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Yttrium Substitution in $MTiO_3$ (M = Ca, Sr, Ba and Ca+Sr+Ba) Perovskites and Implication for Incorporation of Fission Products into Ceramic Waste Forms

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$CaTiO_3$ has been proposed as a ceramic waste form for immobilization of radioactive waste that might include short-lived fission products ^{137}Cs and ^{90}Sr and consequently their decay products ^{137}Ba (stable), ^{90}Y (intermediate), and ^{90}Zr (stable). In order to characterize substitution relations of Y^{3+} for M^{2+} (M = Ca, Sr, Ba singly or in combination) in $MTiO_3$, precursor mixtures with nominal atomic ratios of M:Y:Ti = 0.75:0.25:1 were synthesized by solid-state reactions. To ensure homogeneous starting material and to explore low temperature behavior of the Ca–Y–Ti–O system, coprecipitated xerogel powder was synthesized and heated to various temperatures for different periods of time. All M–Y–Ti–O systems formed two major phase mixtures of perovskite $MTiO_3$ and pyrochlore $Y_2Ti_2O_7$ with low substitution of M^{2+} by Y^{3+} in $MTiO_3$ and Y^{3+} by M^{2+} in $Y_2Ti_2O_7$. The study of xerogel confirmed the tendency of the formation of mixtures of $CaTiO_3$ and $Y_2Ti_2O_7$ phases, even at lower temperature. The temperature dependence of the substitution of Ca^{2+} by Y^{3+} in $CaTiO_3$ appears to be small. Despite the minor substitution of M by Y in the perovskite no significant $^{90}Y^{3+}$ build-up is expected to occur in the waste form due to the rapid decay of $^{90}Y^{3+}$ relative to that of $^{90}Sr^{2+}$.

I. Introduction

An important step to close the nuclear fuel cycle is the immobilization of radioactive waste in stable matrices for long-term storage or geological disposal. Titanate minerals have the capacity to incorporate in solid solution nearly all the elements present in radioactive waste[1,2] and exhibit little driving force for dissolution or alteration in the environment.[3] $CaTiO_3$, orthorhombic perovskite has been proposed as a ceramic waste form for immobilization of waste that might include short-lived $^{137}Cs^+$ and $^{90}Sr^{2+}$ fission products and consequently their decay products (with expected oxidation states indicated) $^{137}Ba^{2+}$ (stable), $^{90}Y^{3+}$ (short lived), and $^{90}Zr^{4+}$ (stable). The changes in composition as a result of the decay chain will be accompanied by changes of cation charge, volume, microstructure, crystal structure, mutual phase solubility limits, and chemical reactivity, in addition to radiation effects. Therefore it is essential to separate the chemical factors that will affect the long-term stability of the waste form from radiological effects.

Previous studies showed that $YTiO_3$ perovskite (containing Ti^{3+}) can be formed under reducing conditions[4,5] but only $Y_2Ti_2O_7$ pyrochlore (with Ti^{4+}) is stable in air. A cubic perovskite was reported in the $Y_xSr_{1-x}TiO_3$ system for x values up to 0.08 from synthesis at 1500°C under a reductive atmosphere.[6] Additional increase in x led to the formation of $Y_2Ti_2O_7$ pyrochlore. A $Ba_6Ti_{17}O_{40}$ phase in addition to the main $BaTiO_3$ perovskite was reported in the $Y_xBa_{1-x}TiO_3$ system for x values of 0.015 from synthesis in air while additional increase in x led to the formation of additional $Y_2Ti_2O_7$ pyrochlore.[7] However, a wide range of $YTiO_3$–$MTiO_3$ (M = Ca, Sr, Ba) solid solutions was observed when samples were made at high temperature via arc-melting under inert atmosphere.[8] Therefore, it is likely that a $CaTiO_3$ perovskite host matrix might be able to accommodate sufficient amount of Y^{3+} decay product under such a reducing atmosphere. In such a scenario, some reduction of tetravalent titanium presumably occurs and charge balance in the perovskite may be dominated by the reaction $M^{2+}+Ti^{4+} = Y^{3+}+Ti^{3+}$. However, the behavior of analogous systems under oxidizing conditions, where trivalent titanium is not present in significant amounts, is less well characterized. Furthermore, no evidence for the existence of $YTiO_3$ under an oxidizing atmosphere has been reported, nor were data found regarding Y^{3+} substitution for Ca^{2+} in $CaTiO_3$ or multicomponent M^{+2} (M = Ca+Sr+Ba) perovskites. The objective of this work is to explore the substitution limits of single and multidivalent M^{2+} cations by Y^{3+} in $MTiO_3$ perovskite waste form compositions, under an oxidizing atmosphere, using nonradioactive analogues for the respective elements, to separate chemical effects from those of radiation damage.

II. Experimental Procedures

(1) M–Y–Ti–O High Temperature Solid-State Synthesis

TiO_2, Y_2O_3, and MCO_3 (M = Ca, Sr, Ba and combinations thereof) preheated precursors were mixed under acetone or

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ethanol with molar composition ratios of M:Y:Ti = 0.75:0.25:1. The mixture was dried and compacted into pellets. The pellets were preheated to 1000°–1200°C for 6 h, cooled, ground under acetone or ethanol, dried, recompacted into pellets, and heated at 1500°C in air for 29 h to undergo solid-state reaction. After completion, the furnace was left to cool to 830°–880°C (taking approximately 0.5 h), before pellet removal for cooling at room temperature. Because solid-state reaction is slow even at 1500°C, we believe the furnace cooling is unlikely to cause significant changes in the compositions of phases present. A mixture of multidivalent cations $MTiO_3$ (M = 0.33Ca+0.33Sr+0.33Ba) was prepared with the same procedure.

(2) Ca–Y–Ti–O Synthesis from Xerogels

Coprecipitated xerogel samples with nominal atomic ratio of Ca:Y:Ti = 0.75:0.25:1.00 were synthesized to explore low-temperature substitution tendencies using homogeneous starting material. One hundred milliliter of an aqueous solution of $Ca(CH_3CO_2)_2$ and $Y(CH_3CO_2)_3$ (ca. 10% by weight) was placed in a distillation apparatus, and the water was distilled until the residue was about one-fourth of the original volume. The water in the distillation flask was replenished and the operation was repeated until CH_3CO_2H ceased to be evolved with the water. The distillation flask, containing a suspension of a white precipitate, was placed on a magnetic stirrer and a 1*M* solution of $Ti[OCH(CH_3)_2]_4$ (calculated stoichiometric amount) in dry $CH_3CH(OH)CH_3$ was added dropwise to the aqueous suspension. During distillation and isopropoxide hydrolysis a weak stream of pure nitrogen or argon was passed through the apparatus to avoid contamination with CO_2. The white residue was separated by centrifugation and decantation and the xerogel was dried in an Abderhalden pistol. Samples of the xerogel powder were calcined at conditions shown in Table I.

(3) Characterization

Phases present, their lattice parameters, and relative amounts were determined by X-ray powder diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer (Madison, WI) operated at 40 kV and 40 mA using Cu*K*α (λ = 1.54056 Å) radiation. JADE 6.1 software (Materials Data Inc., Livermore, CA) and the PDF file version 2.0 (PDF-2 Database, JCPDS-ICDD Newton Square, PA, 1999) were used for phase identification. Rietveld refinement from XRD patterns was used to estimate phase fractions using JADE or FullProf softwares.[9] Quantitative chemical analysis data were collected using a wavelength dispersive spectrometer (WDS) Cameca SX-100 electron microprobe (Cameca Inc., Courbevoie, France), with an accelerating voltage of 15 kEv, a probe current of 10 nA, and beam size of 1 μm. Energy-dispersive spectroscopy (EDS), back-scattered electron imaging (BSE), and characteristic X-ray dot mapping were used to determine the sample chemical homogeneity. $CaTiSiO_5$, TiO_2, $SrTiO_3$, YAG (synthetic Y-garnet, $Y_3Al_5O_{12}$), benitoite (naturally occurring mineral, $BaTiSi_3O_9$), were used as standards for measuring Ca, Ti, Sr, Y, Ba concentrations. Compositions of each phase are presented as an average value of about 10 points, with error given as two standard deviations of the mean. Oxygen concentrations were derived from stoichiometry, assuming M^{2+}, Y^{3+} valencies.

Table I. Heat-Treatment Conditions for the Ca–Y–Ti Xerogel Powder

800°C for 3 h
900°C for 1 h
800°C for 3 h+1100°C for 2 h
800°C for 3 h+1200°C for 2 h
800°C for 3 h+1400°C for 2 h
900°C for 1 h+1500°C for 29 h

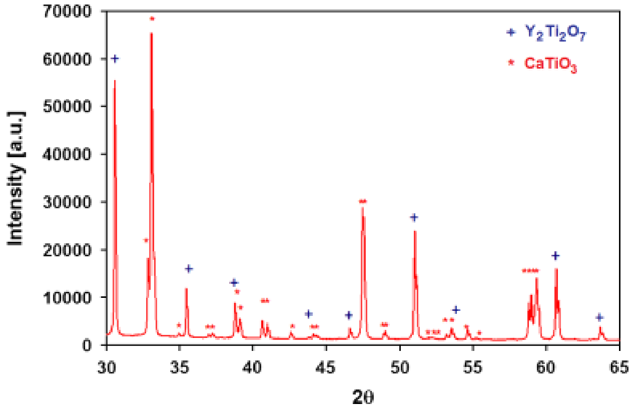

Fig. 1. XRD diffraction pattern of the single divalent cation Ca–Y–Ti–O system that was obtained by solid-state reaction heated to 1500°C for 29 h. Asterisks represent $CaTiO_3$, plus signs represent $Y_2Ti_2O_7$.

III. Results and Discussion

(1) M–Y–Ti–O Treated at 1500°C

All single M^{+2} divalent cation (M = Ca, Sr, Ba) and multidivalent cation (M = Ca+Sr+Ba) M–Y–Ti–O samples formed cubic $Y_2Ti_2O_7$ pyrochlore and $MTiO_3$ perovskite (orthorhombic for M = Ca, cubic for M = Sr, Ca+Sr+Ba, and tetragonal for M = Ba) as major phases when heated to 1500°C for 29 h. The $MTiO_3$–$Y_2Ti_2O_7$ phase separation reflects the structural differences of both phases due to the charge differences between Y^{3+} and M^{2+}. Figure 1 represents a typical XRD pattern, showing the presence of $CaTiO_3$ and $Y_2Ti_2O_7$ phases of the Ca–Y–Ti–O system obtained by solid-state reaction at 1500°C for 29 h. No other peaks than those belonging to these phases were observed for this sample. The presence of the two $MTiO_3$ and $Y_2Ti_2O_7$ major phases was indicated by BSE except for the Sr–Y–Ti–O system which will be discussed below. Figure 2 represents a typical BSE image. It indicates the presence of $CaTiO_3$ and $Y_2Ti_2O_7$ phases obtained from the Ca–Y–Ti–O solid-state reaction at 1500°C for 29 h. The sample shown in Fig. 2 contained large porosity and holes and therefore some dark contrast areas that are shown in the BSE image represent such porosity (and not a third phase). The BSE observations were supported by WDS (see Tables II and III).

Table II shows that the substitution of Y^{3+} for M^{2+} is small in all cases although the Ca–Y–Ti–O system contains a somewhat larger amount of Y in the perovskite than the other $MTiO_3$ systems. This effect is attributed to the relatively small ionic radius of the Ca^{2+} (1.12 Å), closer to Y^{3+} (1.019 Å), as compared with Sr^{2+} (1.26 Å) and Ba^{2+} (1.42 Å)[10] (ionic radius values are

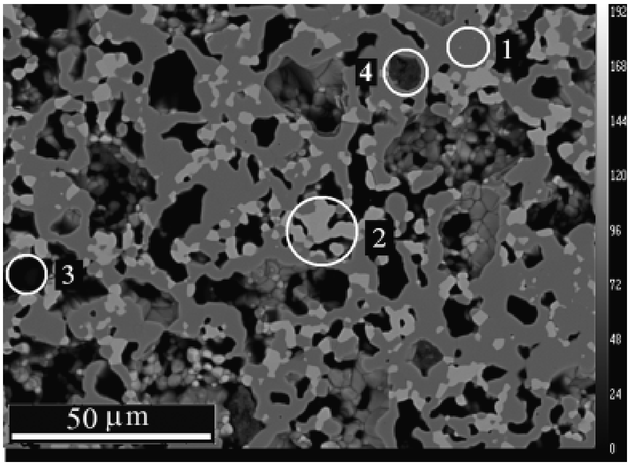

Fig. 2. BSE image of the single divalent cation Ca–Y–Ti–O system that was obtained by solid-state reaction heated to 1500°C for 29 h where 1 is $CaTiO_3$, 2 is $Y_2Ti_2O_7$, 3 is porosity, and 4 is shallow porosity.

Table II. Compositions (at.% Cations) of the Perovskite Phases after Heating at 1500°C for 29 h

	Ti	M			Y
Nominal	20	20			—
M = Ca†	19.8±0.4	18.7±0.3			1.3±0.0
M = Ca‡	20.1±0.4	16.7±0.3			2.6±0.1
M = Ba†	20.2±0.5	18.8±0.4			0.8±0.2
		Ca	Sr	Ba	
M = Ca+Sr+Ba†	19.0±0.4	6.6±0.5	6.7±0.5	5.9±0.5	0.7±0.2

†Synthesized by solid-state reaction. ‡Synthesized from coprecipitated xerogel.

taken for coordination number 8). The substitution of Y^{3+} for Ca^{2+} in the $CaTiO_3$ that was synthesized from xerogel was found to be higher than that in the sample synthesized by solid-state reaction. This could be within the experimental error or could be attributed to diffusion limitation of Y^{3+} in $CaTiO_3$ in the solid-state reaction due to the initially inhomogeneous starting material. Thus, the larger solubility that is observed in the homogeneous xerogel may represent an equilibrium state. Furthermore, the substitution of Y^{3+} for M^{2+} in the multidivalent cation system, with a cubic $SrTiO_3$-like perovskite structure, is similar to that in the single Ba–Y–Ti–O system. Figure 3 demonstrates the chemical homogeneity of the multidivalent cation system obtained from the solid-state reaction at 1500°C for 29 h. Figure 3 also shows Y and Ca/Sr/Ba-rich areas indicating clear separation between the Y and M elements while Ti is distributed relatively homogeneously between perovskite and pyrochlore, as expected. It should be noted that we did not see significant lattice parameter variations in the multidivalent cation perovskite synthesized with yttrium compared with multidivalent cation perovskite with the same M content that were synthesized without yttrium. This supports the low solubility of Y in the perovskite.

Phase separation and mutual substitution limits of Y^{3+} and Sr^{2+} could not be determined by BSE for the Sr–Y–Ti–O single divalent cation system due to the similarity in Z (atomic number) values of Sr and Y. The XRD pattern of the divalent cation Sr–Y–Ti–O system, that was obtained by solid-state reaction at 1500°C for 29 h, did not show any other peaks other than those of pure $SrTiO_3$ perovskite[11] and $Y_2Ti_2O_7$ pyrochlore.[12] A significant substitution of Y^{+3} by Sr^{+2} in the $Y_2Ti_2O_7$ phase, or Sr^{+2} by Y^{+3} in the $SrTiO_3$ phase, could be expected to change the lattice parameters of the phases, due to cation size difference and oxygen concentration changes that are needed to compensate for the charge difference between Sr^{+2} and Y^{+3}. Table III shows that the extent of substitution of Y^{+3} by Sr^{+2}, in the multidivalent cation M–Y–Ti–O system, is within the WDS instrumental error, which indicates a low tendency for Sr^{+2} to be substituted by Y^{+3}.

Figure 4 shows the XRD patterns of all M–Y–Ti–O systems, showing similarity in the peak positions for all $Y_2Ti_2O_7$ phases and therefore similarity in lattice parameters. This supports the low level of substitution observation of Y by M for all M–Y–Ti–O systems.

In the single divalent Ba–Y–Ti–O system, a minor third phase with cation composition (at.%) of Ba:Y:Ti = 27.1±0.5:0.1±0.0:9.2±0.3 is observed in BSE image. The BSE gray image, shown in Fig. 5(a), was converted into a false color image, Fig. 5(b), to emphasis composition differences of the three phases. Weak peaks corresponding to minor phases were observed in the XRD pattern of the Ba–Y–Ti–O system. The minor peaks that could not be assigned to a known phase are very low in intensity, perhaps too low in comparison to the amount of the third phase seen in the BSE image, suggesting that they may belong to some other very minor impurity. We did not investigate this issue further. From Tables II and III it seen that the amount of Ba in $Y_2Ti_2O_7$ is smaller than that expected if all the Ba substituted by Y in the perovskite were to have entered the pyrochlore. This suggests that the Ba–Ti-rich third phase forms from the Ba that did not enter the pyrochlore phase, presumably because of low solubility related to its large radius. A few small spots corresponding to a Ba–Ti-rich phase were also observed in the multidivalent system (which contained Ba) but their composition could not be determined due to small grain size. A third Ba–Ti-rich phase in Ba–Y–Ti–O system was reported previously[7] and supports the observation of Ba–Ti segregation, though phase compositions were found to be different from current study, perhaps due to differences in the synthesis procedure.

Semiquantitative EDS analysis of the Ca–Y–Ti–O xerogel powder indicated cation ratio of Ca:Y:Ti = 0.7:0.2:1. The high-temperature sample that was synthesized from the xerogel powder was similar to the Ca–Y–Ti–O sample that was synthesized from solid-state reaction, though a third minor phase with cation composition (at.%) of Ca:Y:Ti = 6.3±0.3:6.5±0.9:23.8±0.5 was observed. Weak peaks corresponding to a minor phases were observed in the XRD pattern of the Ca–Y–Ti–O xerogel sample. Although they could not be assigned to any known compound(s), they presumably belong to the Ca–Y–Ti third phase seen by microprobe. This phase may result from a slight deviation from the nominal stoichiometry of the xerogel, and is not attributed to segregation due to substitution limits (that was observed in the systems that contained Ba) because such a phase was not observed in the solid-state reaction sample.

(2) Ca–Y–Ti–O Xerogel Low-Temperature Behavior

Figure 6 shows selected XRD patterns of the Ca–Y–Ti–O xerogel powders heated in air (see Table I). The peak evolution confirms the tendency of the powder to separate into two major titanates, $CaTiO_3$ and $Y_2Ti_2O_7$ phases, even from initially homogeneous coprecipitated xerogels formed at room temperatures.

Table III. Compositions (at.% Cations) of the Pyrochlore Phases after Heating at 1500°C for 29 h

	Ti	Y	M		
Nominal	18.2	18.2		—	
M = Ca†	18.4±0.4	16.4±0.9		2.0±0.9	
M = Ca‡	19.4±0.4	14.9±0.3		2.3±0.2	
M = Ba†	18.6±0.4	17.6±0.3		0.1±0.1	
			Ca	Sr	Ba
M = Ca+Sr+Ba†	18.4±0.4	17.1±0.2	1.1±0.2	0.0±0.3	0.0±0.0

†Synthesized by solid-state reaction. ‡Synthesized from coprecipitated xerogel.

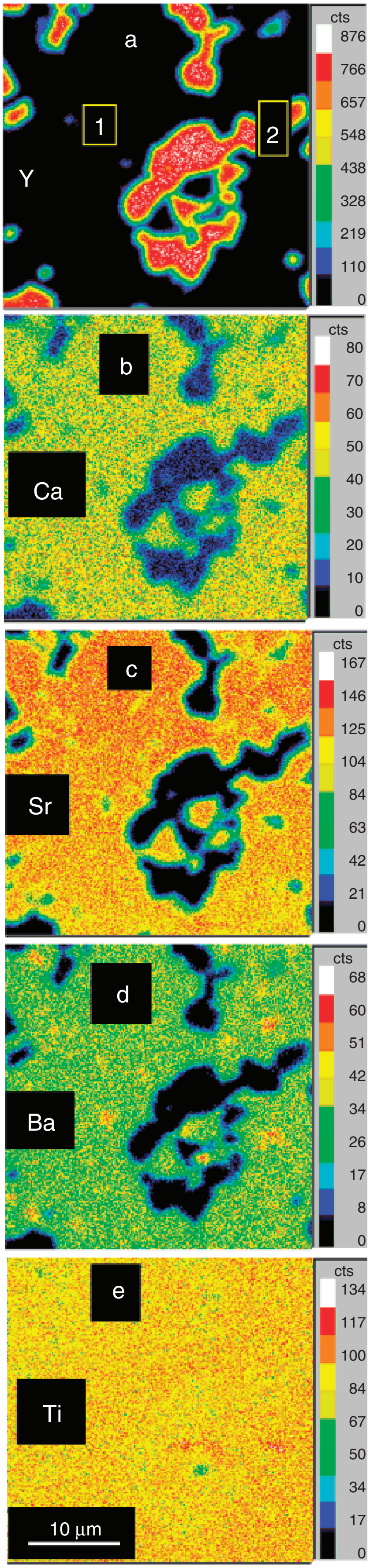

Fig. 3. X-ray dot map images of Y (a), Ca (b), Sr (c), Ba (d), Ti (e) of the multidivalent cation M–Y–Ti–O system that was obtained by solid-state reaction heated to 1500°C for 29 h. 1 is perovskite MTiO$_3$, 2 is Y$_2$Ti$_2$O$_7$.

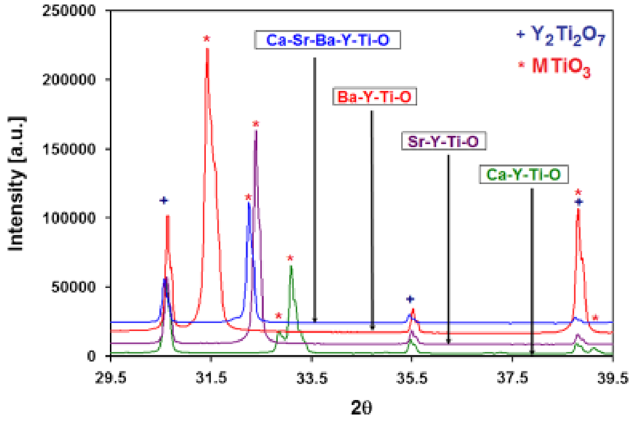

Fig. 4. XRD diffraction patterns of the single divalent cation Ca–Y–Ti–O, Sr–Y–Ti–O, Ba–Y–Ti–O and multidivalent cation Ca–Sr–Ba–Y–Ti–O systems that were obtained by solid-state reaction heated to 1500°C for 29 h. Asterisks represent perovskites MTiO$_3$, plus signs represent Y$_2$Ti$_2$O$_7$.

Figure 7 summarizes the CaTiO$_3$/Y$_2$Ti$_2$O$_7$ mole ratios and the molar volumes of the CaTiO$_3$ and the YTiO$_{3.5}$ phases (obtained from Rietveld analysis) corresponding to all heating conditions applied to the xerogel samples. The samples heated at lower temperatures have smaller CaTiO$_3$/Y$_2$Ti$_2$O$_7$ ratios and smaller YTiO$_{3.5}$ molar volumes than those heated to higher temperatures. The increase in the CaTiO$_3$/Y$_2$Ti$_2$O$_7$ mole ratios with temperature indicates an apparent increase in phase separation at higher temperatures. It is likely that Y$_2$Ti$_2$O$_7$ pyrochlore

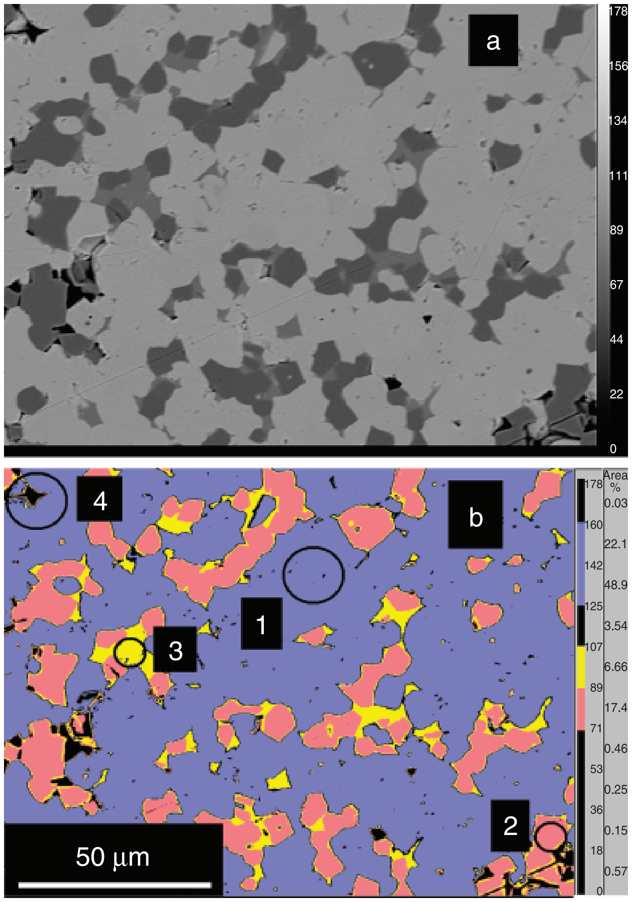

Fig. 5. (a) BSE image of the single divalent cation Ba–Y–Ti–O system obtained by solid-state reaction heated to 1500°C for 29 h and (b) BSE converted image where 1 is BaTiO$_3$, 2 is Y$_2$Ti$_2$O$_7$, and 3 is Ba–Ti-rich phase. Dark area, 4, is porosity.

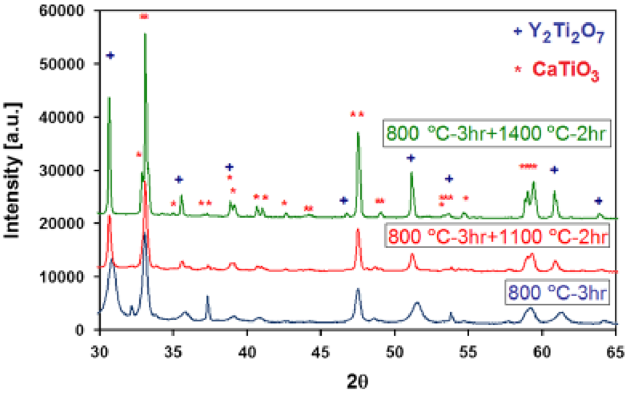

Fig. 6. XRD diffraction patterns of the single divalent cation Ca–Y–Ti–O xerogel samples that were heated in air to 800°C for 3 h (bottom), 800°C for 3 h plus 1100°C for 2 h (middle), 800°C for 3 h plus 1400°C for 2 h (top). Asterisks represent $CaTiO_3$, plus signs represent $Y_2Ti_2O_7$.

formed from the initially homogeneous xerogel accommodates a metastable larger amount of Ca due to slow diffusion at low temperature. When temperature increases, the Ca component apparently leaves the $Y_2Ti_2O_7$ to form more $CaTiO_3$ perovskite phase, inducing an increase in the $CaTiO_3/Y_2Ti_2O_7$ mole ratios and an increase in the $Y_2Ti_2O_7$ molar volume due to the increase of oxygen concentration that is needed for the charge balance compensation between Ca^{+2} and Y^{+3}. Additionally, from Fig. 7 it seen that the $CaTiO_3$ molar volume does not change significantly with temperature. This indicates that the substitution of Ca^{2+} by Y^{3+} in the perovskite $CaTiO_3$ is apparently small even in the initial low-temperature product from xerogel synthesis.

Potential ceramic waste forms containing $CaTiO_3$ perovskite could accommodate Sr as $(Sr_xCa_{1-x})TiO_3$ solid solution. Over the years the ^{90}Sr will decay and produce ^{90}Zr through an intermediate short lived ^{90}Y isotope. This sequence will change cation charge from Sr^{2+} to Y^{3+} to Zr^{4+}, with the surrounding environment a source/sink for electrons. The present study indicates a low substitution level of Ca^{2+} by Y^{3+} in the $CaTiO_3$ host matrix and therefore points to a tendency of the decay product $^{90}Y^{3+}$ to separate from the perovskite waste form into a $Y_2Ti_2O_7$ phase in an oxidizing environment. The substitution of Ca^{2+} by Y^{3+} in the $CaTiO_3$ might be reduced further with the presence of $^{90}Sr^{2+}$ (the original radioisotope) and $^{137}Ba^{2+}$ (the decay product of $^{137}Cs^{+}$, if present in the waste form). The low substitution levels of Ca^{2+} by Y^{3+} in the $CaTiO_3$ host matrix could therefore lead to formation of a separated $Y_2Ti_2O_7$ phase, with a molar volume misfit of 15%, due to the molar volume differences between $CaTiO_3$ (33.7 cm^3/moL) and $Y_2Ti_2O_7$ (38.7 cm^3/moL for $YTiO_{3.5}$). However, due to the rapid decay of $^{90}Y^{3+}$ (half life of 64.1 h), relative to that of $^{90}Sr^{2+}$ (half life of 28.8 yr), the yttrium concentration of the intermediate at secular equilibrium is expected to be far $<1\%$. Thus, no significant $^{90}Y^{3+}$ build-up is expected to occur in the waste form and consequently the current study suggests that the $CaTiO_3$ host matrix could potentially accommodate the small amounts of $^{90}Y^{3+}$ produced in a waste mixture. Because $^{90}Zr^{4+}$ is the final decay product of the $^{90}Sr^{2+}$, its concentration will increase, changing the overall charge balance and stoichiometry. Though Zr^{4+} could be soluble in both perovskite and pyrochlore phases, as a substitute for Ti^{4+}, the presence of other phases, such as $ZrTiO_4$, due to stoichiometry changes, should be considered. Therefore additional work on phase equilibria in the MO–TiO_2–Y_2O_3–ZrO_2 system is desirable.

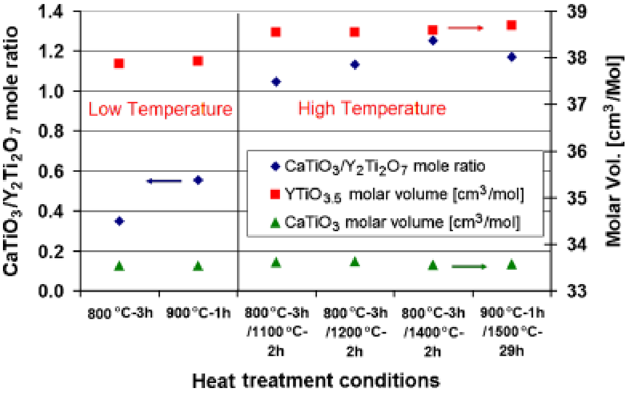

Fig. 7. $CaTiO_3/Y_2Ti_2O_7$ mole ratios (diamond, left Y-axis), molar volumes of the $CaTiO_3$ (triangle, right Y-axis), and the $YTiO_{3.5}$ phases (square, right Y-axis) that obtained from Rietveld analysis for all single divalent cation Ca–Y–Ti–O xerogel heat treatment conditions.

IV. Conclusions

This study shows that in MO (M = Ca, Sr, Ba or a combination thereof)–TiO_2–Y_2O_3 systems there is only very minor substitution of Y in the perovskite phase and of M in the pyrochlore phase under oxidizing conditions. Yet, because the decay of ^{90}Sr produces ^{90}Y as a short living transient intermediate with a very low concentration, it probably can be incorporated into the perovskite waste form. Because $^{90}Zr^{4+}$ is the final decay product of $^{90}Sr^{2+}$ further studies should be addressed to explore the substitution limits of Zr^{+4} with M^{+2} in multicomponent $MTiO_3$ potential waste forms.

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