($YO_{1.5}$)[14]
4	TiO_2 (solid, 25°C) → TiO_2 (dissolved, 702°C)	$\Delta H_4 = \Delta H_{ds}$ (TiO_2)[15]
5	SiO_2 (solid, 25°C) → SiO_2 (dissolved, 702°C)	$\Delta H_5 = \Delta H_{ds}$ (SiO_2)[16]
6	$(2-x)$SrO (solid, 25°C) + $0.67x YO_{1.5}$ (solid, 25°C) + TiO_2 (solid, 25°C) + $2SiO_2$ (solid, 25°C) → $Sr_{2-x}Y_{0.67x}TiSi_2O_8$ (solid, 25°C)	$\Delta H_6 = \Delta H^{o}_{f,ox}$ (sample)

$\Delta H^{o}_{f,ox}$ (ΔH_6) = $-\Delta H_1 + (2-x)\Delta H_2 + 0.67x\Delta H_3 + \Delta H_4 + 2\Delta H_5$; ΔH_{ds} values are found in Table III.

The destabilizing effect in fresnoite compositions with increasing Y could be understood in terms of the basicity difference between SrO and $YO_{1.5}$ as well as the ratio of non-tetravalent cations to tetravalent cations (R_{cat} = (Sr + Y) / (Ti + Si)). A linear relationship between $\Delta H^o_{f,ox}$ and x ($YO_{1.5}$ content), suggesting zero enthalpy of mixing for $Sr_{2-x}Y_{0.67x}TiSi_2O_8$ glasses, within $0 \leq x \leq 1$ are shown in Figure 10. The destabilizing effect of the charge-coupled substitution $3Sr^{2+} = 2Y^{3+}$ on the fresnoite composition could be explained by the basicity difference of SrO and $YO_{1.5}$. The optical basicity of SrO and Y_2O_3 is 1.1 and 1.0, respectively.[18] Since Y_2O_3 is less basic than SrO, this trend was expected. As an additional factor, the ratios of non-tetravalent cations to tetravalent cations (R_{cat} = (Sr + Y) / (Ti + Si)) were examined. The easy crystallization starts when $R_{cat} \leq 0.53$ in Y-substituted Sr-fresnoite system, while it starts when $R_{cat} \leq 0.38$ in Y-substituted Sr-titanite system. R_{cat} also showed a linear correlation with $\Delta H^o_{f,ox}$. Extrapolation of the linearity in $\Delta H^o_{f,ox}$ and R_{cat} showed an endothermic formation enthalpy for glassy $Y_{1.33}TiSi_2O_8$, which was indeed observed. The thermodynamic stability of strontium titanosilicate mineral forms (*e.g.*, fresnoite and titanite) and their glasses may become marginal with increasing Y content.

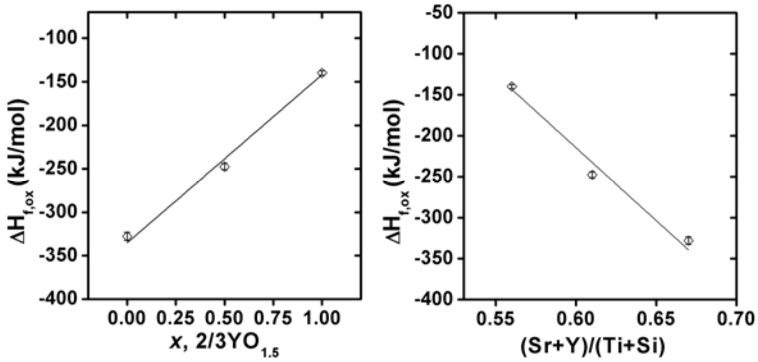

Figure 10. Enthalpies of formation from the constituent oxides ($\Delta H^o_{f,ox}$) of $(Sr_{2-x}Y_{2/3x})TiSi_2O_8$ (x = 0, 0.5 and 1) samples as a function of (A) Y content and (B) (Sr + Y) / (Ti + Si) ratios.

Energetics of Y-substituted Sr-analogues of $CaTiSiO_5$ Titanite

The enthalpy of formation ($\Delta H^o_{f,ox}$) of $SrTiSiO_5$ glass was measured to be −162.9 ± 2.4 kJ/mol as compared with that of titanite ($CaTiSiO_5$) glass, −38.78 ± 3.4 kJ/mol. $\Delta H^o_{f,ox}$ for Y-substituted Sr-titanite samples from constituent oxides was exothermic but became less so with increasing Y content. The thermodynamic stability of the Y-substituted Sr-analogue of crystalline titanite may become marginal with increasing Y content. The destabilizing effect in titanite compositions with increasing Y could be understood in terms of the basicity difference between SrO and $YO_{1.5}$ as well as the ratios of non-tetravalent cations to tetravalent cations (R_{cat} = (Sr+Y)/(Ti+Si)).

Figure 11 shows a linear relation between $\Delta H^o_{f,ox}$ and x ($YO_{1.5}$ content), suggesting zero enthalpy of mixing for $Sr_{1-x}Y_{0.67x}TiSiO_5$ glasses, within $0 \leq x \leq 0.5$. In addition, $\Delta H^o_{f,ox}$ became less exothermic with substitution of Sr^{2+} by Y^{3+}. This behavior indicates a destabilizing effect of the charge-coupled substitution $3Sr^{2+} = 2Y^{3+}$ on the titanite composition. Since Y_2O_3 is less basic than SrO, this trend is expected. An additional factor, the concentration of non-tetravalent cations, further explains better glass forming ability for $Y_{1.33}TiSiO_6$ than for $Y_{0.67}TiSiO_5$. Although tetravalent cations (Ti and Si) do not explicitly form frameworks in titanite composition, their function is distinguishable from that of non-tetravalent cations as in the case of framework silicates. $Y_{1.33}TiSiO_6$ has twice the non-tetravalent cations with respect to the tetravalent cations than $Y_{0.67}TiSiO_5$. The ratios of non-tetravalent cations to the tetravalent cations (R_{cat} = (Sr + Y) / (Ti + Si)) for the samples, $Sr_{1-x}Y_{0.67x}TiSiO_5$, x = 0, 0.25, 0.5, 0.75, and 1, were 0.50, 0.46, 0.42, 0.38, and 0.33, respectively. R_{cat} for $Y_{1.33}TiSiO_6$, which formed a homogeneous glass, was 0.67. This suggests that the easy crystallization starts when $R_{cat} \leq 0.38$. R_{cat} also show a linear correlation (Figure 11B). We note that extrapolation of the linearity in $\Delta H^{o}_{f,ox}$ and R_{cat} shows an endothermic formation enthalpy for E, which is indeed observed.

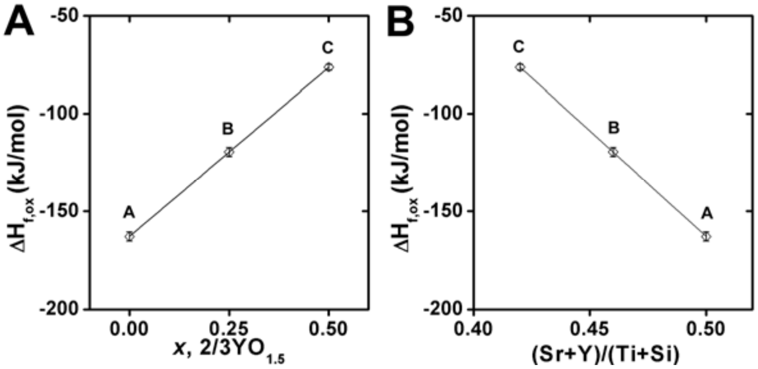

Figure 11. Enthalpies of formation from the constituent oxides ($\Delta H^{o}_{f,ox}$) of $(Sr_{1-x}Y_{2/3x})TiSiO_5$ (x = 0, 0.25 and 0.5) samples as a function of Y content (A) and (Sr+Y)/(Ti+Si) ratios (B).

III. Summary

In summary, we have determined the thermodynamic stabilities of a very durable waste form with Cs- or Sr-loaded mineral phases (e.g., pollucite, fresnoite, titanite), and of the potential decay product series (e.g., Cs-Ba-Ti-Si-O, Sr-Y-Ti-Si-O system). The enthalpies of formation from constituent oxides for the beta decay product series with charge-balance in mineral phases are exothermic but become less so with increasing daughter cation content. Microprobe analysis, XRD, calorimetry and synthesis studies have revealed that the glass-crystal stability in beta decay products is different from the parent compounds. The beta decay product undergoes surface crystallization, while the parent compounds undergoes bulk crystallization. The glass forming ability is in the following order: $Sr_2TiSi_2O_8$ (Sr-fresnoite) > $CaAl_2Si_2O_8$ (anorthite) > $Ba_2TiSi_2O_8$ (fresnoite) > $CaTiSiO_5$ (titanite). The ready glass formation of $Sr_2TiSi_2O_8$, even in the absence of radiation, suggests that amorphous phases may dominate as the Sr and Cs containing waste forms decay. The durability tests suggest that both glassy and crystalline fresnoite exhibit favorable aqueous stability and should be explored further as radioactive waste forms for long-term storage. This combined information on composition, chemical durability, and thermodynamic stability can be used to determine processing windows and to predict long- and short-term stability of multicomponent oxide phases.

4. A description of any products developed under the award and technology transfer activities such as:

A. Publications (list journal name, volume, issue); conference papers; or other public releases of results.

Publications

Tae-Jin Park, Terry J. Garino, Tina M. Nenoff and Alexandra Navrotsky, "The effect of vacancy and Ba-substitution on the stability of the $CsTiSi_2O_{6.5}$ pollucite," *Journal of the American Ceramic Society* (2010) submitted for publication.

Tae-Jin Park and Alexandra Navrotsky, "Thermochemistry and crystallization of glass forming Y-substituted Sr-analogue of fresnoite ($Sr_2TiSi_2O_8$)," *Journal of the American Ceramic Society* **93(7)**, 2055-61 (2010).

Tae-Jin Park, Simon Li and Alexandra Navrotsky, "Thermochemistry of glass forming Y-substituted Sr-analogue of titanite ($SrTiSiO_5$)," *Journal of Materials Research* **24(11)**, 3380-6 (2009).

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Terry J. Garino, Tina M. Nenoff, Tae-Jin Park and Alexandra Navrotsky, "The crystallization of Ba-substituted $CsTiSi_2O_{6.5}$ pollucite using $CsTiSi_2O_{6.5}$ seed crystals," *Journal of the American Ceramic Society* **92(9)**, 2144-6 (2009).

Presentations

Tina M. Nenoff, Terry Garino, Tae-Jin Park and Alexandra Navrotsky, "Fission-product Engineered Waste Forms: The Effects of Decay on Cs-Pollucite," *Materials Research Society (MRS) Spring Meeting,* San Francisco, CA (2010).

Tae-Jin Park and Alexandra Navrotsky, "Thermochemistry and Crystallization Behavior of Titanosilicate Materials: Possible Waste Forms for Radioactive Strontium and Intermediates in Decay Products," (Oral presentation) *239th American Chemical Society (ACS) National Meeting*, San Francisco, CA (2010).

Terry J. Garino, Tina M. Nenoff, David X. Rademacher, Tae-Jin Park and Alexandra Navrotsky, "The Synthesis of Ba-Substituted $CsTiSi_2O_{6.5}$ Pollucite," (Poster presentation) *Engineering Conferences International (ECI) Conferences*, Charleston, SC (2009).

Tae-Jin Park, Tina M. Nenoff, Terry J. Garino, James L. Krumhansl, Mark J. Davis, Paula Vullo and Alexandra Navrotsky, "Thermochemistry of Titanosilicate Minerals Relevant to Nuclear Energy Waste Forms," (Poster presentation) *Geological Society of America (GSA) Annual Meeting*, Portland, OR (2009).

Tae-Jin Park, Tina M. Nenoff, Terry J. Garino, James L. Krumhansl, Mark J. Davis, Paula Vullo and Alexandra Navrotsky, "Thermochemistry of Titanosilicate Materials Relevant to Nuclear Energy Waste Forms," (Poster presentation) *13th International IUPAC Conference on High Temperature Materials Chemistry (HTMC)*, Davis, CA (2009).

Nissim Navi, J. Zabicky, G. Kimmel, E. Goncharov, R. Shneck, M.H. Mintz, and A. Navrotsky, "Enthalpy of Mixing of $Sr_{1-x}Ca_xTiO_3$ and $Sr_{1-x}Ba_xTiO_3$ Perovskite Solid Solutions," *13th International IUPAC Conference on High Temperature Materials Chemistry (HTMC)*, Davis, CA (2009).

Tae-Jin Park, Alexandra Navrotsky, Mark J. Davis, James L. Krumhansl and Tina M. Nenoff, "Thermochemistry of New Fission Product Waste Forms," *Proceedings of Global 2009*, Paris, France (2009).

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Tae-Jin Park, Mark J. Davis, Tina M. Nenoff and Alexandra Navrotsky, "Thermochemistry of new fission product waste forms: (Cs,Ba)-titanosilicates," (Oral presentation) *Materials Research Society (MRS) Fall Meeting,* Boston, MA (2008).

B. Website or other Internet sites that reflect the results of this project.

None.

Networks or collaborations fostered.

UC Davis – Sandia National Laboratories as planned.
Mark Davis at Schott Inc. on fresnoite thermodynamics.
Ben Gurion University on sol-gel synthesis.
Chris Stanek at Los Alamos National Laboratory on high temperature synthesis.

D. Technologies/Techniques.

None.

E. Inventions/Patent applications.

None.

F. **Other products, such as data or databases, physical collections, audio or video, software or netware, educational aid or curricula, instruments or equipment.**

None.

5. List of conference papers/processing:

a. Name of the conference

Materials Research Society (MRS) Meeting
American Chemical Society (ACS) National Meeting
Engineering Conferences International (ECI) Conferences
Geological Society of America (GSA) Annual Meeting
Proceedings of Global 2009
13th International IUPAC Conference on High Temperature Materials Chemistry (HTMC)

b. Location of the conference

San Francisco
Charleston
Portland
Paris (France)
Davis
Washington
Boston

c. Date of the conference

Apr. 5 – 9, 2010
Mar. 21 – 25, 2010
Nov. 8 – 12, 2009
Oct. 18 – 21, 2009
Sep. 15 – 18, 2009
Sep. 6 – 11, 2009
Aug. 16 – 20, 2009
Dec. 1 – 5, 2008

d. Conference sponsor

Materials Research Society
American Chemical Society
Geological Society of America
International Union of Pure and Applied Chemistry
Engineering Conferences International
French Nuclear Energy Society

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