Noncubic layered structure of $Ba_{1-x}K_xBiO_3$ superconductor

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Bismuthate superconductor $Ba_{1-x}K_xBiO_3$ ($x = 0.27 - 0.49$, $T_c = 25$-32 K) grown by an electrolysis technique was studied by electron diffraction and high-resolution electron microscopy. The crystalline structure thereof has been found to be noncubic, noncentrosymmetric and of the layered nature, with the lattice parameters $a \approx a_p$, $c \approx 2a_p$ (a_p is a simple cubic perovskite cell parameter) containing an ordered arrangement of barium and potassium. The evidence for the layered nature of the bismuthate superconductor removes the principal crystallographic contradiction between bismuthate and cuprate high-T_c superconductors.

Superconducting bismuthates including the first discovered $BaPb_{1-x}Bi_xO_3$ (Ref. 1) and $Ba_{1-x}K_xBiO_3$ (BKBO) (Ref. 2) with the highest transition temperature ($T_c = 32$-35 K for $x \approx 0.4$) have the basic characteristics similar to those of high-T_c copper-oxide superconductors.[3] This might favor for a common pairing mechanism. On the other hand, bismuthates have been generally considered to be fundamentally different from cuprates due to two reasons. Bismuthates are nonmagnetic, and they have three-dimensional structures rather than layered two-dimensional ones characteristic of cuprates. Of these two contradictions, the most important one seems to be the latter. The absence of magnetic fluctuations in bismuthates may point to a nonmagnetic nature of the pairing mechanism, whereas it is unlikely that a common superconducting scenario in cuprates and bismuthates does not depend on lattice dimensionality.

The study of BKBO is of a particular interest also for understanding the relation between charge-density waves (CDW's) and superconductivity in high-T_c oxides. The parent compound for BKBO is the perovskite $BaBiO_3$ containing a CDW formed of an ordered arrangement of nonequivalent bismuth ions referred to as Bi^{3+} and Bi^{5+}.[4] This CDW is assumed to be responsible for the semiconducting behavior of $BaBiO_3$ and $Ba_{1-x}K_xBiO_3$ materials with low potassium content ($x < 0.25$). The widely known notion that BKBO superconductors have a simple cubic ABO_3 solid-solution structure of a nonlayered nature, with barium and potassium randomly occupying the A position, was inferred from long-range structural studies of ceramic samples by x-ray[5] and neutron diffractions.[6] A simple cubic structure excludes the existence of a CDW that leads to the conclusion of the total incompatibility of CDW's and superconductivity. However, studies of BKBO by methods sensitive to short-range symmetry, in particular, by the Raman scattering spectroscopy,[7] a paired-distribution function analysis of neutron diffraction data,[8] extended x-ray absorption fine-structure analysis (EXAFS)[9,10] evidence that the local structure of BKBO superconductors is not cubic. An x-ray diffraction study[11] of $Ba_{0.6}K_{0.4}BiO_3$ single crystals grown by an electrolysis technique[12] has revealed supercell reflections assigned to a CDW.

It has been hypothesized[13] that BKBO superconductors may have layered structures with an anisotropic ordered arrangement of potassium and barium. Detailed studies[14] of phase relations in the Ba-Bi-O system have revealed a series of $Ba_nBi_{n+m}O_y$ oxides of ordered layered structures.[15] $Ba_nBi_{n+m}O_y$ are assumed to be matrices transformed, when intercalated with potassium, into superconducting oxides retaining the layered nature of the matrices structures. Besides, Ba-rich oxides with a solid-solution structure that attributed to BKBO superconductors were discovered.[16] Such oxides are formed in two-phase regions of the Ba-Bi-O system. Assuming that the same phenomenon is inherent also in the Ba-K-Bi-O system, we looked for conditions of single-phase growth of BKBO crystals. By varying parameters of the electrolysis technique, we examined the growth process and obtained the data suggesting the existence of individual superconducting phases $Ba_nK_mBi_{n+m}O_y$ with different T_c ($8 - 35$ K).[17]

This paper reports electron diffraction (ED) and high-resolution electron microscope (HREM) studies of superconducting crystals $Ba_{1-x}K_xBiO_3$ ($x = 0.27 - 0.49$, $T_c = 25 - 32$ K) grown by a modified electrolysis technique.[17] We present the evidence obtained by a long-range structural method that the BKBO superconductor has a noncubic structure with layered ordering of barium and potassium.

Superconducting crystals were produced by electrolysis of KOH-$Ba(OH)_2$-Bi_2O_3 melt (K:Ba:Bi=72:1.33:2) with the current of 5.3 mA at 300 °C for 5 h. The anode deposit was a polycrystalline boule consisting of intergrown single crystals. According to an x-ray powder diffraction analysis, the deposit contained several phases of pseudocubic perovskite structure ($a_p = 0.4277 - 0.4310$ nm). The temperature dependence of the magnetic susceptibility χ was measured for four crystals of the cubic shape of $0.5 - 1$ mm³ in volume chosen in the deposit. The crystals displayed similar curves, $\chi(T)$, showing bends at 25, 27, 30, and 32 K that indicates the presence of different superconducting phases.

One of the four crystals was selected for electron microscope studies. It was ground to prepare a suspension with particles of a few micrometers in size which was deposited on holey carbon films. Electron diffraction studies were performed in an electron microscope JEOL JEM-2000FX equipped with a system for an energy dispersive x-ray
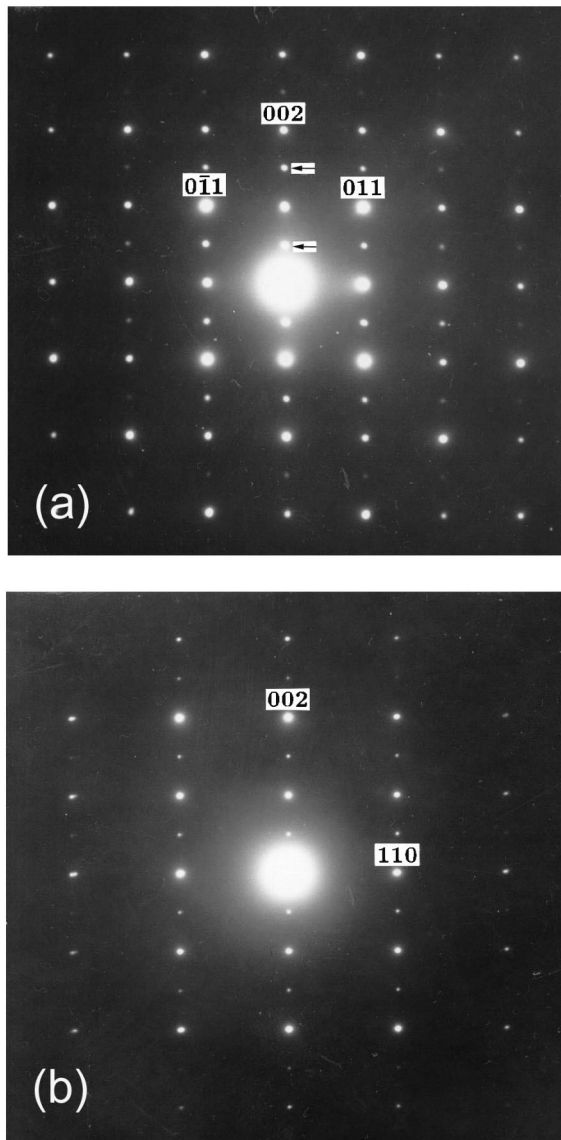
FIG. 1. Electron diffraction patterns of ordered particles displaying supercell spots (arrowed) with the vector $\mathbf{q}=\frac{1}{2}[001]$. (a) [100] zone axis; (b) [1-10] zone axis.
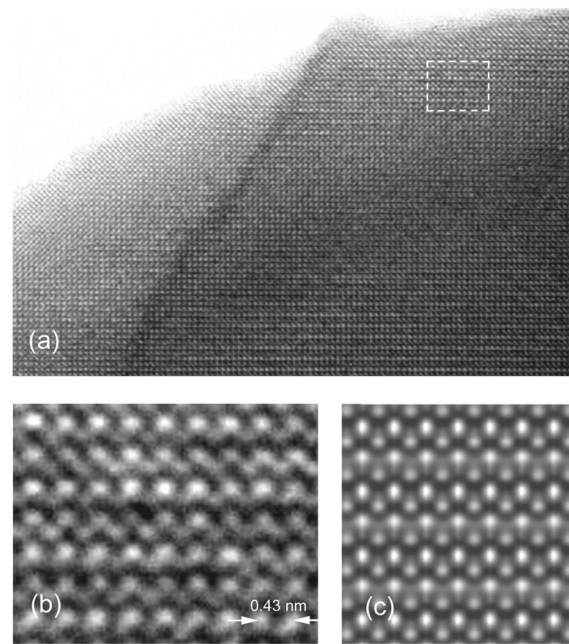

FIG. 2. (a) A [100] HREM image of a particle with the ordering. (b) An enlarged fragment of the Fig. 2(a) image (a dotted rectangle). One may notice the absence of a symmetry center and slightly different sizes of the perovskite blocks in the supercell. (c) A simulated HREM image of the noncentrosymmetric supercell (drawn in Fig. 3) with an ordered arrangement of barium and potassium ions.

(EDX) elemental analysis. High-resolution studies were performed in a microscope Hitachi HF-3000. In order to avoid beam-induced modulations,[18] the experiments were run at minimal electron beam intensity. We examined 40 particles of the ground crystal, EDX spectra, and ED patterns were taken from each particle. Although the full composition range of $Ba_{1-x}K_xBiO_3$ particles was found to be $x = 0.27-0.49$, majority of them had K:Ba:Bi ratio close to average value of 0.38:0.62:1 obtained by summing over all measurements.

Half of the particles exhibited diffraction patterns (Fig. 1) containing supercell reflections with the vector $\mathbf{q}=\frac{1}{2}[001]$ (indexing in terms of a simple cubic perovskite cell) in addition to the basic perovskite reflections. As only two out of three $\langle 100 \rangle$ axial directions are observable at electron microscope studies (due to a limited range of specimen tilt), some of particles not displaying supercell reflections were, in fact,

also of the ordered nature, but those particles were observed in the [001] zone axis when the supercell reflections could not be excited. Assuming that the predominant cleavage at crystal grounding is weak for BKBO superconductors, a lower limit of the relation of all ordered particles to nonordered can be estimated from the above data as 3:1. It indicates that the bulk of the studied crystal was of the ordered state. From the temperature dependence of the magnetic susceptibility, which changed much and sharp at 30 K and smoothly at lower temperatures, it follows that the ordered state is related to $T_c = 30$ K, whereas the nonordered part of the crystal became superconducting at $T_c = 25-27$ K.

The anisotropic orientation of the supercell reflections along only one of the axial directions indicates that the ordered lattice is of noncubic symmetry. As no clear splitting of perovskite spots was observed, which would indicate the presence of twins of a phase with lower crystallographic symmetry, it follows that tetragonal symmetry can be assigned to the ordered lattice. From the magnitude and type of the supercell reflections one may state that the supercell is primitive with the lattice parameters $a \approx a_p$ and $c \approx 2a_p$, it consists of two perovskite blocks.

An [100] HREM image taken from the particle, which displayed supercell spots in ED patterns, is shown in Fig. 2(a). The ordering manifests itself as intensity modulations along the [001] direction with the period of $2a_p$. A detailed picture of the image contrast is shown in Fig. 2(b) presenting the enlarged image of the area near the edge of the particle. It can be visualized that the supercell consists of two perovskite blocks. Matching the corresponding spots in the image

and measurements of the distances between them disclose that the image contrast of the blocks is different, and the blocks are slightly different in size (4–5 %). This indicates that the blocks in the supercell are not equivalent. An important feature of the HREM image in Fig. 2(b) can be noticed, namely, the absence of a symmetry center, which suggests a noncentrosymmetric nature of the supercell structure.

Two crystallographic models of a different nature may be responsible for the appearance of supercell reflections with the vector $\mathbf{q} = \frac{1}{2}[001]$: (1) the model of solid solution with the occurrence of common barium and potassium positions in the perovskite blocks, (2) the model of ordering of barium and potassium.

In the model of solid solution the appearance of the supercell reflections is related to distortions (tilting and/or deformation) of oxygen octahedra surrounding bismuth ions. This approach was applied to explain the origin of supercell reflections with the vectors $\mathbf{q} = \frac{1}{2}\langle 111 \rangle$ observed in diffraction patterns of the perovskite $BaBiO_3$.[4] For our case, a scheme of one-dimensional deformation of oxygen octahedra along the [001] direction without tilting, when octahedra are alternatively different in size with the period of $2a_p$, can only give rise to reflections with $\mathbf{q} = \frac{1}{2}[001]$, because the $a_p \times a_p \times 2a_p$ supercell is not compatible with the presence of tilting.[19] In this scheme, there is a nonequivalency of bismuth ions in neighboring planes rectangular to the [001] axis, which is inter-related with the existence of a CDW.

To establish if the solid solution model is credible, we performed the HREM image simulations using the NCEMSS program[20] with variation of possible parameters affecting the image contrast: ion coordinates, specimen thickness, objective lens defocus value, specimen deviation from the exact zone orientation. The simulation has revealed that no asymmetry in HREM images of centrosymmetric cells is observed, whereas it does occur for noncentrosymmetric ones. However, a trustworthy agreement between simulated images of noncentrosymmetric cells and the experimental images cannot be achieved by varying the parameters. So, we conclude from structural studies that the model of solid solution should be rejected. The model of only oxygen octahedra deformations is not compatible also with superconducting properties of BKBO crystals of the compositions studied here. Quite intensive reflections with $\mathbf{q} = \frac{1}{2}[001]$ (more intensive than reflections with $\mathbf{q} = \frac{1}{2}\langle 111 \rangle$ characteristic of semiconducting $BaBiO_3$) would imply large octahedra deformations, and hence the existence of a very strong CDW, which would result in dielectric properties.

In the model of ordering one of the two cation positions between the oxygen octahedra (A positions) is fully occupied by barium. The second A position is a common site for barium and potassium with the highly prevailing amount of potassium (for $Ba_{0.6}K_{0.4}BiO_3$ composition being close to the average one of investigated particles, the ratio of the occupation factors Ba:K is 1:4 in the second A position). The image simulations [Fig. 2(c)] have shown that the contrast of experimental images can be described in the model of ordering with nonsymmetric ion coordinates. Intensity of the supercell reflections is dictated by a difference in scattering factors of Ba and K.
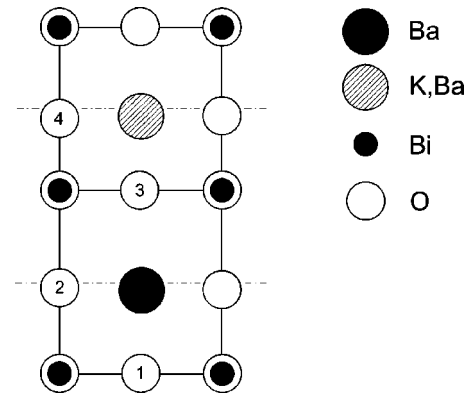

FIG. 3. The [100] projection of a noncentrosymmetric $a_p \times a_p \times 2a_p$ supercell of the $Ba_{1-x}K_xBiO_3$ superconductor. The size of the perovskite block with potassium is slightly smaller than that of with barium. Symmetry planes of the blocks are marked by dotted lines.

Figure 3 illustrates the model of the structure consistent with the HREM images. The tetragonal space group P4mm can be taken as a possible noncentrosymmetric group to describe the lattice symmetry. Barium and potassium are displaced against the centers of the perovskite blocks in parallel manner. Apical oxygens O(2) and O(4) are synchronously displaced from the centers of the edges, that results in distinct positions thereof relative to bismuth ions. Bismuth ions in neighboring BiO_2 planes with planar oxygens O(1), O(3) are nonequivalent in this model as well as in the solid solution one.

The authors of initial studies[21] of BKBO superconductors by EXAFS assumed the existence of only one Bi-O bond length in the structure. The recent EXAFS study[10] has found two distances of oxygen relative to bismuth. It can be assumed that the bond lengths of bismuth with planar oxygens O(1), O(3) (Fig. 3) are close or the same, whereas the bond lengths of bismuth with apical oxygens are clearly different. As the number of apical bonds is smaller than that of planar ones, the contribution of the formers into the general set of Bi-O bonds is insignificant and gives rise to the second-order effect.[10] However, contrary to the assumption put forward in Ref. 10 about the dynamic nature of the occurrence of different Bi-O bonds in BKBO superconductors, our study shows that it is of a static nature.

BKBO superconductors have the formal oxidation state of bismuth ions in the range of 4.35–4.55.[17,22] A part of bismuth ions may be present in the stable oxidation state +3. It is known that Bi^{3+} ions in the structures of bismuth-containing oxides are coordinated with surrounding oxygen ions asymmetrically due to the presence of stereoscopically active lone electron pairs of Bi^{3+} ions. It can be assumed that a collinear orientation of these electron pairs gives rise to the asymmetric structure in Fig. 3.

It is significant that the existence of nonequivalent metal-oxygen distances in the ordered structure of BKBO points to the likely presence of a CDW. This CDW is obviously other than the semiconducting CDW existing in the parent perovskite $BaBiO_3$, because the nonequivalent Bi ions in $BaBiO_3$ have all (six) different Bi-O bonds, whereas such ions in the

ordered BKBO differ with respect to one or two apical oxygens. This is consistent with the x-ray study[11] giving an evidence that splitting of the supecell reflections resulting from the domain structure was sensitive to electric and magnetic fields. Further studies with the use of a quantitative diffraction technique (e.g. neutron diffraction) are needed to reveal the nature of the CDW and details thereof which may be related to the pairing mechanism.

An important point is that the ordered arrangement of barium and potassium ions along the [001] axis results in an anisotropic structure, where stacking of BiO_2 planes with planar oxygens O(1),O(3) along the [001] axis (Fig. 3) endows the structure with the layered nature. This makes the crystalline structure of the ordered BKBO with the separate BiO_2 planes qualitatively similar to crystalline structures of cuprate superconductors with CuO_2 planes that cancels their principal crystallographic contrasting. The difference between them is that cuprates have layered structures with distinct anisotropy, whereas the layered BKBO has a weakly anisotropic structure due to close ion radii of Ba^{2+} (0.138 nm) and K^+ (0.133 nm).

In summary, we have observed a noncubic structure of the superconducting bismuthate $Ba_{1-x}K_xBiO_3$ ($x=0.27-0.49$, $T_c=25-32$ K). The structure is ordered with the lattice parameters $a\approx a_p$, $c\approx 2a_p$ in terms of a simple cubic perovskite cell parameter a_p. It has been revealed that the ordering nature is related to the ordered arrangement of barium and potassium ions, which endows the structure of $Ba_{1-x}K_xBiO_3$ with a layered character being typical for structures of superconducting cuprates. The crystalline cell of the superconductor has been found to be noncentrosymmetric with nonequivalent metal-oxygen distances that may point to the existence of a charge-density wave.

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[1] A.W. Sleight, J.L. Gillson, and P.E. Bierstedt, Solid State Commun. **17**, 27 (1975).

[2] L.F. Mattheiss, E.M. Gyorgy, and D.W. Johnson, Jr., Phys. Rev. B **37**, 3745 (1988).

[3] B. Batlogg, R.J. Cava, L.F. Schneemeyer, and G.P. Espinosa, IBM J. Res. Dev. **33**, 208 (1989).

[4] D.E. Cox and A.W. Sleight, Acta Crystallogr., Sect. B: Struct. Sci. **35**, 1 (1979).

[5] R.J. Cava, B. Batlogg, J.J. Krajewski, R. Farrow, L.W. Rupp, Jr., A.E. White, K. Short, W.F. Peck, and T. Kometani, Nature (London) **332**, 814 (1988).

[6] S. Pei, J.D. Jorgensen, B. Dabrowski, D.G. Hinks, D.R. Richards, A.W. Mitchell, J.M. Newsam, S.K. Sinha, D. Vaknin, and A.J. Jacobson, Phys. Rev. B **41**, 4126 (1990).

[7] N.V. Anshukova, A.I. Golovashkin, V.S. Gorelik, L.I. Ivanova, and A.P. Rusakov, J. Mol. Struct. **219**, 147 (1990).

[8] H. D. Rosenfeld and T. Egami, in *Lattice Effects in High-T_c Superconductivity*, edited by Y. Bar-Yam *et al.* (World Scientific, Singapore, 1992), p. 105.

[9] Y. Yacoby, S.M. Heald, and E.A. Stern, Solid State Commun. **101**, 801 (1997).

[10] A.P. Menushenkov, K.V. Klementev, P.V. Konarev, and A.A. Meshkov, JETP Lett. **67**, 1034 (1998).

[11] C.H. Du and P.D. Hatton, Europhys. Lett. **31**, 145 (1995).

[12] M. Norton, Mater. Res. Bull. **24**, 1391 (1989).

[13] L.A. Klinkova, Sverkhprovodimost: Fiz., Khim., Tekh. **6**, 683 (1993).

[14] L.A. Klinkova, V.I. Nikolaichik, N.V. Barkovskii, and V.K. Fedotov, Russ. J. Inorg. Chem. **44**, 1974 (1999).

[15] V.I. Nikolaichkx, S. Amelinckx, L.A. Klinkova, N.V. Barkovskii, O.I. Lebedev, and G. Van Tendeloo, J. Solid State Chem. **163**, 44 (2002).

[16] V.I. Nikolaichik and L.A. Klinkova, J. Supercond. **10**, 431 (1997).

[17] L.A. Klinkova, V.I. Nikolaichik, N.V. Barkovskii, and V.K. Fedotov, Russ. J. Inorg. Chem. **46**, 715 (2001).

[18] E.A. Hewat, C. Chaillout, M. Godinho, M.F. Gorius, and M. Marezio, Physica C **157**, 228 (1989).

[19] P.M. Woodward, Acta Crystallogr., Sect. B: Struct. Sci. **53**, 32 (1997).

[20] R. Kilaas, NCEM, Lawrence Berkeley Laboratory.

[21] S.M. Heald, D. DiMarzio, M. Croft, M.S. Hegde, S. Li, and M. Greenblatt, Phys. Rev. B **40**, 8828 (1989); S. Salem-Sugui, Jr., E.E. Alp, S.M. Mini, M. Ramanathan, J.C. Campuzano, G. Jennings, M. Faiz, S. Pei, B. Dabrowski, Y. Zheng, D.R. Richards, and D.G. Hinks, *ibid.* **43**, 5511 (1991).

[22] Y. Nagata, H. Samata, T. Uchida, M. Ohtsuka, and A. Mishiro, J. Phys. Chem. Solids **60**, 1933 (1999).