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LETTERS TO THE EDITOR

The Synthesis, by Triethylammoniumoxalate Coprecipitation, and Superconducting Properties of $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$

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Superconductivity has been investigated in the system $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ ($0 \leq x \leq 0.5$). The samples were prepared by triethylammoniaoxalate coprecipitation at ambient oxygen pressure. The superconducting transition temperature, T_c, increased from a value of 85 K ($x = 0$) to 90 K ($x = 0.1$–0.2) and then decreased to 64 K at $x = 0.5$. For compositions beyond the solubility limit ($x = 0.3$), the magnitude of dT_c/dx was high, ca. 45 K from 0.3 to 0.5. The maximum T_c, 90 K, recorded from samples in the range $x = 0.1 \sim 0.2$, were confirmed by magnetization measurements. These results are in contrast to those obtained from the $Y(Ba_{1-x}Sr_x)_2Cu_3O_7$ system, in which T_c decreased monotonically from 93 to 82 K for $0 \leq x \leq 0.5$. © 1991 Academic Press, Inc.

1. Introduction

The enhancement of the superconducting transition temperature, T_c, from 83 to 91 K by the partial substitution of 10% Ca for Y in the $YBa_2Cu_4O_8$ compound (hereafter referred to as 124) was first reported by Miyatake *et al.* (*1*) and confirmed by several groups (*2, 3*). These observations were generally explained on the basis of an increase in the hole concentration in the CuO_2 plane sites, due to the substitution of Y^{3+} by Ca^{2+}. However, this conclusion has recently been questioned by Mangelschots *et al.* (*4*) using Cu nuclear quadrupole resonance (NQR) measurements. These authors suggest that a majority of Ca ions would substitute preferentially at the Ba sites in 124, rather than at the Y location. If this assertion is correct, the observed increase of T_c by Ca doping cannot be simply explained by an increase of the hole concentration. An alternative mechanism, namely the "chemical pressure" effect, may arise from the substitution of Ca^{2+} ions into Ba^{2+} sites and this may play a very important role in enhancement of the T_c in $YBa_2Cu_4O_8$. Moreover, the 124 phase has the highest reported pressure dependence of T_c (*5, 6*) among the high temperature superconducting cuprates. Therefore, we felt it was worthwhile to study the effects of partial substitution of Sr for Ba in the 124 compound.

Here, we use triethylammoniumoxalate coprecipitation at ambient pressure to prepare the solid solution $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$

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($0 \leq x \leq 0.3$). Our results are compared with those reported by Wada *et al.* (*7*) who have synthesized the corresponding compounds by means of a high-oxygen-pressure technique using O_2 hot isostatic pressing (HIP). Moreover, the possible effects of Sr substitution of Ba in $YBa_2Cu_4O_8$ and $YBa_2Cu_3O_7$ are also discussed.

2. Experimental

Stoichiometric amounts of high purity $Y(NO_3)_3 \cdot nH_2O$ (n = 4–6), $Ba(NO_3)_2$, $Sr(NO_3)_2$, and $Cu(NO_3)_2 \cdot 6H_2O$ powders (Merck AG) with a cationic molar ratio of Y : Ba : Sr : Cu = $1 : 2(1-x) : 2x : 4$ (using 0.005 mole of Y^{3+} and x = 0, 0.1, 0.2, 0.3, 0.4, and 0.5) were dissolved in distilled/deionized water. An aqueous solution of oxalic acid (as a precipitant) and triethylamine (as a base) was prepared by mixing 0.025 mole of oxalic acid and 25 ml of triethylamine in 10 ml of water. The solution of the metal nitrate salts was added dropwise into the oxalic acid/triethylamine solution with vigorous stirring. During the mixing, pale blue coprecipitates formed rapidly. The solution was then cooled, with stirring, in an iced-water bath. At this stage, the solution pH reached a value in the region of 9.3 ~ 11.3 and all the metal ions could be nearly completely precipitated from the solution. This was confirmed by the analysis of the various coprecipitates using inductively coupled plasma atomic emission spectroscopic (ICP-AES; Plasmakon S35). After separation of the coprecipitate and filtrate, the former was dried at 120°C in air for 10 hr. The dried powders were then calcined at 700°C in air for 10 hr to eliminate any organic components. The resulting fine black powder was pressed into a pellet and sintered at 830°C in flowing oxygen for 3 days. The sintered samples were then quenched in air.

The structure of the sintered powders was determined on an X-ray diffractometer (XRD) using Cu*Kα* radiation. Chemical compositions of the specimens were examined by energy dispersive X-ray spectrometry (EDS) from a JEM-200CX electron microscope operating at 200 kV. Molybdenum specimen grids were used and background spectra were used to ensure that no copper signals were detected from the sample free area. Bar-shaped samples (1.5 × 2 × 10 mm) were cut from the sintered pellets and used for standard four-point resistivity measurements. Low field magnetization data were taken in an automatic superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

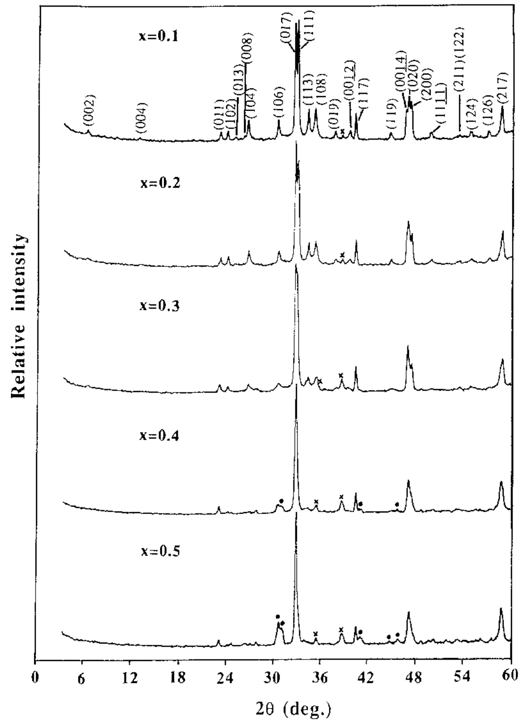

FIG. 1. Powder X-ray diffraction patterns of the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples with x = 0.1, 0.2, 0.3, 0.4, and 0.5. Unidentified and CuO impurities are denoted by ● and ×, respectively.

3. Results and Discussions

In Fig. 1 we show the powder X-ray diffraction patterns of the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$

samples with $x = 0.1, 0.2, 0.3, 0.4$, and 0.5. The samples with $0 \leq x \leq 0.3$ were nearly single phase except a small amount of CuO impurity. When $x \geq 0.4$, unidentified impurities other than CuO were apparent, which indicated that the Sr solubility limit in the 124 phase was around $x = 0.3$ based on our preparation conditions (Section 2). This solubility range may be increased up to 0.4 for preparations under high oxygen pressure and temperature (1000°C) (*7*). A reduction in the lattice parameters (*a*, *b*, and *c*) with an increase in x was observed in our investigations; these findings are similar to those reported by Wada *et al.* (*7*). This change in lattice parameters is most probably due to the substitution of the smaller Sr ion (1.13 Å) into the Ba site (1.35 Å).

Two samples ($x = 0$ and 0.1) were chosen for analysis of their chemical compositions by EDS. Twenty small crystallites from each sample were examined; the average cation ratios for both samples deviated less than 10% from their nominal compositions. Typical energy spectra for both samples are shown in Fig. 2. It is worth pointing out that XRD as well as EDS results rule out the presence of any $YBa_2Cu_3O_7$ phase in our samples.

In Fig. 3 we show the temperature dependence of the normalized resistance of the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples with $x = 0, 0.1, 0.2, 0.3, 0.4$, and 0.5. In the homogenity range of Sr substitution ($0 \leq x \leq 0.3$), all the samples have a metallic behavior in their normal state with room temperature resistivities at the range of 2–4 mΩ cm. In contrast, samples with nominal compositions above the solubility limit ($x \geq 0.4$) have semiconducting behavior in their normal state, concomitant with the higher values of the room temperature resistivities, i.e., 8.4 mΩ cm for $x = 0.4$ and 35.8 mΩ cm for $x = 0.5$. The enhanced normal state resistivities for $x = 0.4$ and 0.5 may arise from the presence of impurity phases (Fig. 1). The $T_{c(\mathrm{onset})}$ for the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ system was at a maximum (90 K) for $x = 0.1$ and 0.2. For compositions $x \geq 0.4$, a significant reduction in T_c was observed from our resistance measurements.

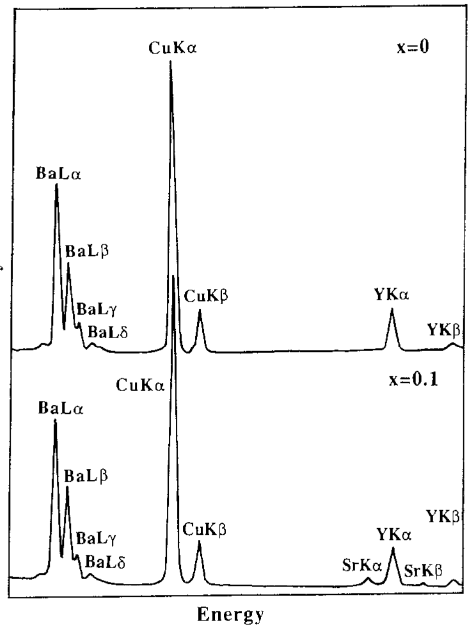

FIG. 2. Typical energy dispersive spectra of $x = 0$ and 0.1 in $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$.

In Fig. 4 we show the temperature dependence of the low field magnetization (5 Oe, field-cooled) of the powder samples having composition $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$. For compositions $0 \leq x \leq 0.3$ the superconducting volume fraction (as gauged from the magnetization measurements, Fig. 4) increased with an increase in x. This result is in contrast to that reported by Wada *et al.* (*7*). A possible reason may be the enhanced homogeneity of the fine powders (average particle size about 0.5 μm) in our chemical coprecipitation samples, as compared with those prepared by solid state reaction. For samples with nominal compositions beyond the solubility limit ($x \geq 0.4$), the superconducting volume fraction was observed to decrease with an increase in Sr content. From the inset of Fig. 4, the diamagnetic signals

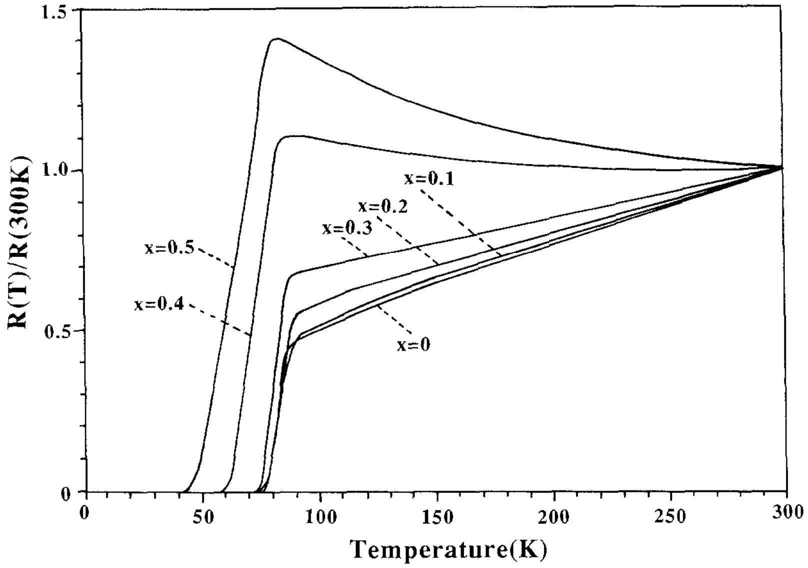

FIG. 3. Temperature dependence of normalized resistance of the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples with x = 0, 0.1, 0.2, 0.3, 0.4, and 0.5.

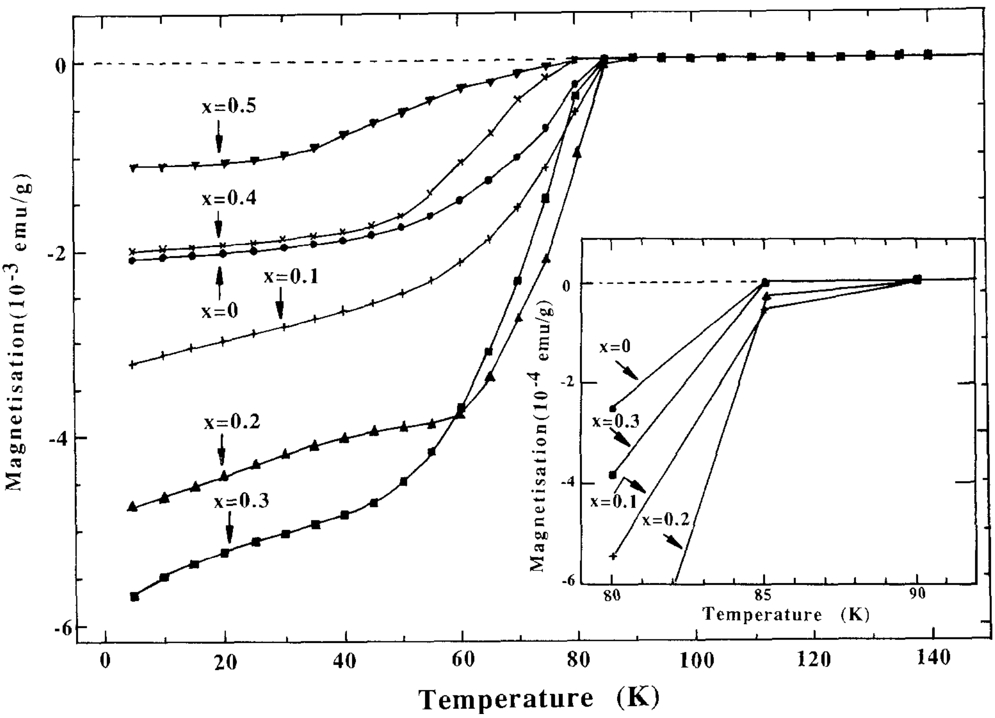

FIG. 4. Temperature dependence of low field magnetization (5 Oe, field-cooled) of the powder samples having composition $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$.

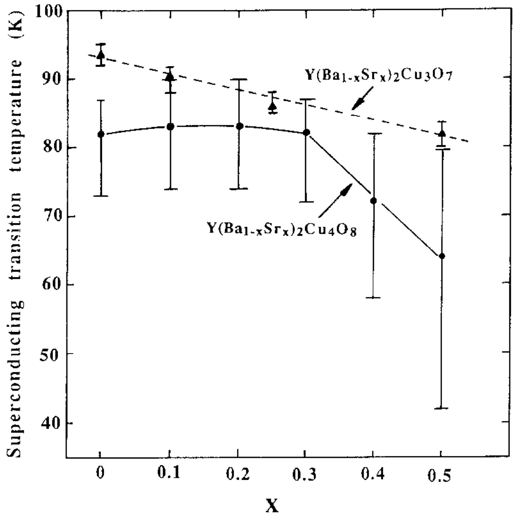

FIG. 5. Superconducting transition temperature, T_c, as a function of Sr content, x, in $Y(Ba_{1-x}Sr_x)_2Cu_3O_7$ and $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$, obtained from Ref. (*8*) and Fig. 3, respectively. The error bars in T_c represent the limiting values for $T_{c(onset)}$, $T_{c(midpoint)}$, and $T_{c(zero)}$.

appeared at 90 K for $x = 0.1$ and 0.2 and 85 K for $x = 0$ samples; these values are consistent with the onset of superconductivity obtained from the electrical resistivity measurements.

In Fig. 5, we show the superconducting transition temperature as a function of Sr content, x, in $Y(Ba_{1-x}Sr_x)_2Cu_3O_7$ and $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ which are derived from Ref. (*8*) and Fig. 3. In the $Y(Ba_{1-x}Sr_x)_2Cu_3O_7$ system, T_c was observed to decrease monotonically from 93 to 82 K with an increasing Sr content up to its maximum solubility limit, $x = 0.5$ (*8*). In contrast, the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ system has a T_c which is nearly constant with compositions up to $x = 0.3$; a small, but reproducible, maximum occurs in the range $x = 0.1 \sim 0.2$. With an increasing Sr content ($x \geq 0.4$), T_c was observed to decrease to a value of 64 K at $x = 0.5$.

The effect of pressure on T_c in $YBa_2Cu_4O_8$ ($dT_c/dp = 5.5$ K/GPa) is about 10 times that observed in $YBa_2Cu_3O_7$ ($dT_c/dp = 0.5$ K/GPa) (*5, 6*). In fact, the T_c of $YBa_2Cu_4O_8$ at 12 GPa leads to superconductivity at 108 K (*9*). This observation may be explained as a result of a decrease in the distance between the apical oxygen and the CuO_2 plane (*10*). A suggestion (*6, 10*) is that increasing pressure leads to an enhanced charge transfer from the double CuO chain to the CuO_2 plane and an increase in the T_c up to its optimum value. Therefore, one may speculate that a similar "chemical-pressure" effect, i.e., the substitution of a small ion into large ion sites, might also be expected to increase T_c in the 124 compound. From the present studies, a small amount of Sr ($x = 0.1 \sim 0.2$) substitution of Ba in $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ leads to an increase in T_c from 85 to 90 K (Fig. 4). Moreover, the partial substitution of Ba by Ca (~10%) in the 124 phase results in a large increase in the volume fraction of the 90 K superconductor (*4*). The restricted solubility range of both Sr and Ca in $YBa_2Cu_4O_8$ effectively limits the maximum value of T_c possible via this chemical approach. However, in order to approach the T_c value of 108 K observed in the 124 structure (*9*), the substitution of ions of a higher charge/radius ratio may be required. In contrast, the optimum T_c appears to have been reached for $YBa_2Cu_3O_7$. The very small pressure effect on T_c in $YBa_2Cu_3O_7$ suggests that increases in T_c due to "chemical pressure" effect will be small. For $Y(Ba_{1-x}Sr_x)_2Cu_3O_7$, strontium substitution ($x > 0$) may lead to enhanced hole carrier concentration, and lower T_c.

Acknowledgments

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