New Superconducting Cuprate Perovskites

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Ten new superconducting cuprate perovskites with T_c's above 77 K are reported. The highest T_c of the new group, and for any superconductor, is observed in $Ba_2Eu_{0.9}Y_{0.1}Cu_3O_x$ which has a resistive midpoint of 94.5 K with a width of 0.7 K. Miessner-effect and ac-susceptibility measurements indicate bulk superconductivity in these materials. Each of these cuprates has a two-to-one ratio of divalent to trivalent ion on the A site of the perovskite-type structure.

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Superconductivity near 30 K in the La-Ba-Cu-O system[1] was shown to occur in a quaternary phase $La_{1.8}Ba_{0.2}CuO_4$ with the K_2NiF_4 structure.[2] This phase identification quickly led to the chemically substituted phase $La_{1.8}Sr_{0.2}CuO_4$ with T_c's near 40 K.[3-6] A superconducting transition extending from 93 to 80 K was recently reported by Wu *et al.*[7] in a mixed-phase Y-Ba-Cu-O system. We subsequently identified the single superconducting phase as having an ordered, defect perovskite structure with composition $Ba_2YCu_3O_{6.9}$.[8] The identification of this phase has prompted us to look for superconductivity in other Cu-based perovskites. This paper reported initial studies on the preparation and properties of new compositions with this structure type.

The substitutional chemistry of the cuprate perovskites is much more extensive than that of the K_2NiF_4 cuprates and many of the substituted phases are high-T_c superconductors. These materials were prepared as described for $Ba_2YCu_3O_{6.9}$,[8] with repeated grindings and refirings (usually two or three) until the material was single phase. Data on lattice parameters and T_c's for these phases are given in Table I. These lattice parameters are based on powder data, except for $Ba_2YCu_3O_{6.9}$ which was determined from a single crystal. All of the compositions listed are single perovskite-type phases, with the exception of $CaBaLaCu_3O_x$ which showed small amounts of additional phases.

Data on the superconducting T_c's given in Table I represent resistive transitions, obtained at a current density of approximately 0.1 A cm^{-2}. Typical resistivity-temperature curves are shown in Fig. 1 and illustrate the linearity in $\rho(T)$ which is commonly found in high-T_c oxide superconductors.[8] As seen in Fig. 1, $\rho(T)$ deviates from linearity at temperatures from 110 to 140 K, which we tentatively ascribe to superconductivity in either a minor phase or a small fraction of the sample with nonbulk stoichiometry. We do not quote these numbers as T_c^{onset}; rather, we report less well-defined and more conservative onsets, namely, the temperature where the curvature of $\rho(T)$ increases most abruptly. This yields on-

TABLE I. Crystallographic and superconducting data for $M_3Cu_3O_x$.

M_3	a (Å)	b (Å)	c (Å)	x	T_c^{onset} (K)	T_c^{mid} (K)	$T_c^{R=0}$ (K)	$\rho(T_c^{\text{onset}})$ ($\mu\Omega$ cm)	$\rho_{300}/\rho(T_c^{\text{onset}})$
Ba_2Y	3.87	3.86	11.67	6.9	93.5	92.5	91	260	2.3
Ba_2Eu	3.88	3.85	11.77	7.1	96	94.5	93.5	740	2.5
$Ba_{2.1}Eu$					96	94.5	92	8500	1.9
Ba_2La	3.934			6.6	77	60	48	39000	1.04
$Ba_{1.8}La_{1.2}$					54	50	47	3400	2.4
BaCaLa	3.877			6.7	81	79.3	77.8	2100	2.5
BaCaY	a				83	80	77		
$Ba_2Y_{0.75}Sc_{0.25}$	3.86	3.84	11.74		92	91	87	1860	2.15
$Ba_2Eu_{0.75}Sc_{0.25}$	3.89	3.87	11.77		96	93	91	3000	1.73
$Ba_2Y_{0.5}La_{0.5}$	3.88	3.86	11.69		92	87	82	4200	1.91
$Ba_{1.5}Sr_{0.5}Y$	3.83	3.82	11.67		91	87	86	1260	2.60
$Ba_2Eu_{0.9}Pr_{0.1}$	3.88	3.86	11.76		85	82	80	1860	1.93
$Ba_2Eu_{0.9}Y_{0.1}$	3.87	3.85	11.77		96	94.5	93.7	320	3.0
$Ba_2Eu_{0.75}Y_{0.25}$	3.87	3.85	11.75		96	95	94	800	2.6

[a]Not single phase.

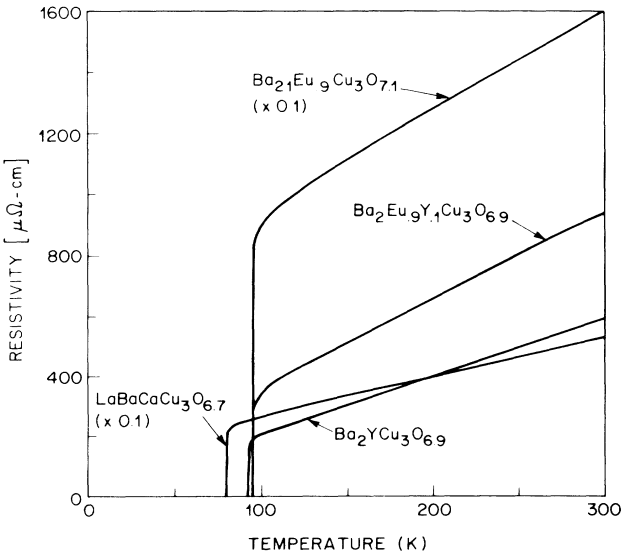

FIG. 1. Resistivity vs temperature for representative samples.

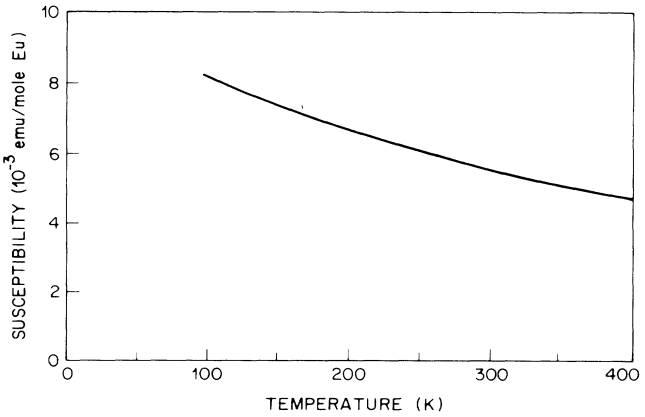

FIG. 2. The magnetic susceptibility above T_c for $Ba_2EuO_{7.1}$ as a function of temperature. The magnitude and temperature dependence are consistent with the $4f^6$ configuration of divalent Eu.

set temperatures typically only a few degrees above the main transition. The transition width of several of these materials are remarkably narrow. In $Ba_2Eu_{0.9}Y_{0.1}Cu_3O_7$, for example, the (10%–90%) transition width is 0.7 K, and the zero-resistance state is achieved at 93.7 K. This is the highest temperature for zero resistance reported to date, as well as the narrowest transition reported in cuprate superconductors. Meissner-effect measurements on Ba_2Y, Ba_2Eu, and $Ba_2Eu_{0.75}Sc_{0.25}$ samples confirmed bulk superconductivity, and ac-susceptibility measurements on the others gave large diamagnetic signals, implying that substantial amounts of these phases are superconducting. The only exception is Ba_2La, which exhibited only a small diamagnetic shift in the susceptibility even at low temperatures. However, $Ba_{1.8}La_{1.2}Cu_3O_x$ gives a substantial ac susceptibility signal.

The resistivity at T_c^{onset} also presented in Table I, along with a residual resistivity ratio $\rho(300\text{ K})/\rho(T_c^{\text{onset}})$. Within each basic chemical system, i.e., Eu- and Y-based materials, there is a rough correlation between the low-temperature resistivity and the residual resistivity ratio, but it is clear that the resistivity cannot be separated into independent components due to phonon and impurity scattering. The strong effect of ternary and quaternary ion substitutions on the resistivity is notable, especially in light of the small effect of these substitutions on T_c. While some of the resistivity can be attributed to intergrain regions in these powder samples, the large Meissner effect and ac diamagnetic signal, along with the relatively high critical currents and absence of "foot structure" in the resistive transition are all indications that the grains in these materials (unlike, e.g., $La_{2-x}Sr_xCuO_4$) are well coupled. In one sample, however, intergrain resistivity probably plays a significant role: $Ba_{2.1}EuCu_3O_7$. Here some excess Ba may have precipitated as BaO or some other insulating phase in the grain boundaries, leading to the extremely high resistivity.

Magnetic-susceptibility data above T_c on $Ba_2EuCu_3O_{7.1}$ are given in Fig. 2. The temperature dependence and the magnitude are characteristic of the $4f^6$ configuration of trivalent Eu with a singlet ground state and an excited triplet several hundred kT higher. This valence state can be inferred also from the lattice parameters, which are only slightly larger than for the Y compound, but considerably smaller than for the La compound. We expected Lu to form this same compound, since it is the other small rare-earth ion. To date, we have not succeeded in obtaining superconductivity at this stoichiometry, but have seen onsets at 96 K at other compositions which were not single phase. It is also notable that the paramagnetic ion Pr^{3+} does not kill superconductivity in small amounts. The compound $Ba_2PrCu_3O_x$, however, does not superconduct.

The La-Ba-Cu-O system is worthy of special mention. It was the report that the superconducting phase[2] had the K_2NiF_4 structure that focused earlier attention on the K_2NiF_4 cuprates. The reported La-Ba-Cu-O perovskites[9,10] were checked for superconductivity without success. We have reexamined this system and found a 30-K wide superconducting transition with an onset at 77 K for the composition $Ba_2LaCu_3O_x$. Even though this is a small amount of superconductivity, $Ba_{1.8}La_{1.2}Cu_3O_x$ gives a large diamagnetic ac-susceptibility signal and it appears clear that this system can give bulk superconductivity at an appropriate La/Ba ratio. This system is notable in that several groups have observed a small amount of superconductivity at approx-

imately this temperature in nominally K_2NiF_4 cuprates.[4,11-13] We believe that such observations were due to small amounts of such a perovskite phase.

It is no coincidence that the M^{2+}:M^{3+} atom ratio is 2 to 1 for most of the superconductors prepared. This stoichiometry provides an appropriate charge balance, which in combination with a tolerable number of oxygen defects can fix the oxidation state of Cu in a desirable valence range (2–2.4). For compounds with a large size difference among the A ions, ordering gives a tripled cell as in $Ba_2YCu_3O_{6.9}$.[8] For the La:Ba compositions, however, where the size difference is smaller, ordering is not necessary and we observe a cubic cell to the limits of our powder diffraction. For the K_2NiF_4-structure cuprates, a Cu-O distance dependence on T_c was reported.[14] For the perovskites we have not been able to identify a relationship with size. It is, however, interesting to note that the in plane Cu-O distance in the layered cuprates are smaller than in the perovskites, but the average of all Cu-O distances is smaller in the perovskites.

In summary, we now have a large class of single-phase, high-T_c superconducting cuprate perovskites. Their availability will allow systematic studies of their physical properties and tests of theoretical models.

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