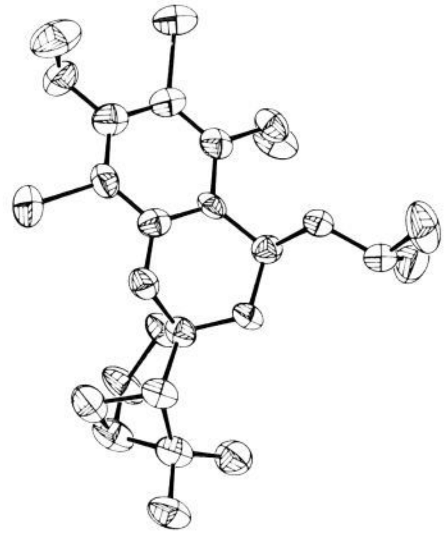

**Figure 1.** X-ray structure of **14b**.[13]

was obtained (20%), the major product isolated was the $\alpha,\beta$-unsaturated ketone **8** (41%).[10] Cyclization of **8** was best achieved with base catalysis in ethanol which delivered a 2:5 mixture of **9** and **10** in excellent yield. Completion of the carbon skeleton was then achieved by appendage of an isobutyl nucleophile at the carbonyl carbon of **9** or **10** and dehydration of the resulting tertiary benzylic alcohol which delivered **11** or **12**, respectively. Catalytic hydrogenation of these alkenes provided the epimers **13a** plus **14a** from **11** and **15a** plus **16a** from **12** (see Scheme I).[11] The production of intractable mixtures containing a multitude of products upon attempted bromination of these intermediates with bromine in methylene chloride was attributed to their acid lability. This obstacle was surmounted by the use of pyridine perbromide.[12] The stereostructures of **9–12**, **13**, and **14** were unambiguously established by single-crystal X-ray analysis (Figure 1) of the crystalline dibromide **14b**. Conversion of the dibromides **13b–16b** into the corresponding dialdehydes **13c–16c** was accomplished by lithium–bromine exchange, carboxylation, methylation, reduction, and partial reoxidation. The $^1H$ and $^{13}C$ NMR spectra of **13c** and **14c** were identical with those of samples prepared by methylation of natural robustadials A and B, respecively. Further, a comparison of optical rotations and CD spectra of **13c** and **14c** with those of naturally derived robustadials showed that the absolute configurations of the (+)-nopinone-derived products are identical with those of the natural products. Therefore, the absolute stereostructures of robustadials A and B correspond to **13d** and **14d**, respectively.

**Acknowledgment.** This research was supported by grants from the National Science Foundation (to R.G.S.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (to W.Y.). We thank Professor J. K. Snyder for a mixture containing authentic robustadials A and B.

**Supplementary Material Available:** Tables of data collection details, fractional atomic coordinates, and anisotropic thermal parameters for non-hydrogen atoms of **14b** as well as analytical and spectral data for all new compounds (12 pages). Ordering information is given on any current masthead page.

---

[10] $^1H$ and $^{13}C$ NMR analysis of **8** is consistent with this alkene being a single geometric isomer. An assignment of configuration has not been made. The epimers **9** and **10** were separated chromatographically (see Supplementary Material) prior to conversion to **11** and **12**, respectively.

[11] Each pair of epimers was separated by HPLC (see Supplementary Material).

[12] McElvain, S. M.; Morris, L. R. *J. Am. Chem. Soc.* **1951**, *73*, 206.

[13] X-ray analysis (Mo Ka radiation): **14b** crystallizes from methanol in the monoclinic space group $P2_1$ with $a = 10.685$ (1) Å, $b = 10.987$ (2) Å, $c = 11.312$ (1) Å, $\beta = 116.14$ (1)°, $V = 1192.15$ (31) Å$^3$, $Z = 2$. Standard direct and difference Fourier methods and least-squares refinement on the basis of 1366 reflections ($I \geq 3\sigma$) for 250 parameters led to final values of $R = 0.046$ and $R_w = 0.049$.

---

# Low-Temperature Synthesis of Superconducting $La_{2-x}M_xCuO_4$: Direct Precipitation from NaOH/KOH Melts

William K. Ham, Gary F. Holland, and Angelica M. Stacy*

*Department of Chemistry*
*University of California, Berkeley*
*Berkeley, California 94720*

*Received April 22, 1988*

The new copper oxide superconductors, $La_{2-x}M_xCuO_4$ (M = Ca, Sr, Ba with $0.05 < x < 0.30$),[1] $RBa_2Cu_3O_7$ (R = Y or other lanthanide elements),[2] and $Bi_2Sr_2CaCu_2O_{8-y}$,[3] generally have been prepared by reactions of intimate mixtures of the metal oxides, carbonates, oxalates, or nitrates at high temperatures (often up to 1100 °C). Product homogeneity is enhanced either through repeated heating and grinding cycles or by coprecipitation of the individual metal salts from aqueous solutions prior to high temperature processing. Disadvantages of this synthetic route include the following: (1) inhomogeneities in the products due to imperfect grindings or to the dissimilar precipitation rates of the salts of rare-earth, alkaline-earth, and copper ions; (2) impurities in the products introduced by multiple grindings and firings; and (3) high cost due to high-temperature processing for extended times. Clearly, there is a need to discover new synthetic routes to copper oxides. Our strategy utilizes molten salts to dissolve the starting materials and directly precipitate the final product. This laboratory has shown previously that single crystals of new barium copper oxides can be prepared from $Ba(OH)_2/BaCl_2$ melts at temperatures above 650 °C.[4] Here, we report the synthesis of superconducting $La_{2-x}M_xCuO_4$ (M = Na, K, or vacancy) from NaOH and KOH melts at 300 °C. This route offers the advantages of a single-step preparation of the product at temperatures much lower than those used in previous syntheses; $La_2CuO_4$ is prepared typically between 900 °C and 1100 °C.

Fused hydroxides are ideal for the preparation of rare-earth–copper oxide superconductors because these solvents melt at low temperatures, dissolve metal oxides, and stabilize high oxidation states. Synthesis at temperatures lower than those required for direct reaction is possible in fused hydroxides since NaOH and KOH melt at 318 °C and 360 °C, respectively, and an equimolar mixture at 170 °C. Molten hydroxide is a Lux–Flood acid–base solvent system, with $OH^-$ in equilibrium with its conjugate acid, $H_2O$, and its conjugate base, $O^{2-}$. Melts can be made more acidic ($H_2O$-rich or low $pH_2O$) or basic ($O^{2-}$-rich) by controlling the water content of the melt. Since the equilibrium concentrations of the dissolved phases of a metal oxide depend on the oxide ion concentration, precipitation of products can be controlled by changing the water concentration of the melt. Finally, the electrochemical-potential window of the hydroxide melts is large enough to allow the existence of metals and oxygen in various oxidation states.[5] In particular, high oxidation states such as $O_2^-$ and $O_2^{2-}$ are stable, and the presence of $Cu^{3+}$ has been reported.[5,6] This is important because all of the copper oxide superconductors

---

[1] Bednorz, J. G.; Müller, K. A. *Z. Phys. B.* **1986**, *64*, 189.

[2] (a) Wu, M. K.; Ashburn, J. R.; Torng, C. J.; Hor, P. H.; Meng, R. L.; Gao, L.; Huang, Z. J.; Wang, Y. Q.; Chu, C. W. *Phys. Rev. Lett.* **1987**, *58*, 908. (b) Hor, P. H.; Meng, R. L.; Wang, Y. Q.; Gao, L.; Huang, Z. J.; Bechtold, J.; Forster, K.; Chu, C. W. *Phys. Rev. Lett.* **1987**, *58*, 1891.

[3] Subramanian, M. A.; Torardi, C. C.; Calabrese, J. C.; Gopalakrishnan, J.; Morrisey, K. J.; Askew, T. R.; Flippen, R. B.; Chowdhry, U.; Sleight, A. W. *Science* (*Washington, D.C.*) **1988**, *239*, 1015.

[4] (a) VerNooy, P. D.; Dixon, M. A.; Stacy, A. M. *Proceedings of the Materials Research Society*; Fall 1987, Boston, MA. (b) Dixon, M. A.; VerNooy, P. D.; Stacy, A. M. *Proceedings of the Materials Research Society*; Spring 1987, Reno, NV.

[5] (a) Claes, P.; Gilbert, J. In *Molten Salt Techniques*; Lovering, D. G., Gale, R. J., Eds.; Plenum: New York, 1983; p 79. (b) Plambeck, J. A. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel-Dekker: New York, 1976; Vol. X, p 283.

[6] (a) Goret, J.; Tremillion, B. *Bull. Soc. Chim. Fr.* **1966**, 67. (b) Eluard, A.; Tremillon, B. J. *Electroanal. Chem.* **1968**, *18*, 277.

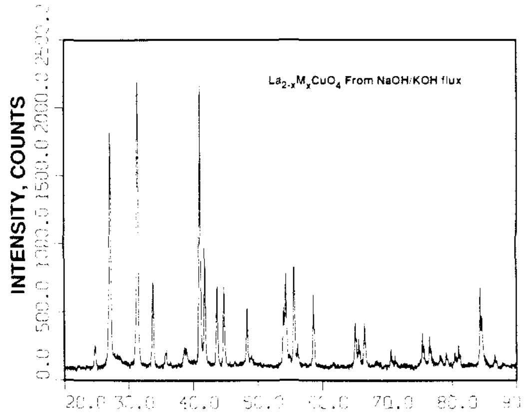

**Figure 1.** X-ray diffraction pattern in intensity versus degrees $2\theta$ for $La_{2-x}M_xCuO_4$ where M = Na, K, or vacancy and $0.0 < x < 0.05$.

are highly oxidized, with formal copper oxidation states greater than two. Thus, these fluxes match our requirements for the low-temperature preparation of homogeneous, highly oxidized rare-earth copper oxides.

Our synthesis starts with a very acidic melt in which CuO and $La_2O_3$ both dissolve (i.e., $Cu^{2+}$ and $La^{3+}$ are stable). Heating at 300 °C results in the slow loss of water, thereby making the melt more basic and the product insoluble. In a typical experiment, 10 g of KOH and 12 g of NaOH (reagent grade), respectively, were placed in a Teflon crucible and melted at temperatures between 200 °C and 300 °C; the melt is acidic because NaOH and KOH contain 0.010 and 0.145 g of water per gram of salt, respectively.[5a] Next, a stoichiometric mixture of 0.10 g (1.3 mmol) of CuO and 0.41 g (1.3 mmol) of $La_2O_3$ were added to the liquid and stirred, producing a blue solution. The temperature was increased and held at 300 °C for approximately 100 h, after which a black solid could be observed in a generally clear, colorless melt. The crucible was removed from the furnace and allowed to cool in air to room temperature. A grey polycrystalline powder was isolated from the cool, solidified melt by dissolving the flux with distilled water. Similar experiments were performed in pure NaOH and pure KOH melts in nickel and $Al_2O_3$ crucibles at temperatures up to 520 °C and times as short as 3 h; analysis of these products showed single-phased materials contaminated with Ni and Al, depending on the crucible.

The precipitates isolated from the Teflon crucibles were characterized by powder X-ray diffraction and EDX microanalysis. The powder pattern is shown in Figure 1; only lines which can be assigned to $La_2CuO_4$ are present. Diffraction lines due to CuO and $La_2O_3$ are absent, indicating that precipitation from the melt was selective for the ternary oxide. Although pure $La_2CuO_4$ is orthorhombic,[7] the powder patterns of the precipitates index to a tetragonal unit cell. This higher symmetry structure also has been reported for $La_2CuO_4$-based structures when (1) alkaline-earth elements are substituted for La ($La_{2-x}M_xCuO_4$, where M = Ca, Sr, Ba and $x > 0.1$),[8] (2) La vacancies are introduced ($La_{2-x}CuO_{4-y}$),[9] or (3) smaller metal atoms, such as Li, are substituted for copper ($La_2Cu_{1-z}T_zO_4$ where T = Li and other small transition metal atoms).[10] The microprobe results showed a La to Cu ratio between 1.9:1 and 2:1 and only very small amounts of Na or K (the quantity was less than 1% by weight). The structure and analytical data are consistent with a doped or nonstoichiometric form of $La_2CuO_4$ and a composition of $La_{2-x}M_xCuO_4$, where M = Na, K, or vacancy, with $0 < x < 0.05$.

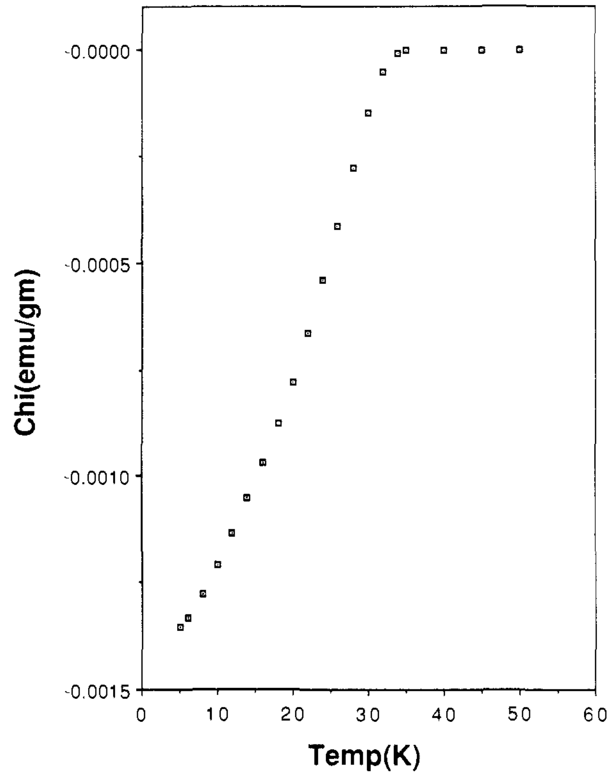

**Figure 2.** Magnetic susceptibility versus temperature for $La_{2-x}M_xCuO_4$ where M = Na, K, or vacancy and $0.0 < x < 0.05$.

We further characterized the samples synthesized in Teflon crucibles by measuring the magnetic properties with a SHE SQUID magnetometer and a field of 12.11 G; the results are shown in Figure 2. Below 35 K, a large diamagnetic signal is observed, indicating the onset of superconductivity in these samples. Superconductivity has been observed previously in $La_{2-x}M_xCuO_4$, where M = Ca, Sr, or Ba and $0.05 < x < 0.30$,[11] and in nonstoichiometric $La_{2-x}CuO_4$;[9] stoichiometric $La_2CuO_4$ does not superconduct. We can understand the presence of superconductivity in our samples if we assume that the valence electron count per formula unit must be similar to that of the alkaline-earth-doped lanthanum–copper oxide superconductors. Half as many alkali metal ions or one-third as many vacancies must be substituted for La compared with alkaline earth atoms. Thus, for $La_{2-x}(Na,K)_xCuO_4$ and $La_{2-x}CuO_4$ superconductivity should be observed for $0.025 < x < 0.15$ and for $0.016 < x < 0.10$, respectively. Since samples precipitated from molten hydroxide fluxes exhibit superconductivity, we propose that the doping levels of Na, K, or vacancies are within the ranges quoted above; these doping levels are consistent with our microprobe analysis.

By employing many of the useful properties of hydroxide melts, we have synthesized a variation of the class of superconductors discovered by Bednorz and Müller.[1] This new route gives direct precipitation of the products and offers the advantages of low temperatures and simplicity in the formation of solid oxide materials. In conjuction with the earlier research at elevated temperatures in $Ba(OH)_2$, this work indicates that hydroxides constitute a solvent of interest for synthesizing new and useful ternary copper oxides.

**Acknowledgment.** We acknowledge the support of the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division of the U.S. Department of Energy under Contract no. DE-AC03-76SF0009.

---

(7) Longo, J. M.; Raccah, P. M. *J. Solid State Chem.* **1973**, *6*, 526.

(8) Nguyen, N.; Choisnet, J.; Hervieu, M.; Raveau, B. *J. Solid State Chem.* **1981**, *39*, 120.

(9) Grant, P. M.; Parkin, S. S. P.; Lee, V. Y.; Engler, E. M.; Ramirez, M. L.; Vazquez, M. L.; Lim, G.; Jacowitz, R. D.; Greene, R. L. *Phys. Rev. Lett.* **1987**, *58*, 2482.

(10) Demazeau, G.; Parent, C.; Pouchard, M.; Hagenmuller, P. *Mat. Res. Bull.* **1972**, *7*, 913.

(11) Tarascon, J. M.; Greene, L. H.; McKinnon, W. R.; Hull, G. W.; Geballe, T. H. *Science* (*Washington, D.C.*) **1987**, *235*, 1373. Fleming, R. M.; Batlogg, B.; Cava, R. J.; Reitman, E. A. *Phys. Rev. B* **1987**, *35*, 7191.