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# Electron density distribution of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ( $x = 0.43$ ) by ultra-short-wavelength x-ray diffraction

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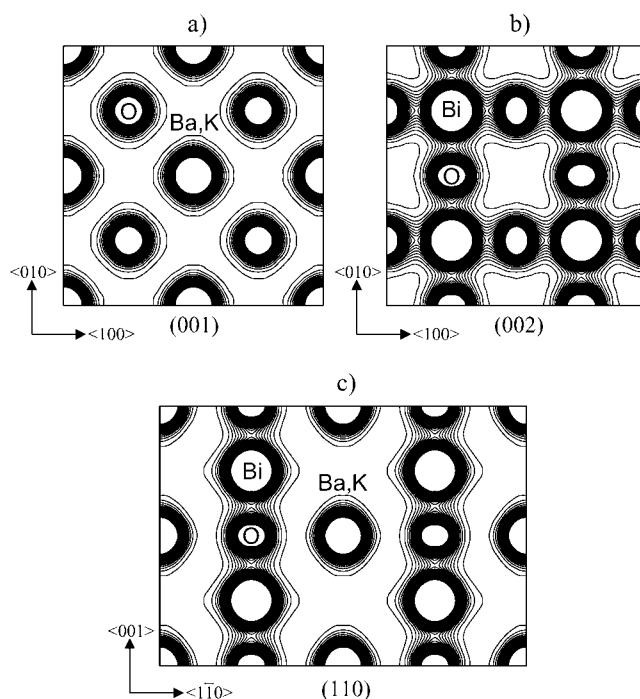
## Abstract

The crystal structure and electron density distribution (EDD) of superconducting  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$  have been studied by the maximum-entropy method using ultra-short-wavelength x-ray diffraction data for a single crystal at 295 and 108 K. It is found that the bonding between the Bi and O atoms is covalent, though there is no overlapping of electron density between (Ba, K) and O atoms. The EDD around O atoms shows spatial anisotropy and the result is in agreement with anisotropic thermal motion of O atoms. No peculiar change of chemical bonding nature appears, comparing the EDD at 295 K with that at 108 K. The calculated EDD for cubic  $\text{BaBiO}_3$  using the first-principles full-potential linearized augmented plane-wave method is compared with the experimental EDD for  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$ .

## 1. Introduction

Perovskite-type  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  in the metallic region is known to be a superconductor with transition temperature  $T_c \sim 31$  K [1, 2] and numerous studies have been carried out so far. The crystal structure of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  has been studied for samples synthesized either by a solid-state reaction method or by an electrochemical one. The samples from the electrochemical method have higher  $T_c$  than those from the solid-state reaction method, which were found to have oxygen deficiencies [3–5]. The magnetic susceptibility of single-crystalline  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  has already been measured by the present authors [6]. Recent neutron and synchrotron x-ray diffraction studies for superconducting samples from the electrochemical synthesis have revealed a smeared structural phase transition from a cubic to tetragonal  $I4/mcm$  structure with a rotation of oxygen octahedra at  $T_s = 245$ – $145$  K for  $x = 0.324$ – $0.410$  [7]. This is in contrast to a neutron diffraction result [8] for samples from the solid-state reaction, in which the structural symmetries at room temperature for  $0 \leq x \leq 0.1$ ,  $0.1 \leq x \leq 0.35$  and  $x \leq 0.35$  were found to be monoclinic, orthorhombic and cubic,

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**Figure 1.** EDDs in  $\text{Ba}_{0.55}\text{K}_{0.45}\text{BiO}_3$  at 295 K obtained by MEM. Contour lines are drawn from 0.2 to  $4.2 \text{ e \AA}^{-3}$  with the interval of  $0.1 \text{ e \AA}^{-3}$ .

respectively. We note here, however, that a weak diffuse scattering at the  $R$  point in reciprocal space is found by an electron-diffraction study [9] for ceramic samples in the cubic phase, in accordance with the neutron-diffraction results [7] for samples from the electrochemical synthesis.

Accurate single-crystal x-ray diffraction study is one of the most indispensable methods to understand the nature of chemical bonding as well as thermal displacement of atoms in materials precisely. In our previous study, we discussed some difficulty in obtaining chemical bonding by use of the conventional Fourier synthesis method due to the termination effect [10]. Recently, a new method, the maximum-entropy method (MEM), has been found to be efficient in determining the electron density and a great number of studies have been reported [11–13].

The purpose of the present study is to determine the crystal structure and to obtain the EDD in  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  ( $x = 0.43$ ) by MEM using single-crystal x-ray diffraction data to understand the electronic structure. We also calculate the EDD of cubic  $\text{BaBiO}_3$  using the first-principles full-potential linearized augmented plane-wave (FLAPW) method and compare it with the EDD in  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  ( $x = 0.43$ ) obtained by MEM.

## 2. Experiment

A single crystal of  $\text{Ba}_{0.53}\text{K}_{0.47}\text{BiO}_3$  was prepared by an electrochemical synthesis technique [14]. The K composition  $x = 0.47$  was determined by means of electron-probe microanalysis (EPMA). The specimen was made spherical with a diameter of 0.278 mm by Takahashi's method, taking about 20 h [15]. The reason for using this geometry was to obtain accurate x-ray structure factors after applying the absorption correction and to obtain good agreement of the intensities between the equivalent Bragg reflections.

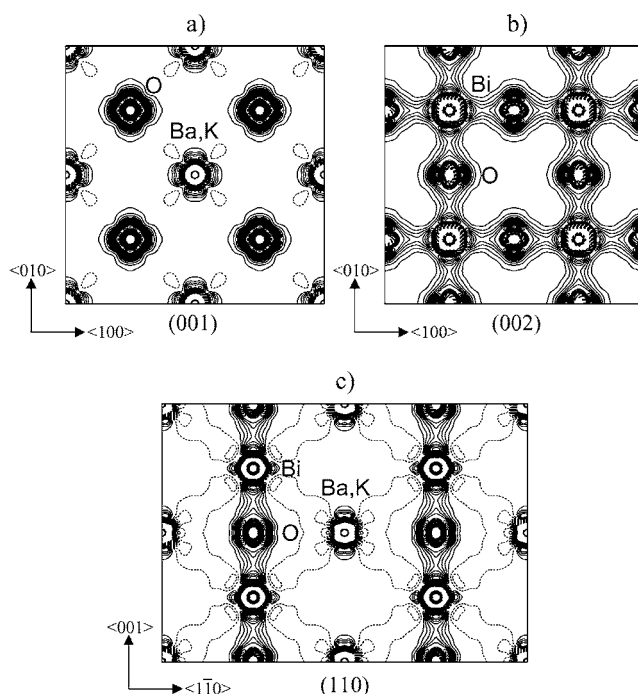
**Table 1.** Experimental parameters for the present measurements of a single-crystal  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$  specimen.

Temperature (K)	295, 108
X-ray wavelength ( $\text{\AA}$ )	0.209 (W $\text{K}\alpha_1$ )
Tube voltage (kV) and tube current (mA)	150 kV and 12 mA
$hkl$ range	$-11 \leq h, k, l \leq 11$
Volume of reciprocal space	Spherical
Maximum of $\sin \theta/\lambda$ ( $\text{\AA}^{-1}$ )	1.3 ( $2\theta < 31.54^\circ$ )
Scan method	$\omega$ scan
Scan width (deg)	0.75
Scan speed ( $\text{deg min}^{-1}$ )	6
Specimen radius (mm)	0.278
Linear absorption coefficient $\mu$ ( $\text{cm}^{-1}$ )	36.418
Transmission factors	
Min.	0.478
Max.	0.481
Number of measured reflections	6019
Number of independent reflections	186
Number of variables	8

Data collection of integrated intensities and lattice parameters was performed on the ultra-short-wavelength x-ray generator (Rigaku) at the Advanced Materials Laboratory, National Institute for Materials Science (AML/NIMS), at 295 and 108 K. The temperature at 108 K was controlled by blowing cooled  $\text{N}_2$  gas across the specimen directly with an accuracy of 1.0 K. An Eulerian cradle (Huber model 512) was used on the two-circle goniometer. In this measurement, we have combined a Ge solid-state-detector (Ge-SSD), a pulse-height analyser (PHA) and a multi-channel analyser to measure diffraction data without a crystal monochromator. The wavelength of the incident beam was 0.209  $\text{\AA}$  (W  $\text{K}\alpha_1$ ). The radiation line was easily selected by using the single-channel analyser with careful adjustment of the window of the PHA. Here, a very high accelerating voltage of 150 kV ( $\times 12$  mA) was used to obtain an efficient photon flux of W  $\text{K}\alpha_1$  radiation, whose exciting voltage is 69.3 kV. The complete data were collected with reflections up to  $\sin \theta/\lambda = 1.3 \text{\AA}^{-1}$ . Detailed experimental information on the measurements is given in table 1.

### 3. Results and discussion

Structural refinements were carried out using the computer program Xtal3.7 [16]. In this analysis, all the reflections were used without removing any specific ones. Structure factors  $F_{obs}$  were obtained after correcting for absorption, scale and isotropic extinction effects [17]. Here, we have treated the temperature parameters for Bi, Ba and K atoms as isotropic and written them as  $U_{iso}$ . On the other hand, that of the O atom is anisotropic,  $U_{11}$  and  $U_{22=33}$ . The thermal parameters  $U_{ij}$  are equal to  $\langle u^2 \rangle_{ij}$ , where  $\langle u^2 \rangle_{ij}$  is the mean square displacement of constituent atoms for component  $ij$ . Neutral atomic scattering factors for all atoms were applied in the refinement [18]. In the structural analysis, the Ba/K anisotropic thermal displacement parameters and these occupations were refined. The sum of the occupations of Ba and K on their common site was constrained to be 1.0. The final structure parameters at 295 and 108 K, thus obtained, are given in table 2, where 186 independent reflections were used for the analysis. It is clear that the present structure analysis has been performed accurately because both the reliability factor,  $R$ , and weighted reliability factor,  $wR$ , are  $< 1.1\%$ .

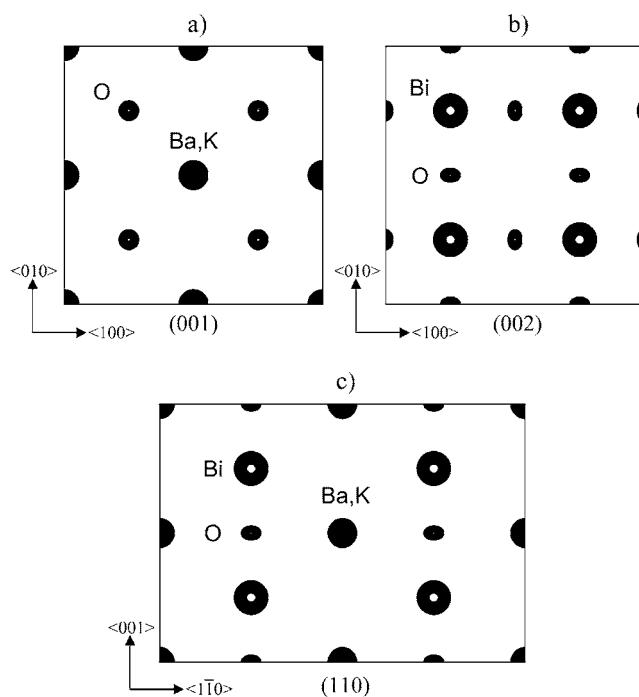


**Figure 2.** The difference electron densities for  $\text{Ba}_{0.55}\text{K}_{0.45}\text{BiO}_3$  at 295 K,  $\Delta\rho(r) = \rho_{\text{obs}}(r) - \rho_{\text{calc}}(r)$ , in (001), (002) and (110) planes ((a)–(c), respectively). The contour lines are drawn from  $-2.0$  to  $2.0 \text{ e } \text{\AA}^{-3}$  with  $0.05 \text{ e } \text{\AA}^{-3}$  intervals. Solid and dotted curves correspond to positive and negative values, respectively.

**Table 2.** Final structural parameters obtained after refinement. Atomic coordinates are Ba, K (0,0,0), Bi (1/2, 1/2, 1/2) and O (0, 1/2, 1/2). The anisotropic thermal parameters are defined as  $\exp\{-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij}\}$ .

Temperature (K)	295	108
Crystal system	Cubic	Cubic
Space group	$Pm\bar{3}m$	$Pm\bar{3}m$
Lattice constant ( $\text{\AA}$ )	4.273 2(3)	4.262 1(3)
$U_{\text{iso}}$ ( $\text{\AA}^2$ ) for Bi atom	0.003 53(2)	0.001 60(4)
$U_{\text{iso}}$ ( $\text{\AA}^2$ ) for Ba atom	0.007 6(1)	0.003 1(1)
$U_{\text{iso}}$ ( $\text{\AA}^2$ ) for K atom	0.015(1)	0.012(2)
$U_{11}$ ( $\text{\AA}^2$ ) for O atom	0.005 2(3)	0.003 3(4)
$U_{22=33}$ ( $\text{\AA}^2$ ) for O atom	0.021 0(4)	0.012 8(4)
$U_{\text{eq}}$ ( $\text{\AA}^2$ ) for O atom	0.015 7(3)	0.009 6(4)
$x$ value in $\text{Ba}_{1-x}\text{K}_x$	0.442(3)	0.423(5)
Extinction $y_{\text{min}}$	0.64 ( $y_{(110)}$ )	0.67 ( $y_{(110)}$ )
$R$ -factor	0.006 2	0.009 8
$wR$ -factor ( $w = 1/\sigma^2 F$ )	0.005 0	0.010 9
Goodness of fit $S$	1.22	1.26

From the temperature dependences of the structural parameters at both 295 and 108 K, no peculiar behaviour was observed in this study. However, the ratios  $U_{22=33}/U_{11}$  for the O atom were equal to 4.20 and 3.88 at 295 and 108 K, respectively. These results show that thermal motion of the O atom in the Ba–K–Bi–O system could be reflected in the breathing

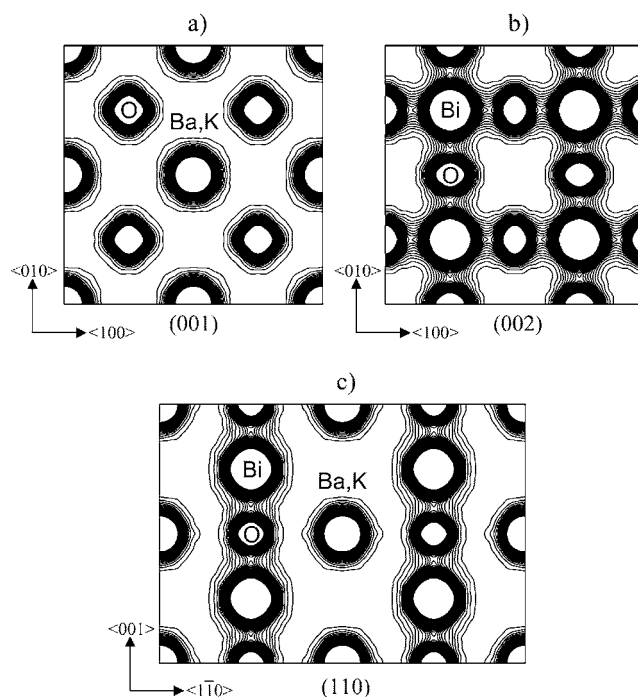


**Figure 3.** EDDs in  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$  at 295 K obtained by MEM. Contour lines are drawn from 10 to 1000  $\text{e} \text{ \AA}^{-3}$  in a logarithmic scale.

mode of the  $\text{BiO}_6$  octahedron. The anisotropy has been reported in the Ba–K–Bi–O system obtained by single-crystal x-ray diffraction [7, 19]. The values of  $U(295 \text{ K})/U(108 \text{ K})$  for Bi, Ba, K and O atoms are equal to 2.21, 2.45, 1.25 and 1.64, respectively. The variation of thermal vibration of light atoms is smaller than that for heavy ones. From the temperature dependence of temperature parameters  $U_{iso}$ , Debye temperatures  $\Theta_D$  for Bi, Ba and K atoms were obtained as 235 K by the formula of lattice vibrations [20]. The observed  $U_{eq}$  of the O atom at  $T = 108 \text{ K}$  is larger than that calculated with the use of  $\Theta_D = 235 \text{ K}$ , where  $U_{eq}$  is equal to  $1/3(U_{11} + 2U_{22=33})$ . It corresponds to a higher Debye temperature for the O atom than for heavy atoms. The same behaviour has been seen in rare-earth hexaborides  $\text{RB}_6$  [21]. The occupation values of K atoms at the Ba sites,  $x$ , are 0.442(3) and 0.423(5) at 295 and 108 K, respectively. From the result, the occupation value used is  $x = 0.43$  in the MEM analysis, which is close to the value  $x = 0.47$  determined by EPMA.

To obtain the EDD in  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$ , the MEM analysis was carried out with the computer program MEED [22]. In the present analysis, the total number of electrons in the unit cell was fixed to be  $F(000)$  ( $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$ ,  $F(000) = 147.09$  [e]) and the unit cell was divided into  $128 \times 128 \times 128$  pixels to ensure good spatial resolution. The number of reflections used was 186 independent reflections in the range of  $\sin \theta / \lambda < 1.3 \text{ \AA}^{-1}$ . The reliability factor of the MEM,  $R_{\text{MEM}}$ , was 0.66 and 0.85% at 295 and 108 K, respectively.  $R_{\text{MEM}}$  is expressed as  $R_{\text{MEM}} = \sum |F_{\text{obs}} - F_{\text{MEM}}| / \sum |F_{\text{obs}}|$ , where  $F_{\text{obs}}$  is obtained by the structural refinement and  $F_{\text{MEM}}$  is the structure factor calculated from the electron density distribution (EDD) obtained by the MEM.

The EDDs in  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$  at 295 K are shown in (001), (002) and (110) planes in figures 1(a)–(c), respectively. The contour lines are drawn from 0.2 to 4.2  $\text{e} \text{ \AA}^{-3}$  with 0.1  $\text{e} \text{ \AA}^{-3}$

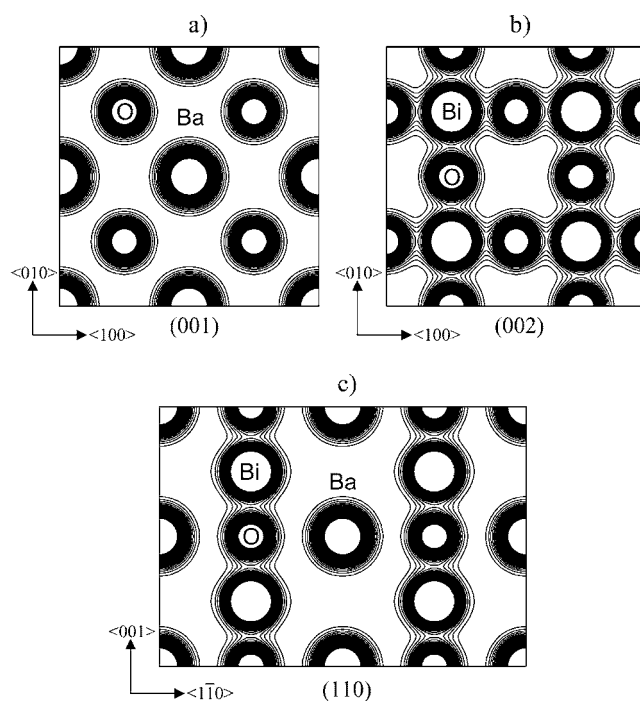


**Figure 4.** EDDs in  $\text{Ba}_{0.55}\text{K}_{0.45}\text{BiO}_3$  at 108 K obtained by MEM. Contour lines are drawn from 0.2 to  $4.2 \text{ e } \text{\AA}^{-3}$  with the interval of  $0.1 \text{ e } \text{\AA}^{-3}$ .

intervals. These planes are four times as large as the unit cell. In these figures, outer EDDs are, in particular, emphasized. From the MEM analysis, strong covalent bonding is clearly found between Bi and O atoms, while no bonding is observed between (Ba, K) and O atoms. It is found that the electron density at the saddle point between Bi and O atoms is  $0.97 \text{ e } \text{\AA}^{-3}$ , located at  $0.95 \text{ \AA}$  from the O atom's position. This value is almost the same as the value of Ti–O bonding in the cubic perovskite  $\text{SrTiO}_3$  reported before [13].

To understand the Bi–O bonding in detail, we have carried out the subtraction of the MEM electron density of  $\rho_{obs}$  directly from that of  $\rho_{calc}$ , which was obtained from the MEM analysis by using calculated structure factors  $F_{calc}$  in the structural refinement.  $\rho_{calc}$  was considered as the spherical electron density of the atoms. The difference electron densities,  $\Delta\rho(r) = \rho_{obs}(r) - \rho_{calc}(r)$ , are shown in (001), (002) and (110) planes in figures 2(a)–(c), respectively. The contour lines are drawn from  $-2.0$  to  $2.0 \text{ e } \text{\AA}^{-3}$  with  $0.05 \text{ e } \text{\AA}^{-3}$  intervals. Solid and dotted curves correspond to positive and negative values, respectively. The height of the Bi–O bonding is smaller than that in figure 1, but it is clearly found that the bonding between the Bi and O atoms appears from the subtraction of the spherical atom electron density. The covalency of the Bi–O bonding is considered to be on account of Bi 6s and O 2p hybridization near the Fermi level [23].

The EDDs at 295 K in  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$  are also shown in (001), (002) and (110) planes with different contour scales in figures 3(a)–(c), respectively, to see the characteristics of inner electrons. The contour lines are drawn from 10 to  $1000 \text{ e } \text{\AA}^{-3}$  in a logarithmic scale. We find the following characteristics from table 2, figures 1 and 3. The fact that  $U_{22=33}$  perpendicular to the Bi–O bond is almost four times as large as  $U_{11}$  for the O atom corresponds to an anisotropic thermal motion of O atoms. It is also realized from figure 3(b) that the EDD of inner electrons



**Figure 5.** EDDs in cubic  $\text{BaBiO}_3$  obtained theoretically by first-principles FLAPW calculation. Contour lines are drawn from 0.2 to  $4.2 \text{ e } \text{\AA}^{-3}$  with the interval of  $0.1 \text{ e } \text{\AA}^{-3}$ .

is elongated perpendicular to inter-Bi–O atoms, while that for O atoms is circular in figure 3(a). It is thought that the shape of the EDD for O atoms is similar to the elliptic one caused by thermal vibration of atoms. The shape is compatible with an anisotropy of thermal atomic displacement parameters for O atoms.

We have tried to find any peculiar change of the EDD at lower temperature. The EDDs in  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$  at 108 K are shown in (001), (002) and (110) planes in figures 4(a)–(c), respectively. The contour lines are drawn from  $0.2$  to  $4.2 \text{ e } \text{\AA}^{-3}$  with  $0.1 \text{ e } \text{\AA}^{-3}$  intervals. Comparing figures 1 and 4, there is no peculiar change between the two figures in terms of Bi–O bonding or anisotropic shape. The electron density at the saddle point between Bi and O atoms is  $1.08 \text{ e } \text{\AA}^{-3}$  and is a little larger than the value at 295 K.

To find the characteristics of the EDD in  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$ , the EDD of the cubic  $\text{BaBiO}_3$  was calculated by the FLAPW method using the WIEN97 computer program package [24]. The exchange and correlation terms by Perdew *et al* [25] were employed. In this calculation, we have used  $Pm\bar{3}m$  as the space group and  $4.355 \text{ \AA}$  as the lattice parameter [8]. The radii of muffin-tin spheres used were 2.3, 1.9 and  $1.6 \text{ au}$  for Bi, Ba and O atoms, respectively. However, the actual structure of  $\text{BaBiO}_3$  is not cubic but monoclinic.

The EDDs in cubic-phase  $\text{BaBiO}_3$  obtained by FLAPW calculations are shown in (001), (002) and (110) planes in figures 5(a)–(c), respectively. Contour lines are drawn at the same scale as in figure 1. In this calculation, we have assumed the temperature is equal to 0 K. The covalent bonding is clearly seen between Bi and O atoms, in good agreement with the EDD in  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$  obtained by the MEM qualitatively, but the EDD at the saddle point between Bi and O atoms is  $0.57 \text{ e } \text{\AA}^{-3}$  and is smaller than that for  $\text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3$ . Further, a spatial anomaly of the O atom is not observed in the calculated EDD. One of the reasons is



that the lowest experimental temperature, 108 K, was still higher than  $T_s$ , which is estimated as  $\sim 100$  K from [5], to observe the order parameter of the smeared structural phase transition.

In summary, the nature of chemical bonding in  $\text{Ba}_{0.55}\text{K}_{0.45}\text{BiO}_3$  is understood from the present structural analysis. As a result of the EDD analysis, strong covalent bonding is found between Bi and O atoms and the result is in good agreement with FLAPW calculation in cubic  $\text{BaBiO}_3$ . The observed spatial anisotropy of the EDD corresponds to the thermal vibration of O atoms.

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