Probing the Entropic Stabilization of High-Entropy Lanthanide Oxysulfates

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We report the synthesis of a series of high-entropy lanthanide oxysulfates ($Ln_2O_2SO_4$), containing 4–7 different lanthanide elements. This was achieved via the thermolysis of a mixture of metal dithiocarbamate precursors in air. The material was investigated by powder X-ray diffraction, and Rietveld refinements were performed to calculate the unit cell parameters and to quantify the phase purity of the samples. Scanning electron microscopy and scanning transmission electron microscopy, with energy-dispersive X-ray spectroscopic mapping, confirm the high-entropy nature of the samples. These analyses reveal a single crystal phase and a uniform distribution of all the included metals from the micrometer to the nanometer scale. The optical properties of these materials were investigated by UV–visible absorption spectroscopy, resulting in direct bandgaps of 4.0–4.1 eV, indirect bandgaps of 3.7–3.9 eV, and Urbach energies ranging from 138 to 581 meV. The synthesis of the analogous high-entropy lanthanide oxysulfides (Ln_2SO_2) allowed us to begin to investigate the stability of these materials by conversion to the oxysulfate while carrying out thermogravimetric analysis and differential scanning calorimetry. The results of this analysis would suggest that the high-entropy samples are thermodynamically stabilized toward oxidation, with the activation energy of the process increasing by 5–28% over the monometallic control. This improved stability could have considerable implications in the development of high-entropy catalysts where extreme operating conditions are required.

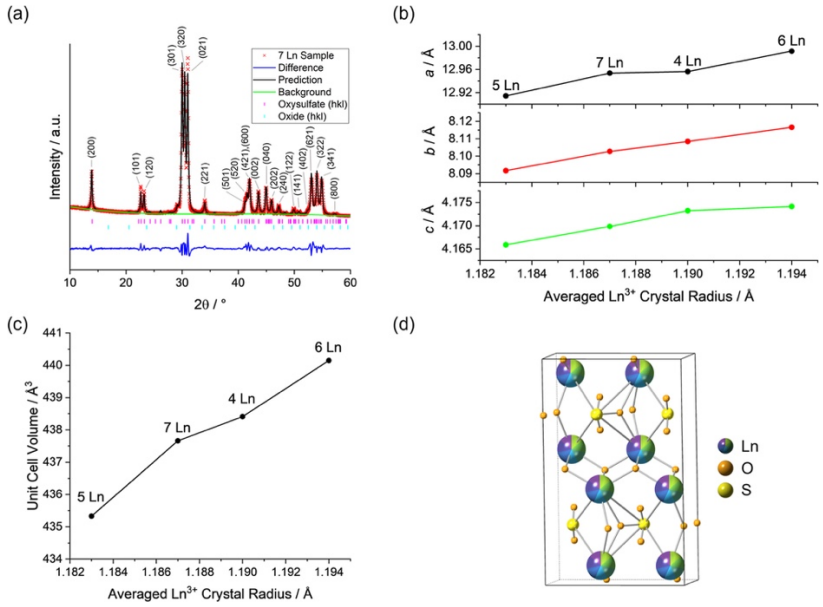


Figure 1. *Plot of the PXRD pattern and Rietveld refinement result for the 7-element oxysulfate sample (*hkl *planes for the oxysulfate phase labeled where I/Λmax > 3%). In the oxide phase found, only the (222) and (400) reflections are observed, at 2θ ≈ 28° and 34°, respectively. (b) Unit cell parameters and the (c) cell volumes extracted from the 4 refinements, plotted against the average crystal radius of the Ln3+ ions contained within the sample, assuming equimolar proportions of each lanthanide. A positive correlation is apparent between the two parameters. Errors on these values are so small as to not be visible when included in the plot. (d) An image of the unit cell; the 'beach ball' shading is used to show the multicomponent lanthanide site that confers high entropy to the material. The anisotropic nature of the material can be seen, with sheets of [Ln2O2]2+ separated by layers of [SO4]2–.*