

## X-RAY AND NEUTRON RIETVELD REFINEMENTS OF BaR<sub>2</sub>CuO<sub>5</sub> AND Ba<sub>5</sub>R<sub>8</sub>Zn<sub>4</sub>O<sub>21</sub> (R=LANTHANIDES)

W. Wong-Ng (1), J. Kaduk (2), B. Toby (1), J. Dillingham (1), and W. Greenwood (1);  
(1) Materials Science and Engineering Laboratory, National Institute of Standards and  
Technology, Gaithersburg, MD 20899; (2) BP-Amoco Research Center, Naperville, IL  
60566-7011.

When Cu<sup>2+</sup> (nine 3d electrons) in Ba<sub>2</sub>YCu<sub>3</sub>O<sub>6+x</sub> is completely substituted by Zn<sup>2+</sup> (ten 3d electrons), the material is not superconducting, presumably due to the result of filling of electronic bands. Therefore, studies of the structures of the Zn-containing compounds in the Ba-R-Zn-O system will enhance the general understanding of superconductivity. The primary goal of this work was to investigate the formation and structure of two series of Ba-R-Zn-O compounds, namely, Ba<sub>5</sub>R<sub>8</sub>Zn<sub>4</sub>O<sub>21</sub> and the “Zn-green phase” BaR<sub>2</sub>CuO<sub>5</sub> (R=lanthanides) as a function of the size of R using X-ray Rietveld refinements. As the powder X-ray diffraction technique is of primary importance for phase characterization, the second goal of this investigation was to supplement the reference diffraction patterns of these compounds for the Powder Diffraction File (PDF).

The structure of the orthorhombic (*Pbnm*) Zn-green phase, BaR<sub>2</sub>ZnO<sub>5</sub>, is similar to that of the Cu-green phase, BaR<sub>2</sub>CuO<sub>5</sub>. Single phase BaR<sub>2</sub>ZnO<sub>5</sub> can be prepared for compounds with R = Sm, Eu, Gd, Dy, Ho, Y, and Er. For R=Tm, second phases also observed. The lattice parameters for compounds with R=Tm to Sm range from  $a=7.01855(9)$  Å to  $7.20452(14)$  Å,  $b=12.25445(17)$  Å to  $2.5882(2)$  Å, and  $c=5.6786(14)$  Å to  $5.81218(11)$  Å, respectively. R is 7-fold coordinated inside a monocapped trigonal prism. These prisms share edges to form wave-like chains parallel to the long b-axis. For smaller R (Yb and Lu), the BaR<sub>2</sub>ZnO<sub>5</sub> structure is not stable. Instead Ba<sub>5</sub>R<sub>8</sub>Zn<sub>4</sub>O<sub>21</sub> along with other mixed phases were observed. The Ba<sub>5</sub>R<sub>8</sub>Zn<sub>4</sub>O<sub>21</sub> type compounds were successfully prepared for R = Eu, Gd, Dy, Ho, Er, Tm, and Yb. Ba<sub>5</sub>R<sub>8</sub>Zn<sub>4</sub>O<sub>21</sub> crystallizes in the tetragonal space group *I4/m*; for R = Yb to Eu,  $a$  ranges from  $13.63502(5)$  Å to  $13.96062(9)$  Å, and  $c$  from  $5.65846(3)$  Å to  $5.78483(5)$  Å. The Zn<sup>2+</sup> ions adopt a 5-fold distorted square pyramidal coordination. Similar to BaR<sub>2</sub>CuO<sub>5</sub>, the 7-coordinate R<sup>3+</sup> also reside in monocapped trigonal prisms. These prisms share edges, and form layers stacked along the  $c$ -axis. There are two types of BaO polyhedra: bicapped square prisms (BaO<sub>10</sub>), and irregular BaO<sub>10</sub> polyhedra. For larger R, Ba<sub>5</sub>R<sub>8</sub>Zn<sub>4</sub>O<sub>21</sub> was not stable, and tetragonal BaR<sub>2</sub>ZnO<sub>5</sub> (La, Nd) and orthorhombic BaR<sub>2</sub>ZnO<sub>5</sub> (Sm) phases were observed instead.