Correlation of the superconducting transition to oxygen stoichiometry in single-crystal $Ba_{1-x}K_xBiO_{3-y}$

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Temperature-dependent positron-lifetime experiments have been performed from room temperature to 15 K on single crystals of the oxide superconductor $Ba_{1-x}K_xBiO_{3-y}$. Results indicate that the filling of oxygen vacancies has a marked impact on the superconducting properties of this system. Cation defect concentrations were below the detectable limit of positron-annihilation-analysis techniques in this material, which is in sharp contrast to identical studies on polycrystalline samples. We find that the positron lifetime in these electrochemically deposited single crystals is determined by the oxygen stoichiometry of the lattice, but there is no experimental signature of strong positron localization. By performing a subsequent oxygen anneal on the crystals, the superconducting transition is sharpened and the onset is raised. The observed change in positron lifetime associated with this annealing procedure is in quantitative agreement with theory.

The highest reported superconducting transition temperature in a copper-free oxide system is 32 K for $x \approx 0.4$ in the $Ba_{1-x}K_xBiO_{3-y}$ (BKBO) system. Superconductivity in potassium-doped $BaBiO_3$ was discovered in 1988 by Mattheiss, Gyorgy, and Johnson,[1] and specific synthesis and structural parameters for the polycrystalline material have been detailed by Hinks *et al.*[2] Recently, a novel electrochemical crystal-growth method has been reported that enables the fabrication of higher-quality superconducting material.[3] Studies of electrochemically deposited material, when contrasted to those of polycrystalline samples, have resulted in significant revisions of superconducting parameters such as the upper critical field and the coherence length.[4,5]

The parent compound to this material, $BaBiO_3$, is monoclinic and possesses an oxygen breathing-mode distortion which results in a periodic arrangement of Bi^{3+} and Bi^{5+} ions.[6] As potassium is gradually substituted on the barium site, the commensurate charge-density wave found in $BaBiO_3$ is suppressed until finally, near half-filling, a metallic superconducting phase is formed. This phase occurs for $0.37 \leq x \leq 0.5$ and has been identified as a cubic perovskite ($Pm3m$) of the form ABO_3 (A=Ba or K; B=Bi). The specific structure consists of bismuth atoms occupying the cell corners and surrounded by linked oxygen octahedra. Potassium and barium atoms are then randomly distributed with the proper stoichiometry in sites between the octahedra. The phase diagram of the material has been determined by neutron diffraction as a function of both potassium concentration (x) and temperature.[6] These studies show that the breathing-mode distortion and octahedral tilt, for given compositions and temperatures, yield numerous structural phase transitions.

We demonstrate a correlation between the superconducting properties of BKBO and the presence of oxygen defects in the lattice. These oxygen vacancies may significantly impact the delicate nature of the previously observed structural phase transitions. Recent theoretical calculations have suggested that the coupling of electrons to high-energy oxygen phonons furnishes a sufficient explanation of superconductivity in the system within the Eliashberg theory.[7] Until the electrodeposited material was synthesized, however, it was difficult to make a definitive statement about the oxygen stoichiometry and its specific relation to superconductivity in this system. The competition between defect populations has been studied previously in the polycrystalline material by using positron-lifetime techniques.[8] Using this same method, the defect structure of electrodeposited single-crystal BKBO has been investigated and the results are reported here.

We have determined, via positron-annihilation studies, that the electrodeposited samples show no signature associated with defects on the metal-atom sites. The only observable defects in the material are oxygen vacancies, and the lifetimes corresponding to these defects match theoretical calculations remarkably well. By performing a high-temperature oxygen anneal, these oxygen vacancies were partially filled and the associated lifetimes dropped accordingly. More importantly, however, the superconducting transition was observed to sharpen and the onset temperature was raised as the oxygen-vacancy level decreased. This indicates a direct correlation between the specific oxygen stoichiometry and superconductivity in BKBO.

Single crystals of BKBO were electrochemically grown using a technique only slightly modified from that reported by Norton.[3] The specific material involved in this study consists of small microcrystallites that form on the anode in a potassium hydroxide flux. This material is then culled by color, since the metallic phase of BKBO is

indicated by a brilliant blue hue. For this study we have chosen material from a growth which has a maximum T_c of 30.8 K with a ΔT_c of 2 K as determined by zero-field-cooled magnetization data.

Magnetization versus temperature was measured for these samples using a superconducting quantum interference device (SQUID) magnetometer,[9] and the superconducting transition was broad ($\Delta T_c = 15$ K) with an onset of 28.0 K. These crystallites have been verified as cubic-phase BKBO with $x = 0.4$ by Rietveld refinement of x-ray-powder-diffraction data. The refined lattice parameters for polycrystalline $Ba_{1-x}K_xBiO_{3-y}$ previously obtained from neutron diffraction[6] were used to determine potassium concentrations. These samples were next annealed under a flowing oxygen atmosphere in a thermogravimetric analysis (TGA) system. Since phase separation of the material is not known to occur until over 500 °C, the result was interpreted as an oxygenation of the already intact barium-potassium-bismuth lattice. Specific thermogravimetric data for this material are shown in Fig. 1. These data were corroborated by weighing the sample with another device before and after oxygenation. The difference in mass between the pre- and postannealed samples was directly correlated to oxygen content. The mass gain of 0.5% corresponds to an increase in oxygen stoichiometry of 0.2 per formula unit. Anneal sequences which hold the sample at high temperature (450 °C) for extended periods of time show a saturation of oxygen intake for the sample, at least using this oxygenation technique.

After the oxygen annealing sequence is complete, magnetization versus temperature was again measured on these samples. As seen in Fig. 2, the superconducting onset is raised by ≈ 2 K and the transition sharpens ($\Delta T_c = 8$ K). The width of the superconducting transition was originally believed to be an indication of variations in the potassium stoichiometry of the sample. However, the phase diagram of this material does not suggest any changes in the potassium doping on the bari-
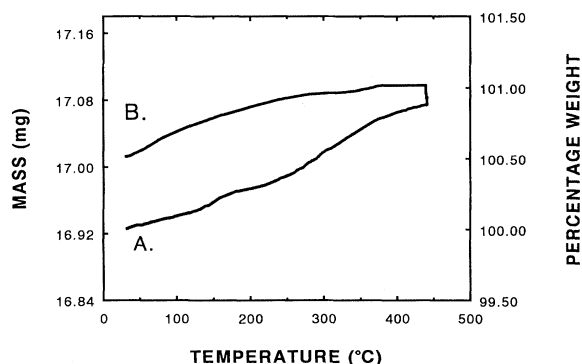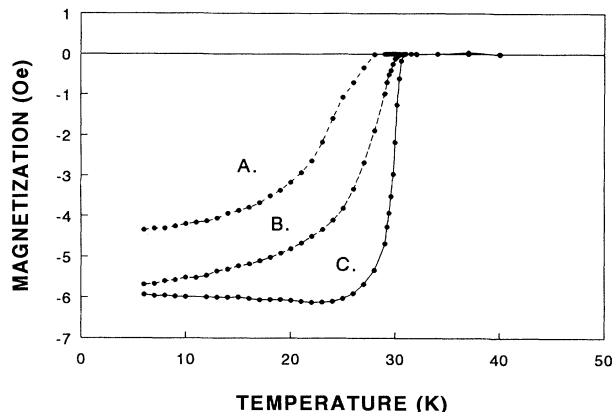

FIG. 2. Magnetization versus temperature data for the (A) as-grown and (B) postannealed samples. The applied field in both cases was 5 Oe. The critical temperature was raised by 1.8 K, and the transition was visibly sharpened going from state (A) to state (B). (C) For comparison, a postannealed single crystal from the same electrochemical growth is shown.

um sublattice at the low temperatures of this oxygen anneal.[2] Our results indicate that oxygen stoichiometry also has an important effect on the transition width. Samples which were quenched from the highest anneal temperature to room temperature and immediately measured show a maximum $T_c = 30.8$ K and the sharpest transition yet observed in this material ($\Delta T_c \leq 2$ K).

In order to examine the defect structure of BKBO more exactly, we have measured the positron-annihilation rates in the electrodeposited material. After initial characterization the crystallites were mounted on either side of a sealed positron source consisting of 20 μCi of ^{22}Na. The positron lifetimes were measured in a BaF_2 fast-fast coincidence spectrometer, with a resolution of 260 ps from a ^{60}Co calibration. The discriminator windows used to determine the resolution were identical to those used in the experiment. The sample was placed in a closed-cycle liquid-He refrigerator, and data were obtained at temperatures ranging from 15 to 300 K. These data were gathered for 10^6 counts (≈ 4 h) and were measured in random order to avoid any effects due to sample degradation. The best fit to the coincidence data was obtained using a single-lifetime model. Attempts to resolve two or more separate lifetimes were unsuccessful, suggesting that the positrons may not be strongly localized at defects in the sample.

The positron lifetime in a material depends on the overlap of the electron- and positron-charge densities.[10,11] Shorter positron lifetimes are associated with regions of higher electron-charge density. For defect-free material, the measured lifetime is almost temperature independent, with only negligible thermal-expansion effects. When defects are introduced, however, the positron can trap at the defect and the resulting change in charge-density overlap leads to a change in the positron lifetime. Since different defects result in different electron- and positron-charge densities, each will have its own characteristic lifetime. The probability of a positron annihilat-

FIG. 1. Thermogravimetric data for electrochemically deposited $Ba_{1-x}K_xBiO_{3-y}$. The sample gains 0.2 formula units of oxygen during the anneal sequence (30 cm^3/min flowing O_2). Positron-lifetime and magnetization versus temperature measurements have been performed (A) before and (B) after oxygenation. The postanneal lattice parameters do not change appreciably, and the postanneal mass is stable.

ing in a particular defect will depend on the defect concentration, the depth of the positron potential well at the defect, and the thermal energy of the positron. This can lead to a temperature-dependent competition between different types of defects. Positrons become localized in shallow defects at low temperatures and increasingly favor deeper traps at high temperatures where the thermal energy is comparable to the depth of the shallow trap.

Theoretical calculations of positron lifetimes have been performed using a first-principles approach based on self-consistent electronic structure calculations using the linear muffin-tin orbital method. This method, which is fully described in Ref. 11, contains no adjustable parameters to describe the electron interaction and has been highly successful in calculations of positron lifetimes for elemental metals, monovacancies in metals, and metal vacancies in BKBO.[11,12] Calculated lifetimes were found to increase with increasing potassium concentration, and so calculations were performed for potassium concentrations ranging from 0% to 100% on the barium sublattice. This produced lifetime ranges of 168–193 ps for the bulk (defect-free) material and 205–215 ps for a bismuth vacancy. For vacancies on the Ba/K sublattice, the calculated lifetime of 248 ps was essentially independent of potassium concentration. For $x \approx 0.4$ and full oxygenation, theory predicts a bulk lifetime of 186 ps. A negligible change of 1 ps is expected for thermal lattice expansion between 10 and 300 K.

Calculations indicate that the metal-atom vacancies provide deep potential wells that strongly localize the positron at the defect. In contrast, oxygen vacancies have almost no effect on the positron wave function, primarily because the electrostatic potential of the crystal lattice favors negative charge at an oxygen-vacancy site. The defect potential is not strong enough to trap the positron, and its charge distribution on the atoms in the unit cell is essentially the same as in the defect-free case. The lifetime can be significantly changed, however, since the electron-charge density at an oxygen vacancy is much lower than that on a filled oxygen site. The annihilation rate is therefore reduced, and the lifetime increases when compared with the defect-free case. This represents a previously unidentified effect where a vacancy-induced lifetime change is due to the reduction in the electron-charge density at the vacancy, not by a change in the positron-charge density caused by defect trapping. The calculated lifetimes for oxygen vacancies range from 168 ps for 0% potassium and a vanishingly small oxygen vacancy concentration (i.e., $BaBiO_3$) to 218 ps for 100% potassium and a substantial number of oxygen vacancies (i.e., $KBiO_2$).

Since the oxygen vacancies change the lifetime without significantly altering the positron-charge distribution, the lifetime can be used as a measure of the number of oxygen vacancies in the sample. The lifetime will vary continuously with changing oxygen-vacancy concentrations, approaching the bulk lifetime values in the limit of vanishing oxygen-vacancy concentration. This behavior contrasts with the lifetime variation associated with positron-trapping defects where the defect lifetime is rela-

tively insensitive to the defect concentration, but the amplitude of its contribution to the total annihilation rate may get smaller as the defect concentration is reduced.

The positron-lifetime values for the pre- and postannealed samples, displayed in Fig. 3, are significantly longer than those expected for defect-free BKBO. However, there is no signature of the metal-atom defects previously observed in the polycrystalline data: The magnitude of the measured single-crystal lifetime is much lower than the lifetime for Ba/K monovacancies, and the temperature independence of our measurements indicates no competition for positron annihilation between different sites in the electrodeposited samples. The close agreement between theoretical calculations for oxygen-vacancy structures and our experimental results leads us to conclude that oxygen defects are responsible for the difference between the predicted defect-free lifetime and that measured experimentally. Calculations predict specific lifetime values for substoichiometric oxygen levels, values which are independent of small changes ($\Delta x \approx 0.05$) in potassium concentration. For oxygen levels between 2 and 3 per formula unit in $Ba_{1-x}K_xBiO_{3-y}$ and $x \approx 0.4$, the theory predicts lifetimes between 178 and 208 ps. Our lowest measured lifetime (202 ps) suggests an oxygen value of $y = 0.8$ for the postannealed sample. The calculated drop in lifetimes associated with the oxygen-mass gain in our samples (0.2 oxygen per formula unit) is 6 ps. Experimentally, we see a 4–5 ps drop after annealing, in excellent agreement with theory. This agreement strongly suggests that the added oxygen fills in oxygen vacancies rather than entering interstitially. It is possible that the observed lifetime shift is associated with an unresolved lifetime component due to positron trapping at defects in the system, but this seems unlikely in view of the temperature independence of the measured lifetime
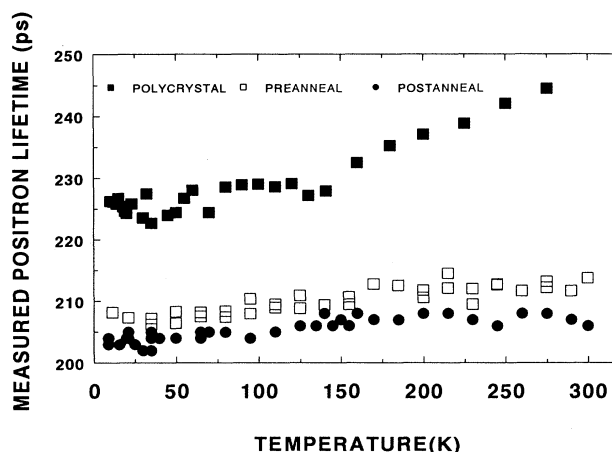

FIG. 3. Positron-lifetime data for the preannealed (open square, ≈ 210 ps) and postannealed (solid circle, ≈ 204 ps) samples. The difference in lifetimes due to oxygenation corresponds well to the change predicted by theory for a $y = 0.2$ oxygen gain. Also included for comparison are data on polycrystalline material (solid square, ≈ 240 ps), indicating a large metal-atom defect signature not seen in single-crystal BKBO.

spectra.

Neutron-powder-diffraction studies on polycrystalline samples of BKBO have observed no oxygen deficiency in postannealed samples.[13] Results have shown that at crucial stages of the synthesis procedure, however, oxygen defects must be introduced in order to achieve the desired potassium substitution in the $BaBiO_3$ lattice. In the electrodeposited material, the potassium/barium stoichiometry is established during growth and lacks a significant defect structure. However, the oxygen vacancies are still substoichiometric after growth, which can strongly influence the superconducting properties. We conclude that any detailed investigations of the electronic properties of single-crystal BKBO should address the question of oxygen stoichiometry.

The disproportionation of charge on the bismuth sublattice is intrinsically tied to oxygen stoichiometry, and numerous oxygen vacancies will undoubtedly affect the strength of the electron-phonon coupling. This electron-phonon coupling can lead to a competition between superconductivity and the formation of a charge-density wave. The existence of charge-density waves (CDW's) has been established in the parent compound $BaBiO_3$,[14] but is still in question in the semiconducting phases of BKBO.[15,16] Regardless of the specific type of electronic transition that occurs, the oxygen-defect stoichiometry is crucial in determining the exact nature of the ordering. The manner by which these oxygen defects are filled may also be crucial in understanding the specifics of the structural phase transition and the competition between CDW's and superconductivity in BKBO.

We have demonstrated that the superconducting properties of single-crystal $Ba_{1-x}K_xBiO_{3-y}$ are extremely sensitive to oxygen stoichiometry. Furthermore, we have shown that the measured positron-annihilation rates are determined by the oxygen-vacancy concentration. We find no lifetime signature characteristic of metal-atom vacancies, in sharp contrast to polycrystalline material. An oxygen-anneal sequence performed on these samples lowers the lifetime rate by filling oxygen defects. This vacancy filling dramatically impacts the superconducting properties of the system by sharpening the transition and raising T_c. Further studies which relate the sensitivity of specific electronic properties to oxygen-defect stoichiometry are being initiated.

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