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Chemically Tailored, Corrosion Resistant, High-T_c Phases

Ji-Ping Zhou,[†] Steven M. Savoy,[†] Jianai Zhao,[†]
David R. Riley,[†] Y. T. Zhu,[‡] A. Manthiram,[‡]
Rung-Kuang Lo,[‡] Damon Borich,[†] and John T. McDevitt[*,†]

Department of Chemistry and Biochemistry and Center for
Materials Science and Engineering
The University of Texas at Austin
Austin, Texas 78712

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One of the major stumbling blocks that has plagued the practical utilization of high-T_c superconductors has been the tendency of the cuprate compounds to degrade chemically when exposed to water, acids, CO_2, and CO.[1–4] Of the technologically important superconductors with transition temperatures above 77 K (i.e., $YBa_2Cu_3O_7$, $Tl_2Ba_2Ca_2Cu_3O_{10}$, $Bi_2Sr_2CaCu_2O_8$, and $HgBa_2Ca_2Cu_3O_9$), $YBa_2Cu_3O_7$ is the preferred material for thin-film applications.[5] Unfortunately, the $YBa_2Cu_3O_7$ compound displays the highest atmospheric corrosion reactivity of the studied cuprate materials.[2]

The $YBa_2Cu_3O_{7-\partial}$ phase possesses a layered structure with a sequence along the *c*-axis of $Cu(1)O_x$-BaO-$Cu(2)O_2$-Y-$Cu(2)O_2$-BaO-$Cu(1)O_x$.[6,7] Any bond length mismatch between the layers can introduce internal stresses.[8,9] We have shown previously that samples of $YBa_2Cu_3O_{7-\partial}$ having intermediate oxygen contents corrode more slowly than samples do with either higher or lower oxygen contents.[10,11] This behavior cannot be explained satisfactorily along the lines of copper valence as previously hypothesized.[12] Rather, lattice stress appears to be an important factor which dictates the decomposition kinetics for this material.

In an effort to relieve the tensile stress and strain which exists in the Ba–O and $Cu(2)O_2$ layers in the $YBa_2Cu_3O_7$ structure, we have considered a number of cation substitution strategies. The La^{3+} substitution in $YBa_{2-y}La_yCu_3O_{7-\partial}$ causes a rapid decrease in T_c due to a disordering of oxygen in the $Cu(1)O_x$ plane and an accompanying transfer of holes from the active $Cu(2)O_2$ sheets to the inactive $Cu(1)O_x$ planes.[13] However, it has been shown[14] that a cosubstitution of Ca^{2+} for Y^{3+} and La^{3+} for Ba^{2+} in the $Y_{1-y}Ca_yBa_{2-y}La_yCu_3O_{7-\partial}$ system can maintain the T_c above 80 K in spite of the fact that an orthorhombic to tetragonal transition occurs at $y \sim 0.4$.

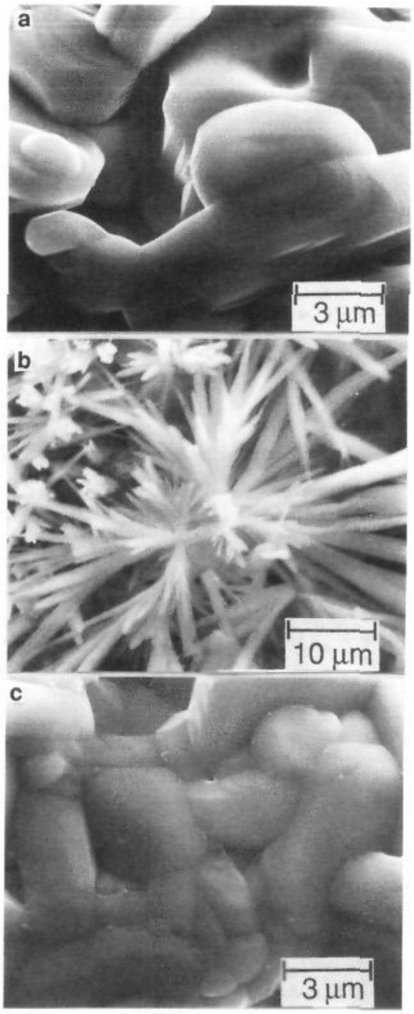

Figure 1. Scanning electron micrographs showing (a) a ceramic pellet of $YBa_2Cu_3O_{6.94}$ before corrosion, (b) the same sample after its exposure to water for 2 days at room temperature, and (c) a $Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_{6.96}$ pellet sample after soaking for 30 days in water at room temperature.

Samples of $Y_{1-y}Ca_yBa_{2-y}La_yCu_3O_{7-\partial}$ were synthesized by solid state reaction methods.[10,14] To explore the environmental reactivity characteristics of the substituted compounds, pellet and powder samples were exposed to liquid water at 25 °C and water vapor at 75 °C for various lengths of time. Scanning electron microscopy (SEM) images were recorded for the samples before and after the water treatment. The results of the SEM study are shown in Figure 1. Here, the unsubstituted pellet sample becomes completely coated with $BaCO_3$ crystallites after soaking in water for 2 days, indicating that the sample has decomposed to a significant extent. The formation of the carbonate salt can be traced to the presence of the atmospheric CO_2 in the chamber as documented previously.[12] On the other hand, pellet samples of $Y_{0.7}Ca_{0.3}Ba_{1.7}La_{0.3}Cu_3O_{6.95}$ and $Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_{6.96}$ appear to be remarkably stable, as almost no reaction with water was observed after 1 month of soaking. In addition to the electron microscopy results, SQUID, 4-probe conductivity, and X-ray powder diffraction (XRD) measurements were obtained before and after the water treatment. Accordingly, all methods demonstrated in a convincing fashion that bulk samples of $Y_{1-y}Ca_yBa_{2-y}La_yCu_3O_{7-\partial}$ display marked increases in their corrosion resistance as compared to the parent compound. Within the $Y_{1-y}Ca_yBa_{2-y}La_yCu_3O_{7-\partial}$ series, the corrosion resistance can be enhanced by increasing *y*. Greater than a 100-fold increase

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[†] Department of Chemistry and Biochemistry.

[‡] Center for Materials Science and Engineering.

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Table 1. Summary of Data for the High-T_c Compounds

sample[a]	T_c (K)	structure (O/T)[b]	lifetime (days)[c]
$YBa_2Cu_3O_{6.94}$	90	O	2.0
$YBa_2Cu_3O_{6.59}$	60	O	4.0
$YBa_2Cu_3O_{6.05}$		T	0.5
$Y_{0.9}Ca_{0.1}Ba_{1.9}La_{0.1}Cu_3O_{6.97}$	85	O	5.0
$Y_{0.8}Ca_{0.2}Ba_{1.8}La_{0.2}Cu_3O_{6.96}$	83	O	10.0
$Y_{0.7}Ca_{0.3}Ba_{1.7}La_{0.3}Cu_3O_{6.95}$	80	O[d]	>80.0
$Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_{6.96}$	80	T	>150.0

[a] Oxygen contents from iodometric titrations[17] and T_c values from 4-probe and SQUID measurements. [b] Orthorhombic vs tetragonal crystal symmetry. [c] Lifetimes were estimated by XRD as the sample exposure time necessary to degrade 50% of sample. [d] This specimen is close to the orthorhombic-to-tetragonal transition.

in the lifetime of $Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_{6.96}$ as compared to $YBa_2Cu_3O_{6.94}$ is noted as illustrated in Table 1.

In addition to the bulk reactivity studies mentioned above, we have also evaluated the environmental reactivity characteristics of high-T_c films. In this regard, the method of laser ablation was utilized to deposit *c*-axis oriented films of $YBa_2Cu_3O_{7-\delta}$ and $Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_{7-\delta}$ onto MgO(100) substrates as 2000 Å thick films. The typical specimens of this type display transition temperatures of 90 and 80 K, respectively.

Aside from a few qualitative descriptions of the reactivity of high-T_c films,[15] little quantitative information is currently available in the literature related to the environmental degradation behavior of thin film samples. To evaluate the reactivity of the superconductor thin-film specimens, resistivity vs time data were recorded for the two materials as they were simultaneously exposed to water vapor that was equilibrated at 75 °C. In this regard, films of $YBa_2Cu_3O_{7-\delta}$ degraded rapidly over a period of 2 h. From the physical appearance of the film, it was observed that the passage of current through the superconductor served to strongly accelerate the corrosion processes, as seen by selective degradation in the vicinity around the electrodes. After stopping the passage of current through the $YBa_2Cu_3O_{7-\delta}$ film, more gradual degradation of the film was noted in regions remote from the contacts. On the other hand, the $Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_{7-\delta}$ film sample showed very little change in its resistance over a period of 10 days.

Within the $Y_{1-y}Ca_yBa_{2-y}La_yCu_3O_{7-\delta}$ class of compounds, measurements of the lattice parameter indicate that the degree of orthorhombicity is decreased with increasing amount of substitution.[14] Interestingly, the most stable compound in the series is the tetragonal material, $Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_{6.96}$ ($a = b = 3.869$ Å, $c = 11.622$ Å), in which the oxygen atoms are disordered in the $Cu(1)O_x$ planes. The dramatic increase in chemical stability may arise from blocking solution access of protic species into the interior of the superconductor by the presence of oxygen at both the *a*- and *b*-axes of the $Cu(1)O_x$ planes. Alternatively, the release of internal stress and strain factors may play an important role, and/or the formation of an oxygen rich surface (~15–30 Å) detected by X-ray photoemission depth profile studies may serve to stabilize the material. Surface passivation for the protection of stainless steel has been shown to enhance the environmental stability of this material.[16] Careful studies are now in progress to determine which of the factors is responsible for the observed behavior.

From the data presented in this paper, it is clear that the cation substitution method represents a successful new strategy for the preparation of chemically stable, high-T_c bulk and thin-film samples. The availability of these stable cuprate phases may facilitate the more rapid commercialization of high-T_c thin-film structures and devices.

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Supplementary Material Available: Resistivity vs temperature curve, X-ray diffraction data, resistivity vs water vapor exposure time curves, and optical photographs of degraded films (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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