

## CRYSTAL STRUCTURES OF $\text{BaSrR}_4\text{Zn}_2\text{O}_{10}$ , $\text{R} = \text{La, Nd, Sm, Eu}$

James A. Kaduk, [Kaduk@PolyCrystallography.com](mailto:Kaduk@PolyCrystallography.com)  
423 East Chicago Avenue, Naperville IL 60540  
Winnie Wong-Ng, [Winnie.Wong-Ng@nist.gov](mailto:Winnie.Wong-Ng@nist.gov)  
100 Bureau Drive, Stop 8520, Gaithersburg MD 20899

The crystal structures of  $\text{BaSrR}_4\text{Zn}_2\text{O}_{10}$  have been determined using synchrotron powder diffraction data collected at 11-BM at the Advanced Photon Source at Argonne National Laboratory.  $\text{BaR}_2\text{ZnO}_5$  have been characterized previously as part of a program to understand the correlations between composition and properties in Cu-based superconductors.  $\text{BaR}_2\text{ZnO}_5$  crystallize in the tetragonal space group  $I4/mcm$  for  $\text{R} = \text{La}$  and  $\text{Nd}$ , and in orthorhombic  $Pbnm$  for smaller lanthanides. Substitution of half of the Ba by Sr (pure Sr analogs have not yet been reported) could be expected to result in interesting structural changes.

All four structures are tetragonal. The Nd, Sm, and Eu compounds crystallize in  $I4/mcm$ , and the trends in lattice parameters follow those of the  $\text{BaR}_2\text{ZnO}_5$ . The unit cells are stiffer along  $c$  than in the  $ab$  plane. Four weak ( $\sim 0.1\%$  relative intensity) peaks in the  $\text{BaSrLa}_4\text{Zn}_2\text{O}_{10}$  pattern could not be attributed to any impurity phase, but corresponded to the 102, 122, 124, and 128 peaks of the tetragonal unit cell. The body centering condition was thus violated, and the true space group is  $P4/ncc$ .

The 10-coordinate sites in all four compounds are occupied by Ba and Sr. The 8-coordinate sites are occupied primarily by the lanthanide cations, but small concentrations of Sr are apparently present at this site for  $\text{R} = \text{La}$  and  $\text{Nd}$ . The tetrahedral Zn sites are similar in all four compounds.

The larger size of the  $\text{R} = \text{La}$  cell apparently results in movement of the Ba/Sr off the center of the 10-coordinate cage. The microstrain profile broadening for  $\text{R} = \text{La}$  is significantly smaller than for the other three compounds, consistent with the idea of local distortions driving the change in symmetry. Almost certainly the Ba and Sr occupy slightly different sites in these compounds, but split site refinements were unsuccessful. The largest errors in the Rietveld plots are in the tails of the peaks, and the errors are not random. Density functional quantum chemical geometry optimizations for Ba-only and Sr-only structures help understand local microstructural distortions and the potential effects of local compositional variations.