

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

**DAWEI FENG¹, PARDHA SARADHI MARAM¹, ALEKSANDRA MIELEWCZYK-GRYŃ², AND
ALEXANDRA NAVROTSKY^{1,*}**

¹Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California Davis, Davis, California 95616, U.S.A.

²Department of Solid State Physics, Gdańsk University of Technology, 80-233 Gdańsk, Poland

ABSTRACT

High-temperature oxide melt solution calorimetry using sodium molybdate ($3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$) solvent at 973 K was performed for the $\text{Na}_{3x}\text{RE}_{0.67-x}\text{TiO}_3$ (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 $\text{Na}_{0.459}\text{La}_{0.522}\text{Ti}_{0.999}\text{O}_3$, $\text{Na}_{0.454}\text{La}_{0.523}\text{Ti}_{0.994}\text{O}_3$, $\text{Na}_{0.380}\text{La}_{0.567}\text{Ti}_{0.980}\text{O}_3$, and $\text{La}_{0.692}\text{Ti}_{0.979}\text{O}_3$, 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 $\text{Na}_{0.442}\text{Ce}_{0.547}\text{Ti}_{0.980}\text{O}_3$ and $\text{Ce}_{0.72}\text{Ti}_{0.96}\text{O}_3$. The *A*-site defect perovskites become more stable relative to oxide components as sodium contents increase. $\text{Na}_{0.5}\text{Ce}_{0.5}\text{TiO}_3$ and $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$ 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