Revision 1

Thermochemistry of Rare Earth Perovskites

$$Na_{3x}RE_{0.67-x}TiO_3 \text{ (RE = La, Ce)}$$
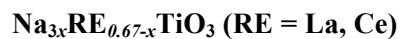
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Abstract

High temperature oxide melt solution calorimetry using sodium molybdate ($3Na_2O \cdot 4MoO_3$) solvent at 973 K was performed for the $Na_{3x}RE_{0.67-x}TiO_3$ (RE = La, Ce) perovskite series. The enthalpies of formation of lanthanum perovskites from oxides (La_2O_3, Na_2O, TiO_2), are -107.25±2.56, -93.83 ± 6.06, -80.68 ± 5.93 and -33.49 ± 4.26 kJ/mol and enthalpies of formation from elements are -1614.05±5.37, -1596.44 ± 7.68, -1594.03 ± 7.58 and -1577.56 ± 6.36 kJ/mol for $Na_{0.459}La_{0.522}Ti_{0.999}O_3$, $Na_{0.454}La_{0.523}Ti_{0.994}O_3$, $Na_{0.380}La_{0.567}Ti_{0.980}O_3$ and $La_{0.692}Ti_{0.979}O_3$, respectively. The enthalpies of formation of cerium perovskites are -99.98 ± 5.78 and -45.78 ± 3.30 kJ/mol from oxides (Ce_2O_3, Na_2O, TiO_2), and -1611.34 ± 6.90 and -1602.06 ± 2.72 kJ/mol from elements for $Na_{0.442}Ce_{0.547}Ti_{0.980}O_3$ and $Ce_{0.72}Ti_{0.96}O_3$. The A-site defect perovskites become more stable relative to oxide components as sodium contents increase. $Na_{0.5}Ce_{0.5}TiO_3$ and $Na_{0.5}La_{0.5}TiO_3$ could be considered as thermodynamically stable endmembers in natural loparite minerals, in which these endmembers are in solid solution with $CaTiO_3$ and other components.

Introduction

Perovskite is a structure of great interest to Earth and materials science (Bruce et al., 2010; Galasso, 1990; Navrotsky and Weidner, 1989). The perovskite structure with stoichiometry ABO_3 is adopted by a huge number of oxides containing A and B cations with different oxidation states. Their exquisite electrical and magnetic and structural properties make them attractive for various technical applications, including solar cells (Grinberg et al., 2013; Mei et al., 2014), sensors (Fergus, 2007), oxygen ion or cationic conductors, and battery materials (Zhang et al., 2014). Nature utilizes $MgSiO_3$-based perovskite as a major phase in in the dense hot ceramic interior of our planet, the lower mantle. From the 670 km seismic discontinuity to the core - mantle boundary, a $MgSiO_3$ - rich perovskite phase, now called bridgmanite after its recent discovery in meteorites (Tschauner et al., 2014), accounts for 50 – 90 % of the lower mantle as the most abundant mineral in the planet (Ito et al., 1990). $CaTiO_3$, the mineral perovskite after which the whole structural series is named, is an important accessory mineral in a number of crustal settings (Chakhmouradian and Wall, 2012; Jones et al., 1996; Lemanov et al., 1999; Mitchell, 2002). This mineral is the host for many ionic substitutions, including those of rare earths (Campbell et al., 1997).

The perovskite mineral loparite (Ce, Na, Sr, Ca)(Ti, Nb, Ta, Fe^{+3})O_3, is the principal ore of the light rare earth elements (LREE) at Lovozero, Russia. Loparite has coupled substitutions, polymorphism, defect chemistry and a tendency to become metamict when containing uranium or in close proximity to uranium minerals (Hedrick et al., 1997). The crystal structures of loparite-(Ce) have been investigated (Mitchell et al., 2000). As rare earths are critical to technological applications, there is increased interest in mining and processing (Hurd et al., 2012). It is significance to understand the energetics of rare earth perovskites for both optimizing the processing of rare earth ores and understanding the paragenesis and occurrences of rare earth minerals.

Perovskites have a 3-dimensional framework structure constructed from vertex-sharing BO_6 octahedra and A-site ions placed in 12-coordinate sites in a cubic close packing of A and oxide ions. Anion vacancies are well known in perovskites (Alariofranco et al., 1982). A-site defects, leading to a family of defect perovskites or bronzoids, are also tolerated in some perovskites such as $La_{0.67}TiO_3$ (abe and Uchino, 1974). Perovskites derived from $La_{0.67}TiO_3$ are of interest because the vacancies at these sites facilitate the electrochemical insertion of alkali metal ions and the subsequent movement of these cations through its structure (Ruiz et al., 2005).

In the ideal cubic case the cell axis, a, is geometrically related to the ionic radii: $a = \sqrt{2}\,(r_A + r_O) = 2(r_B + r_O)$, where r_A, r_B and r_O are the respective radii of A cation, B cation and O anion in the appropriate coordination. Deviations from cubic symmetry, leading to orthorhombic or rhombohedral polymorphs, can be rationalized using the *Goldschmidt tolerance factor*; $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$. The ideal cubic structure is formed for $t = 1$, when the A cation matches in size with the O^{2-} ions to form cubic close-packed layers, and the B cation matches the size of the interstitial sites formed by the oxygens to give an array of corner-shared BO_6 octahedra.

Phase equilibria in La_2O_3 - TiO_2 (Macchesney and Sauer, 1962) and Ce-Ti-O (Bamberger et al., 1994) have been investigated. The oxidation state of cerium remains 3+ in a reductive atmosphere and becomes 4^+ in an oxidative atmosphere, but knowledge of phase equilibria in the Ce_2O_3-CeO_2-TiO_2 system is incomplete. For analogous systems containing sodium oxide, there are few phase equilibrium data available (Kehoe et al., 2013). Thermodynamic data for perovskites in these systems are also sparse (Gong and Zhang, 2012), especially for sodium substitution in these cation deficient rare earth perovskites. The emphasis of the present study is to determine thermodynamic properties in the system $Na_{3x}RE_{0.67-x}TiO_3$ (RE = La, Ce) by measuring heats of formation using high temperature oxide melt solution calorimetry. The energetics of these substitutions and comparison between lanthanum and cerium could help in understanding the A-site substitutions and the occurrence of lanthanum- and cerium-perovskite minerals.

Experimental Methods

Materials

Na$_{3x}$RE$_{0.67-x}$TiO$_3$ (RE = La and Ce) samples were prepared by a standard solid state synthesis method, where Na$_2$CO$_3$, TiO$_2$ and La$_2$O$_3$ or CeO$_2$ (each 99.9 %, pure on metals basis, Alfa Aesar) were thoroughly mixed in stoichiometric ratios and calcined at 1273 K for 3 h. The calcined powder was cold pressed and sintered at 1473 K for 12 h. The sintered pellets were crushed and annealed at 973 K for diffraction and calorimetric experiments. For lanthanum perovskite, the compounds were synthesized in air. The cerium perovskite compounds were synthesized in a reducing atmosphere (5 % H$_2$ in 95 % Ar).

Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer (Bruker-AXS Inc., Madison WI) operated at an accelerating voltage of 40 kV and an emission current of 40 mA with a rotating sample stage attachment using CuK_α radiation (λ = 0.15406 nm). The phases were identified using the Jade 6.1 software package (Materials Data Inc., Livermore CA) equipped with both the International Center of Diffraction Data (ICDD) Powder Diffraction File (PDF) and the Inorganic Crystal Structure Database (ICSD).

The compositions were determined by wavelength dispersive electron probe microanalysis using a Cameca SX100 instrument (Cameca Inc., Gennevilliers, France) on polished samples. The instrument was operated at an accelerating voltage of 15 kV, with a 20 nA beam current and a spot size of 1 μm. The compositions were calculated from an average of 10 data points per sample. The standards used were NaAlSi$_3$O$_8$ (albite), LaPO$_4$, CeO$_2$ and TiO$_2$.

High temperature drop solution calorimetry in molten sodium molybdate (3Na$_2$O·4MoO$_3$) at 973 K was performed in a custom built Tian - Calvet twin calorimeter. The details of the calorimeter and methodology have been described previously (Navrotsky, 1977; Navrotsky, 1997; Navrotsky, 2014).

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Prior to calorimetry, compounds were stored in a desiccator. For each measurement, a ~5 mg pellet was loosely pressed, weighed and dropped from room temperature into $3Na_2O \cdot 4MoO_3$ melt at 973 K. The calorimeter was calibrated using the heat content of corundum. Oxygen was bubbled through the solvent at 5 ml/min and flushed over it at 50 ml/min to stir the melt and retain oxidizing conditions.

Results and discussion

Structure and chemical analysis

All synthesized samples were analyzed using powder XRD. The formation of a phase with the perovskite structure was confirmed for all samples and no secondary phases were detected (see Table 1). The back scattered electron images confirmed homogeneity with no secondary phases. From the microprobe analysis, the chemical compositions were determined as $Na_{0.459}La_{0.522}Ti_{0.999}O_3$, $Na_{0.454}La_{0.523}Ti_{0.994}O_3$, $Na_{0.380}La_{0.567}Ti_{0.980}O_3$, $La_{0.692}Ti_{0.979}O_3$, $Na_{0.442}Ce_{0.547}Ti_{0.980}O_3$ and $Ce_{0.72}Ti_{0.96}O_3$. For $La_{2/3}TiO_3$ and $Ce_{2/3}TiO_3$, the structure was tetragonal with P4/mmm space group (see Table 2).

Table 1: Composition and tolarance factor of $RE_{0.67-x}Na_{3x}TiO_3$ (RE = La and Ce)

Nominal	Microprobe	Tolerance number
$Na_{0.5}La_{0.5}TiO_3$	$Na_{0.459}La_{0.522}Ti_{0.999}O_3$	0.9689
$Na_{0.35}La_{0.55}TiO_3$	$Na_{0.454}La_{0.523}Ti_{0.994}O_3$	0.9578
$Na_{0.65}La_{0.45}TiO_3$	$Na_{0.380}La_{0.567}Ti_{0.980}O_3$	0.9691
$La_{0.67}TiO_3$	$La_{0.692}Ti_{0.979}O_3$	0.8309
$Na_{0.45}Ce_{0.5}TiO_3$	$Na_{0.442}Ce_{0.547}Ti_{0.980}O_3$	0.9748
$Ce_{0.67}TiO_3$	$Ce_{0.72}Ti_{0.96}O_3$	0.8442

Table 2: Calculated latice parameters and space groups of $RE_{0.67-x}Na_{3x}TiO_3$ (RE = La and Ce)

Composition	a (Å)	b (Å)	c (Å)	Space group
$Na_{0.459}La_{0.522}Ti_{0.999}O_3$	5.4781(0)	7.7529(9)	5.4833(1)	Pbnm
$Na_{0.454}La_{0.523}Ti_{0.994}O_3$	5.4760(3)	7.7472(5)	5.4805(3)	Pbnm
$Na_{0.380}La_{0.567}Ti_{0.980}O_3$	5.4753(3)	7.7459(5)	5.4796(8)	Pbnm
$La_{0.692}Ti_{0.979}O_3$	3.8819(3)	-	7.7486(5)	P4/mmm
$Na_{0.442}Ce_{0.547}Ti_{0.980}O_3$	5.4591(2)	7.7295(9)	5.4710(1)	Pbnm
$Ce_{0.72}Ti_{0.96}O_3$	3.8825(2)	-	7.7327(5)	P4/mmm

The lattice parameters observed are smaller for sodium-bearing samples, which show a volume decrease of about 1 %, which is close to the experimental uncertainty. A change from tetragonal to orthorhombic space group is known for these compounds (Ruiz et al., 1999). Ruiz et al. analyzed $Na_{0.42}La_{0.525}TiO_3$ and $Na_{0.24}La_{0.585}TiO_3$ by neutron diffraction and found an orthorhombic superstructure for these compounds, in contrast to undoped material $La_{0.67}TiO_3$, and they attributed this change to the difference between lanthanum and sodium ionic radii (Ruiz et al., 2002). Further X-ray studies confirmed the orthorhombic structures for $Na_{0.425}La_{0.525}TiO_3$, and showed that the system tends to form the tetragonal phase as sodium content decreases.

Enthalpies of formation

The measured enthalpies of drop solution, ΔH_{ds}, of $Na_{3x}RE_{0.67-x}TiO_3$ (RE = La and Ce) were used for determination of the enthalpy of formation from binary oxides, $\Delta H_{f,ox}$, and from elements, $\Delta H_{f,el}$. (see Tables 3, 4 and 5). To be noted, there are two valence states for Ce (3^+ and 4^+). In the high temperature oxide solvent drop calorimetry, the Ce dissolves into the solvent to form Ce^{4+} species. Thereby we first calculated the enthalpy of formation using CeO_2 as a reference and finally calculated the enthalpy of formation using Ce_2O_3 as a reference

Table 3. Thermochemical cycles for the calculation of formation enthalpies of $RE_{0.67-x}Na_{3x}TiO_3$ (RE = La and Ce) from binary oxides

Reactions	ΔH, kJ/mol
(a) Enthalpy of formation of $Na_{3x}La_{0.67-x}TiO_3$ from oxides at 298 K	
$Na_{3x}La_{0.67-x}TiO_{3\,(s,\,298\,K)}=1.5xNa_2O_{(sln,\,973\,K)}+ (0.335-0.5x)\,La_2O_{3(sln,\,973K)}+TiO_{2(sln,\,973\,K)}$	$\Delta H_1=\Delta H_{ds1}$
$Na_2O_{(s,\,298\,K)} \rightarrow Na_2O_{(sln,\,973\,K)}$	$\Delta H_2= -217.56\pm4.25$ (Tessier et al., 1999)
$La_2O_{3\,(s,\,298\,K)} \rightarrow La_2O_{3\,(sln,\,973\,K)}$	$\Delta H_3= -225.10\pm3.16$ (Cheng et al., 2005)
$TiO_{2\,(s,\,298\,K)} \rightarrow TiO_{2\,(sln,\,973\,K)}$	$\Delta H_4= 60.81\pm0.11$ (Navrotsky, 2014)
$1.5x\,Na_2O_{(s,\,298\,K)}+ (0.335-0.5x)\,La_2O_{3(s,\,298\,K)}+TiO_{2(s,\,298\,K)}=Na_{3x}La_{0.67-x}TiO_{3(s,\,298\,K)}$	$\Delta H_5=\Delta H_{f,ox} = -\Delta H_1+1.5x\,\Delta H_2+(0.335-0.5x)\,\Delta H_3+\Delta H_4$
(b) Enthalpy of formation of $Na_{3x}Ce_{0.67-x}TiO_3$ from oxides at 298 K using CeO_2 as reference state	
$Na_{3x}Ce_{0.67-x}TiO_{3(s,298\,K)}+(0.17-0.25x)O_{2(g,973\,K)}=1.5xNa_2O_{(sln,973\,K)}+ (0.67-x)CeO_{2(sln,\,973\,K)}+TiO_{2(sln,973K)}$	$\Delta H_6= \Delta H_{ds2}$
$Na_2O_{(s,\,298\,K)} \rightarrow Na_2O_{(sln,\,973\,K)}$	$\Delta H_2= -217.56\pm4.25$ (Navrotsky, 2014)
$CeO_{2\,(s,\,298\,K)} \rightarrow CeO_{2\,(sln,\,973\,K)}$	$\Delta H_7= 74.37\pm0.75$ (Navrotsky, 2014)
$TiO_{2\,(s,\,298\,K)} \rightarrow TiO_{2\,(sln,\,973\,K)}$	$\Delta H_4= 60.81\pm0.11$ (Navrotsky, 2014)
$O_{2\,(g,\,298\,K)} \rightarrow O_{2\,(g,\,973\,K)}$	$\Delta H_8=21.83$ (Chase, 1998)
$1.5xNa_2O_{(s,\,298\,K)}+ (0.67-x)\,CeO_{2(s,\,298\,K)}+TiO_{2(s,\,298\,K)}=Na_{3x}Ce_{0.67-x}TiO_{3(s,\,298\,K)}+ (0.17-0.25x)O_{2(g,\,973\,K)}$	$\Delta H_{f,ox} = -\Delta H_6+1.5x\Delta H_2+(0.67-x)\Delta H_7+\Delta H_4-(0.17-0.25x)\Delta H_8)$
(c) Enthalpy of formation of $Na_{3x}Ce_{0.67-x}TiO_3$ from oxides at 298 K using Ce_2O_3 as reference state at 298 K	
$0.5Ce_2O_{3(s,\,298\,K)}+0.25O_{2(g,\,298\,K)}=CeO_{2(s,\,298\,K)}$	$\Delta H_9= -185.8\pm2.5$ (Putnam et al., 2000)
$1.5xNa_2O_{(s,\,298\,K)}+ (0.335-0.5x)\,Ce_2O_{3\,(s,\,298\,K)}+TiO_{2(s,\,298\,K)}=Na_{3x}Ce_{0.67-x}TiO_{3(s,\,298\,K)}$	$\Delta H_{f',ox} = \Delta H_{f,ox}+(0.67-x)\,\Delta H_9$

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Table 4. Thermochemical cycles for calculation of enthalpies of formation of $RE_{0.67-x}Na_{3x}TiO_3$ (RE = La and Ce) from elements

Reactions	ΔH, kJ/mol
a) Enthalpy of formation of $Na_{3x}La_{0.67-x}TiO_3$ from elements at 298 K	
$1.5x$ $Na_2O_{(s,\ 298\ K)}$ + (0.335-0.5x) $La_2O_{3(s,\ 298\ K)}$ + $TiO_{2(s,\ 298\ K)}$ = $Na_{3x}La_{0.67-x}TiO_{3(s,\ 298\ K)}$	$\Delta H_{f,ox}$
$2Na_{(s,\ 298K)}$ + ½ $O_{2(g,\ 298K)}$ → $Na_2O_{(s,\ 298K)}$	ΔH_{10}= -417.98±4.2 (Chase, 1998)
$2\ La_{(s,\ 298K)}$ + $3/2O_{2(g,\ 298K)}$ → $La_2O_{3(s,\ 298K)}$	ΔH_{11}= -1791.6±2 (Chase, 1998)
$Ti_{(s,\ 298K)}$ + $O_{2(g,\ 298K)}$ → $TiO_{2(s,\ 298K)}$	ΔH_{12}= -944±0.8 (Chase, 1998)
$3xNa_{(s,\ 298\ K)}$ + (0.67-x)$La_{(s,\ 298\ K)}$ + $Ti_{(s,\ 298\ K)}$ + $1.5O_{2(g,\ 298\ K)}$ = $Na_{3x}La_{0.67-x}TiO_{3(s,\ 298\ K)}$	$\Delta H_{f,el\ 298\ K}$=$1.5x\Delta H_{10}$+(0.335-0.5x)ΔH_{11}+ΔH_{12})+$\Delta H_{f,ox,\ 298\ K}$
b) Enthalpy of formation of $Na_{3x}Ce_{0.67-x}TiO_3$ from elements at 298 K	
$1.5xNa_2O_{(s,\ 298\ K)}$ + (0.67-x) $CeO_{2(s,\ 298\ K)}$ + $TiO_{2(s,\ 298\ K)}$ = $Na_{3x}Ce_{0.67-x}TiO_{3(s,\ 298\ K)}$ + (0.17-0.25x)$O_{2(g,\ 973\ K)}$	$\Delta H_{f,ox}$
$2Na_{(s,\ 298K)}$ + ½ $O_{2(g,\ 298K)}$ → $Na_2O_{(s,\ 298K)}$	ΔH_{10}= -417.98±4.2 (Chase, 1998)
$Ce_{(s,\ 298K)}$ + $O_{2(g,\ 298K)}$ → $CeO_{2(s,\ 298K)}$	ΔH_{13}= -1088.68±1.46 (Chase, 1998)
$Ti_{(s,\ 298K)}$ + $O_{2(g,\ 298K)}$ → $TiO_{2(s,\ 298K)}$	ΔH_{12}= -944±0.8 (Chase, 1998)
Thereby the Enthalpy of formation of $Na_{3x}Ce_{0.67-x}TiO_3$ from elements *at 298 K is*	
$3x$Na(s, 298 K)+ (0.67-x)Ce (s, 298 K)+Ti(s, 298 K) +$1.5O_2$(g, 298 K) = $Na_{3x}Ce_{0.67-x}TiO_{3(s,\ 298\ K)}$	$\Delta H_{f,el\ 298\ K}$=$1.5x\Delta H_{10}$+(0.67-x)ΔH_{13}+ΔH_{12})+$\Delta H_{f,ox,\ 298\ K}$

Table 5. Enthalpies of formation of $RE_{0.67-x}Na_{3x}TiO_3$ (RE = La and Ce) at 298 K

Compounds*	$\Delta H_{ds,\ 298K}$, kJ/mol	$\Delta H_{f,ox,\ 298K}$, kJ/mol	$\Delta H_{f,el,\ 298K}$, kJ/mol
$Na_{0.459}La_{0.522}Ti_{0.999}O_3$	59.38±0.66	-107.25±2.56	-1614.05±5.37
$Na_{0.454}La_{0.523}Ti_{0.994}O_3$	45.91±2.95	-93.83±6.06	-1596.44±7.68
$Na_{0.380}La_{0.567}Ti_{0.980}O_3$	35.12±2.67	-80.68±5.93	-1594.03±7.58
$La_{0.692}Ti_{0.979}O_3$	15.14±2.85	-33.49±4.26	-1577.56±6.36
$Na_{0.442}Ce_{0.547}Ti_{0.980}O_3$	47.48±2.92	-99.98±5.78	-1611.34±6.90
$Ce_{0.72}Ti_{0.96}O_3$	19.98±2.01	-45.78±3.30	-1602.06±2.72

*Calculated based on the microprobe analyses from 10 points data for each sample

Figure 1 shows the formation enthalpy of $Na_{3x}RE_{0.67-x}TiO_3$ (RE = La and Ce) as a function of Na substitution. The enthalpy of formation from oxides becomes more exothermic with increasing sodium content and A-site filling (see Fig. 1). The formation enthalpies become more negative as the sodium substitution grows, implying that the sodium substitution in the A-site vacancies improves the thermodynamic stability of $Na_{3x}RE_{0.67-x}TiO_3$ (RE = La and Ce). For the cerium and lanthanum endmembers, the enthalpies of formation from oxides are less exothermic than values for Na-substitution perovskites with titanium in the B-site. This can be attributed to the existence of empty A-sites. The enthalpies of formation of $Na_{3x}Re_{0.67-x}TiO_3$ (RE = La and Ce) from the oxides become more exothermic with increasing sodium content (see Fig. 1). In addition, the Cerium perovskite tend to be more stable than the Lanthanum perovskite for comparable sodium contents. This could reflect the smaller radius of Ce^{3+} (1.34 Å) than of La^{3+} (1.36 Å) for twelve - fold coordination (Shannon, 1976). Figure 2 shows a linear trend between the enthalpy of formation and the Goldschmidt tolerance factor, where the enthalpies of formation become more negative as the tolerance number increases, as has been noted before for many other perovskite systems (Sahu et al., 2015).
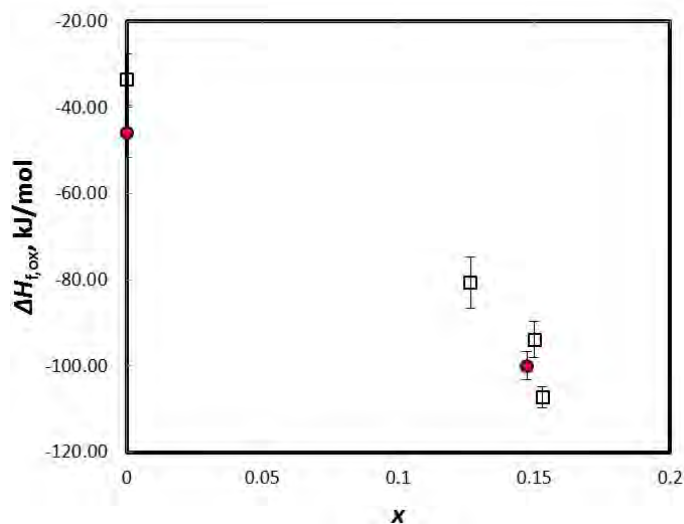
Figure 1: Formation enthalpy of $Na_{3x}RE_{0.67-x}TiO_3$ (RE = La and Ce) as a function of Na substitution, where squares represent lanthanum perovskites, circles represent cerium perovskites.
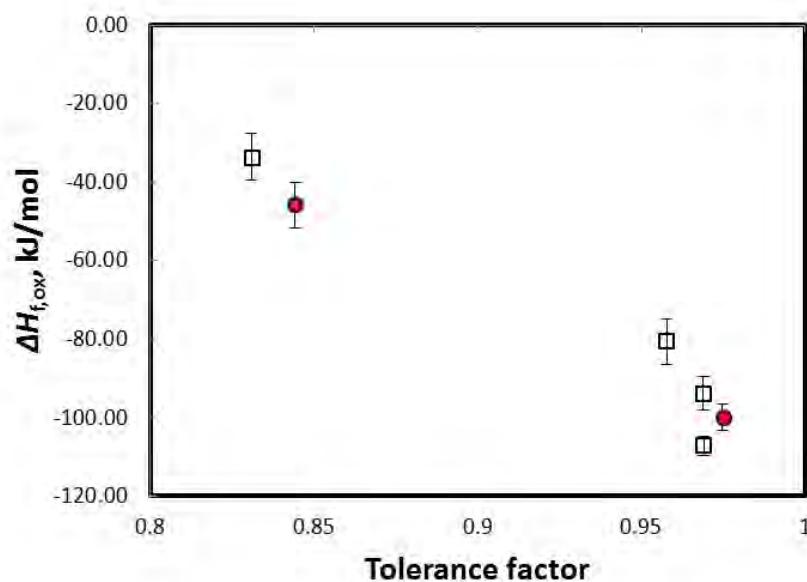

Figure 2: Formation enthalpy of $Na_{3x}Re_{0.67-x}TiO_3$ as a function of tolerance factor, where squares represent lanthanum perovskites, circles represent cerium perovskites.

To be noted the fact that it is 12-fold coordination for cubic structure, while for tetragonal and orthorhombic structures the coordination number is less. As in prior work (Sahu et al., 2015), we use the 12-fold coordination number to calculate the tolerance number. The reasoning behind this is that the

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tolerance factor, calculated for the cubic case, shows the driving force both for distortion and for overall decrease in stability.

Implications

The $RE_{0.67}TiO_3$ perovskite is cation deficient. With increasing sodium content in the A-site, the perovskite become more stable relative to the binary oxides. This reflects both the greater basicity of Na_2O compared to REE_2O_3 and increasing A-site occupancy. When the sodium substitution is 0.5, the A-site is completely filled by a (presumably random) mixture of Na and REE ions which are reasonably well matched in size (for Na^+ and La^{3+} or Ce^{3+}). The ionic radii for Na^+ and La^{3+} or Ce^{3+} are well-matched in size. The ionic radii are close for Na^+ (1.39 Å) and La^{3+} (1.36Å) or Ce^{3+} (1.34 Å), which makes them randomly mixed at A-sites. This leads to greater thermodynamic stability. Further sodium substitution ($3x > 0.5$) is presumably less favorable as there are no more A-site vacancies to fill and materials with $3x > 0.5$ are difficult or impossible to synthesize. Therefore $Na_{0.5}RE_{0.5}TiO_3$ will be considered, in a thermodynamic as well as structural sense, to be an endmember in the $Na_{3x}RE_{0.67-x}TiO_3$ system. It could be incorporated into natural perovskite, $CaTiO_3$, by the charge coupled substitutions $Ca^{2+} = 0.5Na^+ + 0.5REE^{3+}$. Our determination of the energetics of these endmembers is a starting point for future analysis of the thermodynamics of complex perovskites of the loparite family. Such perovskites are important to petrology, rare earth mining, and materials science and technology. Interestingly, most loparite contains cerium more than lanthanum. The more negative enthalpy (and presumably free energy) of formation of the cerium endmember may contribute to this preference. Further calorimetric study of complex rare earth perovskites is underway.

Acknowledgements

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References

Abe, M., and Uchino, K. (1974) X-ray study of the deficient perovskite $La_{2/3}TiO_3$. Materials Research Bulletin, 9(2), 147-155.

Alariofranco, M.A., Joubert, J.C., and Levy, J.P. (1982) Anion deficiency in iron perovskites - the $Sr_xNd_{1-x}FeO_{3-y}$ solid-solution.1. $0.6 \leq x \leq 0.8$. Materials Research Bulletin, 17(6), 733-740.

Bamberger, C.E., Haverlock, T.J., Shoup, S.S., Kopp, O.C., and Stump, N.A. (1994) Compounds of cerium, titanium and oxygen. Journal of Alloys and Compounds, 204(1-2), 101-107.

Bruce, D.W., O'Hare, D., and Walton, R.I. (2010) Functional oxides. Inorganic materials series, Wiley, Chichester, West Sussex.

Campbell, L.S., Henderson, P., and Wall, F. (1997) Rare earth chemistry of perovskite group minerals from the Gardiner Complex, East Greenland. Mineralogical Magazine, 61(2), 197-212.

Chakhmouradian, A.R., and Wall, F. (2012) Rare Earth Elements: Minerals, Mines, Magnets (and More). Elements, 8(5), 333-340.

Chase, M.W., Jr. (1998) NIST-JANAF Themochemical Tables. American Chemical Society, Woodbury, N.Y.

Cheng, J.J., Navrotsky, A., Zhou, X.D., and Anderson, H.U. (2005) Thermochemistry of $La_{1-x}Sr_xFeO_{3-\delta}$ solid solutions ($0.0 \leq x \leq 1.0$, $0.0 \leq \delta \leq 0.5$). Chemistry of Materials, 17(8), 2197-2207.

Fergus, J.W. (2007) Perovskite oxides for semiconductor-based gas sensors. Sensors and Actuators B-Chemical, 123(2), 1169-1179.

Galasso, F.S. (1990) Perovskites and high Tc superconductors. Gordon and Breach Science Publishers, New York.

Gong, W.P., and Zhang, R. (2012) Thermodynamic investigation of the TiO_2-La2O$_3$ pseudo-binary system. Thermochimica Acta, 534, 28-32.

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Grinberg, I., West, D.V., Torres, M., Gou, G.Y., Stein, D.M., Wu, L.Y., Chen, G.N., Gallo, E.M., Akbashev, A.R., Davies, P.K., Spanier, J.E., and Rappe, A.M. (2013) Perovskite oxides for visible-light-absorbing ferroelectric and photovoltaic materials. Nature, 503(7477), 509.

Hedrick, J.B., Sinha, S.P., and Kosynkin, V.D. (1997) Loparite, a rare-earth ore (Ce, Na, Sr, Ca)(Ti, Nb, Ta, Fe+3)O^{-3}. Journal of Alloys and Compounds, 250(1-2), 467-470.

Hurd, A.J., Kelley, R.L., Eggert, R.G., and Lee, M.H. (2012) Energy-critical elements for sustainable development. Materials Research Bulletin, 37(4), 405-410.

Ito, E., Akaogi, M., Topor, L., and Navrotsky, A. (1990) Negative Pressure-Temperature slopes for reactions forming $MgSiO_3$ Perovskite from Calorimetry. Science, 249(4974), 1275-1278.

Jones, A.P., Wall, F., Williams, C.T., and Mineralogical Society (Great Britain). (1996) Rare earth minerals : chemistry, origin and ore deposits. Chapman & Hall, London.

Kehoe, S., Langman, M., Werner-Zwanziger, U., Abraham, R.J., and Boyd, D. (2013) Mixture designs to assess composition-structure-property relationships in SiO_2-CaO-ZnO-La_2O_3-TiO_2-MgO-SrO-Na_2O glasses: Potential materials for embolization. Journal of Biomaterials Applications, 28(3), 416-433.

Lemanov, V.V., Sotnikov, A.V., Smirnova, E.P., Weihnacht, M., and Kunze, R. (1999) Perovskite $CaTiO_3$ as an incipient ferroelectric. Solid State Communications, 110(11), 611-614.

Macchesney, J.B., and Sauer, H.A. (1962) The System La_2O_3-TiO_2 - Phase equilibria and electrical properties. Journal of the American Ceramic Society, 45(9), 416-422.

Mei, A.Y., Li, X., Liu, L.F., Ku, Z.L., Liu, T.F., Rong, Y.G., Xu, M., Hu, M., Chen, J.Z., Yang, Y., Gratzel, M., and Han, H.W. (2014) A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. Science, 345(6194), 295-298.

Mitchell, R.H. (2002) Perovskites : modern and ancient. VII, Almaz Press, Thunder Bay, Ont.

Mitchell, R.H., Burns, P.C., and Chakhmouradian, A.R. (2000) The crystal structures of loparite-(Ce). Canadian Mineralogist, 38, 145-152.

Navrotsky, A. (1977) Progress and new directions in high-temperature calorimetry. Physics and Chemistry of Minerals, 2(1-2), 89-104.

-. (1997) Progress and new directions in high temperature calorimetry revisited. Physics and Chemistry of Minerals, 24(3), 222-241.

-. (2014) Progress and new directions in calorimetry: A 2014 perspective. Journal of the American Ceramic Society, 97(11), 3349-3359.

Navrotsky, A., and Weidner, D.J. (1989) Perovskite : a structure of great interest to geophysics and materials science. American Geophysical Union, Washington, D.C.

Putnam, R.L., Navrotsky, A., Cordfunke, E.H.P., and Huntelaar, M.E. (2000) Thermodynamics of formation of two cerium aluminum oxides, $CeAlO_3(s)$ and $CeAl_{12}O_{19.918}(s)$, and cerium sesquioxide, $Ce_2O_3(s)$ at T=298.15 K. Journal of Chemical Thermodynamics, 32(7), 911-921.

Ruiz, A.I., Lopez, M.L., Pico, C., and Veiga, M.L. (2002) New $La_{2/3}TiO_3$ derivatives: Structure and impedance spectroscopy. Journal of Solid State Chemistry, 163(2), 472-478.

-. (2005) Structural modifications induced by composition in the $La_{1.33-x}Na_{3x}Ti_2O_6$ perovskites: A neutron diffraction study. Chemistry of Materials, 17(6), 1391-1397.

Ruiz, A.I., Lopez, M.L., Veiga, M.L., and Pico, C. (1999) Electrical behaviour of $La_{1.33-x}M_{3x}Ti_2O_6$ perovskites (M=Li, Na and K). International Journal of Inorganic Materials, 1(3-4), 193-200.

Sahu, S.K., Tanasescu, S., Scherrer, B., Marinescu, C., and Navrotsky, A. (2015) Energetics of lanthanide cobalt perovskites: $LnCoO_{(3-\delta)}$ (Ln = La, Nd, Sm, Gd). Journal of Materials Chemistry A, 3(38), 19490-19496.

Shannon, R.D. (1976) Revised effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica Section A, 32(Sep1), 751-767.

Tessier, F., Le Sauze, A., Marchand, R., and Navrotsky, A. (1999) Energetics of nitridophosphates PON and "LiNaPON glasses". Solid-State Chemistry of Inorganic Materials Ii, 547, 389-394.

Tschauner, O., Ma, C., Beckett, J.R., Prescher, C., Prakapenka, V.B., and Rossman, G.R. (2014) Discovery of bridgmanite, the most abundant mineral in Earth, in a shocked meteorite. Science, 346(6213), 1100-1102.

Zhang, J., Zhao, Y.B., Zhao, X., Liu, Z.L., and Chen, W. (2014) Porous perovskite $LaNiO_3$ nanocubes as cathode catalysts for $Li-O_2$ Batteries with low charge potential. Scientific Reports, 4.