Partial suppression of structural distortion in epitaxially grown $BaBiO_3$ thin films

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Thin films of $BaBiO_3$, the parent compound of $Ba_{1-x}K_xBiO_3$ superconducting oxide with $T_c \sim 30$ K, were prepared by pulsed laser deposition and their structures were investigated by x-ray diffraction analysis. It is known that bulk $BaBiO_3$ crystal adopts structures having two kinds of distortions, namely, tilting and breathing of BiO_6 octahedra below 750–800 K. Epitaxial $BaBiO_3$ (001) film was grown on MgO (001) substrate at 773 K. In the film, the BiO_6 tilting mode was suppressed at ambient temperature and the structure was cubic with superlattice breathing distortion. This is the experimental realization of $BaBiO_3$ having cubic structure with only superlattice breathing distortion at ambient temperature. An electric transport measurement showed that the film is insulating. These results show direct experimental evidence for the idea provided by theoretical studies that the breathing distortion solely can open the gap around the Fermi energy of $BaBiO_3$ phase.

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$Ba_{1-x}K_xBiO_3$ (BKBO) is a family of superconductors with a transition temperature (T_c) as high as approximately 30 K that has attracted much attention over the past two decades.[1] Although the metallic and superconducting phases ($x \geq 0.38$) adopt a cubic perovskite structure, the parent compound $BaBiO_3$ (BBO) has superlattice distortions of frozen in breathing and tilting of BiO_6 octahedra and is an insulator. "Breathing" refers to distortion due to the BiO_6 octahedra expanding and shrinking alternately in the perovskite structure. "Tilting" of BiO_6 octahedra brings about the lowering of the symmetry of the structure from cubic to monoclinic or rhombohedral. These features of BBO phase, which are believed to arise owing to charge-density-wave instability, have been a subject of continuing interest in relation to the high-temperature superconductivity of BKBO compounds, which do not contain copper. Many experimental and theoretical studies have been conducted to elucidate the nature of the BBO and BKBO phases.[2–14] Below 750–800 K, BBO has both breathing and tilting distortions and is rhombohedral ($R\bar{3}$) or monoclinic ($I2/m$). Above 750–800 K, the crystal is cubic with only the breathing distortion (space group: $Fm\bar{3}m$). Theoretical analysis of the structural instability predicted that the breathing mode distortion is solely responsible for the generation of the band gap around the Fermi energy of the BBO phase.[7,13,14] However, no BBO sample containing only one of the two distortion modes at ambient or low temperature has been produced.

A useful method to control lattice distortions is to grow thin films on substrates.[15–18] For example, anisotropic stress due to epitaxial growth induces the formation of an orbital ordering structure in $Nd_{0.5}Sr_{0.5}MnO_3$ films on $SrTiO_3$ substrates.[15–17] The strain in epitaxial films has a large effect on the magnetism of the multilayer structure; a $La_{0.5}Ca_{0.5}MnO_3$ layer has been sandwiched between two $Pr_{0.5}Ca_{0.5}MnO_3$ layers on $SrTiO_3$ (001), and the corresponding magnetic and transport properties have been discussed in terms of the stabilized charge ordering and the vibration mode of the Jahn-Teller distortion.[19] Our recent study revealed that a constraining effect of substrates could enable or disable the antiferromagnetic structural transition of CrN thin films, although the films had lattice constants very close to those of bulk CrN.[20] Metal-insulator transitionlike behaviors have also been reported for CrN films.[21]

Here, we report that the growth of BBO thin film can partially suppress its structural distortion. BBO film was grown on MgO substrate, and the structure was elucidated to be cubic with cell parameters twice those of the simple perovskite structure. In other words, the BBO phase showed superlattice breathing but no tilting distortion. Experimental realization of such BBO phase around ambient temperature has not been reported so far, while theoretical studies sometimes assume such virtual structure. Although sophisticated works were reported on thin-film preparation of BBO and BKBO,[22–24] suppression of the structural distortions has not been discussed explicitly so far. In the present study, the thin film with partially suppressed distortion provides important experimental information on the origin of the band gap discussed in the theoretical studies.

A $BaBiO_3$ target disk used for pulsed laser deposition was prepared as follows. BaO and Bi_2O_3 were mixed and well ground using a mortar and then pressed into a disk with 1.6 cm diameter and approximately 5 mm thickness. The disk was calcined at 1073 K for 48 h in an oxygen flow to obtain the $BaBiO_3$ target disk. Another disk prepared by the same procedure was analyzed by powder x-ray diffraction using Cu $K\alpha$ radiation with a Bruker D8-Advance diffractometer, and the diffraction pattern coincided with the reported monoclinic structure having both tilt and breathing distortions. The sample was dissolved in HF and analyzed by inductive-coupled plasma atomic emission spectroscopy (ICP-AES) with a Perkin-Elmer Optima 3000 spectrometer. Ba and Bi in the sample were confirmed to be stoichiometric (1:1). The thin film's synthesis was based on techniques used in our previous studies on metal nitrides.[25–33] The pulsed laser deposition system used in this study was equipped with a KrF excimer laser (COMPex102, Lambda Physics, Goettingen, Germany). The residual pressure of the chamber was less than 10^{-8} Torr. The MgO (001) and $SrTiO_3$ (011) substrates were cleaned in methanol before their introduction into the vacuum chamber. During the deposition, oxygen gas was introduced to the chamber at a pressure of approximately 0.03 Torr. The substrate temperature was 773 K, the

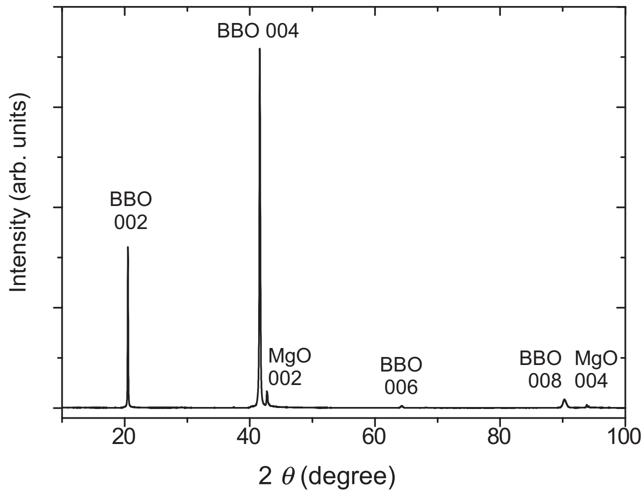

FIG. 1. Conventional $\omega-2\theta$ scan x-ray diffraction patterns of $BaBiO_3/MgO$ film.

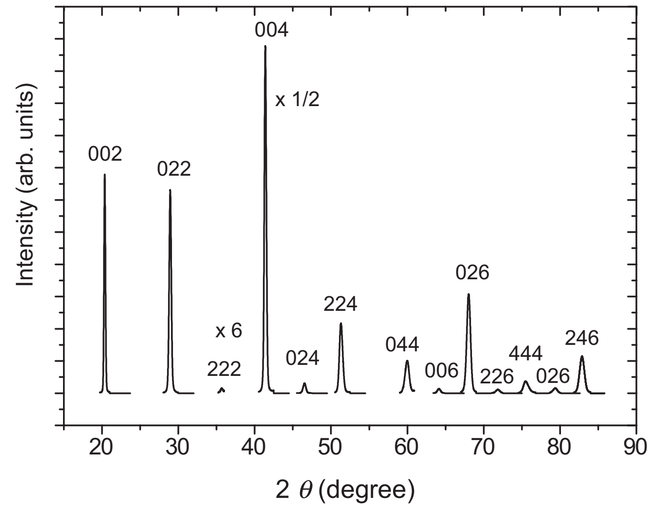

FIG. 2. $\omega-2\theta$ scan x-ray diffraction peaks measured for crystal planes not parallel to the substrate surface.

pulse repetition rate was 4 Hz, and the energy of the laser pulses was approximately 100 mJ. The film thickness was measured with a Digital Instruments D-3100 atomic force microscope operated in tapping mode. The crystal structures of films were characterized by x-ray diffraction using two diffractometers. Conventional $\omega-2\theta$ scans were performed with a Bruker AXS D8-Advance diffractometer using Cu $K\alpha$ radiation with a Ni filter. The $\omega-2\theta$ scans at various Ψ angles[31] were carried out with a Philips X'Pert MRD diffractometer. The incident beam was a Cu $K\alpha$ parallel beam from an x-ray mirror with a crossed slit (0.5 mm width and 5 mm height). The detector was equipped with a parallel-plate collimator and a graphite monochromator (0.27° resolution). The Ba to Bi ratios in the films were determined with a Shimadzu ESCA-3400 x-ray photoelectron spectrometer, which was calibrated with a standard $BaBiO_3$ bulk sample, the composition of which was confirmed by ICP-AES. Magnetic measurements were carried out with a magnetometer (Quantum Design MPMS-5S, USA). The thin film was placed parallel to the applied magnetic field. Electric conduction was checked by the two-probe method, but the resistance was too large to determine ($>30\ \text{M}\Omega$).

Figure 1 shows the x-ray diffraction pattern (conventional $\omega-2\theta$ scan) of BBO film grown on MgO (001) at 773 K. In the diffraction pattern, peaks were observed at positions very close to those expected for the BBO cubic phase. No other diffraction peak was observed except for those of MgO, indicating that BBO grew epitaxially. Figure 2 shows diffraction peaks of the BBO/MgO film with various Miller indices. The measurements at calculated Ψ angles allowed us to detect diffraction peaks from crystal planes not parallel to the substrate surface. Using these peak positions, cell parameters of the BBO phase in the film were determined and are listed in Table I. All the peaks could be indexed as diffractions from a cubic system. Here, doubled cell parameters were used because of reasons that will be discussed in a later section. Bulk-BBO phase adopts a monoclinic structure distorted from a cubic structure at room temperature. To confirm that the BBO phase in the film was cubic, further detailed measurements were carried out for the 444 peak of the cubic structure, as shown in Fig. 3. If the BBO phase adopts a crystal system other than cubic, the diffraction should give several separated peaks (two peaks for the rhombohedral structure and three peaks for the monoclinic structure). In fact, the powder x-ray diffraction pattern of the bulk-BBO (monoclinic) samples had three separated peaks, as shown in Fig. 3(a). Considering the possible orientations of the monoclinic and rhombohedral structures of BBO on the substrate, three measurements were carried out for the thin film to detect the separated peaks, as shown in Fig. 3(b). All three measurements gave one diffraction peak at the same position. These results demonstrate that the BBO phase in the film was cubic and the phase had no tilting distortion of the BiO_6 octahedra.

To obtain more information on the crystal structure of the BBO/MgO film, further x-ray diffraction measurements were carried out for the 333 diffraction peak of the BBO phase. Bulk-BBO has a breathing distortion owing to the BiO_6 octahedra expanding and shrinking alternately in the perovskite structure. If the breathing distortion survives in the cubic structure, the cell parameters are doubled and 333 diffraction peak should be observed. In other words, detection of the 333 diffraction indicates the presence of the breathing distortion in the cubic structure. Figure 4 shows the measurement of the 333 diffraction peak. A clear peak was observed at the expected position. According to all the x-ray diffraction experiments, the BBO phase in the thin film has a cubic structure with cell parameters twice those of a simple perovskite structure and the structure has breathing distortion of the BiO_6 octahedra. Table I also gives cell parameters of BBO grown on $SrTiO_3$ (011) substrate. X-ray diffraction experiments showed the film had (011) orientation and adopted cubic structure with 333 reflection. That is, the film had breathing distortion but not tilting distortion. According to these results, orientation of the thin-film growth does not seem to affect the partial suppression of structural distortion.

The film was epitaxially grown on a substrate but the film was cubic and had lattice constants close to those expected

TABLE I. Structural parameters of thin films and bulk $BaBiO_3$ prepared in this study. t_f is film thickness, C is cubic, and M is monoclinic.

Sample	t_f (nm)	Crystal system	Cell parameters a (nm)	b (nm)	c (nm)	β (deg)
BBO/MgO (001)	42	C	0.87148(9)			90
$BBO/SrTiO_3$ (011)	52	C	0.8698(1)			90
bulk-BBO		M	0.61801(2)	0.61377(3)	0.86622(3)	90.182(4)

from the cell volume of the bulk-BBO (0.8693 nm). It has been reported that bulk-BBO phase adopts three different crystal structures depending on temperature.[2,3,7] Below 750–800 K, the phase has both breathing and tilting distortions and is rhombohedral ($R\bar{3}$) or monoclinic ($I2/m$). Above 750–800 K, the crystal is cubic with only the breathing distortion (space group: $Fm\bar{3}m$). The cubic phase structure observed in the thin film had the same symmetry as that observed for bulk phase above 750–800 K. One possible explanation of the thin-film structure is that the cubic structure, stable at high temperature, was frozen by a constraining effect of the substrates because the substrate temperature (773 K) during the film deposition was in the range of the structural transition temperature. An attempt to deposit BBO film at a lower temperature (723 K) resulted in the formation of (cubic) polycrystalline film. Deposition at a higher temperature (873 K) gave a film with Bi_2O_3 impurities. Recently, Gozar *et al.*[8] analyzed the surface structure of atomically smooth $BaBiO_3$ films using sophisticated methods such as low-energy time-of-flight scattering and recoil spectroscopy and mass spectroscopy of recoiled ions, and they found that the in-plane cell parameter was very close to that of the simple perovskite structure. Our results are similar to their findings in the sense that the BBO film adopted a cubic structure different from the distorted structures reported for the bulk-BBO phase. Another similar phenomenon has been reported for ferroelectric perovskite $BaTiO_3$ films. Bulk $BaTiO_3$ shows structural transition from cubic perovskite structure to a tetragonal structure at T_c. $BaTiO_3$ grown on Pt/MgO substrates (400 nm thickness) had lattice constants very close to those of bulk and showed no anomaly in the temperature dependence of the lattice constants, but the film showed ferroelectric properties at lower temperature.[34] That is, in the films, atomic displacements occurred in the structure without a detectable change in the crystal systems between cubic and tetragonal.

Extensive spectroscopic studies have been conducted on the origin of the gap of BBO phase and changes in the band structure by doping.[4,5,9–12] It is believed that the breathing mode distortion, which is closely related to the valence disproportionation of bismuth ions ($2Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$), is responsible for the generation of the gap around the Fermi energy of BBO. Theoretical studies analyzed the electronic state with the breathing distortion. A recent first-principles band calculation clearly showed that, in the band structure of the cubic BBO, displacement of oxygen (i.e., breathing mode distortion) opens the gap around the Fermi energy.[14]

The present study provides important experimental information concerning the origin of the gap around the Fermi

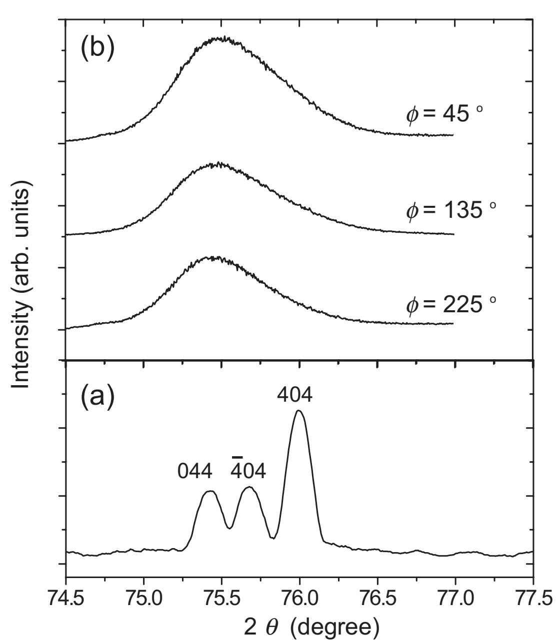

FIG. 3. X-ray diffraction peaks related to 444 (cubic) reflection. (a) Powder pattern of monoclinic bulk $BaBiO_3$; (b) $\omega-2\theta$ scan of $BaBiO_3/MgO$ thin film. In (b), the diffraction peaks were measured for the thin film at different phi angles to check for deviations from cubic structure.

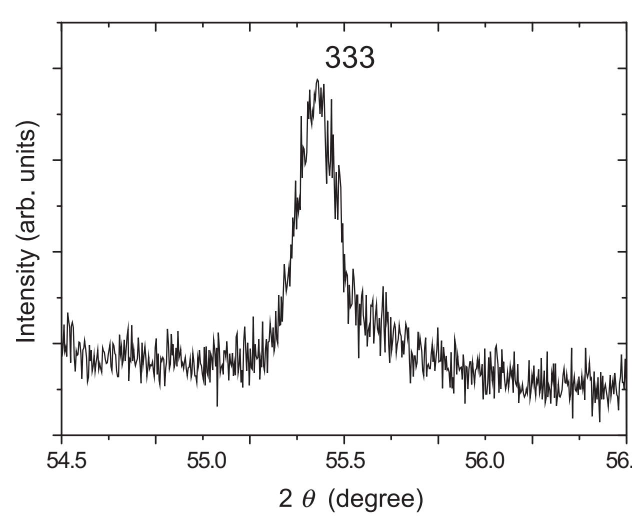

FIG. 4. 333 diffraction peak of the cubic $BaBiO_3$ on MgO with doubled cell parameters.

energies of BBO and BKBO. Our BBO thin film is the experimental realization of $BaBiO_3$ in which breathing occurs but tilting of the BiO_6 octahedra is suppressed in the structure at ambient temperature. An electric transport measurement showed that the film was insulating. These results are direct experimental evidence for the idea provided by theoretical and experimental studies that the breathing distortion solely can open the gap around the Fermi energy of $BaBiO_3$ phase. The information is important because the elucidation of the nature of BBO would contribute to a better understanding of BKBO, a copper-free superconducting oxide having a high transition temperature.

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