Synthesis of Twin-Free, Orthorhombic $EuBa_2Cu_3O_{7-\delta}$ Superconductors at 450 °C by Direct Precipitation from Molten NaOH and KOH

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Polycrystalline samples of the $RBa_2Cu_3O_{7-\delta}$ class of cuprate superconductors (R = Y and many of the rare-earth elements) are prepared typically by heating intimate mixtures of solid reactants (e.g., binary metal oxides). This method involves a two-step process whereby an anneal in oxygen at ~450 °C is required to transform the product obtained at ~900 °C from the oxygen-deficient, tetragonal form into the orthorhombic form that exhibits superconductivity. Here we report a new "low-temperature" synthetic route in which the orthorhombic form of $RBa_2Cu_3O_{7-\delta}$ for R = Nd, Sm, Eu, and Gd is obtained directly by precipitation from a molten NaOH and KOH solution. The characterization of the material containing Eu is reported below.

The essential difference between the synthetic route described here and all methods reported previously for the synthesis of the $RBa_2Cu_3O_{7-\delta}$ class of superconductors is that since the temperature is substantially lower, the superconducting, orthorhombic form is obtained directly. This is accomplished by dissolving the reactants in a wet eutectic mixture of NaOH and KOH and subsequently precipitating the product by removal of water rather than by mixing solid reactants and heating to cause diffusion; we have reported previously a synthesis method similar to the present one for the preparation of superconducting samples of $La_{2-x}M_xCuO_4$ (M = Na, K).[1] Among the advantages of a lower processing temperature for the $RBa_2Cu_3O_{7-\delta}$ class of superconductors is that the material is obtained below the orthorhombic-to-tetragonal phase transition; thereby, the *a*–*b* twinning and the cracking due to the large volume change associated with the solid-state phase transformation are avoided. The materials that precipitate from molten alkali metal hydroxides are relatively large, untwinned plates with rectangular faces; in contrast, samples prepared at elevated temperatures consist of smaller particles with square faces and contain *a*–*b* twin boundaries.

In a typical experiment, 0.050 g (0.63 mmol) of CuO, 0.037 g (0.11 mmol) of Eu_2O_3, 8.5 g of NaOH, and 11.5 g of KOH were placed in an open silver crucible (~20 mL). Barium was introduced in the form of $Ba(OH)_2{\cdot}8H_2O$, and the quantity added was varied from the stoichiometric amount of 0.033 g (0.42 mmol) up to 3.0 g.[2] The mixture was heated to 450 °C, and a clear blue solution formed. To remove water from the melt to induce precipitation, the temperature was held at 450 °C for times ranging from 6 h to 10 days under a constant air flow (rate = 120 cm^3/min); gradually, a dark precipitate formed. Finally, the mixture was cooled to room temperature over 4 h.

The product was isolated by removing the excess hydroxides with distilled water, and the resulting crystalline black powder was filtered and washed with methanol to enhance drying. Analysis of powder X-ray diffraction patterns[3] indicates that the products are predominately $EuBa_2Cu_3O_{7-\delta}$, with small amounts of Eu_2CuO_4 and CuO. The quantity of these impurity phases decreases dramatically as the reaction time is increased and as the amount of $Ba(OH)_2{\cdot}8H_2O$ is increased. The deterioration of the product due to exposure with water was not observed, perhaps because the dissolution of NaOH and KOH raised the pH considerably; if degradation of the surfaces of the particles are of concern, methanol can be substituted for water for the removal of the hydroxides.

It is notable that the desired product is not obtained if pure NaOH or pure KOH is used instead of the eutectic mixture under similar reaction conditions. Furthermore, the superconducting phase forms if other large rare-earth ions (e.g., Nd, Sm, and Gd) are substituted for Eu. However, $R_2Cu_2O_5$ precipitates instead of $RBa_2Cu_3O_{7-\delta}$ for R = Y and Dy.[4] We conclude that $R_2Cu_2O_5$ is less soluble than $RBa_2Cu_3O_{7-\delta}$ in NaOH and KOH under the conditions reported here, and therefore $RBa_2Cu_3O_{7-\delta}$ is only obtained for the larger rare earth ions which do not form the $R_2Cu_2O_5$ phase.[5]

Scanning electron microscopy (SEM)[6] images of the polycrystalline powders showed thin, platelike crystallites typical of $RBa_2Cu_3O_{7-\delta}$. However, the faces of the crystallites were not square as is observed for samples prepared above 900 °C. Instead, the morphology was markedly rectangular as shown in Figure 1. Dimensions for the faces of the crystallites were as large as 30 μm by 130 μm, but unfortunately the crystals had a mosaic structure and were not suitable for analysis by single-crystal X-ray diffraction methods. Since the size of the crystals increased significantly with increased reaction time, further attempts to

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(1) Ham, W. K.; Holland, G. F.; Stacy, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 5214.

(2) The purity and sources of all reagents are as follows: CuO (99.99%) Aldrich; Eu_2O_3 (99.9%) Johnson-Matthey; $Ba(OH)_2{\cdot}8H_2O$ (98%) Aldrich; NaOH and KOH (99.99%) Johnson-Matthey. All reagents were used without any pretreatment.

(3) The powder X-ray diffraction patterns were obtained on a Siemens D500 diffractometer by using Cu Kα radiation. The lattice parameters were obtained from a least-squares refinement of 10 peaks. The figure of merit (average absolute discrepancy) was 0.11 for indexing based on a tetragonal unit cell as opposed to 0.046 for indexing based on an orthorhombic unit cell. The amounts of impurity phases were estimated by refinement of the scale factors of these phases by using GSAS.

(4) Keller, S. W. Thesis, University of California, Berkeley, 1991.

(5) Kimizuka, N.; Takayama, E.; Horiuchi, S. *J. Solid State Chem.* **1982**, *42*, 322. Bringley, J. F.; Trail, S. S.; Scott, B. A. *J. Solid State Chem.* **1990**, *86*, 310.

(6) Scanning electron microscope (SEM) pictures were obtained on a JEOL-35CF scanning electron microscope operating at 20 keV.

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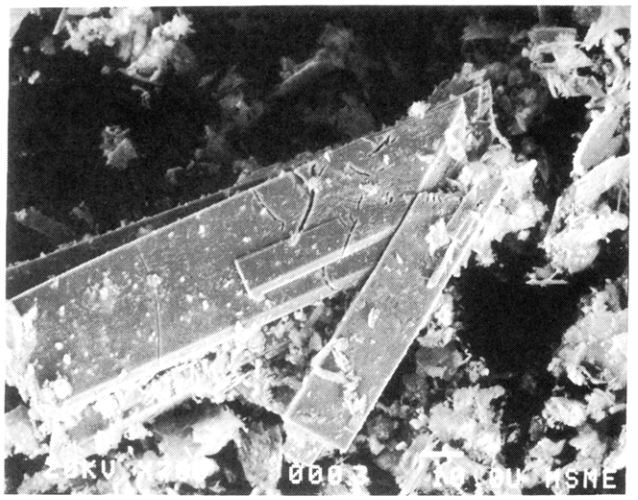

Figure 1. Scanning electron micrograph showing the morphology of the crystallites of $EuBa_{2-x}Cu_3O_{7-\delta}$ precipitated from NaOH and KOH.

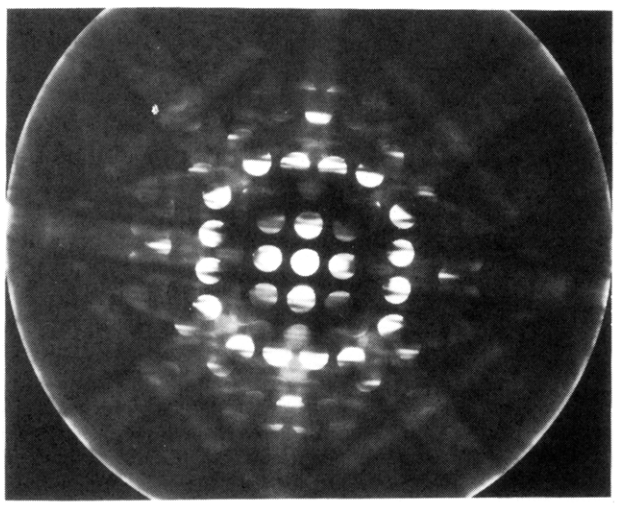

Figure 2. CBED pattern of the [001] crystallographic axis. Note the 2-fold symmetry about the center disc, confirming an orthorhombic rather than tetragonal unit cell.

obtain single crystals should be made by systematic variations of the synthesis conditions reported here.

The convergent beam electron diffraction (CBED)[7] pattern shown in Figure 2 provides definitive confirmation that these samples have an orthorhombic unit cell; the pattern clearly exhibits 2-fold rather than 4-fold symmetry about the [001] crystallographic axis. Since the orthorhombic-to-tetragonal transition for $EuBa_2Cu_3O_{7-\delta}$ in vacuum occurs at 570 °C,[8] whereas the synthesis temperature was only 450 °C, it is not surprising that the product is in the orthorhombic form. It is notable that this is the first direct synthesis of the orthorhombic form; only the tetragonal form can be obtained directly by the previously

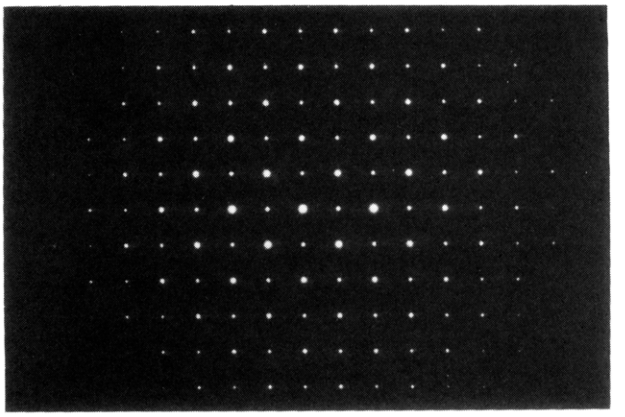

Figure 3. Selected area electron diffraction pattern (SAED) of the [001] zone. The "satellite" spots surround the main diffraction spots are indicative of a small number of oxygen vacancies.[19]

reported synthetic methods due to the higher temperatures that are required.

Another attribute of the samples prepared by this new synthesis route is the absence of a–b twinning. Splitting of the diffraction spots indicative of twinning is not observed in the selected area electron diffraction (SAED)[9] pattern shown in Figure 3. Furthermore, a–b twin boundaries are not observed in the transmission electron micrograph shown in Figure 4a. In contrast, a–b twins are readily observed in the image of a polycrystalline sample of $YBa_2Cu_3O_{7-\delta}$ prepared by solid-state reaction[10] as shown in Figure 4b. Thus, because "oxygen-rich" $EuBa_2Cu_3O_{7-\delta}$ has been obtained at temperatures below the orthorhombic-to-tetragonal transition, the a–b twins associated with the uptake of oxygen and change in symmetry do not form.

The diffraction peaks associated with $EuBa_2Cu_3O_{7-\delta}$ were indexed for an orthorhombic unit cell, and data analysis was performed with the General Structure Analysis System (GSAS) Rietveld least-squares refinement code.[11] The refined lattice parameters are a = 3.891(1) Å, b = 3.896(1) Å, and c = 11.623(9) Å. The a and b lattice parameters for our product are larger and the c parameter is smaller compared with those reported by Le Page *et al.*[12] for $EuBa_2Cu_3O_7$ prepared by solid-state reaction (a = 3.869(2) Å, b = 3.879(3) Å, and c = 11.693(6) Å). The differences in lattice parameters suggest that there are differences in stoichiometry for the samples precipitated from molten hydroxide compared with those prepared at elevated temperatures. The most likely possibilities are substitution of sodium, potassium, and/or europium on the barium site or substitution of alkali metal atoms on the europium site; it is unlikely that there is any substitution of these electropositive cations for copper. Furthermore, the change in lattice parameters cannot be attributed to oxygen nonstoichiometry because the c parameter increases as oxygen is removed from stoichiometric $RBa_2Cu_3O_7$.[13]

(7) The CBED pattern was obtained by using a Phillips EM400 microscope with a strongly converged electron beam of 100 nm in diameter. The range of incident angles in the beam resulted in a diffraction pattern consisting of disks rather than sharp spots. Dynamical scattering of electrons within the specimen gave rise to contrast within individual discs; the symmetry apparent in the pattern can be no lower than that of the diffracting crystals. See, for example: (a) Joy, C. D.; Romig, Jr., A. D.; Goldstein, J. L., Eds. *Principles of Analytical Electron Microscopy*; Plenum Press, New York, 1986. (b) 2-fold versus 4-fold symmetry in: Mansfield, J. F.; Chevacharo, S.; Kingon, A. I. *Appl. Phys. Lett.* **1987**, *51*, 1034.

(8) Grader, G. S.; Gallagher, P. K. *Adv. Ceram. Mater. Spec. Issue* **1987**, *2* (3B), 649.

(9) Electron diffraction patterns were obtained on a Phillips EM400 microscope operating at 100 keV. The diffracting area of the specimen was limited by an aperture to a circular region of 0.3 μm in diameter.

(10) Fortunati, K.; Fendorf, M.; Powers, M.; Burmester, C. P.; Gronsky, R. In *Proceedings of the 47th Annual Meeting of the Electron Microscopy Society of America*; Gailey, G. W., Ed.; San Francisco Press: San Francisco, 1989.

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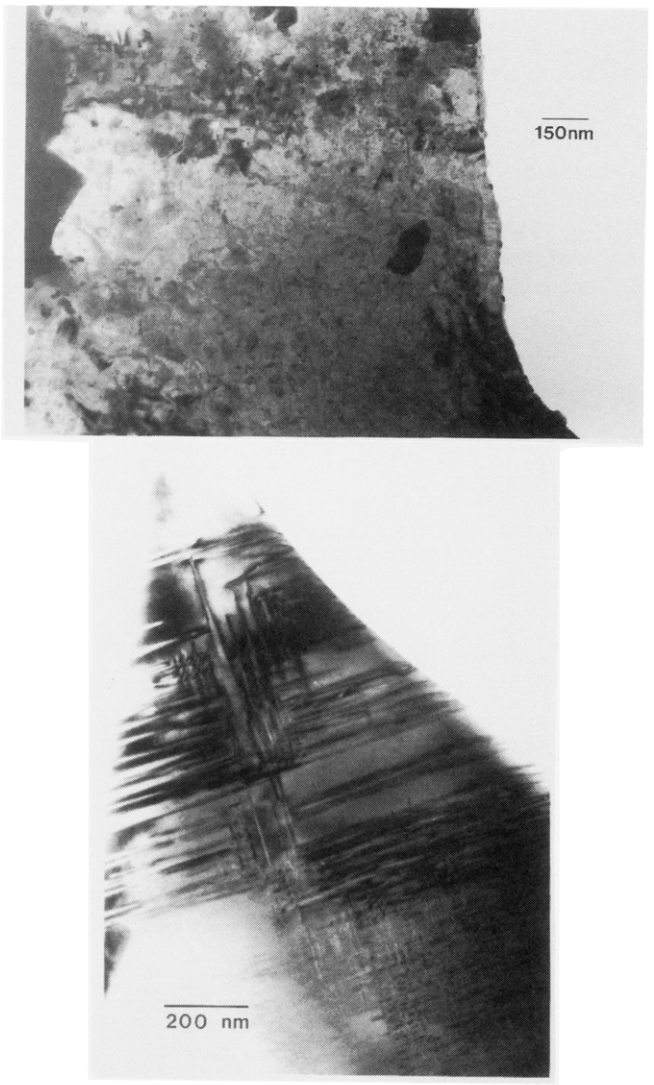

Figure 4. Transmission electron microscope images of (a, top) twin-free $EuBa_{2-x}Cu_3O_{7-\delta}$ prepared by precipitation from NaOH and KOH and (b, bottom) a sample of twinned $YBa_2Cu_3O_7$ prepared at elevated temperatures by solid-state reaction.

Rietveld refinement of the occupancy of the barium and europium sites gave a site occupancy of 0.87(4) for barium and 0.98(3) for europium. Therefore, we conclude that there are deviations in stoichiometry predominantly on the barium site. The low occupancy of the barium site suggests that there are either vacancies on this site or doping of atoms with a smaller electron density, such as sodium or potassium. We also considered partial substitution of europium (which has a larger electron density) for barium since the tendency for ordering might be less at the low synthesis temperature and due to the smaller size difference between europium and barium compared with yttrium and barium. However, since Rietveld refinement of this structural model resulted in a negative occupancy for europium on the barium site, we do not believe that europium is substituted for barium. Moreover, previous reports of substitution of europium for barium have shown that this leads to an overall decrease in the volume of the unit cell compared with stoichiometric samples;[14] in contrast, we observe an increase in the volume of the unit cell.

The composition of the thin, platelike crystals was obtained by wavelength-dispersive X-ray spectroscopy (WDS) by using an electron beam microprobe.[15] Two sets of samples of small crystals were analyzed one polished and one unpolished. The presence of both sodium and potassium was detected for the unpolished samples, whereas these alkali metals were not detected above the detection limit of <0.08 wt % (<0.02 mol of alkali metal/mol of $RBa_2Cu_3O_7$) for the polished crystals. Additionally, silver incorporation from the crucible was considered, but silver was also not detected. The stoichiometry obtained by careful comparison with standards for the polished samples were $Eu_{1.02(3)}Ba_{1.88(4)}Cu_3O_{7.02(5)}$, in excellent agreement with the structural refinement for the barium site occupancy. We believe that the analysis of the polished samples is representative of the bulk; presumably, the alkali-metal atoms are present as salt deposits adhering to the surfaces of the crystals. Therefore, we propose that the superconducting material precipitated is alkali-metal-free but barium-deficient and fully stoichiometric in oxygen.

The WDS results indicate that despite the presence of large quantities of alkali metal ions under the synthesis conditions, sodium and potassium are not incorporated into the bulk. These results are in contrast to previous reports of potassium-doped $EuBa_2Cu_3O_{7-\delta}$[16] and sodium- and potassium-doped $YBa_2Cu_3O_7$ made by solid-state methods.[17] Unfortunately, for materials prepared by solid-state routes it is difficult to prove that the alkali-metal ions are incorporated in the structure because the crystallites are too small to be polished for WDS analysis or for analysis by single-crystal X-ray diffraction. Rietveld refinement of powder diffraction data is not definitive because reduced electron density on the barium site can be modeled either as alkali-metal doping or as vacancies. In light of the results presented here, alkali-metal doping of this class of superconductors should be reinvestigated.

The superconducting behavior of the samples precipitated from molten hydroxide was determined by measuring the magnetic properties on a Quantum Design SQUID (superconducting quantum interference device) magnetometer. Both shielding and Meissner effect measurements were obtained by cooling the sample in zero field and in a field of 50 G, respectively, and subsequently measuring the diamagnetism in a field of 50 G. The onset of superconductivity occurred at approximately 75 K, and the Meissner effect at 5 K was −0.0021 emu/g (20% of the shielding value of −0.011 emu/g). Le Page *et al.*[12] reported

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(15) The composition of the materials obtained was determined by wavelength-dispersive X-ray spectroscopy analysis using an ARL SEMQ electron beam microprobe. Small crystals were mounted in epoxy and polished in order to obtain smooth surfaces for quantitative analysis. The samples and the standards were carbon-coated with 200–500 Å of 99.999% pure graphite. The intensities of the X-ray emissions for the samples were compared with the following standards: BaF_2 for barium, MgO for oxygen, Cu metal for copper, $EuNi_5P_3$ and $EuSi_2$ for europium, orthoclase $KAlSi_3O_3$ for potassium, and nepheline $Na_3(Na,K)(Al_4Si_4O_{16})$ for sodium. Background counts for the wavelength regions of interest were determined by measuring the background fluorescence of synthetic materials with purities in excess of 99.99%.

(16) Felner, I., et al. *Mod. Phys. Lett. B* **1988**, *2*, 713.

(17) Ausloos, A.; et al. *Solid State Commun.* **1988**, *68*, 538. Saito, Y.; et al. *Physica* **1987**, *148B*, 336. Dalichaouch; et al. *Solid State Commun.* **1988**, *65*, 1001. Fartash, A.; Oesterreicher, H. *Solid State Commun.* **1988** *66* 39.

$T_c = 94$ K for $EuBa_2Cu_3O_7$ prepared by solid-state reaction. The large decrease in T_c measured for our samples is consistent with deviations from the ideal stoichiometry; the nominal formal copper oxidation state of +2.4 for our samples is higher than optimum. We are optimistic that T_c can be raised by careful annealing to remove oxygen and/or by adjustment of the synthesis conditions.

In summary, we have prepared the orthorhombic form of $EuBa_2Cu_3O_{7-\delta}$ at 450 °C with a T_c of 75 K. The low T_c relative to that observed for samples prepared at elevated temperatures can be attributed to a deficiency of barium as determined by Rietveld refinement and WDS analyses. These analyses also show that neither sodium, potassium, nor europium are substituted for barium. The simplest model that would account for our data are vacancies on the barium site, although we are hesitant to claim so many vacancies of a large cation. It is conceivable that a number of these vacancies can be accounted for by the formation of stacking faults that produce an apparent barium deficiency; this would be consistent with the large mosaic structure in our crystallites. Barium-deficient stacking faults have been observed in Y–Ba–Cu–O materials produced via solid-state synthesis.[18] While it is not obvious that such defects will cause a lowering of T_c, we will continue to search for such defects by high-resolution electron microscopy.

We conclude that molten alkali-metal hydroxides are useful as solvents for the direct synthesis of the superconducting, othorhombic form of $RBa_2Cu_3O_{7-\delta}$ for R = Nd, Sm, Eu, and Gd. With this synthetic method, it is possible to prepare twin-free materials with relatively large crystallite sizes and to explore the effects of stoichiometry and particle morphology on superconductor device performance.

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