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EFFECTS OF Cd DOPING ON Bi-CONTAINED SUPERCONDUCTORS FROM RAPIDLY QUENCHED AMORPHOUS FILMS

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Abstract The effect of Cd substitution for a part of the Ca atoms in $Bi_2Sr_2Ca_2Cu_3O_q$ and $Pb_{0.2}Bi_{0.8}Sr_{0.8}CaCu_2O_7$ has been studied using the rapid quenched method. The Cd doped films in both systems yielded a highly oriented array of the 80 K phase. The addition of Cd content decreased the resistivity at room temperature and vanished the tailing of superconducting transition. Tc(endpoint) increased from 67K (x=0.0) to 87K (x=0.1) in $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_q$ and from 67 K (y=0.0) to 83 K (y=0.2) in $Pb_{0.2}Bi_{0.8}Sr_{0.8}Ca_{1-y}Cd_yCu_2O_z$.

INTRODUCTION

Since the discovery of Bi-containing superconducting oxides[1], many attempts have been done to prepare their materials. One of the methods for preparing Bi-containing superconducting oxides is rapid quenching of their melts[2-5]. It enables us to obtain uniform, smooth and dense films, and to choose wide variety of compositions due to extended solubility. Amorphous materials, therefore, have a great significance in the search for and designing of superconductors. We have reported[4,5] that amorphous films of $Bi_2Sr_2CaCu_2O_p$ and $Bi_2Sr_2Ca_2Cu_3O_q$ were successfully prepared by the rapid-quenching-after-rapid-melting (RQRM) technique using a Xe arc imaging furnace without any containers. In the present study, we have attempted to substitute a part of the Ca atom in $Bi_2Sr_2Ca_2Cu_3O_q$ and $Pb_{0.2}Bi_{0.8}Sr_{0.8}CaCu_2O_z$ with Cd atom, in order to obtain film possessing higher quality. It is claimed that the substitution of Ca by Cd have not been succeeded by solid state reactions[9].

EXPERIMENTAL METHOD

The powder materials for $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_q$ (x=0.0, 0.4) and $Pb_{0.2}Bi_{0.8}Sr_{0.8}Ca_{1-y}Cd_yCu_2O_z$ (y=0.0, 0.2) were weighed out and wet-mixed with ethanol in an agate mortar using 99.99% Bi_2O_3, $CaCO_3$ and CuO and 99.9% $SrCO_3$, PbO and CdO. They were calcined in air at 800°C for 12h and pulverized, molded and submitted for CIP under 294 MPa to make bar samples 2.5 mm in dia. and 150 mm long. The bar sample was suspended in an FZ arc image furnace (SD-5D, Nichiden Kikai Inc. Tokyo

Japan) in such a position that the tips of the samples were located at the light focuses. The lamp output was 1kW for melting of the sample. Molten droplet on the tops of the bar samples fell down and into a twin roller. They were rapidly cooled and shaped into films about 20μm thick. The films thus obtained were annealed at 835-880°C by various heating schedule on (100) cleavage surface of MgO single crystal in air. X-ray diffraction(CuKα) for the annealed films was carried out. The resistivity of the film was measured by a standard four-probe method using a constant current of 0.5 mA. The microstructure on the fractured surfaces of the heated specimens were observed by using a scanning electron microscope(SEM:S-450, Hitachi Inc. Tokyo Japan).

RESULTS AND DISCUSSION

Although all the rapidly quenched samples contained crystal phases of very small quantities of CaO or CaO-CdO solid solutions, their phases were almost amorphous with $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_q$ and $Pb_{0.2}Bi_{0.8}Sr_{0.8}Ca_{1-y}Cd_yCu_2O_z$ compositions produced by this RQRM method[3]. In the series of $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_q$ samples, the X-ray diffraction peaks of the precipitated crystalline phase shifted to higher angles corresponding to the increase in x:Cd content, indicating the substitution of Ca by Cd[4]. Figure 1 shows the X-ray diffraction patterns of the $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_q$ with (a)x=0.0 and (b)x=0.4 annealed at 870°C for 5 h on (100) MgO single crystal in air. The $Bi_2Sr_2Ca_2Cu_3O_q$ film without the Cd doping shows not oriented thick film of the 80 K phase(Fig.1(a)). The Cd doped film with x=0.4 yielded a highly oriented thick film of the 80 K phase.

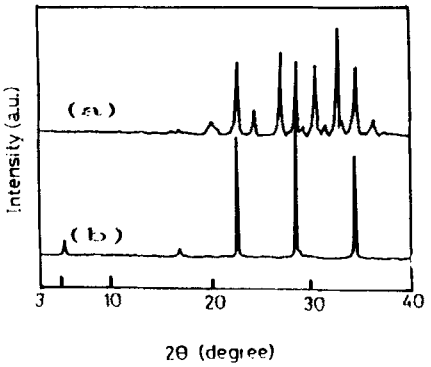

Fig.1 The x-ray powder diffraction patterns of the $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_z$ films, (a)x=0.0,(b)x=0.4 after annealing in air at 870°C for 5h.

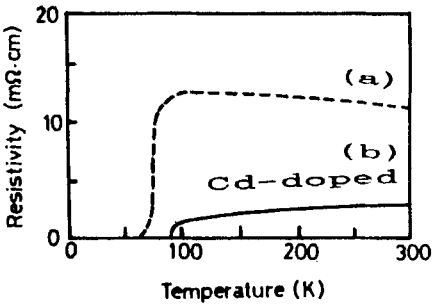

Fig.2 Temperature dependence of the resistivity of the $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_z$ films, (a)x=0.0,(b)x=0.4 after annealing in air at 870°C for 5h.

The value of orientation with (00ℓ) peak estimated by area ratio of (00$\underline{10}$)/(115) was 62. The extent of orientation improved with addition of Cd[4]. The $Bi_2Sr_2Ca_2Cu_3O_q$ (x=0.0) sample had the lattice parameters of a_o=0.541, b_o=0.540 and c_o=3.081 nm. With addition of Cd, $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_q$ had larger the cell volume and increased c axis from c_o=3.081 nm (x=0.0) to c_o=3.089 nm (x=0.4). There are, however, almost no elongation for a and b axes in comparison with c axis.

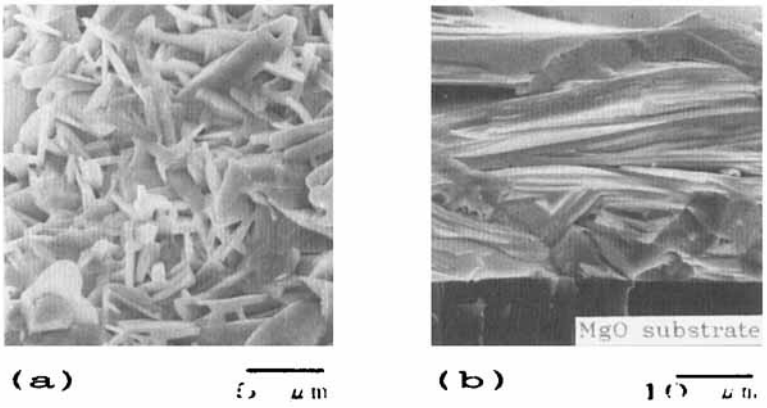

Fig.3 Scanning electron photomicrographs of the fracture surfaces of the specimen annealed (a)at 880°C for 1h (x=0.0) and (b)at 870°C for 5h (x=0.4) in air.

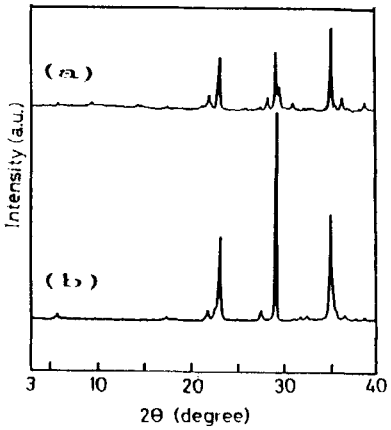

Fig.4 The x-ray powder diffraction patterns of the $Pb_{0.2}Bi_{0.8}Sr_{0.8}Ca_{1-y}Cd_yCu_2O_z$ films, (a)y=0.0, (b)y=0.2 annealed at 880°C for 1h and reheated at 850°C for 5h in air.

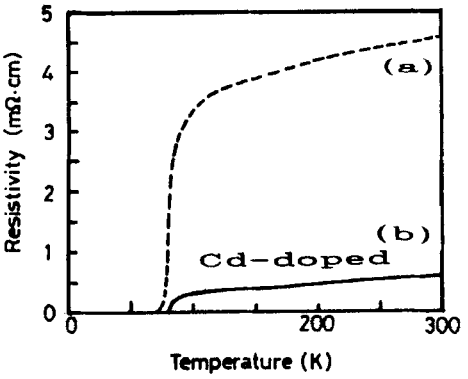

Fig.5 Temperature dependence of the resistivity of the $Pb_{0.2}Bi_{0.8}Sr_{0.8}Ca_{1-y}Cd_yCu_2O_z$ films, (a)y=0.0, (b)y=0.2 after annealing at 880°C for 1h and reheated at 850°C for 5h in air.

These results suggest that Cd doping causes some changes in the cation distribution of Bi, Pb, Sr and Ca, and/or change in oxygen content. Figure 2 shows the resistivity-temperature curve for the samples with x=0.0 and 0.4. The $Bi_2Sr_2Ca_2Cu_3O_q$ (x=0.0) film annealed at 870°C for 5h shows Tc(endpoint)=67 K with a tail. The addition of Cd content (x=0.4) decreases the resistivity at room temperature and vanishes the tailing of superconducting transition, to give the Tc(endpoint) of 87 K without any tail. Annealing of the films with $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_q$ yielded polycrystalline products.

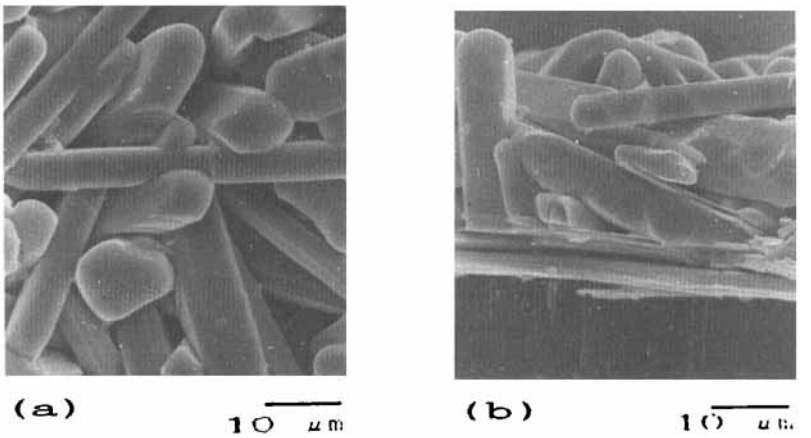

Fig.6 Scanning electron photomicrographs of the (a)as prepared and (b)fractured surfaces of the $Pb_{0.2}Bi_{0.8}Sr_{0.5}CaCu_2O_z$ films annealed at 880°C for 2h and reheated at 840°C for 5.5 h and at 835°C for 10h in air.

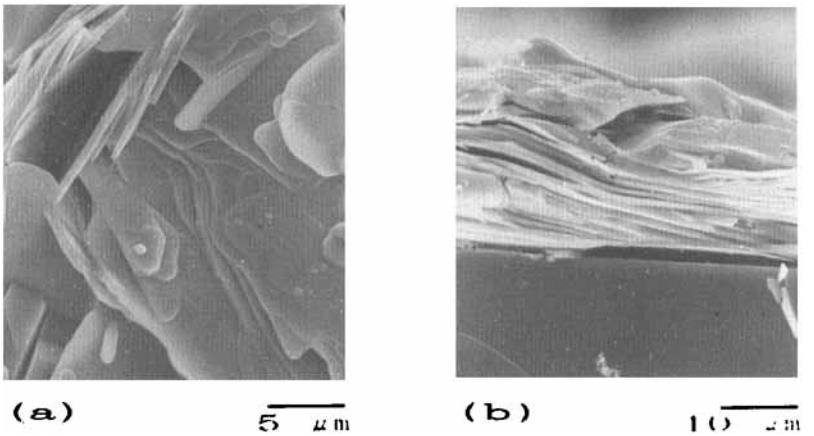

Fig.7 Scanning electron photomicrographs of the (a)as prepared and (b)fractured surfaces of the $Pb_{0.2}Bi_{0.8}Sr_{0.8}Ca_{0.9}Cd_{0.2}Cu_2O_z$ films annealed at 880°C for 2h and reheated at 840°C for 5.5 h and at 835°C for 10h in air.

MgO substrate

Figure 3 shows the fractured surface of the films with (a)x=0.0 and (b)x= 0.4 which consist of plate-like grains for the specimens annealed at 880°C for 1 h and at 870°C for 5 h, respectively. Figure 3(a) shows the plate-like crystal making a card-house structure, while (b) shows the oriented structure in a parallel direction to on (100) MgO single crystal.

The $Pb_{0.2}Bi_{0.8}Sr_{0.8}Ca_{1-y}Cd_yCu_2O_z$ films annealed at 880°C for 1 h were annealed again at various temperatures and times. Similar effects could be observed in $Pb_{0.2}Bi_{0.8}Sr_{0.8}Ca_{1-y}Cd_yCu_2O_z$ to the Pb-free samples in the Bi-Sr-Ca-Cu-O system. For example, these films annealed at 880°C for 1h and 850°C for 5h shows to be also lengthened from c_o=3.068 nm (y=0.0) to c_o=3.077 nm (y=0.2)(Fig.4). As shown in Figure 5, the superconducting transitions became sharp and Tc(endpoint) increased from 67 K (y=0.0) to 83 K (y=0.2), in addition the resistivity at room temperature decreased with the addition of Cd. Figure 6 shows as prepared and fractured surfaces of the $Pb_{0.2}Bi_{0.8}Sr_{0.8}CaCu_2O_z$ and $Pb_{0.2}Bi_{0.8}Sr_{0.8}Ca_{0.8}Cd_{0.2}Cu_2O_z$ films annealed at 880°C for 2h, at 840°C for 5.5 h and at 835°C for 10h in air. The Cd-free film has the surface which consists of rod-like grains (Fig.6(a)) and the fractured surface which consists of stacking the rod-like grains (Fig.6(b)). The surface of the Cd-doped film, however, shows the plate-like grains (Fig.7(a)) and Figure 7(b) showing the oriented array in a parallel direction to on (100) MgO single crystal.

In summary, Cd-doping in Bi-(Pb)-Sr-Ca-Cu-O systems brings about the effects as follows:

1) decreasing the resistivity at room temperature.
2) increasing Tc(endpoint) and vanishing the tailing of transition.
3) growing large the cell volume and increasing c axis.
4) being well oriented along to (00ℓ) plane.

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