

Synthesis and Study of Microstructural Features of BSCCO-2223 Superconductors

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Abstract: The samples of 2223 compound of BSCCO system superconductors were synthesized by using solid state reaction techniques. The samples calcined at 830 °C and sintered at 845 °C showed higher T_c values. The highest value of $T_{c(R=0)}$ at 84 K has been observed in the case of sample calcined at 830 °C and sintered at 845 °C. The study reveals that the calcination around 830°C is advisable for getting the samples with higher values of T_c . The high-resolution transmission electron microscopy (HRTEM) and electron diffraction technique was used to ascertain the presence of 2201, 2212 and 2223 phases in these materials. The transmission electron microscopy and electron diffraction studies revealed the presence of lattice planes, rotational Moire fringes, formation of Bands, and grain boundaries etc. in these samples at some typical regions. The microstructural features of these samples were discussed in relation with the results R-T measurements.

Keywords: Solid State Reaction, Transmission Electron Microscopy, Lattice Imaging, Grain Boundaries, Moire Patterns

1. Introduction

Since the discovery of high T_c superconductors extensive studies have been made [1 – 11] on these oxides. It has been well established that the BSCCO system has three superconducting phases namely very low T_c phase (2201), low T_c Phase (2212) and high T_c Phase (2223). The value of T_c upto 120 K has been reported [12] in the sample of BSCCO system prepared under well controlled conditions. While Pb-doped BSCCO superconductor was reported to show zero resistance upto 125 K [13]. In the present paper the author has focused on synthesizing the 2223-compound of BSCCO superconductors and studying its microstructural features by using the high-resolution electron microscopy and electron diffraction techniques, especially to ascertain the presence of 2201, 2212 and 2223 superconducting phases.

2. Materials and Methods

The samples of 2223 compound of Bi-System Superconductors were synthesized by Solid State Reaction technique. Two sample having the same nominal starting composition were prepared. The stoichiometric composition of the starting material was kept $\text{Bi}_{2.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$. Dry powders of Bi_2O_3 , SrCO_3 , CaCO_3 and CuO with the cation molar ratio Bi:Sr:Ca:Cu::2.2:2:2:3 were thoroughly mixed and ground. The thoroughly mixed powder was divided into two parts.

The first part of the powder was calcined at 800°C twice for 24 hrs each with intermediate grinding. The calcined material was again pulverized and ground to form a fine and homogeneous powder. This powder was then pelletized. These pellets were sintered at 845°C in air for 168 hours. After sintering the pellets were cooled to 500°C at the rate of 2°C/min. These pellets were annealed at 500°C for 24 hrs in air and then cooled to room temperature inside the furnace. The resulting material was named as sample No. 1.

While the second part of the powder, was calcined at 830°C twice for 24 hrs. with intermediate grinding. The calcined

mixture was again pulverized and ground to get a fine and homogeneous powder. The resulting materials were pelletized. These pellets were sintered for 168 hrs. at 845°C in air. After sintering the pellets were cooled to 500°C at the rate of 2°C/min. These pellets were annealed at 500°C for 24 hrs in air and then cooled to room temperature inside the furnace. The resulting material was then named as sample No. 2.

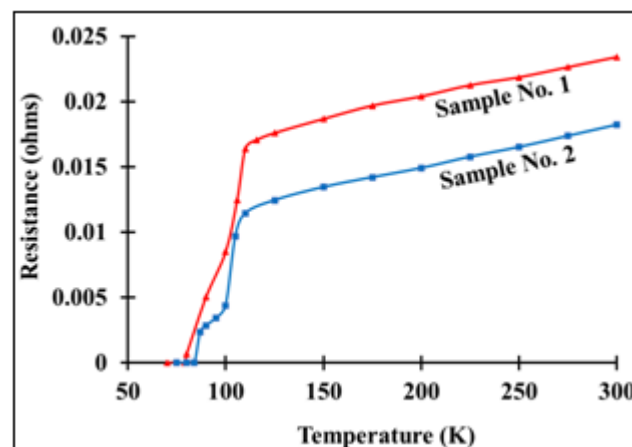


Figure 1: Resistance vs. Temperature Characteristics

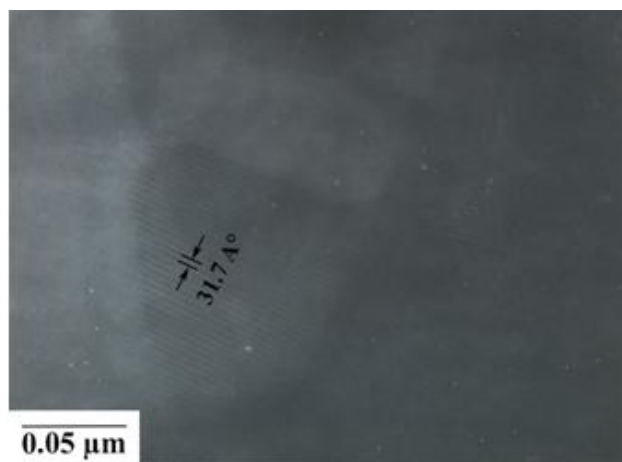
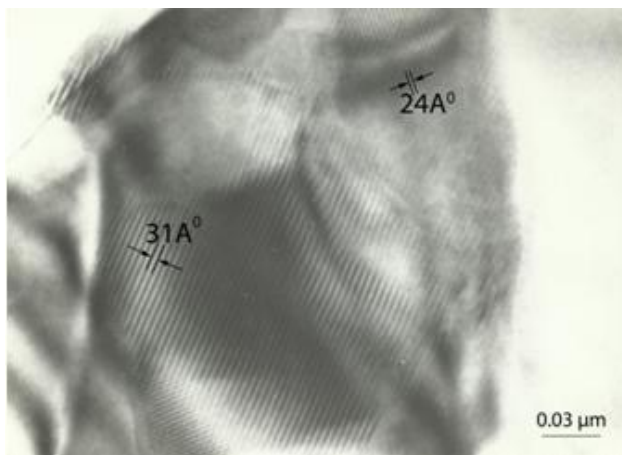
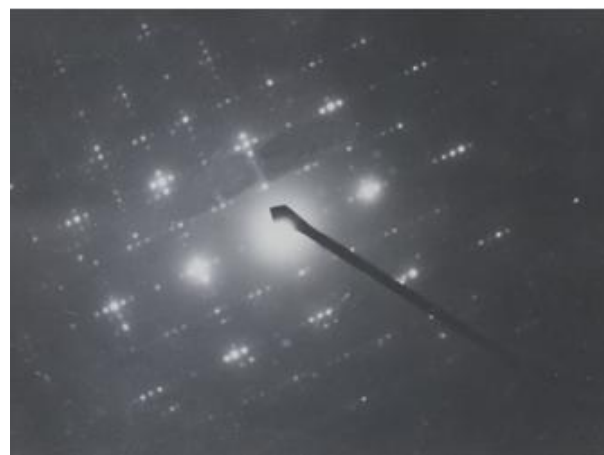
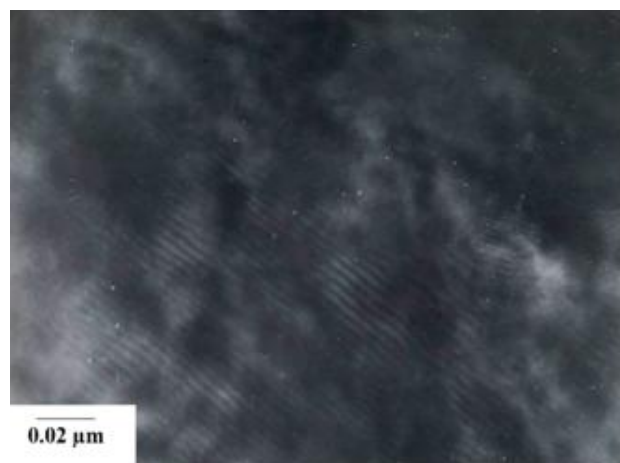
3. Results

The DC four probe technique was used to study the of resistance versus temperature characteristics of the sample Nos. 1 & 2. The resistance vs temperature characteristics of these samples are shown in figure 1. The sample No. 1 showed the metallic behaviour from room temperature to 110 K. It behaved like a superconducting material below 110 K and showed zero resistance at 79 K. Sample No. 2 also showed the metallic behaviour between room temperature and 110 K and showed superconducting properties below 110 K. But the zero resistance was observed at 84 K, in this case. The results of resistance vs. temperature data of these samples have been summarized in the table 1 given below:

Table 1: T_c Values of sample Nos. 1 and 2

Sample	Calcination Temperature (°C)	Calcination Time (hrs.)	Sintering Temperature (°C)	Sintering Time (hrs.)	$T_{c(on)}$ K	$T_{c(R=0)}$ K
1	800	48	845	168	110	79
2	830	48	845	168	110	84

The sample Nos.1 and 2 were investigated by transmission electron microscopy and electron diffraction Techniques to study the microstructural features and also to ascertain the presence of 2201, 2212 and 2223 superconducting phases in these samples. The electron micrographs shown in figures 4(a) to 4(d) depict the microstructural features of sample No. 1. While microstructural features of sample No.2 are shown in figures 4(e) to 4(g).

**Figure 4(a):** Lattice planes of 2212 phase observed in sample No.1**Figure 4(b):** Intergrowth of different phases observed in sample No. 1**Figure 4(c):** Selected Area Diffraction Pattern of Sample No. 1**Figure 4(d):** Wavelike fringes observed in sample No. 1

The electron micrograph in figure 4(a) depicts the high-resolution lattice image of an interesting region of sample No. 1. The lattice spacing between the lattice planes was found to be 31.7 \AA . The electron micrograph of another region of sample No. 1, shown in fig. 4(b) depicts lattice planes being formed from the multiple crystals having different lattice parameters. The grain boundaries were also observed. The electron diffraction pattern of a region of the sample shown in figure 4(c) depicts the main reflection along with the satellite spots along b-axis indicating the modulation in structure, which is incommensurate [14]. The high-resolution electron micrograph of the same sample shown in figure 4 (d) clearly depicts the wavelike fringes. The micrograph shows variation of contrast.

The high-resolution lattice image of sample No. 2 shown in figure 4(e) depicts the lattice fringes having different spacing. The lattice planes having spacing 19.5 \AA were observed in a region of the specimen while another region of the specimen was found to have the lattice planes with lattice spacing 14.76 \AA . The micrograph also depicts grain boundaries. The selected area diffraction pattern of the same region is shown in figure 4(f). The diffraction pattern shows satellite spots indicating the incommensurately modulated structure and fivefold symmetry along b-axis.

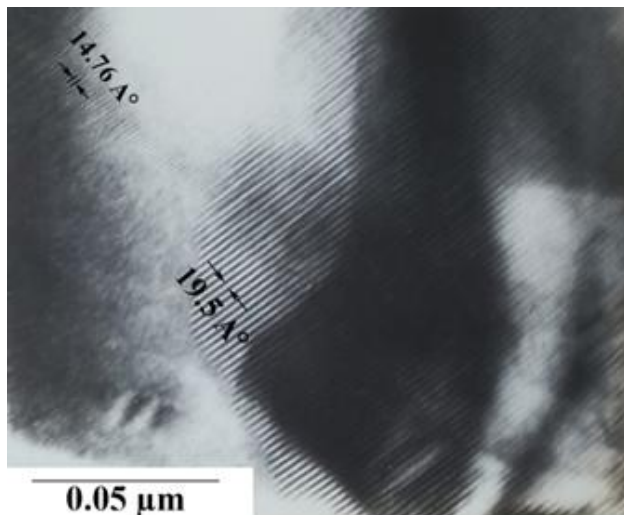


Figure 4(e): HRTEM Lattice image of Sample No. 2



Figure 4(f): Selected Area diffraction Pattern of Sample No.2

The high-resolution image of another interesting region of sample No.2 is shown in fig. 4(g). This micrograph shows the presence band structure in the specimen in an area of the micrograph while the remaining area was found to possess the rotational Moire pattern. The separation between the rotational Moire fringes was observed to be 48.11 \AA . The micrograph also shows the variation in contrast in the region showing the band structure.

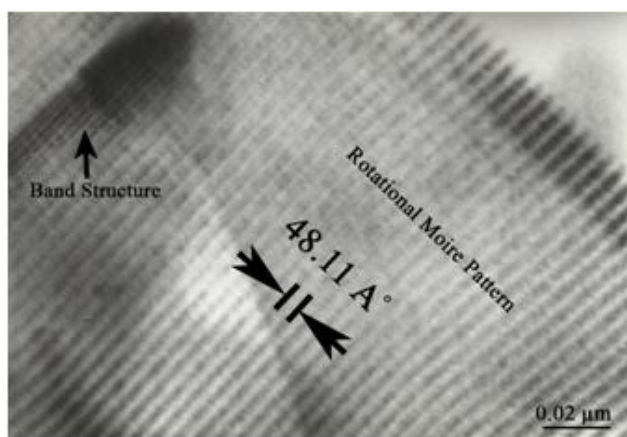


Figure 4(g): Band structure and rotational Moire Pattern observed in sample No. 2

4. Discussions

Figure 1(a) as well as Table 1 indicates that the sample No. 2 calcined at 830°C showed $T_{c(R=0)}$ at little higher value than the sample No.1 calcined at 800°C . These results of T_c measurements indicate that the calcination at 830°C was helpful in enhancing the T_c values in Bi-2223 superconductors. The melting point of Bi_2O_3 is 820°C . When the homogeneous mixture of the powders of Bi_2O_3 , SrCO_3 , CaCO_3 and CuO is calcined at 830°C , the Bi_2O_3 melts and diffuses into the structure of superconducting phases of BSCCO system, in turn creates the conducive conditions for the growth of superconducting phases.

The electron micrograph shown in figure 4(a) depicts the high-resolution lattice image of an interesting region of sample No. 1. The lattice spacing between the lattice planes was found to 31.7 \AA , which very close to the 'c' parameter of the unit cell of 2212 low T_c Phase. The electron micrograph of another region of sample No. 1, shown in fig. 4(b) depicts the lattice planes produced due the presence of overlapping of crystals having different lattice parameters. The grain boundaries and local variation in the lattice spacing was also observed. The electron micrograph clearly shows the presence of lattice planes produced from two or more crystals having unit cells with lattice spacing 24 \AA and 31 \AA indicating the presence of low T_c , 2201 and 2212 phases respectively. The presence of lattice planes with different lattice spacings i.e. 24 \AA and 31 \AA in the specimen is an indication of intergrowth of various superconducting phases in the sample. The electron diffraction pattern of a region of the sample shown in figure 4(c) depicts the main reflection along with the satellite spots along b-axis indicating the incommensurately modulated structure. The satellite spots are due to the double diffraction and are along b-axis. This diffraction pattern also indicated that two-unit cells are overlapping with their 'a' or 'b' axis perpendicular to each other. On indexing the electron diffraction pattern, the lattice parameters were found to be $a = 5.39 \text{ \AA}$ and $b = 27 \text{ \AA}$. The high-resolution electron micrograph of the same sample shown in figure 4 (d) clearly depicts the wave like fringes. These wavelike fringes are nothing but the Moire fringes. The presence of these wavelike fringes may be due to some kind of the defect in structure. The micrograph shows variation of contrast also

The high-resolution lattice image of sample No. 2 is shown in figure 4(e) depicts the lattice fringes having different lattice spacings. The lattice spacing, in one region of the micrograph was observed to be 19.5 \AA while in the other region it was found to be 14.76 \AA . The micrograph also depicts the grain boundaries. The lattice spacings of these fringes do not match with lattice spacings of either of the any constituent powdered materials or any of the superconducting phases. The growth of these unknown structures or the unit cells with lattice spacings 19.5 \AA and 14.76 \AA in these samples may be responsible to create the unfavourable conditions for the proper growth of high T_c phase resulting in the microstructural instability. The selected area diffraction pattern of the same region is shown in figure 4(f). The diffraction pattern shows satellite spots indicating the incommensurately modulated structure and fivefold

symmetry along b-axis. The diffraction pattern basically shows the principal and satellite reflection. There is a periodic variation in the intensity of satellite spots. After indexing the diffraction pattern, 'a' and 'b' parameters of the unit cell were found to be 5.4 \AA and 27 \AA respectively. The high-resolution image of another interesting region of sample No.2 is shown in fig. 4(g). This micrograph shows the presence of rotational Moire patterns as well as the band structure in the specimen. The grain boundaries were also observed. The spacing between the Moire fringes was found to be 48.11 \AA . The formation of Moire pattern having spacing 48.11 \AA can take place when two crystals having unit cells of 2223 phase with c-parameter 36.8 \AA are lying over one another at angle of 45° . These results confirmed the presence of high T_c phase in the specimen. The micrograph also shows the variation in contrast. The presence of bands in a region of the specimen corresponds to the different layers of oxides in the compound which are not fully resolved.

5. Conclusions

The synthesis of 2223 compound of Bi-system has been described and the material thus prepared has been characterized by different techniques. The resistance versus temperature measurements of the sample calcined at $800 \text{ }^\circ\text{C}$ and sintered at $845 \text{ }^\circ\text{C}$ showed lower values of T_c as compared to the sample calcined at $830 \text{ }^\circ\text{C}$ and sintered at $845 \text{ }^\circ\text{C}$. This shows that the calcination at $830 \text{ }^\circ\text{C}$ is advisable to growth of high T_c phase in 2223 compound of BSCCO superconductors and also to get $T_{c(R=0)}$ at higher temperature. The high-resolution transmission electron microscopy and electron diffraction investigations of these samples confirmed the presence of 2201, 2212 and 2223 superconducting phases. The c-parameter corresponding to these phases were found to be 24 \AA , 31 \AA and 30.6 \AA respectively. Some unknown phases with the lattice spacings of 19.5 \AA and 14.76 \AA were also observed. The formation of these unknown phases may be responsible for creating the unfavourable conditions for the proper growth of high T_c phase resulting in the microstructural instability. The electron diffraction study of the samples revealed orthorhombic structure and the values of a and b parameters of the unit cell were found to be 5.4 \AA and 27 \AA respectively. The lattice images, rotational Moire fringes, formation of Bands and grain boundaries etc. have been observed in the 2223 compound of the Bi-system.

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