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Superconducting and Nonsuperconducting Analogs of $Bi_2Sr_2CaCu_2O_8$: The Role of Electronegativity

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The following new solid solution series possessing the structure of the superconducting oxide with an ideal formula $Bi_2Sr_2CaCu_2O_8$ have been characterized: $Bi_{2-x}M_xSr_{3-x}Y_xCu_2O_8$ (M = Pb, Cd), $Bi_{2-x}Pb_xSr_2Ca_{1-x}Y_xCu_2O_8$, and $Bi_2Sr_{3-2x}Na_xY_xCu_2O_8$. While the phase exists over a wide composition range in each series, superconductivity arises only over a limited range. The results are interpreted on the basis of a correlation between electronegativity and charge carrier concentration in the superconducting copper oxides.

Introduction

$Bi_2Sr_2CaCu_2O_8$ is the prototype example of a new family of copper oxide superconductors based on bismuth (*1*, *2*) or thallium (*3*, *4*). The new superconductors contain CuO_2 sheets but not Cu–O chains. The charge carriers (holes) are presumably related to cation deficiencies (*5*) on the Bi and/or Sr sites but may also be influenced by interstitial oxygens. Synthesis of isostructural phases where Bi/Tl and the alkaline earth metals are substituted by other cations of similar size and chemistry is important toward understanding the mechanism of superconductivity in these oxides. Substitution of Sr/Ca by Y or similar rare earths in $Bi_2Sr_2CaCu_2O_8$ which reveals the existence of an insulator–superconductor boundary has already been reported. This in turn indicates that the charge carriers do not arise from overlap of the Bi 6*p* band with the Fermi level (*6*–*8*). We report here on the simultaneous substitutions for Bi by Pb/Cd, and for Sr/Ca by Y or Y and Na, in the $Bi_2Sr_2CaCu_2O_8$ structure, yielding superconducting and nonsuperconducting analogs of the parent oxide. On the basis of the results, we suggest that the occurrence of superconductivity in copper oxides may be correlated with the average electronegativity of all atoms except Cu in the compound.

Experimental

The compounds were synthesized by heating appropriate mixtures of reactants (Bi_2O_3, PbO_2, CdO, SrO_2, CaO_2, Y_2O_3, $NaNO_3$, CuO) at 850 to 900°C for 12–24 hr.

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Purity of the phases was checked by powder X-ray diffraction data using a SCINTAG (PAD IV) automated powder diffractometer. Lattice parameters were derived from the powder diffraction data of single phases. The Cu^{III} content was analyzed by titrimetry (*9*). Superconducting transition temperatures were determined by magnetic flux exclusion measurements.

Results and Discussion

We have investigated substitution for Bi and Sr/Ca in $Bi_2Sr_2CaCu_2O_8$ by other cations of similar crystal chemical properties. We have succeeded in replacing Sr/Ca by equal amounts of Na and Y yielding a new series, $Bi_2Sr_{3-2x}Na_xY_xCu_2O_8$, where phases isostructural with $Bi_2Sr_2CaCu_2O_8$ exist for $0.2 < x < 1.0$ (Table I). Considering that the radii of Na^+ and Y^{3+} (1.16 and 1.015 Å in 8-coordination) are similar to the radius of Ca^{2+} (1.12 Å) (*10*), it is most likely that Na^+ and Y^{3+} substituted for Ca^{2+} in $Bi_2Sr_2CaCu_2O_8$. The Na–Y substituted phases are superconducting ($T_c \sim 70$–77 K) in the limited composition range $0.2 < x < 0.3$.

We have been able to make simultaneous substitution for Bi by Pb, and for Ca by Y in $Bi_2Sr_2CaCu_2O_8$, yielding the new series $Bi_{2-x}Pb_xSr_{3-x}Y_xCu_2O_8$. The phases are isostructural with $Bi_2Sr_2CaCu_2O_8$ in the composition range $0.25 < x < 1.0$ (Table I). The $x = 1$ member, $BiPbSr_2YCu_2O_8$, is insulating with a room-temperature resistivity of $\sim 10^3$ ohm-cm. A single-crystal X-ray diffraction study (*11*) of this compound has shown that it is isostructural with $Bi_2Sr_2CaCu_2O_8$ consisting of double CuO_2 sheets and double $BiPbO_2$ sheets. Chemical analysis shows a small quantity of a higher oxidation state for the cations, equivalent to about 5% Cu^{III} of the total copper in this compound. Assuming the most probable oxida-

TABLE I

COMPOSITION, LATTICE PARAMETERS,[a] AND SUPERCONDUCTING TRANSITION TEMPERATURE (T_c) OF ANALOGS OF $Bi_2Sr_2CaCu_2O_8$

Composition	*a* (Å)	*b* (Å)	*c* (Å)	T_c (K)	%Cu^{III}
$Bi_2SrNaYCu_2O_8$	5.360	5.394	30.20	n.s[b]	8
$Bi_2Sr_2Na_{0.5}Y_{0.5}Cu_2O_8$	5.390	5.420	30.10	n.s	14
$Bi_2Sr_{2.4}Na_{0.3}Y_{0.3}Cu_2O_8$	5.395	5.433	30.04	70	—
$Bi_2Sr_{2.5}Na_{0.25}Y_{0.25}Cu_2O_8$	5.391	5.430	30.32	70	23
$Bi_2Sr_{2.6}Na_{0.2}Y_{0.2}Cu_2O_8$	5.395	5.435	30.02	77	26
$BiPbSr_2YCu_2O_8$	5.369	5.422	30.32	n.s	5
$Bi_{1.25}Pb_{0.75}Sr_{2.25}Y_{0.75}Cu_2O_8$	5.383	5.426	30.37	n.s	16
$Bi_{1.5}Pb_{0.5}Sr_{2.5}Y_{0.5}Cu_2O_8$	5.415	5.425	30.60	70	26
$Bi_{1.75}Pb_{0.25}Sr_{2.75}Y_{0.25}Cu_2O_8$[c]	5.428	5.428	30.70	70	30
$BiCdSr_2YCu_2O_8$	5.425	5.425	30.22	n.s	—
$Bi_{1.25}Cd_{0.75}Sr_{2.25}Y_{0.75}Cu_2O_8$	5.426	5.428	30.28	n.s	—
$Bi_{1.5}Cd_{0.5}Sr_{2.5}Y_{0.5}Cu_2O_8$	5.430	5.432	30.48	68	—
$Bi_{1.75}Cd_{0.25}Sr_{2.75}Y_{0.25}Cu_2O_8$[c]	5.432	5.434	30.65	70	—
$Bi_{1.25}Pb_{0.75}Sr_2Y_{0.75}Ca_{0.25}Cu_2O_8$	5.372	3.410	30.34	n.s	15
$Bi_{1.5}Pb_{0.5}Sr_2Y_{0.5}Ca_{0.5}Cu_2O_8$	5.397	5.399	30.53	85	27
$Bi_{1.75}Pb_{0.25}Sr_2Y_{0.25}Ca_{0.75}Cu_2O_8$	5.389	5.390	30.60	86	29

[a] Last-digit uncertainty in *a* and *b* parameters is <5 and in the *c* parameter it is ~1.

[b] Nonsuperconducting above 4.2 K.

[c] $Bi_2Sr_2CuO_6$ is present as an impurity.

tion states, the ideal ionic formula for this oxide would be $Bi^{3+}Pb^{2+}Sr_2^{2+}YCu_2^{2+}O_8^{2-}$; all members in the series should remain insulating. By contrast, phases in the series become increasingly conducting with decreasing x; they are superconducting for x = 0.25–0.50, with $T_c \sim 70$ K. Chemical analysis shows a considerable amount of a higher oxidation state for the cations in the superconducting phases. Again, attributing the higher oxidation state entirely to copper, 25–30% of total copper would be in the III state (Table I). Similar results are obtained for the $Bi_{2-x}Cd_xSr_{3-x}Y_xCu_2O_8$ and $Bi_{2-x}Pb_xSr_2Ca_{1-x}Y_xCu_2O_8$ series.

A common pattern emerging from the present work is that although phases isostructural with $Bi_2Sr_2CaCu_2O_8$ can be prepared in a number of systems over a wide composition range by suitable choice of cations, superconductivity is restricted to a narrow composition range in each system. In the superconducting compositions, the presence of a considerable amount of Cu^{III} (hole concentration) is indicated by chemical analysis. The occurrence of superconducting and nonsuperconducting analogs of $Bi_2Sr_2CaCu_2O_8$ indicates that while the formation of phases with the $Bi_2Sr_2CaCu_2O_8$ structure is determined by crystal chemical considerations, creation of charge carriers (holes) and hence, superconductivity, are determined by an atomic property other than ionic size. We suggest that a low-average electronegativity of the atoms in a phase enhances the formal trivalent oxidation state of copper and hence, the hole concentration, which, however, must presumably be accompanied by suitable point defects. Our suggestion is based on the fact that strongly electropositive cations generally stabilize higher formal oxidation states for transition elements (*12*). In order to correlate electronegativity with superconductivity, we define an average electronegativity parameter

$$\chi_{av} = \Sigma\chi_i/n,$$

where χ_i is the Pauling electronegativity of the ith atom and n is the number of atoms in the phase excepting copper. Note that we exclude copper atoms in the calculation of χ_{av}. When we plot χ_{av} vs T_c for a number of copper oxides (Fig. 1), we find that superconducting phases lie in the narrow range $2.64 < \chi_{av} < 2.66$. More interestingly, the T_c dependence on χ_{av} is nearly linear in this range. It is significant that $\chi_{av} > 2.66$ for divalent Cu oxides and $\chi_{av} < 2.64$ for trivalent copper oxides. La_2CuO_4 ($\chi_{av} \sim 2.66$) is unique, lying on the borderline; accordingly, it can be rendered superconducting by suitable generation of holes through substitution of La by lower-valent electropositive cations such as Ba, Sr, or Na. Substitution for La in La_2CuO_4 by less electropositive cations, Pb^{II} or Cd^{II}, does not, however, lead to superconductivity (*13*). The other R_2CuO_4 oxides (R = Pr, Nd, Sm, Eu, Gd) possess the right kind of structure with CuO_2 sheets; they cannot be made metallic through p-type doping possibly because $\chi_{av} > 2.66$ for these compounds.

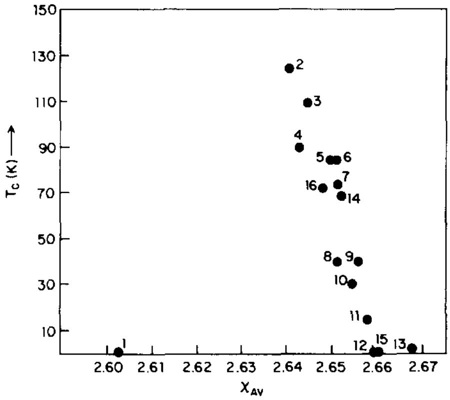

FIG. 1. Plot of χ_{av} vs T_c for copper oxides: (1) $NaCuO_2$; (2) $Tl_2Ba_2Ca_2Cu_3O_{10}$; (3) $Tl_2Ba_2CaCu_2O_8$; (4) $YBa_2Cu_3O_7$; (5) $Tl_2Ba_2CuO_6$; (6) $Bi_2Sr_2CaCu_2O_8$; (7) $Bi_2Sr_{2.5}Na_{0.25}Y_{0.25}Cu_2O_8$; (8) $La_{1.7}Na_{0.3}CuO_4$; (9) $La_{1.85}Sr_{0.15}CuO_4$; (10) $La_{1.85}Ba_{0.15}CuO_4$; (11) $Bi_2Sr_2CuO_6$; (12) La_2CuO_4; (13) $Bi_2Sr_2YCu_2O_8$; (14) $Bi_2Sr_{2.6}Y_{0.4}Cu_2O_8$; (15) $BiPbSr_2YCu_2O_8$; (16) $Bi_{1.5}Pb_{0.5}Sr_{2.5}Y_{0.5}Cu_2O_8$. For definition of χ_{av}, see text. In the calculation of χ_{av} for $YBa_2Cu_3O_7$ only two Cu atoms were excluded.

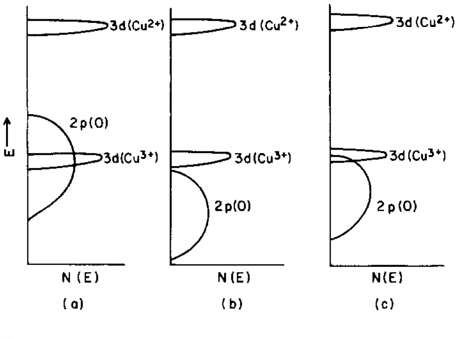

FIG. 2. Schematic energy-level diagram for (a) $Cu^{II}O$, (b) $NaCu^{III}O_2$, and (c) a mixed-valent Cu^{II}–Cu^{III} oxide, e.g., $La_{1.85}Sr_{0.15}CuO_4$.

However, *n*-type doping succeeds (*14*) since there is no need to stabilize Cu^{III}.

The correlation between electronegativity and superconductivity may be understood qualitatively on the basis of a schematic energy-level diagram for copper oxides (Fig. 2). It is generally accepted that superconductivity in copper oxides requires, among other factors, the following: (i) a structure consisting of CuO_2 sheets formed by corner connections of square planar CuO_4 units and (ii) a formal valency of copper which on average must be just above or below 2. Given the right kind of structure, electronegativity seems to be important in stabilizing Cu^{II}/Cu^{III} or Cu^{II}/Cu^{I}. In the absence of electropositive cations, the only accessible oxidation states for copper in the binary Cu–O system are I and II (Fig. 2a). In the presence of strongly electropositive elements such as Na, K, etc., the O(2*p*) states are so much stabilized that Cu^{III} becomes accessible; thus stable trivalent copper oxides such as $NaCuO_2$ and $KCuO_2$ are readily formed (Fig. 2b). For such compositions χ_{av} is less than 2.64. Photoelectron spectroscopy shows the presence of Cu^{III} in such oxides (*15*). When χ_{av} is in the range 2.64–2.66, it is likely that the energy of the 3*d*-manifold of Cu^{III} lies just above the energy of O(2*p*) (Fig. 2c). In such a case, both copper and oxygen would probably be present in a mixed oxidation state. However, the holes created would be localized neither on Cu(3*d*) nor on O(2*p*) because of the strong covalent mixing between them. This indeed appears to be the case with all superconducting oxides.

In summary, the present work shows that phases analogous to $Bi_2Sr_2CaCu_2O_8$ exist in the Bi–Pb–Sr–Y–Cu–O, Bi–Pb–Sr–Ca–Y–Cu–O, Bi–Cd–Sr–Y–Cu–O, and Bi–Sr–Na–Y–Cu–O systems. While the phase exists over a wide composition range, superconductivity is restricted to a narrow range in each system. A correlation between average electronegativity and superconductivity seems to exist in copper oxides. Further work is necessary to render this correlation quantitative.

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