accord with the results of our experimental design.

In conclusion examination of the titanium/polyester interfacial region with Auger electron spectroscopy revealed that a titanium oxide existed between the sputtered titanium metal and polyester film. TiO_x formation most likely resulted from the interaction of the sputtered atoms with film off-gassing products such as water and oxygen. Further analysis by XPS indicated that a titanium carbide like moiety resides at the interface. However, it was not determined whether this species existed as discrete units or was acting to covalently couple the titanium to the polyester substrate. Titanium-polyester oxygen interaction was also suggested by an increase in the fwhm of the Ti_{2p} photopeak following plasma treatment and metallization, which may result in alkoxide or carboxylate linkages. Therefore, a chemical bond and not a mechanical effect must be responsible for the observed increase in adhesion relative to nontreated metallized poly(ethylene terephthalate) films.

Registry No. PET, 25038-59-9; Ti, 7440-32-6; Ar, 7440-37-1; N_2O, 10024-97-2.

Cadmium Substitution in $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$

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The chemical interactions of CdO with $YBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2CaCu_2O_{8+\delta}$, and related oxides are examined. Mixtures of CdO with other oxides (Y-Ba-Cu-O, BaO_2, CuO, Y_2O_3, Bi-Sr-Ca-Cu-O, CeO_2, and CaO) were heated to 800-900 °C under N_2, O_2, air, and 1.5 GPa quasi-hydrostatic pressure. The reacted samples were characterized by powder X-ray diffractometry, thermogravimetric analysis, and dc resistivity and ac magnetic susceptibility measurements. CdO was found to be chemically inert under most of these conditions. When CaO is present, the cubic $CaCdO_2$ is formed. Cadmium(II) can be partially substituted for yttrium(III) (up to 30 mol %) in $YBa_2Cu_3O_{7-\delta}$ without detriment to superconducting properties. Although Cd^{2+} is aliovalent to Y^{3+}, charge compensation is achieved by the formation of additional oxygen vacancies, as evidenced by TGA measurements. This oxygen vacancy formation occurs rather than the expected change in hole concentration in the CuO chains and planes. Also, investigations of CdO substitution by other groups are reviewed.

Introduction

Cadmium(II) is a good candidate for inclusion in the superconducting ceramic compounds for several reasons. It is divalent, has an ionic radius[1] (1.09 Å) similar to those of Ca^{2+} (1.14 Å), Cu^{2+} (0.87 Å), and Y^{3+} (1.04 Å) and lies in the periodic table on a diagonal between copper and thallium. The presence of a filled 4d subshell in cadmium provokes comparison of cadmium compounds with analogous compounds formed by alkaline-earth metals. We have performed a broad search for cadmium-containing compounds related to the familiar high-temperature superconductors. In addition to reactions in air, nitrogen, and oxygen, some samples were heated under high pressure. Since cadmium ions are smaller than barium ions, reaction under high pressure might facilitate the substitution of cadmium for barium. To give a more complete description of the chemistry within these systems, we also summarize for the first time the results of several studies of cadmium substitution.

Experimental Section

Table I. Batches, Processing Conditions, and Results for Cadmium Substitution Experiments[a]

batch	proc conds	products	T_c, K
CdO + BaO_2	air, hi-p, N_2	CdO, BaO_2 (BaO in N_2)	
CdO + CaO	air, hi-p	$CaCdO_2$	
CdO + CuO	air, hi-p	CdO, CuO	
CdO + CeO_2	air, hi-p, N_2	CdO, CeO_2	
2CdO + Y_2O_3	air, hi-p, N_2	CdO, Y_2O_3	
$YBa_2Cu_3O_{7-\delta}$	air, O_2, hi-p	$YBa_2Cu_3O_{7-\delta}$, $BaCuO_2$	92
$Y_{0.9}Cd_{0.1}Ba_2Cu_3O_{7-\delta}$	O_2	$Y_{0.9}Cd_{0.1}Ba_2Cu_3O_{7-\delta}$, $BaCuO_2$	92
$Y_{0.7}Cd_{0.3}Ba_2Cu_3O_{7-\delta}$	O_2	$Y_{\sim 0.8}Cd_{\sim 0.2}Ba_2Cu_3O_{7-\delta}$, $BaCuO_2$, CdO	92
$Y_{0.5}Cd_{0.5}Ba_2Cu_3O_{7-\delta}$	O_2	$Y_{\sim 0.7}Cd_{\sim 0.3}Ba_2Cu_3O_{7-\delta}$, $BaCuO_2$, CdO	90
$YBa_{2-y}Cd_yCu_3O_{7-\delta}$	air, hi-p	$Y_2Cu_2O_5$, CuO, CdO for all y; + $BaCuO_2$, Y_2BaCuO_5 for $y < 2.0$	
$Bi_2Sr_2CaCu_2O_{8+\delta}$	air	$Bi_2Sr_2CaCu_2O_{8+\delta}$, minor phases	80
$Bi_2Sr_2Ca_{0.5}Cd_{0.5}Cu_2O_{8+\delta}$	air	$CaCdO_2$, $Bi_2Sr_2CuO_6$, CaO, CuO, CdO, Bi_2O_3	
$Bi_2Sr_2CdCu_2O_{8+\delta}$	air	$Bi_2Sr_2CuO_6$, CdO, CuO, Bi_2O_3, SrO	

[a] The reaction conditions were: "air" = 850 °C, air, 8 h; "hi-p" = 850 °C, 1.4 GPa, 2.5 h; "N_2" = 900 °C, flowing N_2, 8 h; "O_2" = 900 °C, air, 24 h followed by 500 °C, O_2, 12 h. Products listed are those identified by X-ray diffraction. T_c values are onset temperatures for resistive transitions. Several batches in the $Bi_2Sr_2Ca_{1-z}Cd_zCu_2O_{8+\delta}$ system were made, with slightly different starting compositions but similar results.

CdO powder was ground by mortar and pestle in equimolar ratios with CuO, Y_2O_3, CaO, CeO_2, and BaO_2. Stoichiometric amounts of CdO and other oxides were ground to form mixtures with the following nominal compositions: $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$, where x = 0.1, 0.3, 0.5; $YBa_{2-y}Cd_yCu_3O_{7-\delta}$, where y = 0.5, 1.0, 1.5, 2.0; $Bi_2Sr_2Ca_{1-z}Cd_zCu_2O_{8+\delta}$, where z = 0.5, 1.0. For comparison, undoped $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$ were also prepared. The samples were heated in air, nitrogen, and oxygen and under ~1.5 GPa quasihydrostatic pressure to temperatures between 800 and 900 °C. The exact reaction conditions for each composition are given in Table I. For the samples reacted under high pressure, the following method was used: 2-3-g samples of these powders were packed into silver tubes 6 mm in diameter and ~30 mm

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[1] Ionic radii given are for 6-fold coordination, from: Shannon, R. D. *Acta Crystallogr.* **1976,** *A32,* 751.

0897-4756/91/2803-0428$02.50/0

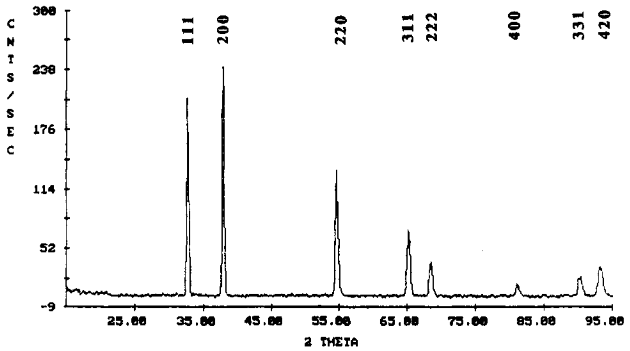

Figure 1. Powder X-ray diffraction pattern for $CaCdO_2$ prepared in air at 850 °C. The diffraction peaks are labeled with respect to Miller planes in the cubic lattice.

in length. These tubes were sealed shut at both ends by propane torch welding. Care was taken not to heat excessively the powders while welding, using a metal heat sink between the weld and the sample volume. Ten to fifteen silver capsules were contained within a machined pyrophyllite cylinder. This cylinder was wrapped in a graphite sleeve, which in turn was wrapped in more pyrophyllite. Pyrophyllite acts as a pressure-transmitting medium. The entire cylindrical sample assembly was pressed within a 75-mm die by a tool steel piston driven by a large hydraulic ram. Up to 10000 A of low-voltage alternating current was passed through the graphite sleeve, resistively heating the contents of the sample assembly. Heating was controlled by feedback from an in situ thermocouple connected to an Omega temperature controller. This controller was interfaced with the power supply via a silicon-controlled rectifier. The reacted powders were analyzed by powder X-ray diffractometry. All suspected superconducting materials were analyzed by ac magnetic susceptometry and dc resistivity measurements. The oxygen-deficient $YBa_2Cu_3O_{7-\delta}$-based samples were analyzed by TGA reduction in 5% H_2/Ar to determine oxygen contents.

Results and Discussion

The starting materials, reaction conditions, and XRD-identified reaction products are summarized in Table I. For all the binary systems examined, no reactions with cadmium oxide were observed except for the formation of $CaCdO_2$ from CaO + CdO. This bright yellow oxide has a cubic structure, and its powder XRD peaks are identified in Figure 1. It was formed under all the conditions where CaO and CdO were intimately mixed and heated.

In $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$, we were able to substitute Cd^{2+} for Y^{3+} to form a superconductor where $x < 0.5$. The X-ray diffraction patterns are shown in Figure 2. These samples are all multiphase, with $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$ being the prominent phase. Although CdO secondary phase peaks are present in all three XRD patterns, there are two reasons to conclude that at least some Cd^{2+} *is* substituting into the major phase lattice. First, all the major-phase reflection angles change with increasing Cd^{2+} content, indicating that the *a*, *b*, and *c* lattice parameters change (*a* and *c* increasing) with increasing Cd^{2+} substitution. Since Cd^{2+} is larger than Y^{3+}, this is what one would expect from Vegard's rule. Second, comparison of the CdO second-phase XRD peak areas from the reacted samples with those of analogous undoped $YBa_2Cu_3O_{7-\delta}$/CdO/$BaCuO_2$/CuO standard mixtures (see Figure 3) shows that the amount of CdO second-phase present in the reacted samples is not enough to account for what was initially included in the batch. The ac magnetic susceptibility and dc resistivity plots are given in Figures 4 and 5, respectively. Note that the increasing presence of secondary phases degrades the superconducting properties, generally lengthening the "tails" (decreasing T_c zero). All the cadmium-substituted samples show superconducting transi-

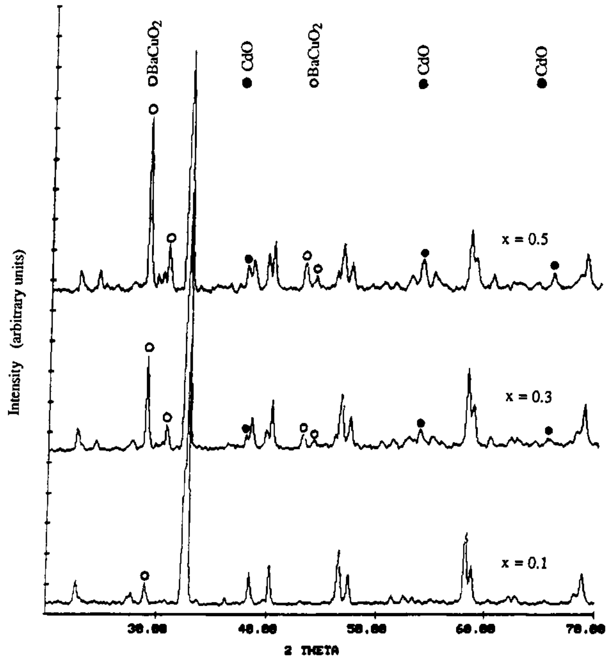

Figure 2. Powder X-ray diffraction patterns for $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$ samples prepared in oxygen. Secondary phase diffraction peaks are labeled by compound. All unlabeled peaks are from $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$; note the shift in reflection angles for these peaks as the cadmium content increases.

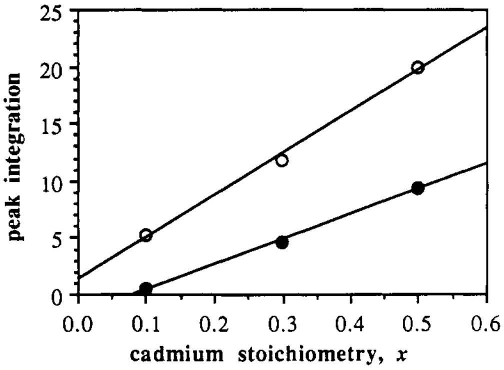

Figure 3. CdO second-phase XRD peak areas. These are the integrated peak areas for the CdO reflection at $2\theta = 55.3$. The closed circles are from the reacted samples described in Figure 2. The open circles are from measurements on stoichiometrically analogous mixtures of $YBa_2Cu_3O_{7-\delta}$, CuO, CdO, and $BaCuO_2$ prepared as XRD standards. One can obtain a crude estimate of the solubility limit by comparing the "leftovers" area for the $x = 0.5$ batch to the standard curve. Reading left and down, the unreacted portion accounts for ~20% Cd, leaving 30% in the superconducting lattice.

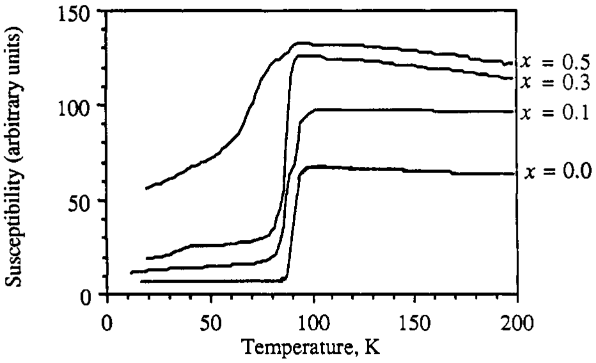

Figure 4. Ac magnetic susceptibility plots for $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$ samples prepared in oxygen. The broad tail for sample $x = 0.5$ results from significant secondary-phase concentration. The sharp onset for sample $x = 0.3$ results from minimized oxygen vacancies.

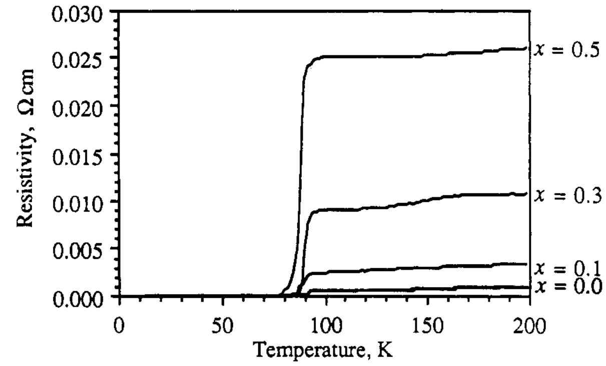

Figure 5. Dc resistivity plots for $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$ samples prepared in oxygen. The same features can be seen in these measurements as in Figure 4. The stepped topography of the normal-state portions of these curves is an artifact of our equipment.

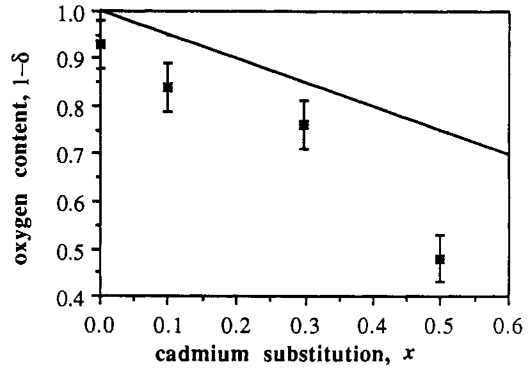

Figure 6. TGA measured oxygen contents in $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$ samples prepared in oxygen. The solid line is the calculated maximum oxygen content, assuming full Cd substitution and matching oxygen vacancies. As cadmium is substituted for yttrium, more oxygen vacancies are required for bulk charge neutrality. Note that the oxygen vacancies are most effectively minimized in samples $x = 0$ (undoped 123) and $x = 0.3$. These two samples also show the sharpest superconducting transition onsets.

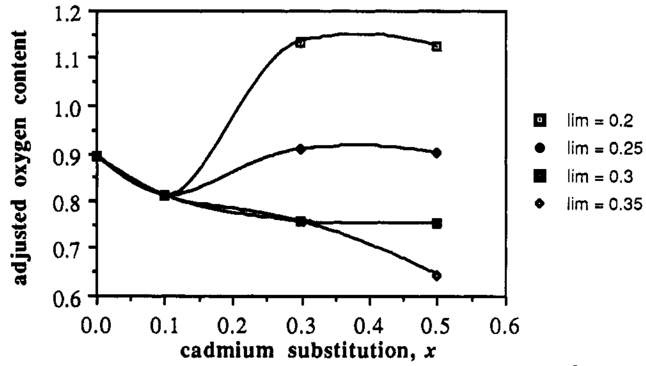

Figure 7. Solubility limit analysis of the TGA measured oxygen contents for $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$ samples prepared in oxygen. The $1-\delta$ values have been "prorated" to reflect dilution by secondary phases beyond different solubility limits. These adjusted oxygen contents correspond to the superconducting phase only. Since dilution effects are canceled, the adjusted oxygen content should become constant once the solubility limit is reached. Note that the curve given by assuming the solubility limit to be $x = 0.3$ gives this result.

tions. This agrees with the results of Chen and Chen,[2] who made $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$ by the same procedure. They claim single-phase substitution to $x = 0.6$, but their XRD patterns and our results indicate that there are still second phases present. In a later report, Chen et al.[3] give further details of the lattice effects for this compound. From the XRD data given in this report, combined with our results, it appears that there is no change in the major peaks beyond $x = 0.3$, only an increase in the secondary-phase peak areas. From this it can be deduced that there exists a substitutional limit of 30 mol % Cd^{2+} for Y^{3+}.

Also in this second report, they give an oversimplistic explanation for the 90 K T_c's, suggesting that the oxygen content remains constant, even though the local ionic charges at the Y^{3+} sites are being changed. This effect can be explained as follows: T_c is proportional to the hole concentration in the CuO_2 layer's Cu $d_{x^2-y^2}$ band, up to some maximum. For the sake of utility, one can consider T_c to be a function of the formal oxidation state of copper. For $YBa_2Cu_3O_{7-\delta}$, the maximum T_c is obtained when $\delta \approx 0$. This gives a formal oxidation state of 2.33 for copper. In the cadmium-doped system, the transition temperature is not changed significantly, so we can assume that the hole concentration is unchanged and the formal oxidation state of copper is still approximately 2.33. Since cadmium is partially substituted for yttrium and overall charge neutrality must be maintained, we can deduce that the oxygen content is lowered with increasing cadmium content. To test this hypothesis, the $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$ samples were reduced in a TGA by a mixture of 5% H_2, balance argon. The results of these measurements are illustrated in Figure 6. T_c onset is determined by the carrier concentration in the bulk phase, and comparison with the theoretical optima given in the graph explains the differences seen in this portion of the transition curves. Furthermore, the TGA data give clues to the substitutional limit. If one considers the superconducting phase in this mixture, the oxygen content should decrease with increasing Cd^{2+} substitution, up to the conjectured solubility limit. Beyond that point, additional CdO causes an increase in secondary-phase content in the mixture, effectively "diluting" the superconducting phase. This dilution effect also causes a decrease in the amount of oxygen measured by TGA, but the effect is more pronounced than that of substitutionally induced vacancies. One can assume different solubility limits and then prorate the oxygen measurements to reflect only the oxygen content in the superconducting phase. These calculations are illustrated in Figure 7. Thus, the TGA data not only are consistent with a decrease in the oxygen content with increasing Cd^{2+} substitution for Y^{3+} but also confirm that the solubility limit is approximately $x = 0.3$.

In $YBa_{2-y}Cd_yCu_3O_{7-\delta}$, we attempted to substitute Cd^{2+} into the Ba^{2+} site, because this would leave the local charge picture unchanged while altering the lattice dimensions. Since Cd^{2+} (1.09 Å) is much smaller than Ba^{2+} (1.49 Å), it was presumed that reaction under high pressure might encourage this substitution. No substitution was found, which agrees with the results of Iguchi et al.,[4] who tried sintering mixed oxides at 920 and 950 °C to form $YBa_{2-y}Cd_yCu_3O_{7-\delta}$. Their XRD patterns also indicate multiphase products containing CdO, $Y_2Cu_2O_5$, and $YBa_2Cu_3O_{7-\delta}$.

Since it is known that $Cu^{2+/3+}$ is vital to these superconductors, we did not try to substitute Cd^{2+} for $Cu^{2+/3+}$. In another paper, Remschnig et al.[5] discussed attempted

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(2) Chen, J. W.; Chen, C. F. *Solid State Commun.* **1989**, *69*, 1079.

(3) Chen, J. W.; Chen, C. F.; Chang, T. C.; Yao, Y. D. *Physica C* **1990**, *165*, 287.

(4) Iguchi, I.; Sugishita, A.; Yanagisawa, M.; Hosaka, S. *Physica C* **1988**, *153-155*, 892.

(5) Remschnig, K.; Rogl, P.; Eibler, R.; Hilscher, G.; Pillmayr, N.; Kirchmayr, H.; Bauer, E. *Physica C* **1988**, *153-155*, 906.

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 $Bi_2Sr_2Ca_{1-z}Cd_zCu_2O_{8+\delta}$, 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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