

Energetics of La, Nd-Containing Hydroxylbastnasite (La_{1-x}Nd_xCO₃OH) Solid Solutions

VITALIY G. GONCHAROV¹, HAYLEA NISBET²,
ANDREW C. STRZELECKI³, HONGWU XU², CHRIS J.
BENMORE⁴, ARTAS A MIGDISOV² AND XIAOFENG
GUO¹

¹Washington State University

²Los Alamos National Laboratory

³Alexandra Navrotsky Institute for Experimental
Thermodynamics, Washington State University

⁴Argonne National Laboratory, IL

Presenting Author: vitaliy.goncharov@wsu.edu

Rare earth elements (REE) are critical materials due to the variety of their technological applications. Hydroxylbastnasites (LnCO₃OH) are one of the common minerals bearing light rare-earth elements (LREE). However, various REE occur as solid solutions in hydroxylbastnasite deposits. To better understand the nature and the formation mechanism of such deposits, and to enable effective processing of such minerals, thermodynamic properties of hydroxylbastnasite solid solutions are of essential importance. In this work, hexagonal La–Nd hydroxylbastnasite (La_{1-x}Nd_xCO₃OH) solid solutions with x values of 0, 0.25, 0.50, 0.75, 1 were synthesized by the hydrothermal method, and characterized via synchrotron powder X-ray diffraction. Thermal decomposition of La_{1-x}Nd_xCO₃OH in an inert environment was examined by thermogravimetric analysis and differential scanning calorimetry coupled with in-situ mass spectrometry. Two-step decomposition pathways were confirmed for La_{1-x}Nd_xCO₃OH solid solutions. The first step corresponded to the release of CO₂ > H₂O > OH mass fragments ($m/z = 44, 18, 17$ respectively), which resulted in the formation of intermediate phases that corresponded to (La_{1-x}Nd_x)₂O₂CO₃. The second step corresponded to the release of CO₂ and led to the formation of the terminal sesquioxides (La_{1-x}Nd_x)₂O₃. The onset of decomposition temperatures followed an inverse parabolic trend. The maximum onset temperatures occurred near $x = 0.50$ and the decomposition temperature of LaCO₃OH > NdCO₃OH. The enthalpies of formation of La_{1-x}Nd_xCO₃OH were then determined by high temperature oxide melt drop solution calorimetry, which confirmed their formation to be thermodynamically stable with respect to their constituent sesquioxides, H₂O, and CO₂. The enthalpies of mixing were then derived with an interaction parameter of 12.58 ± 0.16 kJ/mol, which suggested a regular solution model for mixing of La and Nd within the hydroxylbastnasite lattice. This was consistent with the X-ray diffraction analysis which demonstrated La_{1-x}Nd_xCO₃OH followed a minimal deviation from the Vegard's law. Lastly, we estimated the Gibbs free energy of mixing at various relevant formation temperatures, from which we demonstrated that the favorable formation of La_{1-x}Nd_xCO₃OH solid solution is driven by entropic effects.