# Synthesis of the Electron-Doped Bismuth Oxide $(Ba_{0.6}Bi_{0.4})BiO_{3-x}$

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## Abstract

The electron-doped bismuth oxide $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$ has successfully been synthesized by the two-step heating method. Mixed powders of the starting materials have been pelletized and heated in flowing gas of $N_2$ at 800°C for 12 h. The reacted pellets have been heated at 400°C first in flowing gas of $O_2$ for 24 h and then under a high oxygen-pressure of 600atm at 400°C for 96 h. It has crystallized in a pseudo-cubic symmetry. From the XRD and ICP analyses, the substitution of Bi for Ba has been confirmed, but the product has still remained an insulator.

*Key words:* substitution; electron doping; bismuth oxide; perovskite;

The perovskite $Ba_{1-x}K_xBiO_3$ has the highest superconducting transition temperatute ( $T_c \sim 30$ K at $x \sim 0.4$ ) among oxide superconductors not containing copper[1-3]. The parent material $BaBiO_3$ has a distorted perovskite structure with the monoclinic symmetry because of the size mismatch between the smaller Ba-O plane and the larger Bi-O plane. According to the simple electron-band theory, $BaBiO_3$ has a half-filled band of 6s electrons of $Bi^{4+}$, leading to a metallic behavior. However, the valence state of $Bi^{4+}$ with $6s^1$ is unstable so that $Bi^{4+}$ disproportionates into $Bi^{3+}$ with $6s^2$ and $Bi^{5+}$ with $6s^0$, leading to a CDW insulator[4]. Striking features of the parent material $BaBiO_3$ are the absence of both quasi-two-dimensionality and magnetic order, which are generally believed to be essential to the appearance of the high-$T_c$ superconductivity in the copper oxides. On the other hand, the fact that the superconductivity appears through the carrier doping into the parent material is similar to that in the copper oxides. That is, some superconductors have been found through the hole doping into the parent material. The purpose of this research is to synthesize electron-doped materials of (Ba, Bi)$BiO_3$ by the partial substitution of $Bi^{3+}$ for $Ba^{2+}$ in $BaBiO_3$.

Polycrystalline samples of $(Ba_{0.6}Bi_{0.4})BiO_{3-x}$ were prepared as follows. Mixed powders of the starting materials, $BaO_2$ and $Bi_2O_3$, were pelletized and heated in flowing gas of $N_2$ at 800°C for12 h. Next, the reacted pellets were heated in flowing gas of $O_2$ at 400°C for 24 h and then heated at 400°C for 96 h under a high oxygen-pressure of 600atm. The product was identified by the powder X-ray diffraction(XRD) analysis. The molar ratio of Ba : Bi was determined as 0.59 : 1.41 from the inductively coupled plasma emission spectrometry (ICP). The oxygen content was estimated as 2.92 from the iodometric titration. Polycrystalline samples of $BaBiO_3$ were also prepared for reference by the solid-state reaction in oxygen at 800°C for 12 h.

Fig. 1 shows the XRD patterns of $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$ and $BaBiO_3$. All the peaks of $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$ can be indexed on the basis of the cubic symmetry, indicating the formation of a single phase. The intensity of the 100 peak of $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$ is smaller than that of $BaBiO_3$, indicating that $Ba^{2+}$ ions are partially replaced by heavier ions, namely, $Bi^{3+}$ ions. These results of XRD and ICP suggest that the electron-doped $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$ has successfully been prepared.

Here, we discuss the reason why the substitution of

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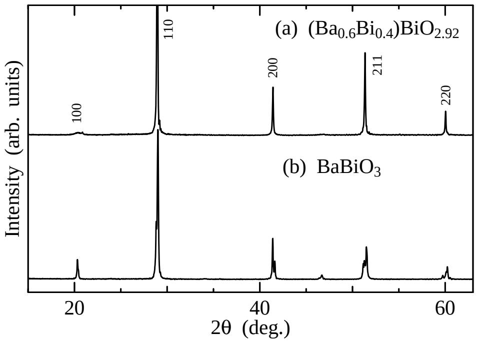

Fig. 1. XRD patterns of (a) $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$ with the cubic symmetry and (b) $BaBiO_3$ with the monoclinic symmetry. The peaks are indexed on the basis of cubic symmetry.

$Bi^{3+}$ for $Ba^{2+}$ has been realized in flowing gas of $N_2$. Even if $(Ba_{0.6}Bi_{0.4})BiO_{3-x}$ is tried to be synthesized in air, the trial results in the formation of $BaBiO_3$, because smaller $Bi^{3+}$ ions are hard to be substituted for larger $Ba^{2+}$ ions on account of the increase in the size mismatch as mentioned above. In the case of the synthesis in flowing gas of $N_2$, on the other hand, a large number of oxygen vacancies may alleviate the size mismatch, because the Coulomb repulsion between $Ba^{2+}$ ions enlarges the Ba-O plane. Moreover, it is likely that the electronic cloud of the $6s^2$ lone pair of $Bi^{3+}$ polarizes toward the oxygen vacancy, leading to the decrease in the effective ionic radius of $Bi^{3+}$ in the direction perpendicular to the polarization direction, namely, the contraction of the Bi-O plane, as shown in Fig. 2. These may be the reasons why the heat-treatment in flowing gas of $N_2$ makes it possible to substitute $Bi^{3+}$ for $Ba^{2+}$. These may also be the reasons why it is hard to compensate oxygen vacancies in this compound fully even through the heat-treatment under high oxygen-pressures.

As for the electrical property, the obtained product of $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$ has been found to be an insulator. One might consider two possible causes for the non-superconductivity; one is the oxygen deficiency and the other is the tilt of the $BiO_6$ octahedron. In the monoclinic $BaBiO_3$, the $BiO_6$ octahedron tilts due to the alleviation of the size mismatch. The size mismatch in $(Ba_{0.6}Bi_{0.4})BiO_3$ without oxygen vacancies is expected to be larger than that in $BaBiO_3$, because the substitution of smaller $Bi^{3+}$ for larger $Ba^{2+}$ causes not only the contraction of the Ba-O plane but also the decrease in the average valency of Bi ions, namely, the enlargement of the Bi-O plane. Thus, the tilt of the $BiO_6$ octahedron is supposed to still remain in $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$, though the slight oxygen deficiency must contribute to the alleviation of the size mismatch. The tilt of the $BiO_6$ octahedron leads to the decrease in the overlap between the Bi6s and O2p orbitals, resulting in the decrease in the gain of the transfer energy. Accordingly, $6s^2$ electrons in the $Bi^{3+}$ site tend to localize. That is, it seems that the tilt of the $BiO_6$ octahedron operates to suppress the transition to metal or superconductivity in $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$. In fact, the superconductivity appears only in the cubic $Ba_{1-x}K_xBiO_3$ without the tilt of the $BiO_6$ octahedron [3]. By the way, the reason why the crystal symmetry of $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$ is cubic may be due to the disorder on both Ba and Bi sites. $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$ could be expressed as $(Ba_{0.6}Bi^{3+}{}_{0.4})(Bi^{3+}{}_{0.7}Bi^{5+}{}_{0.3})O_{2.92}$. This disorder on both sites interferes with the long range forces which are necessary for a cooperative displacement of atoms to give lower symmetry. The symmetry is believed to be lower locally.

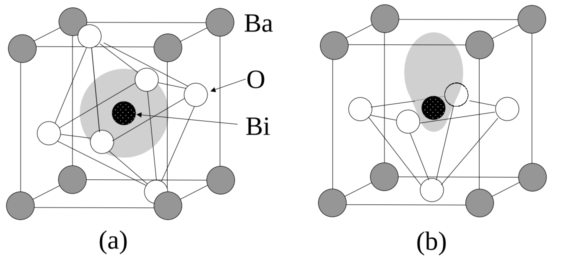

Fig. 2. Schematic structures of (a) $BaBiO_3$ and (b) $BaBiO_{3-x}$ with an oxygen vacancy. In the latter, the electronic cloud of the $6s^2$ lone pair of $Bi^{3+}$ polarizes toward the oxygen vacancy.

In conclusion, the electron-doped bismuth oxide $(Ba_{0.6}Bi_{0.4})BiO_{2.92}$ has successfully been prepared by heating the starting materials in flowing gas of $N_2$ at 800°C for the substitution, followed by annealing at 400°C first in flowing gas of $O_2$ and then under a high oxygen-pressure of 600atm for the compensation for oxygen vacancies. The product has been found to be insulating. This may be due to the oxygen deficiency and/or the tilt of the $BiO_6$ octahedron.

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