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The Preparation and Magnetic Behavior of $EuBa_2Cu_{3-y}M_yO_{6.5+x}$ (M = Ni, Co, Al, and Zn) and Some Related Compounds

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The substitution limits and the change in T_c produced by substituting selected comparably sized cations for copper in the high-T_c superconducting phase, $EuBa_2Cu_3O_{6.5+x}$, are determined. The elements, M = Ni, Co, Zn, and Al, substitute for copper only to a limited extent to produce $EuBa_2Cu_{3-y}M_yO_{6.5+x}$ phases. Attempts to completely replace the copper ions and retain the orthorhombic structure were unsuccessful. As substitution progressed, a tetragonal phase became stabilized and the superconducting transition temperature, T_c, decreased sharply. Magnetic properties and superconducting transition temperatures of the maximally substituted phases and of $EuBa_2Cu_3O_{6.5+x}$ and $BaCuO_{2+x}$ are reported.

Introduction

Bednorz and Mueller (*1*) and subsequently Wu *et al.* (*2*) demonstrated the high-temperature superconducting behavior of the systems X–Ba–Cu–O for X = La and Y, respectively. Recent research on these and related phases has been directed toward enhancing understanding of both the mechanism responsible for this superconductivity and the structural limits of the superconducting phases. The cuprate perovskites with the compositions $LnBa_2Cu_3O_{6.5+x}$, where Ln represents a trivalent lanthanoid element or yttrium, are particularly interesting because these trivalent ions not only have little influence on the observed superconductivity (*3–9*), but also as Ln is varied produce relatively little change in cell parameters (*3, 6*). Published data demonstrate that the composition and the variable valence of the copper play a peculiarly important role in determining the superconducting critical temperature, T_c.

Analytical and structural analysis results have shown that in the $LnBa_2Cu_3O_{6.5+x}$-type superconductors Cu is present in two distinct oxidation states, 2+ and 3+ (*10, 11*). On the basis of bond distances and bond strength calculations it has been suggested that the Cu^{2+} ion is coordinated in CuO_5 pyramids while the Cu^{3+} ion is found in square planar coordination, the Cu(1) site at (0, 0, 0) (*10*). The superconductivity is probably confined to the [CuO_2–BaO–CuO–BaO–CuO_2] structural unit (*6*). In view of these observations, insight into the role the Cu–O arrangement has on the su-

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perconducting behavior of the material might be provided by examining the effect caused by substituting for Cu similarly sized species which potentially can exhibit either the 2+ or the 3+, or both the 2+ and 3+, oxidation states. To our knowledge, when this work was initiated, the effects that substituting another element for Cu had on both the structure and the superconducting critical temperature, T_c, had been examined only minimally.

The partial insertion of Ni^{2+} ions into the copper–oxygen chains in $Y_{0.75}Sc_{0.25}Ba_2Cu_{2.4}Ni_{0.6}O_7$ is described by Iqbal *et al.* (*12*). The effect that substituting Fe and Ag for Cu has on the superconductivity in $YBa_2Cu_3O_7$ was investigated by Felner *et al.* (*13*) and Cahen *et al.* (*14*), respectively. In these three cases the superconductivity was strongly affected with the transition temperature, T_c, lowered. Compounds of the composition $YBa_2(Cu_{0.9}M_{0.1})_3O_{6+y}$, i.e., 10 mole%, where M = Ti, Cr, Mn, Fe, Co, Ni, and Zn were examined by Xiao *et al.* (*15*). They found the Zn-substituted phase not to exhibit the Meissner effect. The Ti-, Cr-, and Mn-substituted phases exhibited slightly reduced T_c, the Ni-substituted phase showed moderately reduced T_c, and the Fe- and Co-substituted phases evidenced drastically reduced superconducting temperatures. However, they did not present any evidence that the specimens examined were monophasic. Siegrist *et al.* (*16*) subsequently demonstrated from single crystal studies on Al-substituted $YBa_2Cu_3O_{7-y}$ that substitution occurs only at the copper site and, more specifically, at the Cu(1) site located at (0, 0, 0) in space group *Pmmm*, the ion in square planar coordination. Studies on $YBa_2Cu_{3-x}Ni_xO_{7-y}$, for x = 0.25 and 0.50, indicated further that the superconducting transition temperature, T_c, is lowered as substitution occurs, and point out that copper cannot be replaced completely by Ni (*17*).

Since most experiments had been effected at apparently arbitrarily selected substitution values, we undertook preparatory X-ray powder diffraction studies on $EuBa_2Cu_{3-y}M_yO_{6.5+x}$ phases, where M = Ni^{2+}, Co^{3+}, Al^{3+}, and Zn^{2+}, to determine substitution limits for copper, if any existed, and the extent to which the orthorhombic structure was affected as copper ions were replaced. The M ions selected have the following (CN 6) radii (in Å, where HS = high spin and LS = low spin) Ni^{2+} (0.83), Ni^{3+} (0.70 LS, 0.74 HS), Co^{3+} (0.68 LS, 0.75 HS), Al^{3+} (0.68), and Zn^{2+} (0.88), respectively, in comparison with 0.68 Å for Cu^{3+} and 0.71 Å (CN 4) for Cu^{2+} (*18*). (CN 4 radii are not available for the comparison.) To demonstrate the effect on superconducting properties magnetic susceptibility measurements were made in a 0.1-kG field on maximally substituted specimens. The magnetic behavior of three compounds which were observed in the Eu_2O_3–$BaCO_3$–CuO system, Eu_2BaCuO_5, $Eu_3Ba_3Cu_6O_{13.5+x}$, and $BaCuO_{2+x}$ is also presented (*19*).

Experimental

Specimens were prepared by mixing appropriate molar proportions of Eu_2O_3 (99.9%, Research Chemicals, Phoenix, AZ), $BaCO_3$, NiO, Co_2O_3, and Al_2O_3 (reagent grade, J. T. Baker, Co., Phillipsburg, NJ), and CuO and ZnO (reagent grade, Mallinckrodt, St. Louis, MO). Specimens were mixed intimately by grinding in an agate mortar, placed in SiO_2 boats, and heated in a tube furnace in air for 24 hr at 950°C. The sintered materials were then reground in an agate mortar, annealed in a dynamic oxygen atmosphere at 900°C for 12 hr, and cooled to ambient temperature at a rate of 50°C hr^{-1}. The reaction products were analyzed by X-ray diffraction with Cu*K*α ($\lambda\alpha_1$ = 1.54050 Å) radiation in a 114.59-mm Guinier–Haegg camera. NBS-certified Si (a = 5.43082(3) Å) served as the internal standard; film measurements were effected with a modified Charles Supper reader. The programs ITO9 (*20*) and TREOR (*21*) were used for indexing the observed reflections. Lattice parameters were refined by the program APPLEMAN (*22*). All calculations were effected on a VAX 11/750 computer.

The magnetic susceptibility of comparably substituted phases was measured with a SHE SQUID magnetometer in a field of 0.1 kG over the temperature range 5–120 K. Specimens were formed into pellets ~3–5 mm thick in a hydraulic press under a pressure of ~30,000 psi and were held at fixed positions in contact with He in the SQUID. Transition temperatures, T_c (at $H = 0.1$ kG), were established by the onset of diamagnetic character in the susceptibility. Resistance measurements were made as a function of temperature on pressed pellets in a home-built four-probe device.

Results and Discussion

The mixed metal oxide phases, $EuBa_2Cu_{3-y}M_yO_{6.5+x}$ for M = Co, Ni, Al, and Zn, were synthesized in the form of black powders. Lattice parameters for selected compositions are presented in Table I. These phases are isostructural with the previously described oxide, $EuBa_2Cu_3O_{6.5+x}$ (*19*). The systems $EuBa_2Cu_{3-y}M_yO_{6.5+x}$ evidence solid solution only in the region $0 < y \leq 0.3$ for M = Ni, Zn, and Al, and $0 < y \leq 0.6$ for M = Co. Beyond these composition limits reflections indicative of a second phase appeared in the X-ray diffraction pattern.

The value of y for Ni substitution agrees reasonably well with the Ni solubility limit of $y = 0.5$ reported in (*17*) for $YBa_2Cu_{3-y}Ni_yO_{7-x}$, a value the authors indicate "may overestimate the upper limit of the nickel solubility." On the basis of M^{3+} ionic radii Co and Ni should behave similarly, so the great difference in their substitutability almost certainly relates to their very different crystal field stabilization and oxidation potential values.

The ionic radii of Co^{3+} and Ni^{3+} are spin dependent, with the high spin radius larger than the low spin value. Since site size is controlled principally by 0.71 Å (CN 4) or (CN 5) Cu^{2+} ions, the oxide field would probably be weak, and the M^{3+} ions high spin. However, in contrast to cobalt, nickel does not commonly exhibit a 3+ oxidation state in the solid state, particularly with oxide anions (*23*); nickel oxidizes more readily to the (CN 6) 4+ state (LS radius = 0.62 Å). Thus nickel is probably present either in the 2+, or much less likely, the 4+ oxidation state. Regardless of the ultimate oxidation state of Ni in the product, it must substitute into the lattice in the 2+ oxidation state where its size is approximately the same as that of Zn^{2+}. Thus zinc and nickel would be expected to exhibit similar solubilities, and they do. And because of the size mismatch between these ions and Cu^{2+} and Cu^{3+}, limited substitutability would be expected.

The reactant cobalt, on the other hand, is initially in the 3+ oxidation state and should substitute readily into the lattice with the extra oxide anions required for charge balance filling adjacent vacant anion sites. The cobalt will either remain in the 3+ oxidation state (its decomposition temperature of 895°C is below the initial 950°C heating temperature (*24*)), or will possibly decompose and then reoxidize when heated at 900° in pure oxygen. The absence of a significant volume change between the initial heated and after oxygen heated Co-substituted specimens (Table I) suggests that it remains in the 3+ oxidation state. If it indeed does remain in the 3+ oxidation state, only 0.4 of the 2.4 moles of Cu in the formula unit would need to oxidize to Cu^{3+} to achieve the ideal composition, $EuBa_2Cu^{II}_{2.0}Cu^{III}_{0.4}Co^{III}_{0.6}O_7$. By analogy to the oxygen analysis results on $YBa_2Cu_3O_{7-y}$ (*11*), and based upon the 0.3-Å^3 volume change ob-

TABLE I

LATTICE PARAMETERS, CELL VOLUME, AND INDEXING FIGURE-OF-MERIT DATA OF $EuBa_2Cu_3O_{6.5+x}$, $BaCuO_{2+x}$, AND $EuBa_2Cu_{3-y}M_yO_{6.5+x}$ (M = Ni, Zn, Co, Al) PHASES

Composition	Symmetry[a]	Lattice parameters[b] a (Å)	b (Å)	c (Å)	V (Å^3)	F.M.[c]	Remark[d]
$EuBa_2Cu_3O_{6.5+x}$	O	3.857(2)	3.900(2)	11.749(5)	176.7	36	i.h.
	O	3.840(2)	3.900(2)	11.712(4)	175.4	27	a.h.
	O	3.869(2)	3.879(3)	11.693(6)	175.5	—	(6)
$BaCuO_{2+x}$	O	9.924(5)	5.647(2)	4.745(2)	265.9	23	i.h.
	T	3.8634(3)		11.563(2)	172.6	176	a.h.
$EuBa_2Cu_{2.7}Ni_{0.3}O_{6.5+x}$	O	3.858(1)	3.901(1)	11.694(3)	176.0	43	i.h.
	T	3.900(2)		11.564(5)	175.9	18	i.h.
	O	3.8621(1)	3.898(1)	11.6773(3)	175.8	36	a.h.
	T	No solution			—	—	a.h.
$EuBa_2Cu_{2.7}Zn_{0.3}O_{6.5+x}$	O	3.886(2)	3.913(3)	11.719(5)	178.2	20	i.h.
	T	No solution			—	—	i.h.
	O	3.8957(9)	3.8960(8)	11.961(2)	177.4	11	a.h.
	T	3.8917(4)		11.697(1)	177.2	44	a.h.
$EuBa_2Cu_{2.7}Co_{0.3}O_{6.5+x}$	O	3.895(3)	3.898(3)	11.720(6)	177.9	26	i.h.
	T	3.8976(7)		11.713(2)	177.9	53	i.h.
	O	3.894(1)	3.899(1)	11.701(2)	177.6	40	a.h.
	T	3.8954(5)		11.705(1)	177.6	49	a.h.
$EuBa_2Cu_{2.4}Co_{0.6}O_{6.5+x}$	O	3.903(2)	3.916(2)	11.658(3)	178.2	14	i.h.
	T	3.9062(8)		11.680(4)	178.2	34	i.h.
	O	3.909(1)	3.902(2)	11.684(2)	178.2	30	a.h.
	T	No solution			—	—	a.h.
$EuBa_2Cu_{2.7}Al_{0.3}O_{6.5+x}$	O	3.883(2)	3.893(2)	11.722(3)	177.2	26	i.h.
	T	No solution			—	—	i.h.
	O	3.881(4)	3.893(5)	11.715(6)	177.1	15	a.h.
	T	No solution					a.h.

Note. In those cases in which the data could be indexed on both tetragonal and orthorhombic symmetry both solutions are presented.

[a] O, orthorhombic; T, tetragonal.

[b] The estimated standard deviations (in parentheses) refer to the last digit indicated.

[c] Figure-of-merit according to (*31*).

[d] i.h., initial heating; a.h., after heating in O_2.

served when $y = 0.3$ and the absence of a volume change when $y = 0.6$ (Table I), the likelihood of such limited oxidation seems probable.

The problem then is not so much the enhanced substitutability of Co^{3+}, but the absence of this level of substitution for comparably sized Al^{3+}. In contrast to Co(III), Al(III) exhibits numerous oxide phases (*25*). Thus, the absence of substitutability is probably related more to the greater stability of the Al^{3+} ion in other aluminum containing species, e.g., MAl_2O_4 phases, over that in the mixed Eu–Ba–Cu–Al–O phase than it is to size effects. In other words, as its concentration increases, Al(III) can achieve greater stability in MAl_2O_4 and related phases than it can in this quarternary compound.

The results reported herein and the above discussion are based on the assumption that these ions substitute at a copper site. X-ray powder diffraction intensity calculations indicate that the substitution site cannot be determined from powder diffraction intensities (*26*). However, a number of factors provide strong support for the proposed substitution mode. In a single-crystal study of $SmBa_2Cu_{2.79}Al_{0.21}O_{6.5}$, Siegrist *et al.* (*16*) established that Al substitutes for copper. Garbauskas *et al.* (*27*), from an analysis of X-ray single-crystal data, rejected the hypothesis that Cu substituted into the Y site at a level of 0.2 mole fraction, and indicated that substitution at any level is unlikely. Veal *et al.* (*28*) examined $YBa_{2-x}Sr_xCu_3O_{7-y}$ specimens as a function of x and determined that the unit cell volume decreased from 173.55 Å^3 at $x = 0.0$ to 169.21 Å^3 at $x = 1.0$. Miceli *et al.* (*29*) examined $YBa_2Cu_{3-x}Co_xO_{7-y}$ specimens by neutron diffraction and concluded that Co preferentially occupies the Cu(1) site. Tarascon *et al.* (*3*) and LePage *et al.* (*6*) determined the effect of different lanthanoids (*Ln*) on the unit cell volume of $LnBa_2Cu_3O_{7-y}$ and found a regular, but small volume decrease from 177.5 Å^3 for Ln = La to 171.4 Å^3 for Ln = Yb. In the present work the unit cell volumes either remain constant or *increase* slightly with increasing mole percentage of the substituted cation. Since the cations used in this work are smaller than either the lanthanoids or Sr, were they to substitute in either of these sites the unit cell volumes should decrease, not increase. Furthermore, if substitution were to occur at either the Eu or Ba site, reflections of other phases of these ions would probably be seen in the X-ray diffractograms.

When the initial content of the substituting element exceeded the limits outlined above, a mixture of oxides resulted. Reactants mixed in molar ratios designed to yield pure $EuBa_2Ni_3O_{6.5+x}$ and $EuBa_2Co_3O_{6.5+x}$ yielded mixtures of the initial oxides and $BaMO_{2-x}$-type phases (*30*).

Some of the powder X-ray diffractograms (Table I) could be interpreted on both tetragonal and orthorhombic symmetries with lattice parameters very close to those of the $EuBa_2Cu_3O_{6.5+x}$ modifications (*19*). In these cases both the tetragonal and the orthorhombic parameters are tabulated along with appropriate figure-of-merit values (*31*). These figure-of-merit (M_{20}) values are reported by the indexing programs and do not consider space group extinctions. Thus slight M_{20} differences such as the 40 and 49 (O vs T) values observed for the y = 0.3 Co-substituted species are probably insignificant, and the true symmetry cannot be ascertained from powder diffraction data alone. Other observed differences are larger and most likely significant. It thus appears that the 950°C oxygen treatment does not alter the orthorhombic symmetry of the Ni- or Al-substituted specimen, but does convert the initially orthorhombic Zn-substituted material to tetragonal symmetry, and the initially tetragonal $y = 0.6$ Co-substituted specimen to orthorhombic symmetry. They symmetry changes are assumed to be reflective of oxidation of some of the Cu^{2+} ions.

Lattice parameters of most of the products heated in oxygen refined to values slightly shorter than those of products heated only in air, but in no case was the cell volume change upon heating as great as that of the unsubstituted $EuBa_2Cu_3O_{6.5+x}$ phase. The shorter parameters presumably result from oxidation of some Cu^{2+} ions and their absence suggests that substitution inhibits oxidation of the copper. More detailed chemical analysis data are needed to verify this hypothesis. It is noteworthy that after being heated in oxygen only the Zn-substituted specimen retained the tetragonal modification over the orthorhombic form by a significant figure-of-merit edge (*31*). As discussed later, this material exhibited paramagnetic behavior at all temperatures. Siegrist *et al.* (*16*) found that Al substituted in $YBa_2Cu_{3-x}Al_xO_7$ over the range of $0 < x < 0.22$, a range relatively

TABLE II

OBSERVED MAGNETIC PROPERTIES OF SELECTED Eu-Ba-(Cu, *M*)-O COMPOUNDS (*M* = Ni, Cu, Zn, Co, AND Al) AND $BaCuO_{2+x}$ DETERMINED AT 0.1-kG AND 5 K AND TEMPERATURES AT WHICH MAGNETIC BEHAVIOR CHANGED FROM DIAMAGNETIC TO PARAMAGNETIC

Compound	Magnetic properties at 5 K		T_t
	Magnetism[a]	χ_M (emu/mole)	(K)
$EuBa_2Cu_3O_{6.5+x}$	s dia-	-83.12×10^{-1}	91.5
Eu_2BaCuO_5	m para-	2.67×10^{-2}	—
$Eu_3Ba_3Cu_6O_{13.5+x}$	s para-	85.58×10^{-2}	—
$BaCuO_{2+x}$	m dia-	-2.51×10^{-1}	82.5
$EuBa_2Cu_{2.7}Ni_{0.3}O_{6.5+x}$	m dia-	-8.45×10^{-1}	55.5
$EuBa_2Cu_{2.7}Zn_{0.3}O_{6.5+x}$	m para-	3.31×10^{-2}	—
$EuBa_2Cu_{2.7}Co_{0.3}O_{6.5+x}$	m dia-	-4.87×10^{-1}	26.0
$EuBa_2Cu_{2.7}Al_{0.3}O_{6.5+x}$	m dia-	-11.49×10^{-1}	52.5

[a] s, strong; m, medium.

close to that reported herein for the Eu analog.

The magnetic properties of selected compounds at 5 K are summarized in Table II. Only the Zn-substituted compound $EuBa_2Cu_{2.7}Zn_{0.3}O_{6.5+x}$ is paramagnetic at 5 K. This observation is consistent with that of Tarascon *et al.* (*17*) on $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_4$, which for $x > 0.05$ evidenced paramagnetic susceptibility and semiconductivity and Xiao *et al.* (*15*) on $YBa_2Cu_{2.7}Zn_{0.3}O_{6+y}$. The Eu_2BaCuO_5 and $Eu_3Ba_3Cu_6O_{13.5+x}$ phases also have positive magnetic moments. In Fig. 1 the temperature dependence of the magnetic susceptibility of representative samples is presented. The *M*-substituted phases $EuBa_2Cu_{2.7}M_{0.3}O_{6.5+x}$, where *M* = Co, Ni, and Al are superconducting. Our transition temperatures, T_c, for Co- and Ni-substituted $YBa_2Cu_{2.7}M_{0.3}O_{6.5+x}$, 26 and 55.5 K, respectively, compare favorably with those reported by Xiao *et al.* (*15*), 21.2 and 66.3 K. Our transition temperature for the Al-substituted phase is 52.5 K. The ef-

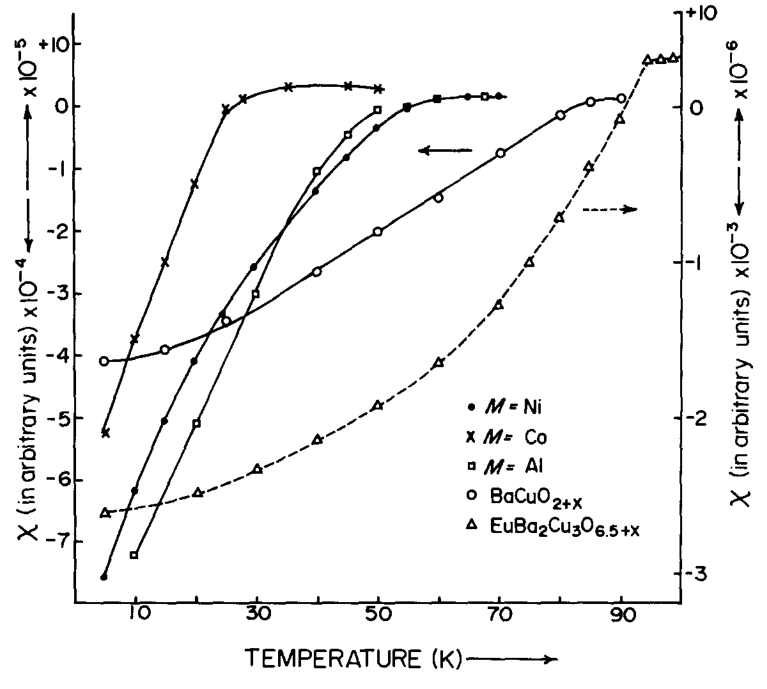

FIG. 1. A plot of the magnetic susceptibility (in arbitrary units) vs temperature for $EuBa_2Cu_3O_{6.5+x}$, $BaCuO_{2+x}$, and $EuBa_2Cu_{2.7}M_{0.3}O_{6.5+x}$ (*M* = Ni, Co, and Al) in a 0.1-kG field. The right ordinate applies only to the $EuBa_2Cu_3O_{6.5+x}$ graph. Note that the scale multiplication factor changes at zero.

fect of Ni substitution on the superconductivity of $La_{1.85}Sr_{0.15}CuO_4$ is discussed in (*32*); the same mechanism probably prevails here. The pure, superconducting $EuBa_2Cu_3O_{6.5+x}$ phase evidences a transition at 91.5 K, in good agreement with the literature value (*33*).

The tetragonal modification (see Table I and Fig. 1) of $BaCuO_{2+x}$ exhibited a magnetic susceptibility behavior that at first glance appears akin to that of the "123" compound, suggestive that it might exhibit superconductivity. Its resistivity was consequently measured as a function of temperature; it is a semiconductor. Even though its behavior is not identical to that of the typical superconducting phases, the similarities suggest that systematic studies on the crystallographic and magnetic properties of substituted $BaCuO_{2+x}$ oxides as a function of x might be worthwhile.

In summary, Ni, Co, Zn, and Al ions substitute presumably for Cu only to a limited extent, and attempts to completely replace the Cu and retain the same structure were unsuccessful. As substitution occurs, the tetragonal phase becomes stabilized, and the superconducting transition temperature decreases sharply. These observations suggest that the size of the substituting cation is of minor importance in determining whether or not superconductivity occurs and they support the hypothesis that the electron energy levels associated with the different Cu states are critical for superconducting behavior.

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