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SINGLE CRYSTAL GROWTH OF SUPERCONDUCTING COMPOUND Bi-Sr-Ca-Cu-O

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Single crystals of high temperature superconductors in the system Bi-Sr-Ca-Cu-O have been prepared by a flux method. The d.c. electrical resistivity showed that the metal to superconductor transition is at 82K. SEM showed a layered structure, while X-ray diffraction analysis indicated an ortho-rhombic structure with a=5.39 (2) A°, b=5.35(2) A° and c=30.65(3) A°.

Key words: Single crystal, Super conductors, Systems Bi-Sr-Ca-Cu-O.

Introduction

In the Bi-Sr-Ca-Cu-O system Maeda *et al.* [1] reported the bulk superconductivity at 75K and evidenc of superconductivity at 120 K (onset). We now know that there are three superconducting phases having the general formula $Bi_2Sr_2Ca_{z-1}Cu_zO_y$ where z=1,2,3 and these phases have transition temperatures of 10, 80 and 110K. The preparation of 110K phase of $Bi_2Sr_2Ca_2Cu_3O_y$ has some difficulties with respect to 80K phase. Many studies dealing element substitution have been made to separate the high-T_c phase from the low-T_c phase. Partial substitution of Pb for Bi has been reported to be effective in preparing the high-T_c phase [2,3]. It is also reported [4,5] that the partial replacement of Bi with Pb and Sb is also capable of giving 110 K phase when annealed for three days at 850-865°, compared to 10-days annealing time needed to prepare the samples of the same quality substituting Bi by Pb only.

Materials and Methods

Materials are more easily prepared in polycrystalline form compared to single crystals. But single crystals are important for investigation of their physical properties, since the physical properties of materials are ideally studied in single crystals: here the periodicity of the lattice structure is preserved throughout the volume of the solid. In this paper we report the preparation and preliminary information of superconducting single crystals.

Preparation. The single crystals were grown by a flux method. The composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ showed a high-T_c phase, when prepared as a polycrystalline phase [6]. Therefore, the above starting composition with the addition of extra PbO as a flux was used to prepare the single crystals. The raw materials used were; Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO of atleast 99.9% purity. These reagents were weighed and mixed in the proper atomic proportions Bi:Pb:Sr:Ca:Cu=1.6:0.4:2:2:3. The weights were measured within an accuracy of 1 mg. The mixture was ground for an hr using an agate mortar and pestle. An excess amount of PbO was used as a flux, which is similar to the method used for other 80K class superconductors, 4334, [7]. The pulversized material was mixed with the 10 (wt%) PbO. The mixture of 50 g of ground material was placed in the Al_2O_3 crucible. The typical heat treatment was as follows:

The temperature in the muffle furnace was raised to 840° and held for 10 hrs. The sintered material was reground and melted at 1060° for 2 hrs. After this the temperature was decreased at 950° at the rate of 10°/hr. and held for 12 hrs, then lowered to 850° at the rate of 5°/hr. Finally the temperature was decreased to room temperature at a rate of 120°/hr. In the final products, deep black single crystals stacking one to the other with typical dimensions of 3.0 x 1.5 x 0.5 mm^3 were found in the crucibles. The single crystals from the flux were separated manually. One example is shown in Fig. 1.

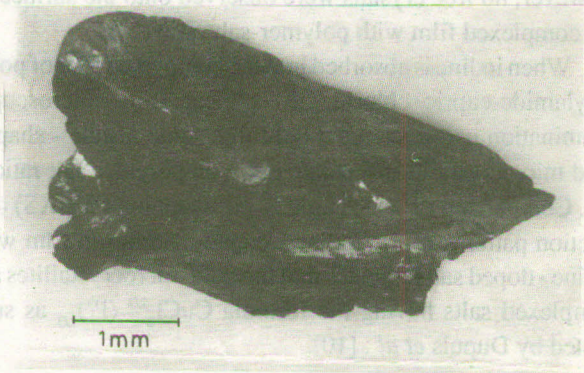

Fig. 1. A typical superconducting single crystal of Bi-Sr-Ca- Cu-oxide.

Results and Discussion

A true superconductor not only shows zero resistance but also excludes a magnetic field completely, the Meissner effect. The positive test for superconductivity behaviour of our samples was the observation of the Meissner effect. The visual demon-

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stration [8] of this effect showed that the crystals were superconducting at the liquid nitrogen temperature. To confirm, whether the material was single crystal or not, it was examined by X-ray Laue back-reflection photographs. Laue back-reflection patterns show excellent crystallographic features (Fig. 2), suggesting the formation of single crystals.

Single crystals were also examined by X-ray powder diffraction studies. Since the amount of single crystals available was small. Therefore, Debye-Scherrer powder pattern were taken. On analysis the superconducting phase was identified to be ortho-rhombic structure with a=5.39(2) Å, b=5.35(2) Å and c=30.65(3) Å. No peaks corresponding to high-T_c phase appeared in the XRD. This result confirmed the formation of the low-T_c phase. It is evident that the starting composition (2223) has been decomposed to (2212) the low-T_c phase. These results are in good correspondence with the result of Hoshizaki *et al.* [9]. They reported that in the heating process, the high-T_c phase of 2223 decomposed to the low-T_c phase of 2212 at about 910°. It is also reported that the single crystals of the low-T_c phase, 2212 of several millimeters in size have been prepared [10-12].

Small size could not allow to measure the directional resistivity of the crystals as it needed reshaping of the specimen and therefore, resistance versus temperature was measured as described below.

To know about the transition temperature of the crystals, the biggest piece was chosen for resistance measurement. The temperature dependence of the resistance of the crystal was measured directly by the standard four-probe method, within the range 77-300K. High quality silver paste was used to ensure good electrical contacts between the electrode and the crystal surface. A current of 10mA was used in the experiments. Figure 3 shows the temperature dependence of resistance, normalized to 300K, of the single crystal specimen of starting composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$, grown by flux technique using 10% PbO as flux.

From this graph, it is evident that the zero critical temperature is 82 ± 1K, which agrees to the low-phase transition superconductors. Though the starting composition of the material was that of high-T_c phase, but the results of X-ray diffraction and d.c electrical resistivity measurements confirmed the formation of low-T_c phase, suggesting that most probably low-phase is more stable compared to the high-phase in the system Bi-Sr-Ca- Cu-O.

Scanning electron microscopy on Bi-Sr-Ca-Cu-O single crystals has been carried out using Jeol 35 CF Microscope at an operating voltage of 25 KV. The samples used were of approximate dimensions of 3.0 x 1.5 x 0.5 mm^3. They were mounted on brass stub with their flat surface facing the electron beam. Secondary electron images taken from the surface show a homogeneous spread of the main composition with some occasional inclusions of a secondary phase. The occurrence of such a secondary phase is shown in the scanning electron micrograph of Fig. 4a as a light grey area. Wave length dispersive X-ray analysis (WDS) is underway to find out its composition.

The crystals show highly textured lamellar structure which can be seen in Fig. (4b) where stacks of ab plane [12] are grown along c-direction. This type of texture growth has been observed in almost all compositions of Bi-Sr-Ca-Cu-O superconductors whether doped or undoped with Pb. The development of such a texture, however, is very much dependent on the heat treatment given to the sample [13,14].

To summarize we have successfully prepared single crystals of Bi-Sr-Ca-Cu-O with a PbO flux method, whose T_c is 82 ± 1K which agrees to the low-T_c phase (2212) class of superconductors. 'SEM' studies explain that the specimen is

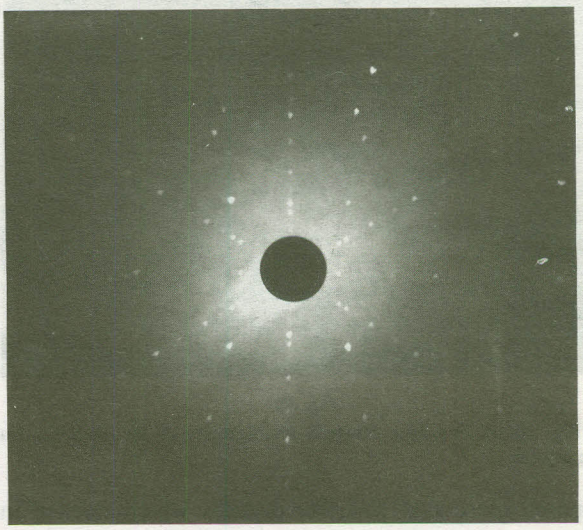

Fig. 2. X-ray Laue back-reflection photograph for superconducting single crystals.

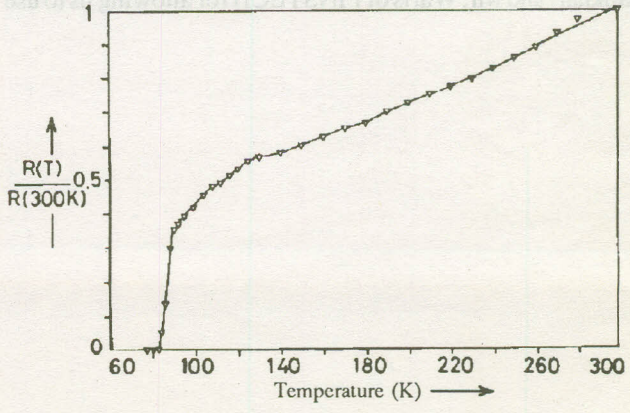

Fig. 3. Normalized resistance R(T)/R(300K) of superconducting single crystals as a function of temperature.

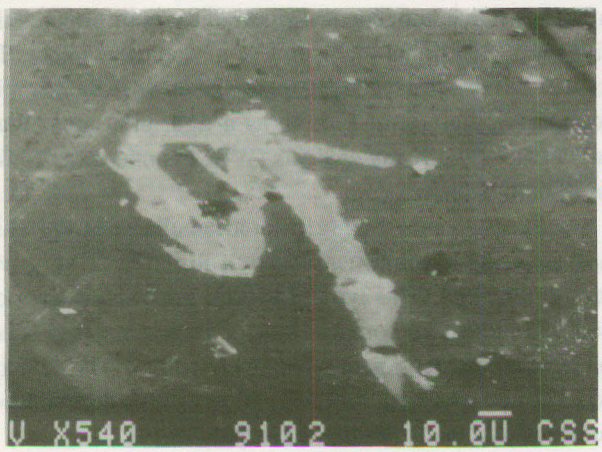

Fig. 4a.

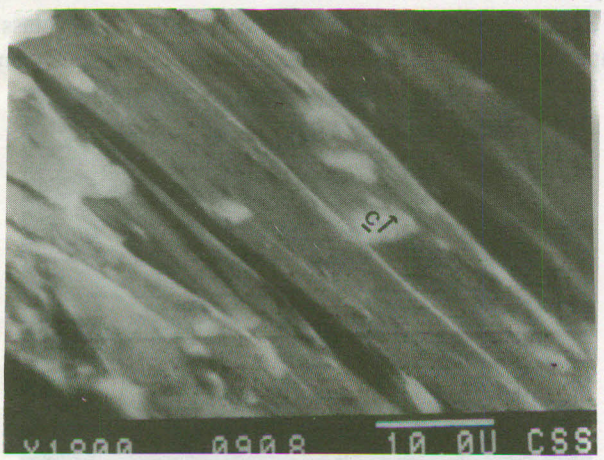

Fig. 4b.

Fig. 4(a,b). Scanning electron micrographs of the Bi-Sr-Ca-Cu-O single crystal.

composed of several platelike crystals which stacked in a layered structure in the direction of thickness.

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