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Preparation and characterization of superconducting $BiSrCaCu_2$-oxide

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The preparation of a high-temperature superconducting phase of the Bi–Sr–Ca–Cu–O system is described. The surface morphology of calcined and sintered material has been studied. The sintered material, thus prepared, has been characterized by electron microscopic techniques. The structure at various local regions has been investigated by electron diffraction and lattice imaging. The composition has been determined by electron probe micro-analysis. The study revealed intergrowth in the system, giving various values of the *c* parameter in local regions.

1. Introduction

The discovery of superconductivity in the La–Ba–Cu–O system [1] around 30 K and in the Y–Ba–Cu–O system [2] around 90 K has generated tremendous interest amongst scientists and technologists. After the discovery of these high-T_c superconducting systems, extensive efforts have been made to search for newer superconducting oxide compounds. As a result a number of new oxide compounds without rare-earth elements have been found to show higher values of T_c. The first such compound belonged to the Bi–Sr–Cu–O system and was investigated by Michel *et al.* [3]. They found a maximum value of the transition temperature as 22 K in the Bi–Sr–Cu–O system. Since then a number of workers have studied various compounds of the Bi–Sr–Ca–Cu–O system which showed higher values of T_c. The highest value of T_c (up to 120 K) has been achieved recently in the Bi–Sr–Ca–Cu–O system as reported by Chu *et al.* [4]. Extensive efforts have been made to get zero resistance at higher temperatures. The doping of lead into the Bi–Sr–Ca–Cu–O system gave interesting results. In lead-doped samples, zero resistance has been achieved at 125 K by Haung *et al.* [5]. The structural characterization of these materials has been done by X-ray diffraction [6], neutron diffraction [7] and electron diffraction techniques [8]. It has been found that superconducting phases of the Bi–Sr–Ca–Cu–O system have an orthorhombic structure based on the $Bi_4Ti_3O_{12}$ type of structure [9]. The unit cell dimensions of the orthorhombic phase are $a = 2^{1/2}a_0$, $b = 5\,(2^{1/2})a_0$ and $c = 8\,a_0$ where a_0 is the unit cell dimension of cubic perovskite.

In the present paper we describe the preparation conditions of high-T_c superconducting phases of the Bi–Sr–Ca–Cu–O system and report measured T_c values for sintered material. The surface structure and surface morphology of sintered material and various phases grown in it have been investigated by using scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS), respectively. Electron microscopic and electron diffraction studies have also been carried out to determine the microstructure of the sintered material.

2. Experimental procedure

Samples of high-T_c 1:1:1:2 compound were prepared by using Bi_2CO_3, $SrCO_3$, $CaCO_3$ and copper oxide powders. Powders having appropriate ratios were mixed and ground in an agate pestle and mortar. After grinding the powder thoroughly, it was calcined at 800 °C for 3 h in air and slowly cooled to room temperature in the furnace. The resulting material was again ground to fine powder and heated at 800 °C for 2 h in air and cooled slowly to room temperature. The material was then ground to fine powder and pelletized. These pellets were heated at 850 °C for 3 h in air and annealed at 400 °C for 5 h in air before the furnace was cooled to room temperature.

The electrical resistivity of the sintered pellet was measured as a function of temperature by the standard d.c. four-probe method. The surface structure and elemental analysis of sintered material were investigated by using a Jeol scanning electron microscope (Model JSM-35 CF) and the Kevex energy-dispersive spectrometer attached to the SEM, respectively. The internal structure was investigated by transmission electron microscopy (TEM) and electron diffraction techniques by using a Jeol transmission electron microscope (Model JEM-200CX). Specimens for TEM examination were prepared by crushing the pellet and grinding it into a homogeneous fine powder in an agate pestle and mortar. The powder was sprinkled on copper grids having a Formvar film as support. Specimens were also prepared by suspending the fine powder in acetone by using an ultrasonic bath and then pouring a drop of the suspension on a copper grid having a support film. The specimens were dried and loaded in the TEM for examination.

3. Results and discussion

Fig. 1 shows the variation of resistance as a function of

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temperature. It is observed from the curve in Fig. 1 that the material is superconducting in behaviour. It does not consist of a single phase. The onset of a superconducting transition is observed in the sample at temperatures of 108, 80 and 64 K. The transitions occurring at three temperatures reveal that there are at least three different phases present in the material which are superconducting in behaviour, and each transition corresponds to a different phase.

The surface structure and morphological features of the sintered pellets were studied with SEM. Fig. 2 shows a micrograph revealing the morphology of phases as observed by SEM. The elemental composition of the material was determined with the EDS attachment of the SEM. It was observed that the composition of the material changed after the process of calcination and sintering, and the material showed the formation of a number of phases. The most commonly observed phases showed the compositions 2:2:2:3, 2:2:1:2, 1:1:1:3 and 1:1:1:2 as the ratios of Bi:Sr:Ca:Cu, and the grains showing these compositions have been marked as A, B, C and D, respectively, in Fig. 2. Similar studies on Bi–Sr–Ca–Cu–O phases prepared under different conditions have been done by the authors and the results have been reported in an earlier paper [10].

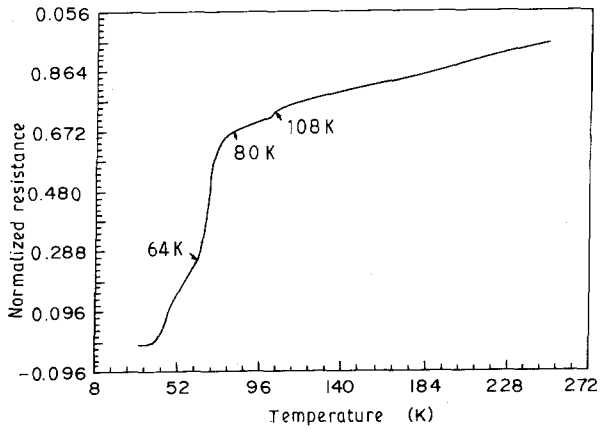

Figure 1 Curve showing the variation of electrical resistivity with temperature of a sintered pellet of the material.

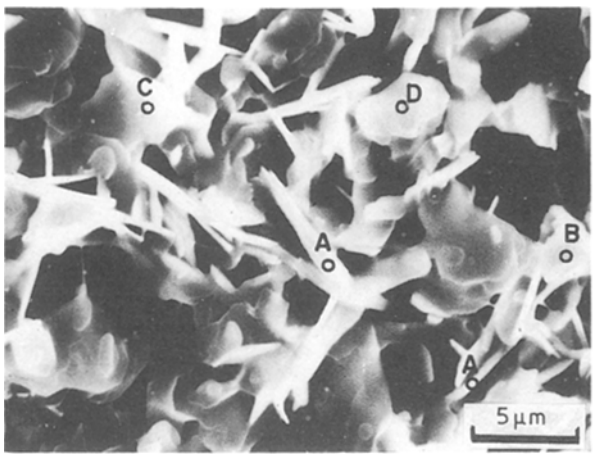

Figure 2 SEM micrograph of a sintered pellet of $BiSrCaCu_2O_x$ showing the surface morphology of grains, depicting different compositions.

In order to study the internal structure of the material, specimen grids prepared by the techniques discussed above were examined by TEM. On scanning the grid it was found that the sample had a few regions which were transparent to the electron beam. At these suitable regions of the sample electron micrographs and selected-area diffraction patterns were recorded.

Fig. 3 shows the electron micrograph of a certain region of the material revealing grain boundaries and structural features. A selected-area diffraction pattern of the same region has been depicted in Fig. 4. In the figure it is observed that there are two types of diffraction spots. One, which is bright, is due to the main reflections and the other, comprising satellite spots along the *b* axis, is due to the modulated structure. In this case the beam is along the [0 0 1] direction. Careful observation of the diffraction pattern reveals that the distance between the satellite spots is not equal. This shows the incommensurate character of the structure [11]. The satellite spots along the *b* axis indicate a five-fold superstructure: the lattice parameter *b* is observed to be five times the *a* parameter. After indexing the diffraction patterns the *a* and *b* parameters are found to be 0.538 and 2.69 nm, respectively.

Some other grids prepared from the same sample

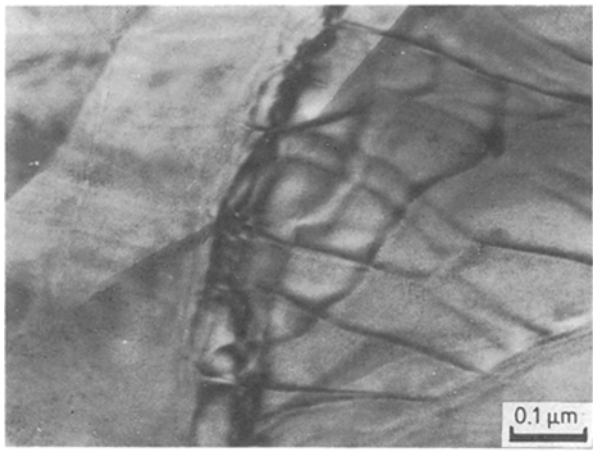

Figure 3 Electron micrograph of sintered material revealing grain boundaries and structural features.

Figure 4 Electron diffraction pattern of superconducting $BiSrCaCu_2O_x$ phase.

were also examined. The electron diffraction examination of a transparent region showed diffraction pattern as shown in Fig. 5. These patterns are indicative of microdomains in the material which are at 90° to each other. Similar results have also been reported by Ganapathi *et al.* [12].

Fig. 6 shows a lattice-resolution image of some different regions of the sample. In the lattice-resolution image the dislocations are clearly observed in region A. In region B the lattice planes are observed showing different values of interplaner spacing.

During the examination of the sintered material it is observed that the Bi–Sr–Ca–Cu–O system also shows intergrowth structure. TEM studies at high resolution showed lattice planes resolved as depicted in Fig. 7. The figure also shows isolated dislocations in the regions encircled.

Figure 5 Electron diffraction pattern showing the presence of microdomains in $BiSrCaCu_2$-oxide.

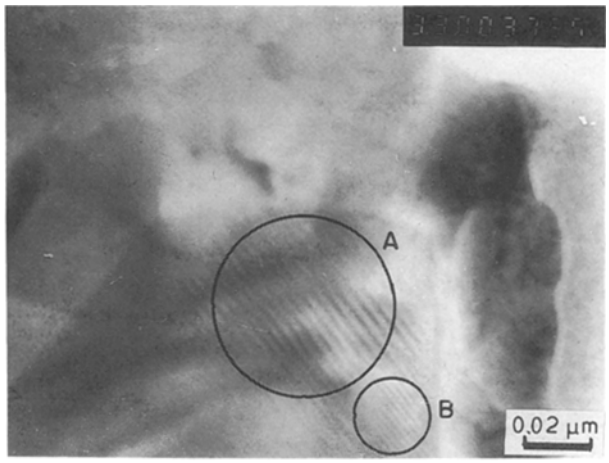

Figure 6 Electron micrograph depicting a lattice resolution image showing dislocations.

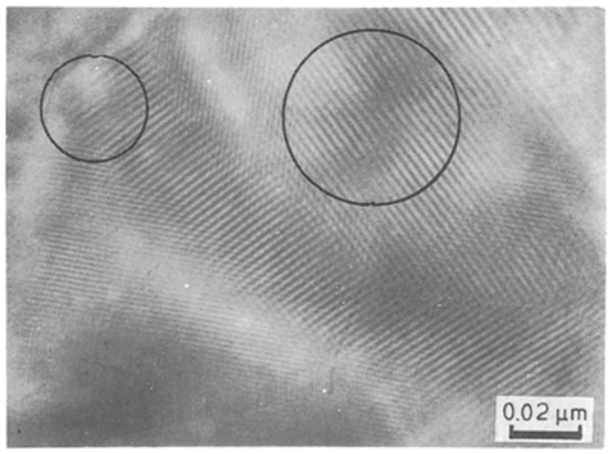

Figure 7 Electron micrograph showing different values of the c parameter at a region in $BiSrCaCu_2$-oxide revealing intergrowth in the phase under examination.

4. Conclusions

The electrical resistivity measurements on $Bi_1Sr_1Ca_1Cu_2$-oxide in the present study reveal that the onset of a superconducting transition occurs at 108, 80 and 64 K, indicating the presence of at least three different phases in the material which are superconducting in behaviour. The SEM study of these samples shows the formation of four distinct phases. Transmission electron microscopy and electron diffraction studies show that various phases are formed in the material. The prominent phases have an orthorhombic structure. The study also gives evidence of intergrowth structure with varying values of the c parameter.

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