substitution of Cd^{2+} for $Cu^{2+/3+}$ in $YBa_2Cu_3O_{7-\delta}$. They reported that while no chemical substitution was found above 2%, the T_c of their product was minimally affected by increasing Cd^{2+} content. This effect was probably due to the presence of undoped $YBa_2Cu_3O_{7-\delta}$ in the multiphase sample. They did claim a homogeneous compound for up to 2% substitution, reporting that the lattice parameter decreased with Cd^{2+} concentration. This claim is contradicted by the fact that Cd^{2+} is larger than both Cu^{2+} and Cu^{3+}.

Overall, CdO is relatively inert toward the $YBa_2Cu_3O_{7-\delta}$ system, since it can react only when batched as a stoichiometric replacement for Y_2O_3. Otherwise, CdO remains an inert second phase. This reinforces earlier work of Sherwood et al.,[6] who determined that Cd and CdO, when sintered together with stoichiometric $YBa_2Cu_3O_{7-\delta}$, remain as separate phases.

In the case of $Bi_2Sr_2Ca_{1-x}Cd_xCu_2O_{8+\delta}$, CdO doping failed to form a superconducting compound. Where CaO and CdO were both present, $CaCdO_2$ was made. This was also observed by Yoshimura et al.,[7] who tried unsuccessfully to make $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_y$ films. This indicates that preferential formation of $CaCdO_2$ prevents the synthesis of a cadmium partially substituted $Bi_2Sr_2CaCu_2O_{8+\delta}$. Without CaO, the CdO remains unreacted, giving a multiphase product. Ac magnetic susceptibility measurements show T_c = 80 K for the undoped sample and no $T_c > 10$ K for all the CdO-doped samples. This also agrees with results of Niwa et al.[8] These workers tried substituting several different cations into the Ca^{2+} site, with Cd^{2+} among those attempted. They also found that CdO remains unreacted when heated with Bi_2O_3, SrO, and CuO. These results contradict and explain reports by Konstantinov and Karbanov[9] of a cadmium-substituted bismuth-based superconductor. Although they claimed that cadmium is part of their superconducting phase, they admit that their samples were multiphase. A significant set of "unidentified" peaks in their XRD spectra correspond to CdO or $CaCdO_2$, again matching our results and those of other groups. This mistake illustrates that care must be used when interpreting XRD spectra and that the difference between "nominal composition" and "compound stoichiometry" is extremely important.

Conclusion

Except where CaO is also present, CdO remains chemically inert relative to several binary systems and the $Bi_2Sr_2CaCu_2O_{8+\delta}$ system. CaO and CdO easily react at temperatures above 800 °C to form a bright yellow cubic oxide, $CaCdO_2$. Cd^{2+} can be stoichiometrically substituted for Y^{3+} in $YBa_2Cu_3O_{7-\delta}$ to form $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$, where $x \leq 0.3$. This solubility limit is much less than that given in earlier reports.[2,3] Also, this aliovalent substitution is accompanied by additional oxygen vacancies, maintaining overall charge balance. This further reinforces the importance of oxygen nonstoichiometry in this chemical system. Otherwise, the nonreactivity of CdO with *stoichiometric* $YBa_2Cu_3O_{7-\delta}$ could be useful for applications requiring insulating layers between superconducting thin films.

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Registry No. CdO, 1306-19-0; Cd, 7440-43-9; $CaCdO_2$, 133494-86-7; $Y_{0.9}Cd_{0.1}Ba_2Cu_3O_7$, 126853-76-7; $Y_{0.7}Cd_{0.3}Ba_2Cu_3O_7$, 126853-75-6; $Y_{0.5}Cd_{0.5}Ba_2Cu_3O_7$, 126854-04-4.

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Superconductivity at 32 K in Electrocrystallized Ba-K-Bi-O

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A technique for the low-temperature, isothermal, isopotential electrochemical deposition of superconducting, highly crystalline materials in the Ba-K-Bi-O system has been developed. The current state of the art for this method of producing large (5-mm diameter), well-faceted crystals in this system is presented. The materials produced have been chemically and physically characterized by using SEM, EDX, PXRD, and magnetic methods.

Introduction

The bismuth-based system of oxide superconductors (Ba-M-Bi-O),[1,2] given sufficient development, may give rise to the long sought after room-temperature superconductor. This conclusion is supported from two quite different approaches. First, the electron-phonon interaction is so strong in $BaBiO_3$ that the frozen phonon mode or commensurate charge density wave is stable to 800 K[3]. The T_c of a system or material may be considered to have as its upper limit the temperature of this phase transition.

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A second approach,[4] which is less qualitative, utilizes the relationship between average electronegativity and T_c and predicts that the T_c of the hypothetical (at this time) compound $Ba_{1.6}Rb_{0.4}BiO_4$ of this system should approach 276 K. Few other systems currently display the high probability of future rises in T_c that this system displays.

It is important to recognize that the Ba–K–Bi–O system displays several modes of instability. At high temperatures, the potassium oxide component is volatile under standard oxide ceramic synthesis conditions.[5] At intermediate temperatures, the potassium becomes insoluble in the perovskite phase,[6] and even at lower temperatures, the oxygen content becomes unstable.[7] An early study of the parent compound $BaBiO_3$ indicated that bismuth can partially occupy the barium site.[8,9] More recent studies have also shown that barium can apparently substitute for a large percentage of the bismuth.[10]

It is interesting to note that years ago, Matthias predicted that high-T_c materials should be intrinsically unstable, and he suggested that one should look for materials that could not be synthesized or that had to be tricked (i.e., are metastable) into existence.[11] The best-known high-T_c superconductor, $YBa_2Cu_3O_7$, appears to provide an excellent example of the wisdom of this approach. The oxygen stoichiometry of this copper-based material is thermally unstable, reflecting the lack of normal filling in the valence band or its occupation by holes. Fortunately, a structurally "identical" material ($YBa_2Cu_3O_{6.5}$) is thermally stable, and this material is readily converted into fully oxidized $YBa_2Cu_3O_7$ via oxidation at reduced temperatures. It is possible that all high-T_c systems will not be as amenable to high-temperature crystal growth and that low-temperature approaches to crystallization of materials must be developed. The utilization of low-temperature synthetic techniques allows for the exploration of new regions of the phase diagram of chemical systems and allows the discovery of materials not accessible via high-temperature techniques due to the presence of large activation energies intrinsic to massively reconstructive phase transformations.

The molten salt electrocrystallization method has a number of potential advantages to offer in the synthesis of novel conducting materials. It would appear to be particularly well suited to the Ba–K–Bi–O system.[12] Conducting phases are preferentially synthesized in electrocrystallization because electrochemical potential losses (*iR* drop) are minimal in such phases. Growth of nonconductors is self-limited by a process commonly referred to as electrode passivation. There is nearly instantaneous nucleation of the desired phase under proper conditions. Because nucleation and growth occur only on the selected electrode area, there are only a limited number of nucleation sites, leading to a reduced number of nucleated crystals, in comparison to many crystallization techniques. The relative supersaturation can be set electronically (potentiastatically), and the reaction can be stopped or quenched quickly. All of the crystalline product can be readily and quickly extracted from the growth solution.

The anodic electrocrystallization technique is exceptionally well suited for the preparation of large single crystals in the Ba–K–Bi–O system for at least two reasons. First, a successful flux or solution-based growth technique requires significant solubility of the reagents to enable diffusion to provide significant mass transport. The product phases $(Ba_{1-x}K_xBiO_3)$(BKBO) are not very soluble in KOH and therefore would cause recrystallization of BKBO to be a slow crystal growth process in this system. However, $Ba(OH)_2$ and Bi_2O_3 are relatively soluble in KOH. The electrochemical oxidation of Bi from an average formal +3 to a >+4 oxidation state yields an insoluble product that grows on the substrate. The large change in solubility accompanying the rather large change in average formal Bi oxidation state may readily be understood in terms of the associated change in Madelung energy. The second most important feature impacting crystal growth in this system is the intrinsic necessity of oxygen or oxidizing agent transport to the growing crystal/solution interface. Such oxidative power is readily delivered electrically, but chemical oxidation requires diffusion of oxygen across the ambient gas/condensed phase interface. This latter process results, in our experience, in the formation of a solid polycrystalline surface barrier film of the oxidized product phase, which impedes further oxygen transport. In the electrochemical system, oxidative power is delivered only to the desired crystal/solution interface.

A fast, isopotential method operative at temperatures below the oxidative instability temperature could afford the best route to preparation of the large, homogeneous, single-crystalline samples required for a satisfactory experimental and theoretical investigation of this anomalous,[13] high-T_c system. Experiments leading to the preparation and characterization of nearly optimum materials are described here.

Experimental Section

Preparation. Deposition experiments have been performed at a variety of temperatures, including the range from 150 to 350 °C. Low-temperature electrodeposition experiments, are performed in readily obtainable Teflon (TFE, tetrafluoroethylene) crucibles (Cole-Parmer). Teflon is the only container material we have identified that does not contaminate the melt with long-term contact. Potentiostatic deposition is performed utilizing a three-electrode, one-compartment-cell geometry. A high-current synthetic potentiostat (Bioanalytical Systems, SP-2) system was employed for these studies. The working electrode (positive, or biased anodically) can be platinum, gold, or silver. Other metals have not been evaluated. The deposited film protects this electrode from anodic dissolution. A 1-mm diameter silver wire electrode (Aesar, 99.9%) is most commonly used. The counter electrode (negative or biased cathodically) used is a 1-mm-diameter platinum wire (Aesar, 99.99%), which is rapidly coated with a thick polycrystalline layer of bismuth metal during use. The reference electrode, which is placed in close proximity to the working electrode, appears to be relatively stable and is particularly appropriate to this system, consists of a polycrystalline bismuth metal (Johnson, Matthey, 99.5%) rod, cast to a diameter of 1 mm. The reference electrode's potential is related to the pO_2, pH_2O, and to the bismuth salt concentration in the solution. This electrode system does not introduce impurities detectable by EDX (energy-dispersive X-ray analysis) into the product phase. The temperature of the cell, its envelope, and a high heat capacity metal thermal ballast cup holding the assembly is controlled by using a temperature controller (Omega) to drive a hotplate. In

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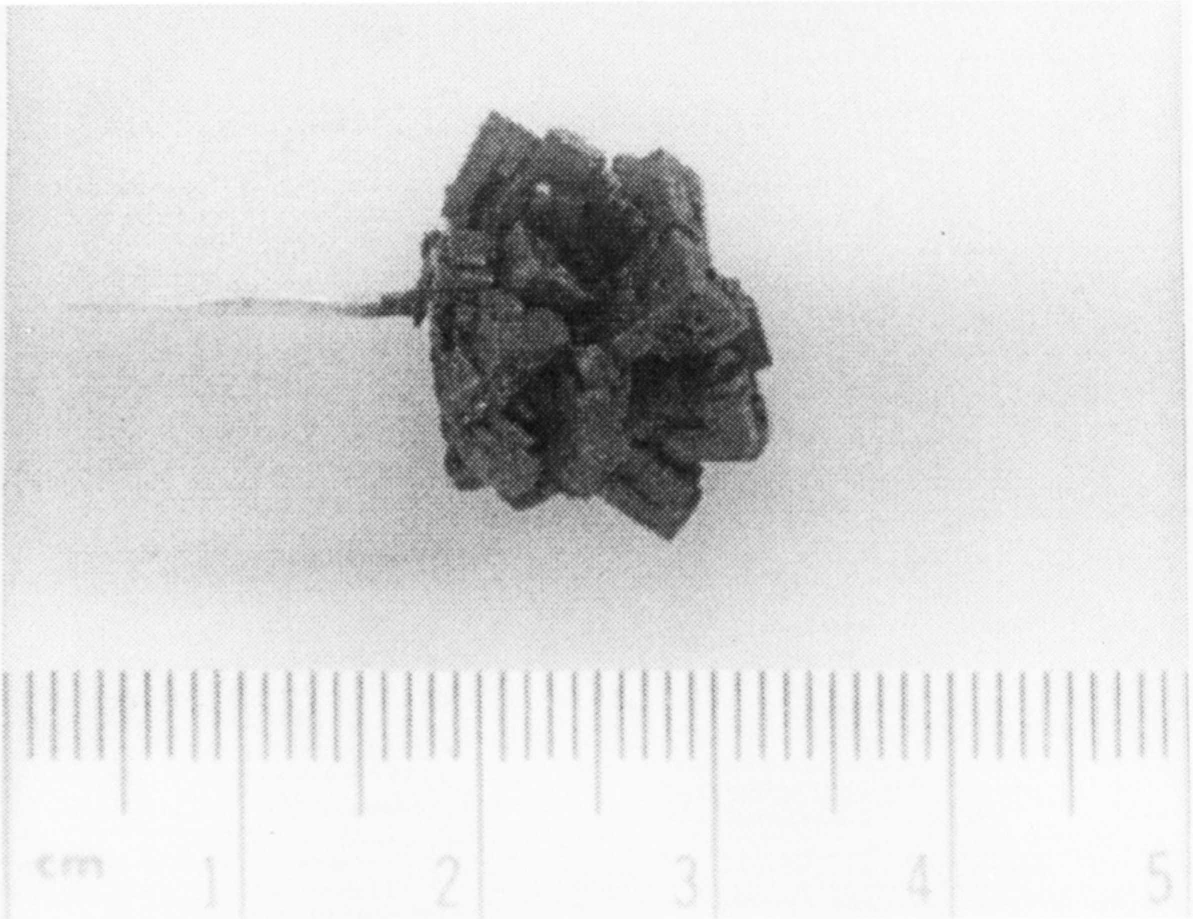

Figure 1. Photograph of BKBO crystal cluster grown on Ag electrode for 66 h at 260 °C (potential = 0.7 V).

an average deposition, 20 g of KOH (Baker, Reagent) is placed in a 15-cm^3 crucible and melted at the reduced melting point of 180 °C. The lowered melting point is presumed to result from the known high water content of commercial KOH.[14] After an operating temperature is achieved, the other components of the melt (typically 1.60 g of Ba(OH$_2$·8H$_2$O (Aldrich, 98%) and 2.37 g of Bi_2O_3 (Aesar, 99%)) are added with stirring to aid dissolution. A quiescent solution is maintained during deposition in order to avoid incorporation of particles from this saturated solution into the growing deposit. Maintenance of an inert atmosphere is necessary in order to avoid "spontaneous" or air oxidation of this chemical system. This "spontaneous" oxidation can be quite rapid at elevated temperatures. A quartz cell holder contains the cell, supports the electrodes, and allows maintenance of a water vapor saturated nitrogen cover gas flow (ca. 3 cm^3/min) over the cell. The constant pH_2O may influence the long-term stability of the reference electrode potential.

Upon sedimentation of excess, undissolved Bi_2O_3, electrolysis of the crystal-clear solution is begun at an applied potential typically between 0.6 and 0.9V vs the Bi reference electrode. Deposition begins immediately and is terminated by withdrawing the crystal laden electrode from the melt after any desired period of time. The useable time is limited by the depletion of Bi from the solution through deposition of Bi metal (cathodic) and Bi oxides (anodic), to periods on the order of 48 h for the system described above. Scaleup of the apparatus is readily accomplished. Samples are air cooled, rinsed, ultrasonically cleaned in distilled water, and then allowed to air dry. Some compositions, most notably the highest T_c materials, have been observed to change color rapidly when in contact with the atmosphere. Other samples appear quite stable.

Characterization. Visual examinations of the samples were made using an inverted optical metallographic microscope (Leco/aus JENA).

Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analyses were performed using a Phillips Model 505 SEM equipped with a Tracor Northern 5500 data acquisition system and semiquantitative analysis software. Multiple sites were probed with 25-kV excitation by using a 100-nm spot size. Data were collected over the range 0–25 kV. The M line of Ba, the K line of K, and the L line of Ba were fit to yield atomic percentages of these elements.

X-ray diffraction patterns were acquired by using a Scintag XDS 2000 θ/θ X-ray powder diffraction system. Data were taken for 2θ values in the range 15–60° and analyzed on the system's Microvax.

Magnetization studies were performed using a Model MPMS2 SQUID magnetometer (Quantum Design, Inc.). The sample was cooled in zero field to 5 K and then a 5-Oe field was applied. The magnetization was measured as a function of temperature to 35 K to obtain the diamagnetic shielding curve. The sample was then cooled in the applied 5-Oe field to 5 K and remeasured to 35 K to obtain the Meissner curve. The trapping curve was obtained by cooling the sample to 5 K in a 5-Oe applied magnetic field and then setting the field to zero and measuring the magnetization as a function of temperature to 35 K.

Results and Discussion

A representative cluster of crystals is shown in Figure 1. Crystals with [100] facets greater than 0.5 cm in length are present.

Optical Microscopy. Materials prepared with deposition times of 6 h have been observed to grow as dendrites along [111]. At lower growth temperatures the nuclei and earliest grown crystals are metallic bronze in color. The later grown crystals are bright blue in reflection. It could be expected that these colors reflect the electronic properties of the material, which are governed by their K content. Materials grown at higher temperatures appear to be more homogeneous, perhaps due to the lower vis-

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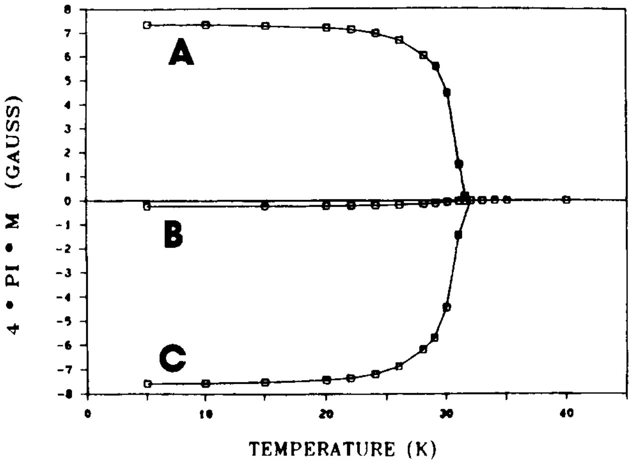

Figure 2. Magnetization plot for a BKBO crystal (A) trapping, (B) field cooled, and (C) zero field cooled.

cosity and thus better mass transport of the flux system.

SEM/EDX. EDX analysis shows that the bronze colored, early crystallized material grown at low temperatures displays a composition roughly corresponding to $Ba_{0.8}K_{0.2}BiO_3$. The later material, which composes the bulk of the material displays the approximate stoichiometry $Ba_{0.6}K_{0.4}BiO_3$, the well-known superconducting composition. Mapping of the composition along the growth direction has been performed. As anticipated, there is a K concentration gradient along this line. Although it may be an artifact of the crystal growth process, the gradient appears to be discontinuous.

X-ray Diffraction. Analysis of the X-ray diffraction pattern for the low-temperature-grown material indicates significant broadening of the peaks, which are readily indexed as cubic. The pattern is not readily refined and indicates some spread in lattice constants, consistent with the EDX and optical observations. Material grown at higher temperatures gives much sharper diffraction peaks. The intensities are not well fit by using Rietveld methods; however, there may be significant texture, which was not refined in our experiments. The lattice parameter for the highest T_c material refines to be 4.2913 Å. This lattice parameter translates to the formulation $Ba_{0.636}K_{0.364}BiO_3$.[15] This composition is quite near that predicted for the metal/insulator phase boundary at 0 K, which is also where the highest T_c should occur.[15]

Magnetic Measurements. Ac Squid measurements indicate that the product prepared at lower temperatures is superconducting and has a low T_c (~20 K onset) and broad (~8 K) superconducting transition. These findings support the conclusions that this crystalline product is inhomogeneous and very likely is strained by the gradient in lattice parameter produced by the gradient in K content. In contrast, the material shown in Figure 1 displays an unusually high T_c. The magnetic transition, displayed in Figure 2, is sharp (2 K width), and the onset (ca 31.8 K) is far above transition temperatures usually reported for powders of this material.

The quite high T_c onset observed for this material was unexpected but may not be difficult to explain. The use of a low-temperature synthetic procedure can allow one to avoid the instabilities detailed earlier. Compositional instabilities related to the metal/insulator phase boundary are not expected to be relevant for the stoichiometries produced, at the synthesis temperature. The use of this alternative preparation technique leads to the production of material with a T_c approximately 10% higher than normally observed for ceramically prepared powders. It must be noted, however, that powders are not usually synthesized with targeted compositions of $X = 0.3643$.

There are two reports of the low temperature preparation of BKBO in which the fine-grain polycrystalline material produced display unusually high T_c of 32[16] and 34 K.[17] These results would appear to indicate that there is an essential difference between the ceramic and low-temperature chemical approaches to production of this material and illustrates the importance of further research in low-temperature synthetic techniques.

The electrodeposition reaction can be viewed as a Bismuth oxide polymerization process resulting in a 3-D polymer stuffed with K and Ba cations. That is, a polymer cross-linked in two dimensions perpendicular to the growth direction is formed and incorporates ions from the melt as growth progresses. The reason for utilizing potentiostatic control of the electrode process was to maintain a constant rate of polymerization and therefore to maintain a steady-state doping rate. This is only possible if the solution composition remains constant, a situation best approximated by use of large solution volumes. Relatively long deposition times necessarily lead to compositional variation in the product in closed systems. Solution or local depletion of Ba content drives the dopant profile to higher K contents with increasing time. The use of higher temperatures leads to higher deposition currents, due to faster mass transport rates. Higher temperatures also lead to crystals with a more cubic morphology, presumably due to higher surface ionic mobilities.

Annealing does not appear practical in view of the thermal sensitivity ofthese materials. Annealing at 400 °C in air (1 h) has not been found to improve the less than ideal materials or to have detrimental effects on the high-T_c crystals. This indicates that the oxygen content of these materials is relatively stable.

Large regions (3-mm diameter) of the larger crystals do appear to be homogeneous via EDX analysis, and small single crystals grown quite quickly may be quite homogeneous. Therefore this method, with little further development, can deliver extraordinarily large, high-quality, high-T_c crystals. These crystals may be of great value for (1) optical studies, which are highly surface sensitive, (2) temperature-dependent X-ray structural studies, which require reasonably small samples, (3) magnetization and flux pinning studies, (4) heat capacity studies, (5) tunneling studies. Some of these studies are now underway.

From limited preliminary work, it appears that this deposition process is also directly applicable to the Ba–Rb–Bi–O and Ba–K–Rb–Bi–O systems.

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Registry No. Ba–K–Bi–O, 118145-70-3.

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