Superstructures in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-y}$ and $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$

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Abstract. The perovskite compounds $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ and $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x = 0.9, 0.5, 0.25$) have been investigated by high resolution electron microscopy and selected area electron diffraction. Several superlattices produced by *in situ* electron beam reduction have been observed. Ordered atomic arrangements in the reduced materials are discussed.

Keywords. $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-y}$; $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$; high resolution electron microscopy; superstructure; oxygen diffusion.

1. Introduction

Although the transition temperature (T_c) of metal oxide superconducting materials has recently advanced to over 120 K, the BaBiO_3 -based superconductors, $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ and $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, with relatively low T_c (about 30 K and 12 K respectively), are still of great interest due to their pseudocubic structures. The bismuth valence in BaBiO_3 has long been debated. A few workers have suggested that bismuth exists entirely of Bi^{4+} cations (McGuire and O'Keefe 1984). Most, however, believe in the existence of a charge density wave corresponding to the ordered arrangement of—nominally— Bi^{3+} and Bi^{5+} on the perovskite B-sites, and resulting in a monoclinic distortion of the perovskite cell (e.g. Cox and Sleight 1979). Oxygen-deficient barium bismuthate (BaBiO_{3-y}) has been investigated by thermogravimetric analysis and electron-diffraction (Chaillout and Remeika 1985). It was concluded that oxygen vacancy ordering existed in two phases— $\text{BaBiO}_{2.97}$ and $\text{BaBiO}_{2.77}$. Our own previous electron diffraction studies on BaBiO_3 and BaPbO_3 initially showed the expected $\sqrt{2} \times \sqrt{2} \times 2$ superunit cell (Zhou *et al* 1989). BaPbO_3 is very stable under the electron beam. However, in BaBiO_3 , superlattices, evident from high resolution electron microscopy (HREM) images and selected area electron diffraction (SAED) patterns, develop after exposure of the sample to the electron beam for 10–30 min. It was concluded that oxygen diffusion from BiO_6 octahedra in the BaBiO_3 perovskite lattice is responsible for the superstructure formation, and that oxygens associated with Pb^{4+} cations are much less readily removed.

Electron beam-induced superstructures in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-y}$ have been observed recently (Hewat *et al* 1989). They proposed that the superstructures arose from the partial ordering of Bi^{3+} and Bi^{5+} and displacements of the Bi^{3+} cations or oxygen anions rather than an ordering of oxygen vacancies or potassium cations. Others have observed the appearance of additional spots in SAED patterns under intense electron beam exposure (Pei *et al* 1989). These were put down to the loss of either potassium or oxygen from the beam-heated area, but no experimental details were given. In this present work, electron microscopy results are reported for the superconducting phase $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ and for compositions in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$

system. Structural models of superlattices for the reduced materials based on oxygen vacancy ordering are proposed.

2. Experimental

Compositions in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system ($x = 0.9, 0.5, 0.25$) were prepared using a three-step solid-state reaction method. Appropriate quantities of $\text{Ba}(\text{NO}_3)_2$, Pb_3O_4 and Bi_2O_3 were initially fired at 650°C in air for 5 h in order to decompose the $\text{Ba}(\text{NO}_3)_2$. The resultant powder was reground, then fired twice at 800°C in flowing oxygen for 12 h with an intermediate grinding. All samples were checked for complete reaction using powder X-ray diffraction. Final sample compositions were checked by energy-dispersive X-ray emission spectrometry (EDS) and were found to be homogeneous. Samples were also checked after two of the three firings. These had a range of Pb/Bi compositions, the range in x being approximately ± 0.1 about the nominal composition. $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ was prepared by the two-stage reaction developed by Hinks *et al* (1988).

SAED patterns were recorded on a JEM-200CX electron microscope operating at 200 kV, in which a $\pm 45^\circ$ double tilting specimen stage was used. The composition of each crystal from which SAED patterns was obtained was examined by EDS. HREM images were recorded on another JEM-200CX electron microscope, where a modified specimen stage was used with point resolution of 0.195 nm (Jefferson *et al* 1986). Image magnification was ca. $500\,000\times$. Superlattices were produced in a vacuum $5 \times 10^{-7}\text{ m bar}$ when specimens were exposed to electron beam irradiation with a current density of ca. $0.1\text{--}1.0\text{ A cm}^{-2}$. Exposure times were between 10 min and 1 h, depending on the composition of the specimen.

3 Results and discussion

Initial SAED patterns obtained from $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ showed the expected simple cubic perovskite cell. In figure 1(a), a pattern taken down the $[110]$ direction, the diffraction spots which indicate the presence of a $\sqrt{2} \times \sqrt{2} \times 2$ supercell (as is observed in BaBiO_3) are absent. Figure 1(c) shows a pattern taken down the $[001]$ direction after 10 min exposure to the electron beam. This pattern reveals the development of a four-fold repeat in the $[110]$ direction together with a two-fold repeat in the $[1\text{--}10]$ direction, indicating a $2\sqrt{2} \times \sqrt{2}$ superlattice in the (ab) plane. After a further 20 min in the electron beam, a different pattern was observed (figure 1(d)) which corresponds to a 4×4 superlattice in the (ab) plane.

SAED patterns taken immediately on $\text{BaPb}_{0.1}\text{Bi}_{0.9}\text{O}_3$ samples are shown in figures 2 (a, b). Figure 2(a) shows the presence of a $\sqrt{2} \times \sqrt{2} \times 2$ supercell, which is absent in the cubic $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ (figure 1(a)). After 10 min beam exposure, an SAED pattern was taken down the $[111]$ direction (figure 2(c)). This reveals a one-dimensional four-fold repeat in the $[110]$ direction, and is consistent with a $2\sqrt{2} \times \sqrt{2}$ superlattice. A corresponding HREM image, viewed down the $[111]$ direction shows a striped pattern indicative of a one-dimensional superlattice. It should be noted that the contrast on this image is very sharp. This suggests that the

Figure 1. SAED patterns from $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. (a) Initial pattern viewed down the $[110]$ direction of the simple perovskite lattice; (b) initial pattern viewed down the $[001]$ direction; (c) after 10 min beam exposure viewed down $[001]$; and (d) after a further 20 min beam exposure viewed down $[001]$.

superlattice cannot be due exclusively to the ordered arrangement of B-site cations—there must also be a large local lattice distortion consistent with oxygen vacancies.

For $\text{BaPb}_{0.5}\text{Bi}_{0.5}\text{O}_3$ specimens, initial SAED patterns showed no satellite diffraction spots (figure 3(a)). After beam irradiation, a superlattice similar to that observed for $\text{BaPb}_{0.1}\text{Bi}_{0.9}\text{O}_3$ appears (figure 3(b)). However, a rather longer exposure time (15 min) is required to induce such a superlattice.

Initial SAED patterns taken on samples of the superconducting composition $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ again showed no evidence of superlattices, other than the

Figure 2. SAED patterns and HREM image of $\text{BaPb}_{0.1}\text{Bi}_{0.9}\text{O}_3$. (a) Initial pattern viewed down the $[110]$ direction of the simple perovskite lattice; (b) initial pattern viewed down the $[111]$ direction; and (c) after 10 min beam exposure viewed down $[111]$.

Figure 3. SAED patterns from BaPb_{0.5}Bi_{0.5}O₃ viewed down the [111] direction. (a) Initial pattern; and (b) after 15 min beam exposure.

$\sqrt{2} \times \sqrt{2} \times 2$ supercell due to deviation from cubic symmetry (figure 4(a)). Prolonged exposure to the electron beam (for over 40 min) resulted in the observation of a $2\sqrt{2} \times \sqrt{2}$ superlattice (figure 4(b)). The corresponding HREM image showed clearly a striped pattern indicative of a four-fold repeat, similar to that shown for BaPb_{0.1}Bi_{0.9}O₃ (figure 2(c)). Evidence for microtwinning of this superstructure was gained from HREM imaging—a microtwin boundary is visible in figure 4(c).

All the superstructural SAED patterns observed in BaPb_{1-x}Bi_xO₃ samples are identical to those seen in lead-free BaBiO_{3-y}, except that the intermediate $\sqrt{2} \times 3\sqrt{2}$ superlattice found previously in the latter compound has not been observed in any of the Pb-doped compositions. The duration of electron beam exposure required to produce these superlattices, however, seems to be strongly dependent on the concentration of Pb in the sample. The higher the Pb content, the greater the time that is necessary to cause the superstructure. This ties in with the previous work on BaBiO₃ and BaPbO₃, where superlattice formation is observed readily in BaBiO₃, but not at all in BaPbO₃. Current thermogravimetric analysis and high temperature X-ray diffraction studies on BaBiO₃ and BaPbO₃ in an inert atmosphere also indicate that oxygen contained in BaBiO₃ diffuses out of the compound at a much lower temperature as does that in BaPbO₃ (Dalton *et al* 1990). This finding strongly supports the idea that it is oxygen diffusion out of the sample under the electron beam that is responsible for the formation of the superstructures observed in SAED patterns and HREM images. It follows that for samples in the BaPb_{1-x}Bi_xO₃ system, oxygens associated with the Bi sites must be more labile than those adjacent to Pb cations, and therefore oxygen vacancies will be produced preferentially next to Bi cations. The observation of superlattices in all compositions studied implies that the Pb and Bi cations must be ordered in some way. A random arrangement of Pb and Bi on the perovskite B-sites would be expected to result in a random arrangement of oxygen

Figure 4. SAED patterns and HREM image for $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ viewed down the $[001]$ direction. (a) Initial pattern; (b) after 40 min beam exposure; and (c) HREM image after 40 min exposure showing twin defects.

Figure 5. A structural model of the (ab) plane in $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{2.875}$, showing a $\text{BaPb}_{0.5}\text{Bi}_{0.5}\text{O}_{2.75}$ layer. The Bi ions occupy the square pyramidal sites and Pb ions the octahedral sites.

vacancies, and no superstructure would be visible in SAED patterns. Pb and Bi ordering has been proposed by others (Shebanov *et al* 1983).

A model for the reduced material, $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-y}$ is proposed in figure 5. The diagram shows one MO_6 octahedral plane ($M = \text{Pb}, \text{Bi}$) with an ordering of oxygen vacancies, forming a $\sqrt{2} \times 2\sqrt{2}$ superlattice. Two Bi cations occupy the square-pyramidal sites associated with each anion vacancy. The composition of this plane would be $\text{Pb}_2\text{Bi}_2\text{O}_{11}$. If such a plane alternates with a Bi-free plane along the c-axis, then we will have a three-dimensional unit cell which gives a $\sqrt{2} \times 2\sqrt{2} \times 2$ superlattice based on the perovskite subcell. The composition of this model is $\text{Ba}_8\text{Pb}_6\text{Bi}_2\text{O}_{23}$ or $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{2.875}$. A similar model can be developed for $\text{BaPb}_{0.5}\text{Bi}_{0.5}\text{O}_{3-y}$ where each octahedral plane has the composition $\text{Pb}_2\text{Bi}_2\text{O}_{11}$, implying a whole crystal composition of $\text{BaPb}_{0.5}\text{Bi}_{0.5}\text{O}_{2.75}$.

Results from $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ also indicate an ordering of oxygen vacancies in reduced samples. In potassium-free BaBiO_3 , one can understand the formation of the oxygen vacancy superstructure in terms of the B-site ordering of Bi^{3+} and Bi^{5+} . However, $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ has cubic structure, with all Bi sites equivalent, making the existence of a superstructure in reduced samples rather surprising. A possible explanation is that the A site cations ($\text{Ba}^{2+}, \text{K}^+$) are ordered, since, by local charge considerations, an oxygen vacancy is more likely to reside next to a monovalent

potassium ion than next to a barium ion of charge + 2. An alternative explanation is that the production of the first oxygen vacancy causes a local distortion in the previously cubic structure, with the result that certain oxygens in the vicinity are destabilised, and others become more tightly bound.

Further studies are currently under way on other compositions in both the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ and $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ systems in an attempt to understand the exact nature of these fascinating compounds.

References

- Chaillout C and Remeika J P 1985 *Solid State Commun.* **56** 833
Cox D E and Sleight A W 1979 *Acta Crystallogr.* **B35** 1
Dalton M, Gameson I, Edwards P P and Singh K K 1990 (in preparation)
Hewat E A, Chaillout C, Godinho M, Gorius M F and Marezio M 1989 *Physica* **C157** 228
Hinks D G, Dabrowski D, Jorgensen J D, Mitchell A W, Richards D R, Shiyu Pei and Donglu Shi 1988 *Nature (London)* **333** 836
Jefferson D A, Thomas J M, Millward G R, Tsuno K, Harriman A and Brydson R D 1986 *Nature (London)* **323** 428
McGuire N K and O'Keefe M 1984 *Solid State Commun.* **52** 433
Shebanov I A, Fritsberg Ya V and Gaevskis A P 1983 *Phys. Status Solidi* **A77** 369
Shiyu Pei, Zaluzec N J, Jorgensen J D, Dabrowski B, Hinks D G, Mitchell A W and Richards D R 1989 *Phys. Rev.* **B39** 811
Zhou W, Dalton M, Singh K K, Jefferson D A and Edwards P P 1989 (submitted for publication)