Thermochemistry of rare earth perovskites Na$_{3x}$RE$_{0.67\times}$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$_x$RE$_{0.67\times}$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$_{0.49}$La$_{0.42}$Ti$_{0.99}$O$_3$, Na$_{0.43}$La$_{0.32}$Ti$_{0.98}$O$_3$, Na$_{0.40}$La$_{0.30}$Ti$_{0.98}$O$_3$, and La$_{0.62}$Ti$_{0.37}$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$_{0.42}$Ce$_{0.54}$Ti$_{0.98}$O$_3$ and Ce$_{0.72}$Ti$_{0.37}$O$_3$. The A-site defect perovskites become more stable relative to oxide components as sodium contents increase. Na$_{0.67}$Ce$_{0.33}$TiO$_3$ and Na$_{0.49}$La$_{0.51}$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 ideal cubic case the cell axis, $a$, is geometrically related to the ionic radii: $a = \sqrt[6]{2} (r_A + r_B) = 2(r_B + r_O)$, 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: $t = (r_A + r_B) / \sqrt{2} (r_O + r_B)$. The ideal cubic structure is formed for $t = 1$, when the A cation matches in size with the O$^-$ 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.

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Phase equilibria in La$_2$O$_3$.TiO$_3$ (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.