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Superconductor-to-Insulator Transition in the $Bi_2Sr_{3-x}Y_xCu_2O_{8+y}$ System

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The compositions $Bi_2Sr_{3-x}Y_xCu_2O_8$ have been prepared with the structure of superconducting $Bi_2Sr_{3-x}Ca_xCu_2O_8$. The range of x in $Bi_2Sr_{3-x}Y_xCu_2O_8$ is roughly 0.2 to 1.0 and chemical analysis shows that the Cu^{III} concentration increases with decreasing x. The compositions are superconducting ($T_c \sim$ 65–72 K) for $x = \sim 0.2$ to 0.4. Insulating behavior is observed in the region from $x = 0.5$ to 1.0. This insulating region would not be expected if the Bi 6p band overlapped the Fermi level, as indicated by recent band structure calculations for $Bi_2Sr_2CaCu_2O_8$. © 1988 Academic Press, Inc.

Introduction

The occurrence of superconductivity adjacent to a metal–insulator boundary is an established feature of many systems as the composition is varied. For oxides, insulator-to-superconductor transitions occur as function of x in the system $SrTiO_{3-x}$ (*1*), A_xWO_3 (*2*), $La_{2-x}A_xCuO_4$ (*3*), and $YBa_2Cu_3O_{6+x}$ (*4*). Superconductivity at highest temperatures is found in the systems $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (*5, 6*), $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ (*7*), and $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ (*8, 9*) where n ranges from 1 to 3 in bulk phases. We report here on an $n = 2$ system of the $Bi_2Sr_2CaCu_2O_8$ type, which shows an insulator-to-superconductor transition as the composition is varied. Similar behavior has been reported for $Bi_2(Sr,Ca)_{3-x}Y_xCu_2O_8$ systems (*10, 11*).

Experimental

The compounds were synthesized by reacting Bi_2O_3, SrO_2, Y_2O_3, and CuO in stoichiometric ratios at 900°C for 12 to 24 hr. Purity of the phases was checked by powder X-ray diffraction data using a SCINTAG (PAD IV) automated powder diffractometer. The Cu^{3+} content was analyzed by titrimetry. Superconducting transition temperatures were determined by magnetic flux exclusion measurements.

Results

The range of x in the $Bi_2Sr_{3-x}Y_xCu_2O_8$ system was determined from X-ray diffraction data. The a, b, and c lattice parameters varied smoothly form $x = \sim 0.2$ to 1.0 (Fig. 1). Outside this range, impurity phases

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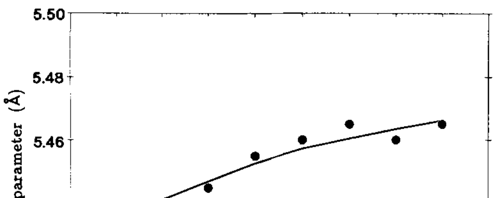

FIG. 1. (Top) Variation of a (average a and b) lattice parameter as a function of x for $Bi_2Sr_{3-x}Y_xCu_2O_{8+y}$. (Bottom) Variation of c lattice parameter as a function of x for $Bi_2Sr_{3-x}Y_xCu_2O_{8+y}$.

were detected in addition to the $n = 2$ phase. The c axis decreases with increasing x, as might be expected, since Y^{3+} is smaller than Sr^{2+}. However, there is an increase in the a axis with increasing x which can be attributed to the decrease in the copper oxidation state which leads to longer Cu–O distances within the copper oxygen sheets. Compositions are superconducting for $x = \sim 0.2$ to 0.4 ($T_c \sim$ 65–72 K). Chemical analysis indicated a substantial Cu^{III} concentration for superconducting compositions such as $Bi_2Sr_{1.7}Y_{0.3}Cu_2O_8$. However, the Cu^{III} concentration decreases sharply with increasing concentration of Y (Fig. 2). The decrease in Cu^{III} concentration also results in loss of superconductivity and in a change to insulating behavior. Electrical resistivity measurements on pressed powders indicate that for $x = 0.5$ to 1.0 the compounds are semiconductors; as x increases the room temperature resistivity also increases.

Discussion

$Bi_2Sr_{3-x}Ca_xCu_2O_8$ phases are known over a range of x that does not include $x = 0$ (*6*). The nonexistence of $Bi_2Sr_3Cu_2O_8$ apparently arises because the cation site between the adjacent CuO_2 layers requires a relatively small cation such as Ca^{2+}. Although some substitution of Ca^{2+} by Sr^{2+} occurs, complete substitution is unknown in any of these layered copper oxides, including the $n = \infty$ member, (Sr,Ca)CuO_2 (*12*). However, Y^{3+} is smaller than Sr^{2+}, and thus Y^{3+} can serve to decrease the average size of the cation between the adjacent CuO_2 layers.

An understanding of the $Bi_2Sr_{3-x}Y_xCu_2O_8$ systems is complicated by our lack of understanding of the $Bi_2Sr_{3-x}Ca_xCu_2O_8$ system where there are interrelated unresolved compositional and structural issues. Written as $Bi_2Sr_{3-x}Ca_xCu_2O_8$, no Cu^{III} would be present in this compound. This would seem

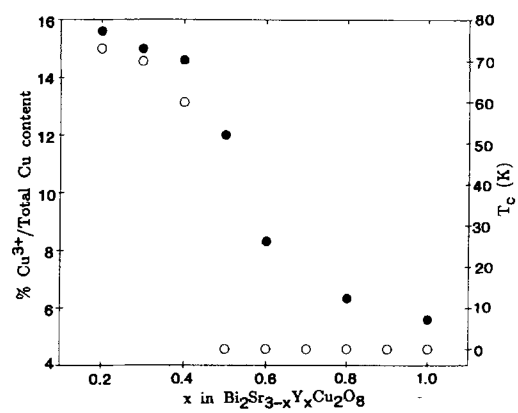

FIG. 2. Variation of Cu^{3+} content (filled circles) and T_c (open circles) as a function of x for $Bi_2Sr_{3-x}Y_xCu_2O_{8+y}$.

inconsistent with the observed superconductivity; furthermore, chemical analysis shows a significant Cu^{III} content (*6*). The defect giving rise to Cu^{III} might be oxygen interstitials, but current evidence suggests that Cu^{III} is probably present even without such interstitials. Structural refinements show that there is no significant oxygen content between the adjacent CuO_2 layers (*6*). There is evidence for oxygen between the adjacent Bi–O layers in certain preparations (*13*). However, this interstitial oxygen causes a decrease in T_c and presumably results in oxidation of Bi^{III} to Bi^{V} rather than of Cu^{II} to Cu^{III}. Another defect mechanism for producing Cu^{III} would be cation vacancies on the Sr^{2+} site. Some microprobe data appear to support the possibility (*14*), but recent crystallographic results (*15*) indicate that a deficiency of Bi^{3+} is more likely than a deficiency of A^{2+} cations. The suggestion that Bi^{3+} might substitute for Ca^{2+} between adjacent CuO_2 layers adds a further complication since this would push the average oxidation state of copper below 2.

Given the evidence for Cu^{III}, the $Bi_2Sr_{3-x}Ca_xCu_2O_8$ and $Bi_2Sr_{3-x}Y_xCu_2O_8$ formulations must be regarded as idealized. Whatever the cause for Cu^{III}, the substitution of Y^{3+} for A^{2+} should result in a decreased average oxidation state for copper. In fact a decreased Cu^{III} content is observed both for the $Bi_2Sr_{3-x}Cu_2O_8$ and $Bi_2(Sr,Ca)_{3-x}Y_xCu_2O_8$ systems (*10, 11*). For the $Bi_2Sr_2YCu_2O_8$ end member one might expect the presence of some Cu^{I}. We have XANES experiments underway on $Bi_2Sr_2YCu_2O_8$ to search for Cu^{I}.

Another suggestion based on band structure calculations (*16*) is that the Cu^{III} content in $Bi_2Sr_2CaCu_2O_8$ results from an overlap of the Bi 6*p* band with the Cu $d_{x^2-y^2}$–O $2p\sigma$ band at the Fermi level. This proposal makes little sense on chemical grounds since it would be akin to oxidation of Cu^{II} by Bi^{III}. The band structure calculations are misleading because they are based on an idealized structure whose Bi–O distances differ widely from the real structure. In an oxidized system, the Bi 6*p* band is expected to lie well above the Fermi level. The insulating regions in the $Bi_2(Sr,Ca)_{3-x}Y_xCu_2O_8$ systems furnish further proof that the Bi 6*p* band does not overlap the Fermi level.

A metal–insulator boundary has now been found in the systems $La_{2-x}A_xCuO_4$, $YBa_2Cu_3O_{6+x}$, and $Bi_2Sr_{3-x}Y_xCu_2O_8$. In the former two systems, it has been shown that the insulating state is associated with antiferromagnetism (*17, 18*). Recent muon spin resonance studies have shown that $Bi_2Sr_2YCu_2O_8$ is also antiferromagnetic with a Néel temperature of about 210 K (*19*). Thus in these three systems, long-range magnetic order is apparently destroyed through Cu^{III} doping before superconductivity can arise.

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