

## Thesis Summary

Nature of chemical bonds in double perovskite-type oxide BaBiO<sub>3</sub> and related oxides visualized by synchrotron-radiation X-ray diffraction

(放射光X線回折により可視化された二重ペロブスカイト型酸化物BaBiO<sub>3</sub>および関連酸化物の化学結合の性質)

Zhao Qing

Perovskite-type oxide BaBiO<sub>3</sub> has attracted extensive research interests since the discovery of superconductivity in the doped solid solutions (Ba, K) (Pb, Bi) O<sub>3</sub>. Considering the charge balance, the Bi ion normally will take average 4+ valence state in the compound. However, as the Bi ion is referred to be a “valence skipper”, hence, the Bi ions are suggested to exhibit charge disproportionation from average Bi<sup>4+</sup> valence state to Bi<sup>3+</sup> and Bi<sup>5+</sup> valence states with equal ratio. BaBiO<sub>3</sub> is supposed to be not a simple perovskite, but a *B*-site ordered double perovskite with two different *B*-sites in the compound. The charge ordering accounts for the fact that BaBiO<sub>3</sub> is electrically semiconductor with a band gap. However, clear experimental evidence of Bi charge order is lacking.

Accurate electron charge density distributions of BaBiO<sub>3</sub> have been obtained by the high-resolution synchrotron-radiation powder X-ray diffraction data using the maximum entropy method/Rietveld method. The charge ordered Ba<sub>2</sub>Bi<sup>3+</sup>Bi<sup>5+</sup>O<sub>6</sub> double perovskite adopts four structures, i.e., monoclinic  $P2_1/n$ , monoclinic  $I2/m$ , rhombohedral  $R\bar{3}$ , and cubic  $Fm\bar{3}m$  phases upon heating progress. We investigate these phase transitions at charge density level, such as the change of chemical bonding nature and possible modifications in charge density. We found BaBiO<sub>3</sub> forms a two-dimensional covalent layer with  $P2_1/n$  symmetry, a three-dimensional

covalent network with  $I2/m$  and  $R\bar{3}$  symmetry, and an ionic structure consisting of isolated  $\text{Bi}^{3+}$  ions and  $[\text{Bi}^{5+}\text{-O}_6]^{7-}$  octahedron upon heating progress.

In order to discover the novel oxides with intriguing properties, engineered local environments of cations coordinated with oxygen ions in oxides is an effective pathway. Here we present the successful synthesis of  $\text{BaBiO}_{2.5}$  with layered structure enabled by a non-topotactic phase transformation from the perovskite-type oxide  $\text{BaBiO}_3$ . Using the maximum entropy method/Rietveld method based on the high-resolution powder synchrotron-radiation X-ray diffraction data, we successfully found that Bi ions form unusual chemical bonds with four coordinated oxygen ions that results in an asymmetric coordination geometry. One ionic bond and three covalent bonds of Bi-O bonds are successfully visualized in this layered structure that is owing to the hybridization of O  $2p$  and Bi  $6p$  orbitals. Specifically, we find that this unusual structure shows the near-infrared photoluminescence different from the ordinary Bi-containing systems. Experimental and quantum chemistry calculations motivate us to propose the excitonic nature of near-infrared photoluminescence. Our work highlights that creating materials with unusual Bi-O bondings and Bi coordination geometry will provide a pathway to discover the materials with new physical properties. We believe this work may stimulate interests in exploring a series of materials containing heavier p-block elements, thus providing prospects for discovering systems with unconventional properties.