Observation of a structural-fluctuation enhancement in the vicinity of superconducting transitions in $Ba_{1-x}M_xBiO_3$ (M=K,Rb)

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Features of structural fluctuations related to the cubic-to-orthorhombic transition in $Ba_{1-x}M_xBiO_3$ (M=K, Rb) have been investigated in detail by means of electron diffraction. A fluctuation due to the softening of the R_{25} mode, which is responsible for the transition, is detected as diffuse scattering at the R point in the reciprocal space of the cubic phase. When x is reduced from $x=0.5$ to a transition composition in the cubic phase, the fluctuation is enhanced remarkably at lower temperatures. Because the fluctuation of the R_{25} mode results in those of spontaneous strains, the fluctuations of the A_{1g} and E_g strains are understood to be enhanced near the superconducting transition.

Among superconducting oxides such as $YBa_2Cu_3O_z$, there exist the Ba oxides, $Ba_{1-x}K_xBiO_3$ (BKB), $Ba_{1-x}Rb_xBiO_3$ (BRB), and $BaPb_{1-y}Bi_yO_3$ (BPB), which basically have the simple perovskite structure and are not characterized by the Cu-O layer. In the case of the Ba oxides, the hybridized orbital between 6s (Bi,Pb) and 2p (O) has been understood to be responsible for superconductivity.[1,2] Because of the existence of the large oxygen-isotope effect for the superconductivity,[3,4] a mechanism of the superconductivity in the Ba oxides should be explained in terms of the phonon-mediated mechanism.

In our previous work on BPB with a maximum T_c of about 12 K,[5,6] the structural transitions existing in BPB with $0\le y<0.8$ were found to be basically due to the condensation of the R_{25} mode, which is one of the rotation (tilt) modes of the oxygen octahedron involved in the perovskite structure. A fluctuation related to the R_{25} displacement in the cubic phase was observed as diffuse scattering appearing at the R point, the major contribution of which presumably comes from thermal diffuse scattering due to the softening of the R_{25} mode. The most important feature found in the work is that the fluctuation of the R_{25} displacement also exists in the tetragonal phase, where the superconductivity appears. On the basis of these results, it was pointed out that in BPB there would be correlation between the fluctuation of the R_{25} displacement and the superconductivity, both of which are directly related to atomic displacements of the oxygen atoms of the octahedra. Note that the superconductivity in the Ba oxides has been discussed often in terms of the breathing mode characterized by the expansion and the contraction of the octahedra.[1,2,7,8]

Both BKB and BRB have been reported to exhibit superconductivity with a maximum T_c of about 30 K.[9–11] The structural phase diagram in BKB was determined in detail by neutron powder diffraction.[12] According to the diagram, the crystal system at room temperature changes as follows: the monoclinic system in $0\le x<0.1$, the orthorhombic one in $0.1\le x\le 0.35$, and the cubic one in $0.35\le x$. The superconductivity in both oxide systems is found in the cubic phase and the highest T_c is obtained in the vicinity of the phase boundary between the cubic and orthorhombic phases. In addition, our recent work on structural transitions in BKB and BRB showed that the cubic-to-orthorhombic transition is interpreted as being due to the condensation of the R_{25} mode, just as in BPB.[13,14] Because the superconductivity in both oxide systems appears in the cubic phase, it is thus experimentally easy to obtain direct evidence for the correlation between the fluctuation of the R_{25} displacement and the superconductivity. From this standpoint, we have examined features of the fluctuation of the R_{25} displacement related to the cubic-to-orthorhombic transition in order to elucidate the existence of the correlation in the Ba oxides.

In this paper, we first report features of the structural transitions of BKB and BRB, which have been experimentally obtained by means of transmission electron microscopy. Then, a change in the intensity of diffuse scattering on cooling in the cubic phase is shown, indicating the enhancement of the fluctuation related to the R_{25} displacement. On the basis of experimental results obtained in the present work, we point out the correlation between the fluctuation and the superconductivity, and further discuss what displacements would be responsible for the electron-phonon coupling in the superconductivity of the Ba oxides.

Powder samples of BKB and BRB were prepared from $BaCO_3$, Bi_2O_3, KO_2 and Rb_2CO_3 by calcinating in two steps; 993 K for 1 h in the Ar atmosphere and then 693 K for 1 h in the O_2 one. After the powder samples were pressed into pellets, the pellets were sintered in the same conditions mentioned just above. A change in electrical resistivity with respect to temperature was examined in order to check superconducting temperatures T_c of ob-

tained pellets. A soft-phonon-mode behavior can be observed as a change in intensity of thermal diffuse scattering in electron diffraction because its intensity is inversely proportional to the square of the frequency of a phonon mode. In the present experiment, the intensity of the diffuse scattering related to the soft mode was measured by photodensitometry from an electron-diffraction pattern taken at each temperature. The electron microscope used was an H-800-type transmission electron microscope with a low-temperature stage equipped with a liquid-helium reservoir. A high-temperature stage was also used for a heating experiment. The present experiment was then carried out in a temperature range between about 23 and 700 K. Specimens for the experiment were flakes obtained by crushing the pellets. A composition x of each flake was also measured by energy dispersive x-ray spectroscopy (EDX).

In order to understand the correlation between the cubic-to-orthorhombic transition, particularly the fluctuation of the R_{25} displacement, and the superconductivity, features of both the crystal structures and their fluctuations in $0.1 < x \leq 0.5$ have been examined by means of electron diffraction. As a result, it has been found that there is no difference between BKB and BRB with respect to both the structures and the behavior of the structural transitions. Figure 1, for instance, shows electron-diffraction patterns of BKB with $x = 0.3$, taken at room temperature and 533 K, respectively. Note that diffraction spots are indexed in terms of the $2a_0 \times 2a_0 \times 2a_0$ supercell where a_0 is a lattice parameter of a pseudocubic perovskite structure. At room temperature, superlattice spots with weaker intensity are observed in addition to fundamental spots with stronger intensity, which are due to the simple perovskite structure as a basic structure. From the analysis of other diffraction patterns as well as Fig. 1(a), the superlattice spots are found to be located at a zone boundary of the first Brillouin zone of the cubic perovskite structure along the $\langle 111 \rangle$ direction, the R point. This implies that atomic displacements at room temperature for $x = 0.3$ should result from the condensation of a phonon mode at the R point. As shown in the previous paper,[13,14] intensities of superlattice spots can be explained within an experimental error as being due to the $R_{25}^x + R_{25}^y$ displacements with the same rotation angles of the oxygen octahedra about the x and y axes. That is, the atomic displacements determined experimentally are identical to those expected from the condensation of the R_{25}^x and R_{25}^y modes at the same time and the crystal system is then orthorhombic.

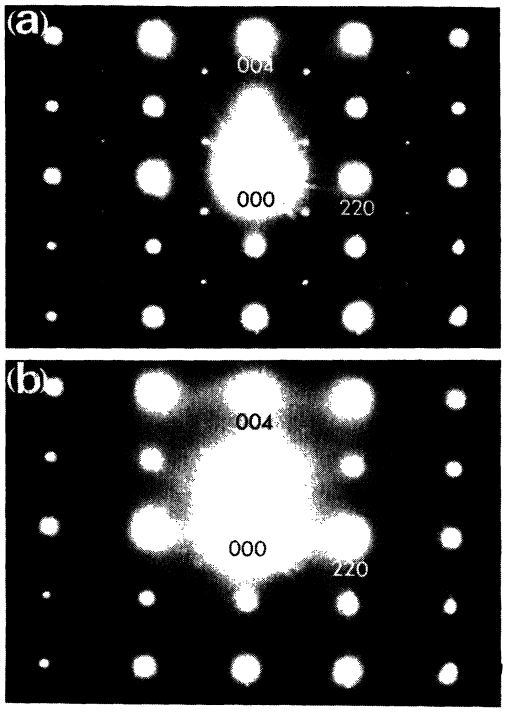

FIG. 1. Electron-diffraction patterns of BKB with $x = 0.3$, taken at room temperature (a) and 533 K (b), respectively. An electron incidence for these patterns is parallel to the $[1\bar{1}0]$ direction.

When the temperature increases, the intensities of the superlattice spots decrease and the spots eventually change into diffuse spots at the transition temperature of about 520 K, as shown in Fig. 1(b). This implies that the orthorhombic-to-cubic transition occurs around 520 K on heating. In addition, it is obvious that the diffuse spots are due to the fluctuation of the R_{25} displacement in the cubic phase.

It is time to show features of the fluctuation of the R_{25} displacement in the cubic phase. A change in intensity of the diffuse spot at the R point with respect to temperature is shown in Fig. 2. A specimen used here is BRB with $x = 0.4$, which does not exhibit the cubic-to-orthorhombic transition and has a T_c of about 20 K, which is defined as a midpoint in the temperature range where the electrical resistivity decreases rapidly. As is easily seen in Fig. 2, the intensity of the diffuse spot at 24 K is much stronger than that at room temperature and the change in the intensity is perfectly reversible during the cooling and heating cycle. The intensity of a diffuse spot at each temperature was then measured from an electron-diffraction pattern by means of photodensitometry. The procedure to measure the intensity is exactly the same as that reported in the previous paper.[6] Figure 3 shows the temperature dependence of the intensity of the diffuse spot located at 3/2 3/2 3/2 in recipro-

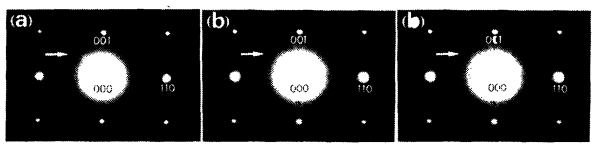

FIG. 2. Electron-diffraction patterns of BRB with $x = 0.4$, taken at room temperature (a), 24 K (b), and room temperature (c), respectively. An electron incidence for these patterns is parallel to the $[1\bar{1}0]$ direction. In the observation, the specimen is first cooled from room temperature (a) to 24 K (b) and then heated up to room temperature (c). In each pattern, there is diffuse scattering, showing the fluctuation of the R_{25} mode, as indicated by an arrow.

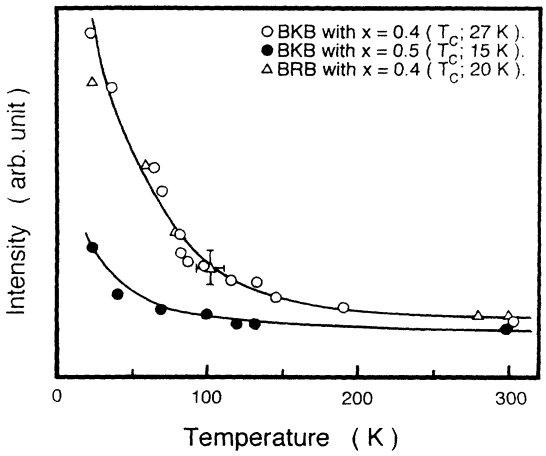

FIG. 3. Change in diffuse intensity as a function of temperature for BKB with $x=0.4$ and 0.5 and BRB with $x=0.4$. In the figure, a difference between a signal from the diffuse spot and that from the background, obtained by photodensitometry, is plotted as a measured intensity.

cal space of the cubic structure for BKB with $x=0.40$ and 0.50 and BRB with $x=0.40$, none of which undergo the cubic-to-orthorhombic transition. A value of a midpoint T_c for each sample, determined by electrical resistivity, is also shown in the figure. The intensity is found to increase with decreasing temperature. This implies that the fluctuation of the R_{25} displacement becomes remarkable on cooling. In particular, the large fluctuation exists at the lowest temperature in the present experiment for BKB and BRB with $x=0.4$. It is worth noticing that the highest T_c is obtained in the vicinity of the phase boundary; that is, around $x=0.4$. These facts suggest the correlation between the superconductivity and the fluctuation of the R_{25} displacement in the Ba oxides. Because the low-temperature stage used covers a temperature range above 23 K, basically only the fluctuation in the normal state can be investigated in the present work. In Fig. 3, only one plotting point in the superconducting state, at 23 K for BKB with $x=0.4$, is actually shown. Precisely, it can therefore be said that there is a correlation between T_c and the structural fluctuation in the normal state. On the basis of the correlation, an effect of the fluctuation related to the R_{25} displacement should be taken into account in the discussion of the mechanism of the superconductivity in the Ba oxides.

In the Landau theory[15] for the structural transition due to the softening of the R_{25} mode, the order parameter is the degenerate set of the soft-mode coordinates (Q_1,Q_2,Q_3). Note that the coordinates transform with respect to operations of the point group Oh like the components of an axial vector. Because of this, the order parameter can be coupled to the spontaneous strains, $e_1+e_2+e_3$ (A_{1g} at Γ),

$$[2e_3-e_1-e_2,\sqrt{3}(e_1-e_2)](E_g)\ ,$$

and (e_4,e_5,e_6) (T_{2g}). Hence, there are the following coupling terms,

$$\begin{aligned}&C_1(Q_1^2+Q_2^2+Q_3^2)(e_1+e_2+e_3)\\&+C_2[(2Q_3^2-Q_1^2-Q_2^2)(2e_3-e_1-e_2)\\&\quad+3(Q_1^2-Q_2^2)(e_1-e_2)]\\&+C_3(Q_2Q_3e_4+Q_3Q_1e_5+Q_1Q_2e_6)\end{aligned}$$

in the free energy. From these coupling terms, in the cubic phase, the fluctuation of the R_{25} displacement is understood to result in the fluctuation of the spontaneous strain. Although there is no volume strain (A_{1g}) at the transition, as shown in $SrTiO_3$,[13,16] its local fluctuation should exist in the cubic phase. The local fluctuation related to the spontaneous strains is eventually enhanced in the vicinity of the transition. Note that, with respect to one oxygen octahedron, dynamic distortions for the A_{1g} and E_g strains are exactly identical to those for the A_{1g} and E_g modes at the R point, respectively. The A_{1g} mode at the R point is the so-called breathing mode.

The Bi,Pb(6*s*)-O(2*p*) bands, which are responsible for the superconductivity in the Ba oxides, can be described in terms of the tight-binding model.[1,2,7,17] In this model, the electron-phonon coupling is due to the change in both the transfer integral and the site energy due to an atomic displacement. As the site energy term basically leads to the same result as that of the transfer term, as pointed out by Shirai, Suzuki, and Motizuki,[7,17] only the transfer term should be discussed in order to understand features of the electron-phonon coupling. It is worth noticing that the transfer integral strongly depends on a change in bond length. Because the fluctuations of the A_{1g} and E_g strains must influence high-energy oxygen phonons which accompany a change in the length of the Bi(Pb)-O bond, the oxygen phonons should play an important role in an electron-phonon coupling. It should be remarked that Shirai, Suzuki, and Motizuki[7,17] explained T_c in the Ba oxides in this model, although they have not specified which phonon modes are crucial for the electron-phonon coupling in the case of BPB.

As has been pointed out, the breathing mode is important for the electron-phonon coupling in the Ba oxides. However, Shirai, Suzuki, and Motizuki[7,17] showed that, unlike BKB, T_c in BPB cannot be reproduced in terms of the A_{1g} and E_g modes at the R point. In addition, when x decreases from $x=0.50$ in BKB, T_c increases and is saturated in the vicinity of the structural transition.[12] That is, the saturation of T_c suggest a direct correlation between the superconductivity and the transition. Therefore, the superconductivity in the Ba oxides, BPB, BKB, and BRB, seems to be basically explained on the basis of the high-energy oxygen phonons influenced by the fluctuation of the spontaneous strains. The sufficient explanation of the superconductivity in both BKB and BRB should, however, require the contribution of the breathing mode because T_c of about 15 K is obtained in BKB with $x=0.5$, where the fluctuation of the R_{25} mode is relatively unremarkable, as shown in Fig. 3.

In summary, the present experiment shows the existence of the structural fluctuation related to the R_{25} mode in the whole cubic phase of $0.4\le x\le 0.5$, which is

responsible for the cubic-to-orthorhombic transition in $0.1 \leq x < 0.4$. As x approaches the transition composition from $x = 0.5$ in the cubic phase, the fluctuation becomes much more remarkable at lower temperatures. From the fact that the highest T_c is obtained near the phase boundary between the cubic and orthorhombic phases, it is understood that there is the correlation between T_c and the fluctuation related to the R_{25} mode in the normal state. Further, the fluctuations of the A_{1g} and E_g spontaneous strains resulting from the soft R_{25} mode seem to play a crucial role in the electron-phonon coupling on the basis of the simple discussion in terms of the tight-binding model.

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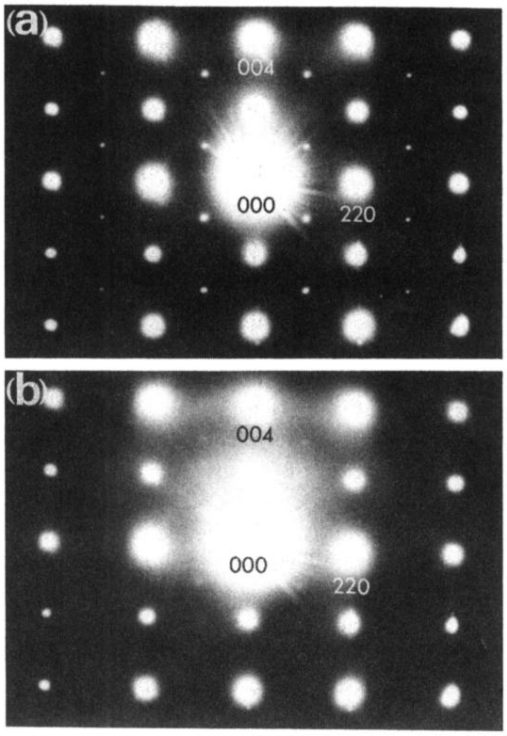

FIG. 1. Electron-diffraction patterns of BKB with $x = 0.3$, taken at room temperature (a) and 533 K (b), respectively. An electron incidence for these patterns is parallel to the $[1\bar{1}0]$ direction.

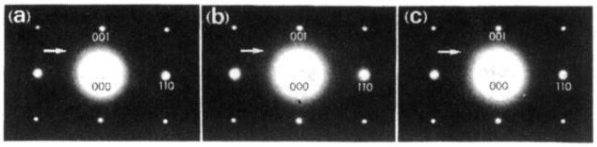

FIG. 2. Electron-diffraction patterns of BRB with $x=0.4$, taken at room temperature (a), 24 K (b), and room temperature (c), respectively. An electron incidence for these patterns is parallel to the $[1\bar{1}0]$ direction. In the observation, the specimen is first cooled from room temperature (a) to 24 K (b) and then heated up to room temperature (c). In each pattern, there is diffuse scattering, showing the fluctuation of the R_{25} mode, as indicated by an arrow.