Thermochemistry of rare earth perovskites Na$_{3x}$RE$_{0.67-x}$TiO$_3$ (RE = La, Ce)

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**ABSTRACT**

High-temperature oxide melt solution calorimetry using sodium molybdate (3Na$_2$O·4MoO$_3$) solvent at 973 K was performed for the Na$_3$RE$_{0.67}$TiO$_3$ (RE = La, Ce) perovskite series. The enthalpies of formation of lanthanum perovskites from oxides (La$_2$O$_3$, Na$_2$O, TiO$_2$), are $-107.25 \pm 2.56$, $-93.83 \pm 6.06$, $-80.68 \pm 5.93$, and $-33.49 \pm 4.26$ kJ/mol and enthalpies of formation from elements are $-1614.05 \pm 5.37$, $-1596.44 \pm 7.68$, $-1594.03 \pm 7.58$, and $-1577.56 \pm 6.36$ kJ/mol for Na$_{0.459}$La$_{0.547}$Ti$_{0.98}$O$_3$, Na$_{0.434}$La$_{0.523}$Ti$_{0.99}$O$_3$, Na$_{0.389}$La$_{0.567}$Ti$_{0.98}$O$_3$, and La$_{0.692}$Ti$_{0.979}$O$_3$, respectively. The enthalpies of formation of cerium perovskites are $-99.98 \pm 5.78$ and $-45.78 \pm 3.30$ kJ/mol from oxides (Ce$_2$O$_3$, Na$_2$O, TiO$_2$), and $-1611.34 \pm 6.90$ and $-1602.06 \pm 2.72$ kJ/mol from elements for Na$_{0.442}$Ce$_{0.547}$Ti$_{0.98}$O$_3$ and Ce$_{0.72}$Ti$_{0.98}$O$_3$. The A-site defect perovskites become more stable relative to oxide components as sodium contents increase. Na$_{0.0}$Ce$_{0.72}$TiO$_3$ and Na$_{0.0}$La$_{0.98}$TiO$_3$ could be considered as thermodynamically stable end-members in natural loparite minerals, in which these end-members are in solid solution with CaTiO$_3$ and other components.

**Keywords:** Rare earth perovskites, calorimetry, enthalpy of formation, loparite

**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 the dense hot ceramic interior of our planet, the lower mantle. From the 670 km seismic discontinuity to the core-mantle boundary, a 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 several 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 three-dimensional framework structure constructed from vertex-sharing $BO_6$ octahedra and $A$-site ions placed in 12-fold coordinated sites in a cubic close packing of $A$ and oxide ions. Anion vacancies are well known in perovskites (Alario-franco 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 $r_A$, $r_O$, and $r_B$ 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 $O$ atoms to give an array of corner-shared $BO_6$ octahedra.

Phase equilibria in La$_2$O$_3$-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.