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TITLE BARIUM POTASSIUM BISMUTH OXIDE. SYNTHESIS AND PHYSICAL PROPERTIES

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ABSTRACT

A series of compounds $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ have been prepared and characterized over the range of compositions ranging from $x = 0.3$ to 0.5 . A neutron powder diffraction analysis has been carried out for the composition $x = 0.4$ at room temperature and at 10 K. Examination of the superconducting properties as a function of x indicates superconductivity occurs over a narrow range of compositions close to $x = 0.4$, with T_c of 29 K. Specific heat measurements indicate conventional electron-phonon interactions may play a role in promoting superconductivity in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. Magnetization loops and examination of the time dependent magnetization indicate that $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ has a low value of J_c due to very weak pinning.

INTRODUCTION

The discovery of superconductivity in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ (T_c 29 K) [1,2] has added a new compound to the group of perovskite-related high transition temperature superconductors. This new compound is of interest for a number of reasons. First, $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ is cubic, implying that two dimensional features present in all of the layered CuO_2 superconductors discovered to date are not necessary for high temperature superconductivity in oxides. Second, the barium potassium bismuth oxide (BKBO) material is diamagnetic in the normal state and lacks any signature of magnetic order [3], implying that the magnetism prevalent in the Cu compounds is not necessary to achieve superconductivity. Additionally, BKBO is closely related to the prototypical high temperature superconducting oxide, $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ (T_c 13 K) [4], the former prepared by A site doping and the latter prepared by B site doping of the parent compound BaBiO_3 .

The parent compounds La_2CuO_4 and BaBiO_3 are one electron short or in excess of a filled shell configuration, respectively. La_2CuO_4 is antiferromagnetic while BaBiO_3 is a diamagnetic charge density wave material. Partial substitution of La^{3+} with a divalent ion (e.g. Sr^{2+}) in La_2CuO_4 or partial substitution of Ba^{2+} with a univalent ion (e.g. K^+) in BaBiO_3 leads to formal oxidation and the addition of a few charge carriers to the parent compounds. This doping leads to the suppression of antiferromagnetism in La_2CuO_4 , and to the suppression of the charge density wave in BaBiO_3 and to the onset of superconductivity in both classes of compounds.

Several important questions regarding the mechanisms of superconductivity in the high temperature superconductors may be assessed by considering the similarities and differences among the cuprates and the bismuthates. The goal of our recent work is to examine a number of the physical properties of BKBO in an effort to attempt to elucidate these similarities and differences. In this paper, we will discuss the synthesis, the effect of K^+ doping on magnetic properties and structure, flux creep and heat capacity of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$.

SYNTHESIS

We have followed the excellent lead of Hinks [5,6] in the preparation of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$. Hinks defined the region of stability where potassium may be substituted into the lattice of BaBiO_3 , and the region of stability of BKBO under one atmosphere of O_2 . We include details of the synthesis for completeness. For successful and reproducible synthesis of BKBO, it must be emphasized that strictly anhydrous conditions be employed. Most of the commonly used potassium reagents for synthesis are deliquescent, and the presence of water leads to volatilization of potassium from the reaction mixture during the high temperature stages of the synthesis. All operations such as weighing, grinding, pressing, etc. are best carried out in a dry box (< 1 ppm H_2O), and that the materials be transferred rapidly from the dry box to furnace tubes continuously purged with scrupulously dry gases. Gross potassium volatilization is indicated by a white film of potassium hydroxide on the cold exit zone from the furnace tube. Any potassium that is not incorporated into the lattice of BKBO, either from insufficient reaction time or

from potassium compositions beyond the range of solubility, will eventually result in the formation of KOH and subsequently K_2CO_3 at the grain boundaries upon exposure to ambient atmosphere.

We have had the greatest deal of success in preparing BKBO ($x \leq 0.5$) from $BaBiO_3$, KX , and Bi_2O_3 in stoichiometric quantities. $BaBiO_3$ is simply prepared from $Ba(NO_3)_2$ and Bi_2O_3 that have been ground to powders and fired in gold crucibles (Pt is attacked) at $825^\circ C$ in air for 1 hour followed by regrinding and reheating for 2-4 hours. Here, X may be nitrate, superoxide, oxide, or, if higher temperatures are used, carbonate. We have also found that " $Ba_{1-x}BiO_y$ " (y and phase identification unknown) and a stoichiometric amount x of potassium salt leads to successful preparation of BKBO. We have also utilized the reaction of stoichiometric quantities of $BaBiO_3$ and $KBiO_2$ [7] with some success. In our experience, it appears that potassium superoxide is the potassium reagent of choice due to higher reaction rates. The conditions for preparation of the BKBO phases described here are given in equations 1 and 2.

The rate at which the reaction mixture is heated or cooled in Ar does not appear to be critical. The rate at which the oxygenation is carried out is important, as the rate at which oxygen is taken up by the reduced material is very rapid at temperatures approaching $400^\circ C$, rapid enough that there could be temperature excursions exceeding those under which BKBO is stable in oxygen. Therefore, we typically ramp the temperature up from $350^\circ C$ to $415^\circ C$ over a period of one hour, hold at that temperature for two to four hours, and then ramp down to $200^\circ C$ in four to six hours. This gives material having very reproducible magnetic properties for the composition near $x = 0.4$. Several plots of magnetization versus temperature for $Ba_{0.6}K_{0.4}BiO_3$ derived from this synthetic procedure are shown in figure 1.

The material thus prepared yields microcrystalline porous pellets. In order to prepare higher density material, we have found it useful to melt the material. Melting the material is carried out in gold crucibles at temperatures in excess of $875^\circ C$ under Ar [8]. By slow cooling of the melt through the freezing point and then cooling to room temperature followed by oxygenating as in equation 2, dense, highly faceted, large grained ($0.25 - 0.5$ mm) superconducting samples may be prepared.

STRUCTURE

Given the widespread occurrence of structural instabilities in superconducting materials and in perovskites, it has been of interest to determine if such instabilities occur in the BKBO system as they do in the parent compound $BaBiO_3$ [9, 10]. Many of the structural aspects of the BKBO system have been elucidated by Hinks and Jorgensen et al [5], Schneemeyer et al [11], Wignacourt et al [12], and Kwei et al [13]. These studies have shown a rich structural chemistry in the BKBO system, both as a function of temperature and potassium content. Of primary interest is the structural behavior around the superconducting transition. One of us has determined the structure of superconducting BKBO at 297 and 10 K by neutron powder diffraction [13]. The composition studied was $Ba_{0.58}K_{0.42}BiO_3$, as determined by analysis of the site occupancies. This composition is close to the composition determined by chemical analysis of $Ba_{0.60}K_{0.38}BiO_x$. The neutron diffraction results indicate that the structure at room temperature is cubic ($a = 4.28686(4) \text{ \AA}$) and remains cubic ($a = 4.2802(1) \text{ \AA}$) down to 10 K, well below the superconducting transition temperature of 29 K. The anisotropic thermal parameters for the oxygen atoms are oblate along the Bi-O-Bi axes indicating a rocking motion or possible disorder involving a tilting of the oxygen octahedra. Similar behavior has been noted in compositions of lower potassium content [11,12]. The observed displacement of the oxygen atoms perpendicular to the Bi-O-Bi axes in the potassium doped materials is perhaps related to the tilting of the oxygen octahedra observed in the parent compound [11,12,13].

We have examined the change in lattice parameter in BKBO as a function of nominal potassium content, x , to establish a correlation useful in tracking potassium loss resulting from the various synthetic schemes, and use the lattice parameter as a more reliable parameter to investigate the effect of potassium content on physical properties such as susceptibility. Using the synthetic scheme outlined above, we prepared a series of BKBO samples ranging from $x = 0.3$ to 0.5 keeping the conditions as identical as possible. The data are shown in figure 2. As has been observed by others, the lattice parameter decreases with increasing potassium content, consistent with the smaller ionic radius of potassium relative to barium. For comparison, data from neutron diffraction/Rietveld analysis [5]

and Schneemeyer's single crystal x-ray determination [11] have been included. It can be seen that the trend in lattice parameter vs. nominal potassium content reflects that from Rietveld analysis of potassium site occupancy.

SUPERCONDUCTING PROPERTIES OF BKBO: THE EFFECT OF POTASSIUM CONTENT

Diagrams of property versus composition are useful in determining structural and physical property sensitivities in multicomponent systems. Such phase diagrams have been found to be useful in examining the effect of dopants on the structure and superconductivity in the La_2CuO_4 family, and a phase diagram of T_c vs. potassium content has been presented in the literature [5] in an attempt to define the compositional boundaries of superconductivity in the BKBO family. It is likely that such diagrams suffer from uncertainty in the actual composition relative to the starting composition due to variable volatilization and loss of potassium from the material during synthesis.

Prior investigation of the T_c vs. x phase diagram are somewhat in disagreement as to the K/Ba ratio that gives rise to superconductivity in BKBO. In an early determination by Hinks et al [5], the appearance of superconductivity and maximum T_c are reported to appear near $x = .25$; Schneemeyer et al [11] indicate that the onset is somewhat less than $x = 0.4$.

We prepared the series of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ compounds where the starting composition x was varied as $x = .3, .33, .36, .38, .40, .42, .44, .47$, and $.5$. Samples were prepared using identical reaction conditions. Samples having potassium contents close to $x = .4$ were made in duplicate. The samples were characterized by x-ray diffraction using SiO_2 as an internal standard for accurate determination of lattice parameters. All samples were found to be cubic. Some samples contained a minor amount of BaBiO_3 . The magnetic susceptibility of the samples was determined as a function of temperature by zero field cooling (zfc) to 5 K, adjusting the field to 50 gauss, and then recording the magnetization while warming to above 34 K. The sample was then field cooled (fc) in 50 gauss to 5 K to record the Meissner value.

A plot of T_c versus either starting composition x or lattice parameter indicates there is little or no correlation among those variables. T_c 's of 29 K are found across the range of stoichiometry studied, with a few samples having T_c 's of 20 - 25 K. Examination of the zfc shielding value versus x (or lattice parameter) indicates a sharp maximum in the shielding occurs at x close to 0.4 (figure 3). Examination of all samples we have prepared in addition to those prepared for the studies reported here show an obvious trend in increasing Meissner fraction as T_c increases to 29 K. At $15 < T_c < 20$ K, the Meissner fraction is < 5 -10% and increases smoothly to 25 to 30% at T_c of 29 K. These three features suggest that superconductivity in the BKBO family occurs over a very narrow range with the optimal concentration of potassium being close to 0.4. This conclusion is significantly different than that arrived at by Hinks et al [5], where the phase diagram of superconductivity was found to be quite broad, ranging from $x = 0.25$ to 0.5. Our results suggest that the material with x far from 0.4 may not be superconducting at all, but rather there may exist local compositional inhomogeneities which have the correct stoichiometry to give rise to a superconducting transition. We have encountered many samples where potassium content is far from $x = 0.4$ as indicated by lattice parameter and have large zfc shielding, even 100%, but that have essentially no fc Meissner effect. This situation is suggestive of the "eggshell effect", where the surface or a subsurface shell of the grains are superconducting, but the interiors are not. If all of this is correct, then we must address the question of why are there transitions at temperatures less than 29 K? The lattice parameters over the range of stoichiometry of interest change by over 1 %. We suggest that the observation of T_c 's lower than 29 K arise from material of the proper stoichiometry but suffer from mechanical strain due to lattice mismatch. Such strain is known to have an effect on transition temperatures in other systems such as Nb_3Sn [14].

The phenomenon of large zfc shielding ($> 90\%$) and small ($< 5\%$) fc flux expulsion also occurs in very dense, large grained material prepared from the melt as described above. These analyses are consistent with the "eggshell" model, with only a small fraction of the bulk being superconducting, this fraction being located at or near the outer surfaces of the grains. In an attempt to understand this phenomenon, we have characterized samples from the melt both structurally and compositionally with powder x-ray diffraction and electron probe microanalysis (EPMA). Close examination of what appear to be single diffraction lines at large values of 2θ are actually multiple peaks having d spacings consistent with a range of stoichiometry of $x \sim .24$ to $.40$. This range of stoichiometry was confirmed by EPMA which indicated the grain edges had a stoichiometry of $x = .4$, with fluctuations within the grains down to $x = .3$ (figure 4). The EPMA also shows the grain boundary to consist of a phase close to KBiO_3 . This compound is highly deliquescent [7], and oozes to the surface of polished surfaces prepared for metallography and solidifies perhaps as K_2CO_3 and Bi_2O_3 . Assuming the 'eggshell' model, grinding of the sample should reduce the zfc shielding, while the fc Meissner fraction should remain the same. In fact, this is exactly what is observed. The zfc shielding value decreased from $> 90\%$ of the value expected for complete diamagnetism to 50 - 60% of that value after reducing the grain size from $> 200\mu\text{m}$ to approximately $10\mu\text{m}$. Again this behavior is consistent with

the superconductivity in the BKBO family occurring over a very narrow range of composition close to $x = 0.4$. An alternative explanation could be that the compound degrades upon grinding to a fine powder hence reducing the shielding value, or that the penetration depth λ is on the order of 10 μm in this compound. We believe these alternatives are unlikely.

HEAT CAPACITY OF $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$

Specific heat measurements on a sample of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ [15] in the temperature range of 1.6 to 40 K were performed between zero applied field and 10 T. The technique used was a quasi-adiabatic thermal relaxation method that allows an accurate absolute determination of heat capacity but is limited in its ability to detect small relative changes due to experimental scatter which is typically on the order of a few percent. The heat capacity measured for $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ is field independent from 4 to 35 K. The zero field heat capacity data plotted as C/T vs. T^2 appear in figure 5. The data demonstrate that for temperature greater than 4 K, there is significant curvature indicative of non-Debye-like behavior ($C/T \neq \gamma + \beta T^2$). The Debye temperature Θ_D derived from this analysis drops from a value of $\Theta_D = 280$ K at $T = 35$ K to a value of $\Theta_D = 210$ K at $T = 4$ K. If this interpretation of the data is appropriate, then the decrease in Θ_D with decreasing temperature implies that soft phonon modes are present in this material at low temperatures. Soft phonon modes are usually associated with considerable electron-phonon interactions. Hence, the lattice softening evident in the specific heat data indicates that conventional phonon-mediated interaction may be responsible, at least in part, for the high superconducting transition temperature exhibited by $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$.

The parent compound BaBiO_3 undergoes a charge density wave displacement of the oxygen atoms, indicating that soft modes may be a general feature of the barium bismuthate family. The phonon coupling responsible for the CDW distortion in BaBiO_3 is thought to arise from rocking or tilting of the oxygen octahedra [12, 13] mentioned above. It is possible that the same phonon mode is responsible for the superconducting transition in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$.

FLUX CREEP IN $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$

Magnetization M vs. magnetic field H loops at a variety of temperatures were obtained on samples of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ [16]. At 5 K, the $M(H)$ curve becomes reversible above about 0.8 T (figure 6). At 20 K, the loop exhibits no hysteresis above 0.3 T. The onset of reversibility occurs at fields an order of magnitude lower than that for other high T_c phases [17]. This lack of hysteresis in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ at such low fields is consistent with small values of the intragranular critical current density J_c as calculated from the Bean model where $J_c = 15 \Delta M/R$ where ΔM is the width of the loop and R is the particle radius. The value calculated from this model is $J_c = 3 \times 10^5 \text{ A/cm}^2$ in zero applied field. The J_c drops off rapidly with increasing field as indicated by the shape of the hysteresis loop; J_c can be taken as zero when the loop is completely collapsed. These features suggest that the pinning in this material is very weak. Preliminary results indicate that J_c and perhaps pinning may be larger in the large grained material processed from the melt. If the larger J_c is related to increased pinning in the melted material, this could also explain the smaller Meissner fraction we observe. However, because of the compositional inhomogeneities and the arguments concerning the effect of composition vs. the appearance of superconductivity discussed above, we feel this explanation is unlikely.

We have examined the pinning in the smaller grained material in more detail using magnetization decay as a function of time from which the average pinning energy can be deduced using the flux creep model (see ref. 16). These relaxation data were obtained by zero field cooling the sample to the temperature specified, and then applying a field of 0.1 T. Analysis of the relaxation data as a function of temperature yields a volume pinning energy U_0 of $0.08 \pm 0.02 \text{ eV}$, consistent with the small value of J_c observed for this material. This value of pinning energy is small relative to those measured for other non-Bi containing superconductors. Values for other materials (all at 1 T and low temperature far from T_c) range from: 0.01 eV - BiSrCaCuO_x [18]; 0.18 eV - Y-123 [17]; and 0.33 eV - TlBaCaCuO_x [17].

It is interesting to note that the lowest pinning energies arise from bismuth containing materials. It should be noted that in examining these relative pinning energies, extrinsic pinning due to defects may be important. For example, Y-123 is well known contain large quantities of defects in the form of twin boundaries, while the thallium cuprates are known to possess several types of structural modulations. In $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$, these types of defects do not occur. Because of the longer coherence lengths in this material, it is also possible that intrinsic pinning is less likely to be an important consideration. Hence, it is unclear whether the pinning energies measured are directly related to their intrinsic pinning properties.

SUMMARY

We have described the synthesis and characterization of the family of compounds $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ for $x < 0.5$. We have investigated the superconductivity in this series and find that the range of composition for the appearance of superconductivity may be quite narrow, and located close to the composition $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. Melt processing of material of this nominal composition results in dense, large grained material. This dense material has considerable compositional variation across individual grains, and exhibits magnetic properties suggestive of surface superconductivity. Clearly, further work is necessary to attempt to improve the melt processing of this material to relieve the compositional problem while retaining the density.

The structure of superconducting $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ has been determined to remain cubic from room temperature to 10 K. This behavior is unique in that most superconductors exhibit significant structural alteration close to the superconducting transition. Measurement of the specific heat of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ suggests that lattice softening occurs with decreasing temperature implying that electron-phonon interactions may be important for superconductivity in this compound.

Magnetization versus field loops and the magnetization time dependence show that $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ has a significantly lower values of J_c and U_0 relative to other high temperature superconductors. All of these various physical measurements discussed here are important in attempting to determine the mechanism of superconductivity in the perovskites, as well as in determining what influences the ultimate current density these materials can accommodate.

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Figure 1. Magnetization vs. temperature, $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ at 50 gauss.

Figure 2. Lattice parameter vs. x for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$.

Figure 4. X-ray diffraction (top) and EPMA line scan (bottom) indicating compositional inhomogeneity in large grained BKBO from the melt.

Figure 5. Plot of heat capacity data for $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$.

Figure 6. Left: Hysteresis loops (positive field shown for clarity). Right: Time dependent magnetization data.