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EFFECT OF Ni SUBSTITUTION ON T_c IN THE (Bi,Pb)-Sr-Ca-Cu-O SYSTEM

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ABSTRACT

Properties of a series of superconducting compounds of nominal composition $(Bi_{0.7}Pb_{0.3})SrCa(Cu_{1.5-x}Ni_x)O_\delta$, where x ranges from 0 to 1.1 have been investigated using electrical resistivity, ac magnetic susceptibility and X-ray powder diffraction measurements. Up to $x = 0.2$ composition, T_c drops down to $\sim$ 60 K rather fast. From $x = 0.2$ to 0.95 the material remains superconducting with T_c around $\sim$ 50K. For $x \geq 1.0$, the material becomes semiconducting. The fact that even the compound with Ni : Cu = 0.95 : 0.55 is superconducting with T_c around 50 K may suggest the magnetic disorder introduced by Ni is smaller in this material than in the Ni-doped $YBa_2Cu_3O_{7-\delta}$ material, where even the samples with Ni : Cu = 0.75 : 2.25 have lost their superconducting properties.

MATERIALS INDEX: bismuth, superconductor, nickel

Introduction

The discovery of high temperature superconductivity in 1988 in the Bi-Sr-Ca-Cu-O system with T_c around 20 K by Michel et al [1] and later work by Maeda et al [2] and Chu et al [3,4] on Bi-based systems with T_c upto 100 K showed the distinct possibility of preparing high T_c materials without the need of rare-earth elements. Tanako et al [5] reported an onset of 116 K in the (Bi,Pb)-Sr-Ca-Cu-O system. Superconductivity with onsets 100-120 K in different (Bi,Pb)-Sr-Ca-Cu-O systems have been reported by several workers [6-8]. Effect of Sb substitution on T_c in the (Bi,Pb)-Sr-Ca-Cu-O system has recently been reported by Dou et al [9].

The ionic size and the orbital structure of the 3d elements are close to those of Cu. Therefore, one would expect the 3d elements to occupy the Cu sites if they are introduced into the (Bi,Pb)-Sr-Ca-Cu-O structure. $Ni(3d^8,4s^2)$ is the member adjacent to $Cu(3d^{10},4s)$

in the periodic table and partial substitution of Cu with Ni should produce substantial changes in the superconducting properties of the (Bi-Pb)-Sr-Ca-Cu-O system, as in the case of $YBa_2Cu_3O_{7-\delta}$ system [10-12], because of the presence of a significantly large local magnetic moment of Ni atoms. Honig et al has recently reported their observation of superconductivity in the $La_{2-x}Sr_xNiO_4$ system with T_c as high as 70 K and co-existence of antiferromagnetism and superconductivity below 20 K [13,14]. Their results suggest the possibility of exchange mediated pairing in nickelates, since Ni^{2+} ions in these componds are in the spin S=1 state. An insight into the possible presence of similar effect in the Bi-based material may be gained by introducing Ni into the structure.

In the case of $YBa_2Cu_3O_{7-\delta}$, doping with 10% Ni has supressed the T_c by about 30 K, which has been attributed to the effect of magnetic impurity scattering [11]. Ni doped samples of this material with Ni : Cu = 0.75 : 2.25 have lost their superconducting properties [10]. It is interesting to see what kind of effect Ni doping would have on the superconducting properties of the (Bi,Pb)-Sr-Ca-Cu-O system. In this paper we report the electrical resistivity, magnetic susceptibility and XRD studies of the series of compounds, $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1(Cu_{1.5-x}Ni_x)0_\delta$ where x ranges from 0 to 1.1.

Experimental

Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO and NiO powders were used as raw materials. Samples were prepared by mixing, dry grinding and firing appropriate quantities at 820°C in air for 12 h. Pellets were pressed from the calcined powder and sintered at 860°C in air for 60 h. Resistivity of the pellet samples were measured in a closed cycle refrigerator, model Daikin V202A5L using the four probe technique with pressed indium contacts. The sample currents used were in the 1-5 mA range. The sample temperature was measured by a gold-chromel thermocouple. For superconducting samples, the Meisner effect was demonstrated by observing the deflection of a vertically suspended small SmCo magnet. AC magnetic susceptibility was measured by using a Hartshorn bridge arrangement. Both coils were fixed to the cryo-tip and the sample was inserted into one coil, after making the null adjustment. Phase setting of the lock-in analyser was adjusted so as to measure the in-phase signal, correspond to the variation in the bridge inductance. Both the resistivity and the susceptibility measurements were computer controlled.

Results and Discussion

Figures 1 and 2 show the temperature dependance of electrical resistance of samples with nominal composition $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1(Cu_{1.5-x}Ni_x)0_\delta$, where $x = 0$ to 1.1. All these samples were prepared in the same manner and heat treated under the same conditions. Undoped material with $x = 0$ exhibited superconductivity with onset of resistivity transition at 120 K and zero resitivity at 100 K. These results are in agreement with the earlier reports [6-9]. Substitution of Ni for Cu in the ratio 0.1 : 1.4 atomic ratio depressed the T_c onset to 80 K and the zero resistivity temperature to 70 K. Further addition of Ni upto $x = 0.95$ depressed the T_c onsets to values in the 60-50 K range. At $x = 1.0$ composition the material became semiconducting, and for compositions with $x \geq 1.0$ the material remained semiconducting with high resistivity. The results have been checked for reproducibility using different samples. The presence of a small resistivity hump around 200 K in all the Ni doped samples is note worthy.

Meisner effect was observed in all Ni doped samples with $x \leq 0.95$. Samples with $x =$ 1.0 did not show any Meisner effect when tested with a small SmCo magnet. Fig. 3 shows

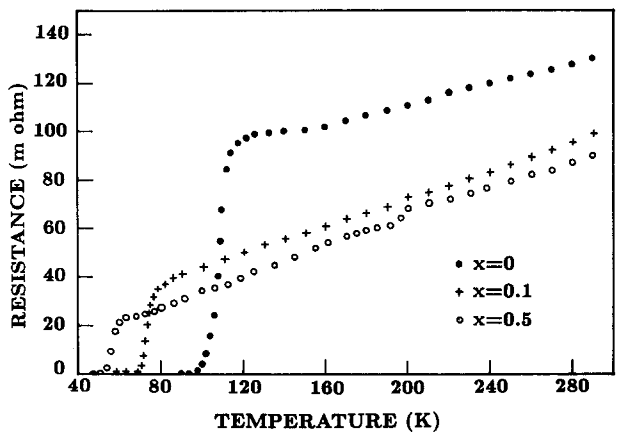

FIG. 1
Temperature dependence of resistance of $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1(Cu_{1.5-x}Ni_x)O_\delta$ for x = 0, 0.1 and 0.2.

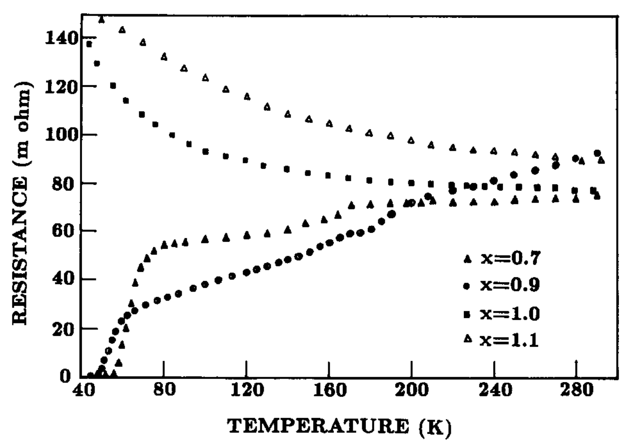

FIG. 2
Temperature dependence of resistance of $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1(Cu_{1.5-x}Ni_x)O_\delta$ for x = 0.5, 0.7, 0.9, 1.0 and 1.1.

the temperature dependance of ac magnetic susceptibility for pure and Ni substituted samples. Pure $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.5}O_\delta$ samples exhibit a sharp transition at 110 K which corresponds to the mid-point of resistivity transition. The transition temperatures for $x = 0.2$ and $x = 0.5$ samples are 60 K and 50 K respectively. All these samples have small Pauli-like paramagnetism above T_c and are diamagnetic below T_c. The sample with $x = 0.7$ shows only a weak diamagnetic effect. The sample with $x = 1.0$ shows Pauli paramagnetism at all temperatures. The appearance of a peak like structure around 50 K for this sample may be due to the presence of a small amount of the superconducting phase as an impurity. It is interesting to note the presence of a small hump around 200 K

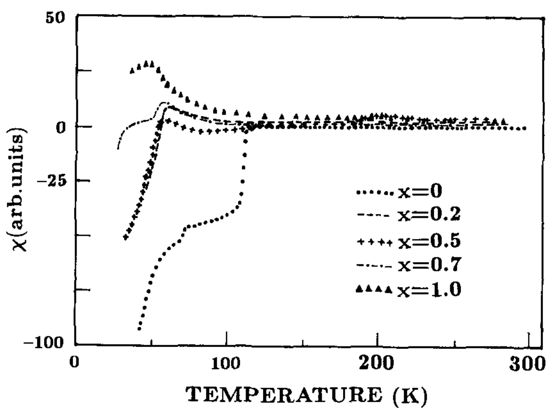

FIG. 3
Temperature dependence of ac magnetic susceptibility of $Bi_{0.7}Pb_{0.3})Sr_1Ca_1$ $(Cu_{1.5-x}Ni_x)O_\delta$ for x = 0, 0.2, 0.5 and 1.0.

in the $\chi \sim$ T curves of most Ni doped samples. The presence of similar humps around 200 K in the R$\sim$T and $\chi \sim$ T curves in some Ni-doped samples may be an indication of the presence of a very small fraction of a new superconducting phase with $T_c \approx 200$ K. Further work to confirm this possibility is in progress.

Fig. 4 shows the variation of T_c with the concentration of Ni. Up to $x = 0.2$ composition, T_c drops down to $\sim$ 60 K rather fast. From $x = 0.2$ to 0.95, the material remains superconducting with $T_c \approx 50$K. For $x \geq 1.0$, the material becomes semiconducting. X-ray diffraction patterns of samples with $x = 0$, 0.2, 0.9 and 1.0 are shown in Fig. 5. XRD pattern of $x = 0$ sample exhibits the characteristic peaks of the undoped material [6,9]. These peaks are retained up to $x = 0.2$ composition suggesting that Ni is actually substituted for Cu. The accompanying drop in T_c up to $x = 0.2$ is presumably caused by the magnetic disorder introduced by the Ni^{2+} - ions which have substantially large magnetic moments compared to Cu^{2+} - ions. As x is increased further, new peaks starts to appear, and at $x = 1.0$, the material becomes non-superconducting and does not show the characteristic XRD pattern of the original material. Up to $x = 0.95$ composition, the presence of new peaks in the Ni doped material at $2\theta = 17.5°$, 20°, 21.5°, 29.5°, 30°, 42°, 52.5° and 55°, which are not observed in the XRD pattern of the original compound, is evidently due to the formation of impurity phases. The intensity of these peaks has increased while the intensity of the peaks at $2\theta = 23°$, 25°, 27°, 29°, 33°, 47°, and 50° characteristic of the undoped material, has gradually diminished as x is increased from 0.2 to 0.9. Faint peaks at these positions were also observed with the $x = 0.95$ samples, but they have disappeared completely at $x = 1.0$ when the material has become semiconducting.

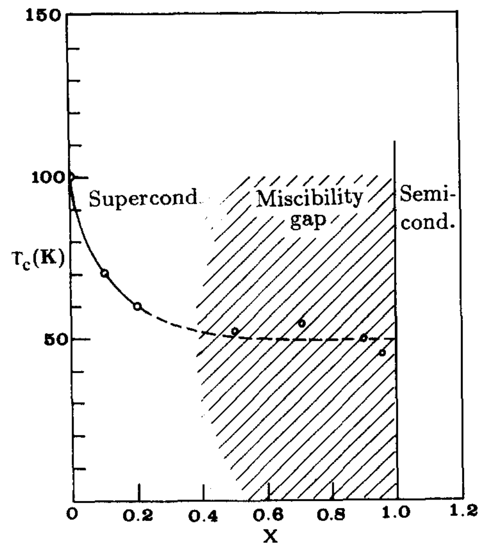

FIG. 4
Variation of critical temperature of the $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1(Cu_{1.5-x}Ni_x)O_\delta$ with x.

Based on the electrical resistivity, magnetic susceptibility and XRD data, it can be suggested that Ni is actually incorporated in to the structure only up to about $x = 0.2$ composition, or 15 atomic %, resulting a drop in T_c. Further addition of Ni up to about $x = 0.95$ nominal composition has given rise to impurity phases of increasing volume fraction, until the multiphase material becomes completely non-superconducting at $x = 1.0$. The formation of different phases in the material as the Ni concentration is gradually increased, can be illustrated as shown in Fig. 4. Up to about $x = 0.2$ the material consists of only the superconducting phase where some of the Cu sites are occupied by Ni. As x is increased from 0.2 to 0.95, the volume fraction of the superconducting phase starts to diminish and a non-superconducting impurity phase, with increasing volume fraction starts to appear. This multiphase region can be represented by a miscibility gap. For $x \geq 1$ the material becomes completely semiconducting.

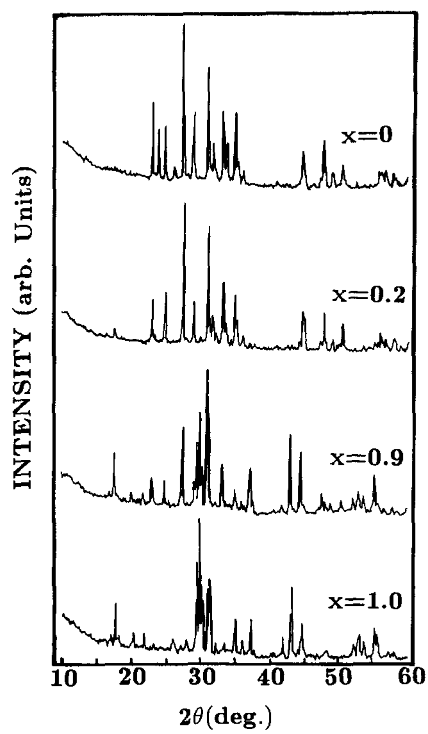

FIG.5
X-ray diffraction patterns of the system, $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1(Cu_{1.5-x}Ni_x)O_{7-\delta}$ for x = 0, 0.2, 0.9, and 1.0.

It is interesting to note that even the multiphase material with Ni: Cu = 0.95 : 0.55 is superconducting with T_c around 50K. This may be compared with the case of Ni doped $YBa_2Cu_3O_{7-\delta}$ material where it has been reported that the superconductivity is retained and Ni is actually substituted for Cu only up to about 10 atomic % and that the superconductivity is destroyed when the nominal composition of Ni exceeds Ni : Cu = 0.75 : 2.25 atomic ratio [10-12]. In this material Ni presumably occupies the Cu sites in the CuO_2 planes whereas CuO chains are expected to play a subordinate role in superconductivity. In the Bi system, however, only one type of CuO configuration, namely the Cu-O_2 planes, appears to exist [15]. Therefore, at low Ni concentrations with $x \leq 0.2$, the substituted Ni atoms presumably occupy the Cu-sites in the Cu-O_2, planes. The drop in T_c in the Ni doped material could arise due to pair breaking effect caused by the conduction and d-electron exchange scattering.

The multiphase samples of the Bi- system with $x = 0.2$ to 0.95 have retained the characteristic XRD peaks of the original undoped system, in addition to the peaks due to one or more non-superconducting phases, and exhibits superconductivity with T_c around 50 K. Eventhough the samples with up to 0.95 Ni and 0.55 Cu atomic ratio appear to have a multiphase nature, the fact that they are superconducting with a rather high T_c suggests that the magnetic scattering and the presence of non-superconducting phases in the Ni doped Bi material has a more moderate effect in destroying the superconductivity compared to the case of Ni doped $YBa_2Cu_3O_{7-\delta}$ material.

Conclusions

From above observations, it can be concluded that substitution of Ni for Cu in the atomic ratio of up to 0.95 : 0.55 in $(Bi_{0.7}Pb_{0.3})SrCaCu_{1.5}O_6$ retains the superconducting properties with T_c above 50 K, but at higher Ni concentrations the superconductivity is completely destroyed. Actual substitution of Ni for Cu appears to be limited to the atomic ratio of Ni : Cu = 0.20 : 1.30. The drop in T_c in the Ni doped material is attributed to the pair breaking effect caused by the conduction and d-electron exchange scattering. Ni addition has a more moderate effect in destroying the superconductivity in the Bi material than in the $YBa_2Cu_3O_{7-\delta}$ material.

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