Physica C 209 (1993) 516-518
North-Holland

PHYSICA C

The synthesis and superconductivity of a new type of Bi-1212 phase $(Bi, Cd)Sr_2(Y, Ca)Cu_2O_z$

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Received 26 January 1993

A novel series of Bi-1212 superconducting cuprates $(Bi_{1-x}Cd_x)Sr_2(Y_{1-y}Ca_y)Cu_2O_z$ has been discovered in this work. The structure was suggested to be that of $(Bi, Cu)Sr_2YCu_2O_z$ with Cd^{2+} ions substituting into the Cu^{2+} sites in the rock-salt-type (Bi, Cu)O layers. The superconductivity was induced in the as-prepared samples by treatment under oxygen pressure of 10 atm at 800°C with a composition of $(Bi_{0.27}Cd_{0.73})Sr_2(Y_{0.7}Ca_{0.3})Cu_2O_z$. The zero-resistivity temperature is 26 K.

1. Introduction

Since the discovery of the Bi–Sr–Cu–O system [1], a family of Bi-based superconducting cuprates $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ $(n=1, 2, 3)$ has been formed [2,3]. These cuprates can be described as intergrowths of Bi_2O_2 double layers with oxygen-deficient perovskite slabs. However, Bi-cuprates with a BiO monolayer had not been discovered. One of the most interesting focuses is whether the cuprates with a BiO monolayer could be formed. Recently, A. Ehmann et al. [4] reported a new family of superconducting cuprates $(Bi_{0.5}Cu_{0.5})Sr_2YCu_2O_z$ (Bi-1212). Its structure is similar to that of $(Pb, Cu)Sr_2(Y, Ca)Cu_2O_y$ [5,6] (fig. 1), in which Cu^{2+} ions need to partially substitute Bi^{3+} ions in the BiO monolayer in order to form the Bi-1212 phase.

The Cd^{2+} ion is particularly interesting for investigation owing to its position in the periodic table, ionic size and intrinsic chemical reactivity. Many works on Cd^{2+} doping have been reported [7–9]. With Cd^{2+} partial substitution, Parise et al. [10] have investigated $(Tl_{1.75}Cd_{0.25})Ba_2CuO_{6+\delta}$ and T.P. Beales et al. [11] have prepared $(Pb_{0.5}Cd_{0.5})Sr_2(Y_{0.7}Ca_{0.3})Cu_2O_y$ the superconducting temperature of which is up to 92 K. In these two systems, Cd^{2+} ions mainly substitute within the rock-salt-type layers incorporating Tl^{3+} or Pb^{4+}.

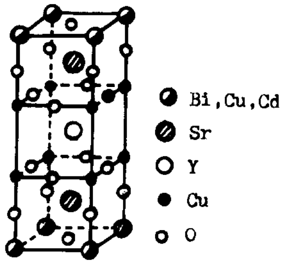

Fig. 1. The schematic structure of $(Bi, Cd)Sr_2YCu_2O_z$.

In this work, we successfully prepared a new type of Bi-1212 cuprate, $(Bi, Cd)Sr_2(Y, Ca)Cu_2O_z$, and superconductivity has been induced in this system.

2. Experimental

Samples with nominal compositions of

$(Bi_{1-x}Cd_x)Sr_2(Y_{1-y}Ca_y)Cu_2O_z$ $(0.5 \leq x \leq 0.8$, $0 \leq y \leq 0.4)$ were prepared by solid state reaction. The starting materials with the appropriate ratios of Bi_2O_3, CdO, $SrCO_3$, Y_2O_3, $CaCO_3$ and CuO were thoroughly mixed and heated at 900°C in air for 24 h. After grinding and pressing into pellets, the samples were calcined at 990°C in flowing O_2 and cooled to room temperature. The as-prepared samples were annealed at 500–800°C in flowing O_2 for 18 h and then quenched to room temperature, or cooled in furnace, or cooled at a rate of 1°C/min, respectively. Some samples were treated at higher O_2 pressure (≈ 10 atm) at 800°C in sealed quartz tubes. The X-ray powder diffraction (XRPD) patterns were taken by a Japan Rigaku Dmax γ_A diffractometer with high-intensity Cu Kα radiation. A scan rate of 0.05°/s was applied to record the patterns in the 2θ range of 5° to 65°. Temperature dependence of electrical resistance was measured by a standard four-probe technique. The temperature was determined by a calibrated Rh/Fe resistance thermometer and the voltage was recorded with a Keithley 181 nanovoltmeter. The resolution of the voltage measurement is 1×10^{-8} V.

3. Results and discussion

The samples with nominal compositions $(Bi_{1-x}Cd_x)Sr_2YCu_2O_z$ were prepared in the range of $0.5 \leq x \leq 0.8$. From the XRPD patterns of the samples, we have found that sintering in oxygen atmosphere is necessary to eliminate the impurity phases (e.g. 2212 phase). The single phase sample was obtained at the optimum composition of $(Bi_{0.27}Cd_{0.73})Sr_2YCu_2O_z$. For $x=0.7$, peaks due to perovskite phase ($SrBiO_3$ type) were observed, and, for $x=0.8$, some unknown impurity phases appeared.

Figure 2(a) shows the XRPD pattern of the $x=0.73$ sample. In this pattern, all the peaks can be indexed using a tetragonal unit cell with lattice parameters $a=3.804(7)$, $c=11.92(8)$ Å, which are close to those of $(Bi_{0.5}Cu_{0.5})Sr_2YCu_2O_z$ $(a=3.815$, $c=11.73$ Å) [2]. It shows that the Cd-containing sample has a slightly shorter a-axis and a longer c-axis than the (Bi, Cu)-1212 sample. The changes in the parameters indicated that the Cd^{2+} ions are readily incorporated into the 1212 phase. The crystal structure of (Bi, Cd)-1212 phase is suggested to be the (Bi, Cu)$Sr_2YCu_2O_z$ structure as shown in fig. 1, where the Cd^{2+} ions may replace the Cu^{2+} ions in the rock salt-type layer.

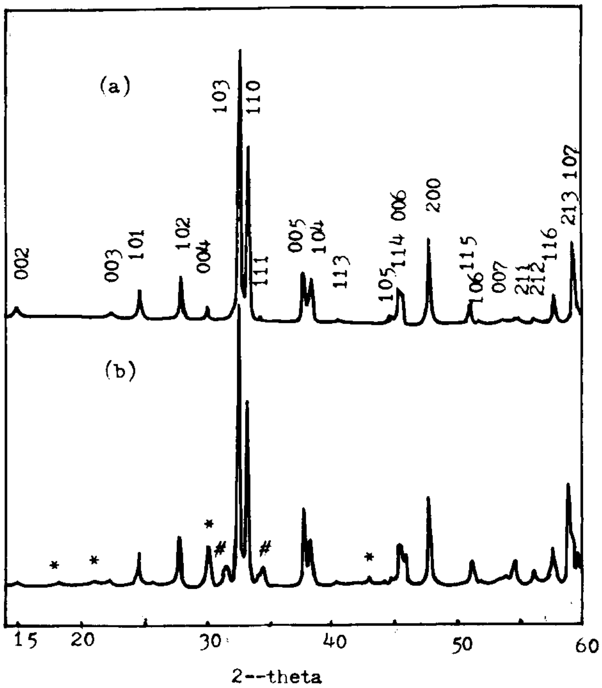

Fig. 2. The X-ray powder diffraction patterns of the samples $(Bi_{0.27}Cd_{0.73})Sr_2(Y_{1-y}Ca_y)Cu_2O_z$. (a) $y=0$, (b) $y=0.3$, annealing at oxygen pressure of 10 atm, *, perovskite phase; #, unknown phase.

In order to induce superconductivity, calcium ions are doped into the samples of $(Bi_{0.27}Cd_{0.73})Sr_2(Y_{1-y}Ca_y)Cu_2O_z$. Perovskite phase and unknown phases were observed when $y > 0.2$ and the impurity phases became much greater when $y > 0.3$. This value is probably the substitution limit for Ca^{2+} ions under the present preparation conditions and attention was concentrated on the samples with $x \leq 0.3$. Samples annealed in flowing O_2 did not show superconductivity down to 4.2 K. After annealing under O_2 pressure (≈ 10 atm) at 800°C, $y=0.3$ samples became superconductive; this means that oxygen content plays an important role in the superconductivity of (Bi, Cd)Sr_2(Y, Ca)Cu_2O_z. The corresponding R versus T curve is shown in fig. 3, the transition temperature $T_{c\,\mathrm{onset}}$ is 34 K, the zero resistivity temperature 26 K. Figure 2(b) is the XRPD pattern of this sample, where we can see that

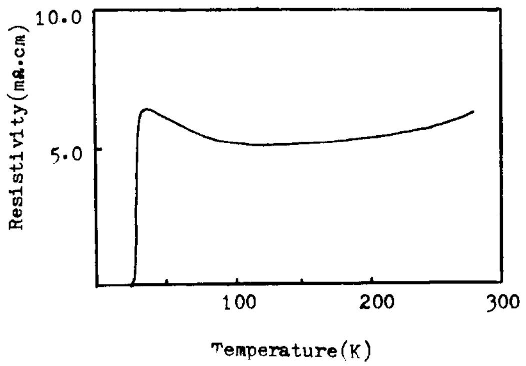

Fig. 3. Temperature dependence of resistivity for the sample of $(Bi_{0.27}Cd_{0.73})Sr_2(Y_{0.7}Ca_{0.3})Cu_2O_z$ with $T_{\mathrm{conset}}=34$ K, $T_{\mathrm{czero}}=26$ K.

no other Bi-cuprate (e.g. 2212) phase is observed. The crystal structure of 1212 phase is not affected by the high oxygen pressure treatment.

Compared with the (Bi, Cu)-1212 cuprate ($T_c=68$ K), the (Bi, Cd)-1212 system has lower transition temperature, which may be due to a carrier concentration that is still not in the proper range. In fact, the treatment condition for the higher superconducting temperature is not optimized. It is possible that, with higher oxygen pressure treatment, the superconducting transition temperature could be further increased.

4. Conclusion

A new type of Bi-based cuprate $(Bi_{0.27}Cd_{0.73})Sr_2(Y_{1-y}Ca_y)Cu_2O_z$ $(0 \leq y \leq 0.3)$ has been prepared. The crystal structure is an analogue to that of the (Bi, Cu)-1212 phase with Cd^{2+} doping in the rock-salt-type BiO monolayer. Superconductivity has been observed in this system, the zero resistivity temperature being 26 K in the $y=0.3$ sample. However, an optimum preparation condition for the highest superconducting temperature has not been determined.

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