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STRUCTURE AND TRANSPORT PROPERTIES OF MELT PROCESSED $Ba_{1-x}K_xBiO_3$

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ABSTRACT

Single-phase samples of $Ba_{1-x}K_xBiO_3$ ($0<x<0.5$) have been synthesized from the melt followed by a two-step annealing procedure. In the first step, potassium is incorporated into the oxygen-deficient material under reducing conditions. Low-temperature oxygen annealing fills the oxygen vacancies without potassium loss. Samples are cubic, bulk superconductors for $x>0.35$ with T_c gradually decreasing as x increases. At 10K, with decreasing potassium content, the symmetry reduces to tetragonal at $x=0.35$, orthorhombic at $x=0.2$ and finally to monoclinic at $x=0.1$. Normal state resistivity displays metallic behavior for $0.40<x<0.5$, phonon-assisted variable-range hopping behavior for $\sim 0.15<x<0.30$ and semiconducting behavior for $x<0.15$.

INTRODUCTION

Two classes of high-temperature oxide superconductors, one based on Cu-O[1] and the other based on Bi-O[2], have several common features. Both systems have semiconducting parent compounds which upon doping, become metallic and superconducting with an unusually high superconducting transition temperature for their low electronic density of states at the Fermi level[3]. Another common feature is the similarity of the local structures based on a corner linked metal ion-oxygen octahedra which may provide similar optical phonon vibrations of oxygen ions and a similar electron-phonon interaction. However, unlike the 2-dimensional directional bonds involving copper d-orbitals in the case of copper oxides, the Bi-based oxides form a true 3-dimensional network based only on simple s- and p-orbitals. Because of their simple electronic structure and the fact that Bi-based oxides, unlike copper oxides, are nonmagnetic, it is possible that the nature of the pairing interaction responsible for high-temperature superconductivity will be revealed first for the $Ba_{1-x}K_xBiO_3$ system.

Single-phase samples in the $Ba_{1-x}K_xBiO_3$ system can be prepared for $0.0<x<0.5$ by a two step procedure[4,5]. In the first step, potassium is incorporated into the compound during a low-oxygen partial pressure firing in the 700-800^{0}C range. Each composition, x, requires a specific oxygen partial pressure and temperature. The potassium containing material is then quenched to room temperature. Oxygen vacancies

formed during the potassium incorporation are filled in the next step - a low temperature (~400^{0}C) firing in pure oxygen. Multiphase samples are obtained if the wrong conditions are used in the first step or if oxygen annealing is done at too high a temperature.

We have recently concluded a structural, transport and superconducting investigation of the samples prepared using the standard ceramic powder synthesis method[6]. The perovskite structure of the undoped $BaBiO_3$ [7] parent compound is monoclinic with frozen-in breathing modes (oxygen atom displacements around the Bi sites) and rotational (octahedral tilt along the $[110]_p$ axis) distortions of the Bi-O_6 octahedra. At room temperature, as x increases, the frozen-in breathing mode distortion disappears near x=0.1. For 0.1<x<0.3 the structure is orthorhombic with only a rotational distortion present. For x>0.3 (at room temperature) samples have a simple cubic structure. However, several structural facts are not adequately resolved for samples prepared by powder synthesis methods due to the compositional inhomogeneities caused by the low synthesis temperature. For example, values of the orthorhombic strain, in samples with compositions close to the orthorhombic-cubic phase transition, were near the detectability limit due to the peak broadening caused by compositional inhomogeneity. Thus, it was not possible to unambiguously rule out the existence of a tetragonal phase present between the orthorhombic and cubic phases.

While $BaBiO_3$ is known to be semiconducting with an activation energy of ~300meV[8], our resistivity measurements showed phonon-assisted variable-range hopping behavior, $\rho \sim \exp[-(T_0/T)^{1/4}]$, between 160 and 300K for 0.3<x<0.45[9]. For higher doping levels, samples are metallic up to the solubility limit, x=0.5. Only samples which are cubic at low temperature (x>0.37) are bulk superconductors with T_c gradually decreasing from 30 to 22K as x increases to 0.5. However, the transition between superconducting and nonsuperconducting phases was smeared as seen from a constant resistive onset temperature for 0.3<x<0.37. Also, the transitions between metallic and nonmetallic compositions were not well defined and, in particular, did not correlate very well with structural changes.

To improve sample quality we have developed a new melt-process method of synthesis for $Ba_{1-x}K_xBiO_3$ system[10]. While the powder method described above gives a low-density product not adequate for many experimental measurements, the melt-process method yields very homogeneous and nearly 100% dense material. The new process involves melting the stoichiometric oxide mixture under a N_2 curtain followed by quenching the melt onto copper plates. The quenched material is then fired using the same sequence as for the powder samples.

Several experiments performed on high-quality, melt-processed material lead to the conclusion that $Ba_{1-x}K_xBiO_3$ is a phonon mediated, weak coupling ($\lambda \leq 1$) superconductor[11]. The high T_c comes from the large average energy of the mediating phonons $\langle\omega\rangle$ due to strong electron interaction with the high-energy optic modes. Here, we report structural and transport results obtained for melt-processed material. These results agree quite well with the earlier study done for material prepared by powder methods. However, due to improved quality of the present samples, it is now possible to more precisely define phase boundaries and transport properties for each phase.

RESULTS

The high quality of the melt-processed material was evident from the small values of

the peak broadening in the raw neutron diffraction data[12]. We interpret this narrowing of peak broadening as resulting from improved sample homogeneity. Rietveld refinements of the neutron diffraction data, obtained at room temperature and below, show the same general features as for material prepared by powder synthesis methods. Thus $BaBiO_3$, and compositions up to x=0.1, are monoclinic, space group I2/m. The breathing mode distortion, as measured by the monoclinic angle, rapidly decreases with increasing x from α=90.25 deg for x=0.0 to 90.08 deg for x=0.1 at 10K. Samples with x=0.15 are orthorhombic, space group Ibmm. However, we find that the x=0.2 composition is indeed tetragonal, space group I4/mcm. Higher compositions, up to x=0.3 at room temperature and up to x=0.35 at 10K, are also tetragonal. Samples with x=0.3 transform to the simple cubic structure, space group Pm3m, just above room temperature. Compositions beyond x=0.3 at room temperature and x=0.35 at 10K have the simple cubic structure. The observation of the tetragonal structure, having a rigid octahedral tilt around the $[001]_p$ axis, whose presence could not be confirmed before, puts the observed structures in a sequence, I2/m→Ibmm→I4/mcm→Pm3m which leads to a continuous increase in symmetry. This sequence of transitions is characterized by first the disappearance of the breathing mode distortion followed by the loss of the octahedral tilts.

Resistive measurements were performed on the same set of samples. It is, thus, possible to correlate the observed resistive behavior with the structural changes. Figure 1 shows resistivity as a function of inverse temperature for several compositions. Samples with x=0.0, 0.05 and 0.1 show semiconducting behavior with activation energies of E_g=300, 246 and 240meV, respectively. The measured activation energy for pure $BaBiO_3$ is the same as reported in the literature from resistive measurements[8] but much smaller than the optical gap, ~2eV[13]. The presence of activated, semiconducting behavior for x=0.0-0.1 can be understood on the basis of charge disproportion of Bi^{+4} into $Bi^{+4+\delta}$ and $Bi^{+4-\delta}$ (commensurate charge density wave) resulting from the breathing mode distortion[7]. This distortion opens a gap at the Fermi surface of the half-filled band of $BaBiO_3$. However, the resistively measured gap does not scale in a simple way with the breathing mode distortion. The value of activation energy initially rapidly decreases and eventually saturates near 240meV.

Plots of resistivity (on a logarithmic scale) vs inverse temperature show marked deviations from simple activated behavior for x≥0.15. The data show curvature at low temperature which increases with doping level. To explain the data for 0.15≤x<0.3, the gap would need to be strongly temperature dependent with its value decreasing rapidly with temperature. This interpretation is difficult to reconcile with the structural data since it is not theoretically possible to create a semiconducting gap from octahedral tilts alone. To explain the presence of a gap, local charge disproportion or a long-range incommensurate charge density wave, was invoked[14,15]. Such an incommensurate charge density wave was initially observed by electron diffraction[16] but not in neutron diffraction experiments[6]. It was subsequently shown that the incommensurate charge density wave ordering was induced by the electron beam[17].

Another interpretation relies on the observation that throughout the studied temperature range, the resistivity can be well approximated by a $\rho \sim \exp[-(T_0/T)^{1/4}]$ relation. Such behavior is characteristic of phonon-assisted, variable-range hopping conductivity. Hopping conductivity does not require a semiconducting gap, i.e. the electronic states are localized at the Fermi energy. The reason for the electron localization may be the disorder introduced by a random substitution of potassium for barium ions.

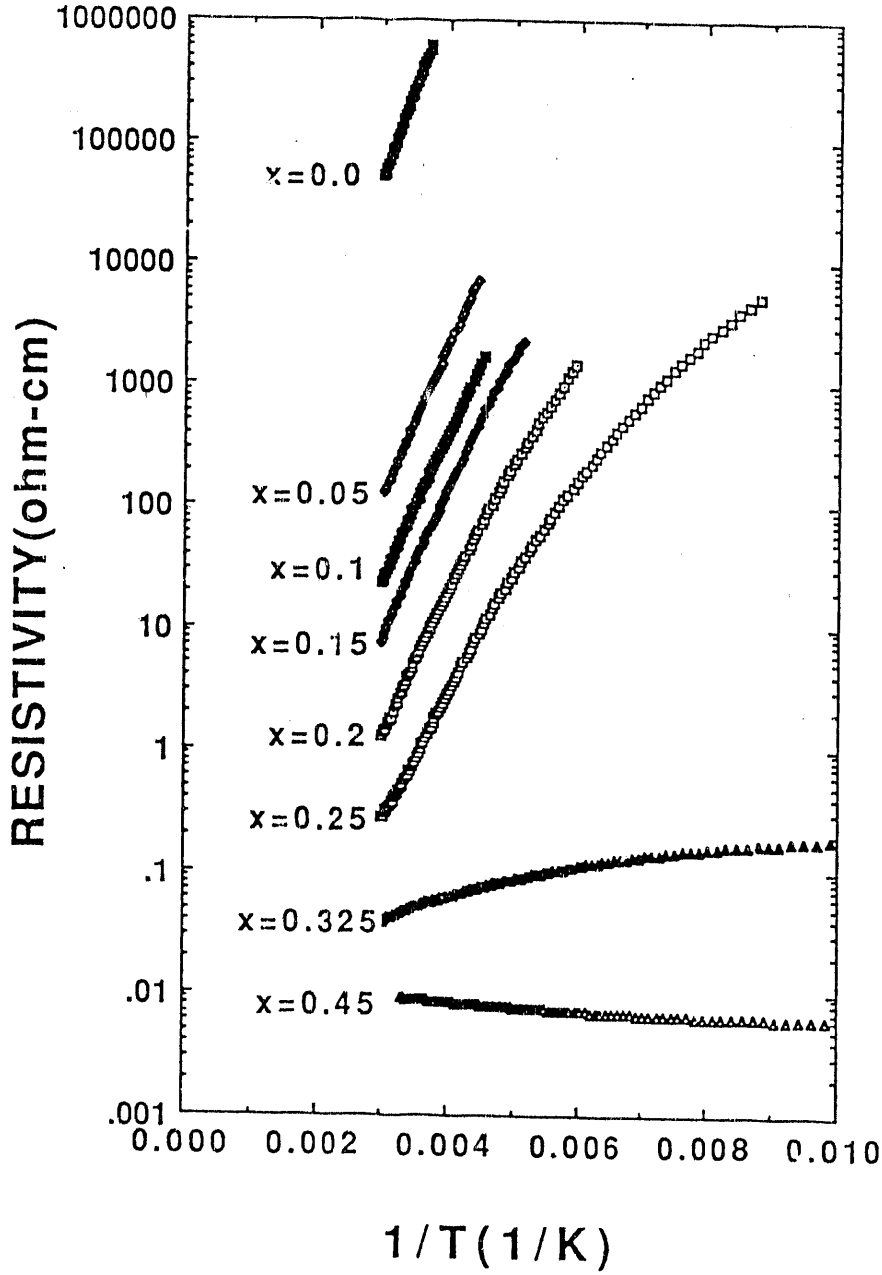

Fig. 1. Resistivity as a function of inverse temperature for several compositions of $Ba_{1-x}K_xBiO_3$.

This interpretation is obviously more consistent with structural results.

Figure 2 shows the normalized resistance for several compositions with x>0.3. In general, samples in the 0.3<x<0.4 range show mixed behavior which cannot be expressed in any simple form. This is consistent with the structural data that shows (in this compositional and temperature range) the samples transform from tetragonal to simple cubic structure. The fraction of the superconducting phase, as determined from AC susceptibility measurements, rapidly increases in this range and attains bulk volume near x=0.35. Samples are metallic and superconducting for x>0.4. In that compositional range, samples are simple cubic. It is, thus, natural to assign metallic and superconducting properties exclusively to the simple cubic structure.

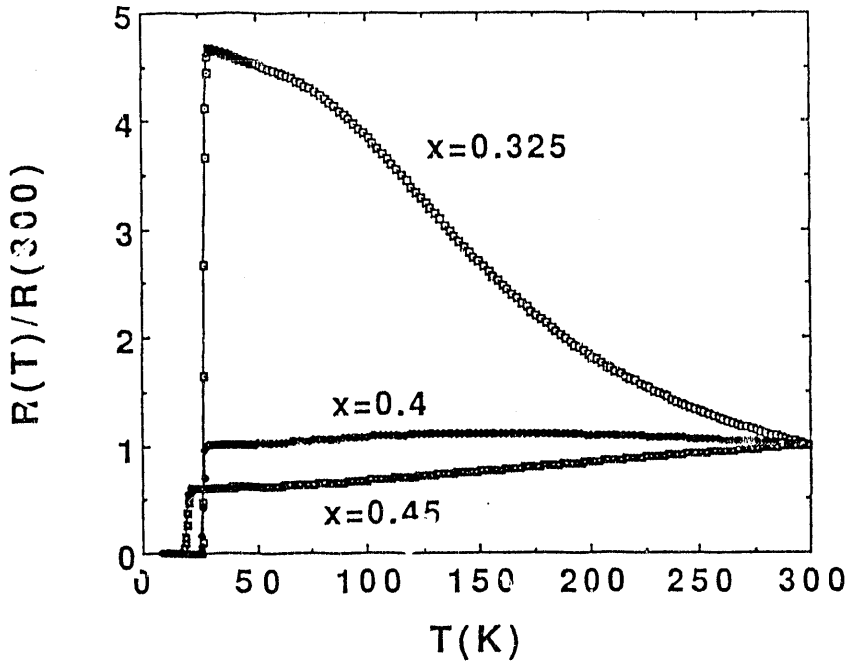

Fig.2. Normalized resistance for the $Ba_{1-x}K_xBiO_3$ samples with x=0.325, 0.4 and 0.45.

CONCLUSION

We have studied structural and transport properties of $Ba_{1-x}K_xBiO_3$ using high-quality, melt-processed samples. For 0.0<x≤0.1, the structure is monoclinic with two distinct Bi sites leading to a semiconducting gap which is observed from the resistivity measurements. For 0.1<x≤0.3, only Bi-O_6 octahedral tilts are present and the structure is orthorhombic (for 0.1<x<0.2) and tetragonal (for 0.2<x<0.3). The resistivity in this range can be approximated by gapless, phonon-assisted variable-range hopping behavior. Only the simple cubic structure, present for x>0.35 at 10K, is metallic and superconducting.

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REFERENCES

1. J.G. Bednorz and K.A. Muller, Z. Phys. B 64, 189 (1986).
2. A.W. Sleight, J.L. Gilson and P.E. Bierstedt, Solid State Commun. 17, 27 (1975); L.F. Mattheiss, E.M. Gyorgy and E.M. Johnson Jr, Phys. Rev. B 37, 3745 (1988).
3. R.J. Cava and B. Batlogg, MRS Bulletin vol. XIV, 49 (1989).
4. 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 332 , 814 (1988).
5. D.G. Hinks, B. Dabrowski, J.D. Jorgensen, A.W. Mitchell, D.R. Richards, Shiyou Pei and Donglu Shi, Nature 333, 836 (1988).
6. Shiyou 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. D.E. Cox and A.W. Sleight, Solid State Commun. 19, 969 (1976).
8. T.D. Thanh, A. Koma and S. Tanaka, Appl. Phys. 22, 205 (1980).
9. B. Dabrowski, D.G. Hinks, J.D. Jorgensen, R.K. Kalia, P. Vashishta, D.R. Richards, D.T. Marx and A. W. Mitchell, Physica C156, 24 (1988)
10. D.G. Hinks, A.W. Mitchell, Y. Zheng, D.R. Richards and B. Dabrowski, Appl. Phys. Lett. 54, 1585 (1989).
11. D.G. Hinks, B. Dabrowski, D.R. Richards, J.D. Jorgensen, S. Pei and J.F. Zasadzinski, Mat. Res. Symp. Proc. Vol. 156, 357 (1989).
12. B. Dabrowski, D.G. Hinks, J.D. Jorgensen, D.R. Richards, Shiyou Pei, Y. Zheng and A.W. Mitchell (to be published in Journal of Non-Crystalline Solids).
13. S. Tajima, S. Uchida, A. Masaki, H. Takagi, K. Kitazawa, S. Tanaka and S. Sugai, Phys. Rev. B 35, 696 (1987).
14. E. Jurczek and T.M. Rice, Europhys. Lett. 1, 255 (1986).
15. C.M. Varma, Phys. Rev. Lett. 61, 2713 (1988).
16. Shiyou Pei, N.J. Zaluzec, J.D. Jorgensen, B. Dabrowski, D.G. Hinks, A.W. Mitchell and D.R. Richards, Phys. Rev. B 39, 811 (1989).
17. E.A. Hewat, C. Chaillout, M. Godinho, M.F. Gorius and M. Marezio, Physica C 157, 228 (1989).

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