

## Rare-earth perovskites along the $\text{CaTiO}_3\text{-Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$ join: Phase transitions, formation enthalpies, and implications for loparite minerals

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### ABSTRACT

The mineral loparite is the principal ore of the light rare earth elements (LREE) with solid solution compositions in the quaternary system perovskite-lueshite-tausonite-loparite ( $\text{CaTiO}_3\text{-NaNbO}_3\text{-SrTiO}_3\text{-Na}_{0.5}\text{Ln}_{0.5}\text{TiO}_3$ ) ( $\text{Ln} = \text{La, Ce, Pr, Nd}$ ). In this study, perovskite solid solutions  $\text{Ca}_{1-2x}\text{Na}_x\text{La}_x\text{TiO}_3$  ( $0 \leq x \leq 0.50$ ) along the perovskite-loparite join were synthesized using solid-state sintering methods. XRD analysis indicates that as the Na+La content increases, the structure changes from orthorhombic to tetragonal. The enthalpies of formation at 298 K from the constituent oxides ( $\Delta H_{f,\text{ox}}^\circ$ ) and from the elements ( $\Delta H_{f,\text{el}}^\circ$ ) have been determined using high-temperature oxide melt solution calorimetry in molten  $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$  at 973 K. Enthalpy of formation from oxides  $\Delta H_{f,\text{ox}}^\circ$  becomes more exothermic with increasing Na+La content, suggesting a stabilization effect of the substitution  $\text{Ca}^{2+} \rightarrow 0.5\text{Na}^+ + 0.5\text{La}^{3+}$ . The observed trend of increasing thermodynamic stability with decreasing structural distortion is in agreement with that seen in many other  $\text{ABO}_3$  perovskites. The thermodynamic stability of perovskite solid solutions  $\text{Ca}_{1-2x}\text{Na}_x\text{La}_x\text{TiO}_3$  ( $0 \leq x \leq 0.50$ ) along the  $\text{CaTiO}_3\text{-Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  join provides insights into the natural occurrence of loparite minerals  $(\text{La,Na,Sr,Ca})(\text{Ti,Nb,Ta,Fe}^{3+})\text{O}_3$ .

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