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Lattice Imaging of Superconducting Phases Formed in Undoped and Pb-Doped 1112-BSCCO Compounds

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Abstract: ***In the present paper the author has reported the systematic study on the preparation of undoped and Pb-doped BSCCO superconductors having starting stoichiometric composition 1112 and prepared by the solid-state reaction technique. The efforts were made to correlate the variations in the preparatory conditions with temperatures dependance of electrical resistance of these samples. The Transmission Electron Microscopy and Electron Diffraction techniques were used study the lattice parameters, grain boundaries, dislocations, Moire patterns and microstructure of these samples. The efforts were made to identify the various superconducting phases formed in these samples through lattice imaging and electron diffraction techniques. The analysis of these results is also being reported in this paper.***

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

1. Introduction

It is well established, from the studies of BSCCO superconductors carried out by several workers [1-8], that BSCCO system has three superconducting phases; very low T_c phase (2201), low T_c phase (2212) and high T_c phase (2223). The highest value of T_c was reported [9] to be 120 K in BiSrCaCuO System superconductors. The doping of BSCCO superconductors, especially with Pb was found to be highly successful in enhancing the high T_c superconducting phase in BSCCO superconductors. In Pb-doped BSCCO superconductors the zero resistance has been achieved at 125K by Huang et al [10]. In the present paper the author has focused on reporting the results obtained by preparing the un-doped and Pb-doped compounds of 1112-BSCCO superconductors by solid state reaction technique under different calcination, sintering and annealing conditions. The main emphasis was to identify the 2201, 2212 & 2223 superconducting phases formed in these compounds by using lattice imaging technique, i.e. high-resolution electron microscopy and electron diffraction techniques. The efforts were also made to correlate the variations in the preparatory conditions with temperatures dependence of electrical resistance of these samples. The High Resolution Transmission Electron Microscopy and Electron Diffraction techniques were also used study the grain boundaries, dislocations and Moire patterns etc. of these samples.

2. Materials and Methods

The samples of undoped and Pb-doped 1112 compound of Bi-System Superconductors were synthesized by Solid State Reaction technique. Three undoped samples and one Pb-doped sample were prepared for this study.

The three undoped samples having the same nominal starting composition were prepared under different preparatory conditions. The stoichiometric composition of the starting material was taken $Bi_1Sr_1Ca_1Cu_2O_x$. Dry powders of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO with the cation molar ratio Bi:Sr:Ca:Cu::1:1:1:2 were thoroughly mixed and ground. The thoroughly mixed powder was divided into three parts.

The first part of the powder was calcined at 800°C for 13 hrs. 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 850°C in air for 2 hours. After sintering the pellets were cooled to 500°C at the rate of 1°C/min. These pellets were annealed at 500°C for 6 hrs in air and then cooled to room temperature inside the furnace. The resulting material was named as sample No. 1.

The second part of the powder, was calcined at 800°C for 5 hrs. in air. Later it was cooled to room temperature inside the furnace. The calcined mixture was again pulverized and ground to get a fine and homogeneous powder. It was again calcined at 820°C for 2 hrs. in air and was allowed to cool to room temperature inside the furnace. This material was again pulverized to form a fine and homogeneous powder and then was pelletized. These pellets were sintered at 850°C for 3 hrs. in air and were cooled to 400°C at the rate of 1 °C/min. These pellets were annealed at 400°C for 5 hrs. in air and then cooled to room temperature inside the furnace. The resulting material was named as sample No. 2.

The third part of the powder, was calcined at 800°C for 3 hrs. in air. Later it was cooled to room temperature inside the furnace. The calcined mixture was pulverized and ground to get a fine and homogeneous powder and then it was pelletized. These pellets were sintered at 850°C for 3 hrs. in air. After sintering the pellets were cooled to 500°C at the rate of 1°C/min. These pellets were annealed at 500°C for 6 hrs. in air and then cooled to room temperature inside the furnace. These pellets were again put in the furnace and were partially melted at 900°C for 1 minute. After partially melting these pellets were cooled to 820°C at the rate of 1 °C/min. These pellets were then annealed at 820°C for 2 hrs. Later these pellets were allowed to cool to room temperature

inside the furnace. The resulting material was named as sample No. 3.

The Pb-doped sample having the stoichiometric composition $Bi_{0.7}Pb_{0.3}Sr_1Ca_1Cu_2O_x$ of the starting material was also prepared by solid state reaction technique. Dry powders of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO with the cation molar ratio Bi:Pb:Sr:Ca:Cu::0.7:0.3:1:1:2 were thoroughly mixed and ground. This mixture was calcined at 830°C for 48 hrs. 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 432 hours in air. These pellets were then cooled to room temperature at the rate of 2°C/min. The resulting material was named as sample No. 4.

3. Results

The DC four probe technique was used to study the of resistance versus temperature characteristics of the sample Nos. 1, 2, 3 & 4. 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 70 K. It behaved like a superconducting material below 70 K and showed zero resistance at 35 K. this sample also showed a sudden dip in its resistance at 45 K. Sample No. 2 also showed the metallic behaviour between room temperature and 108 K and showed superconducting properties below 108 K. But the zero resistance was observed at 41.4 K. In this sample the superconducting transitions were also observed at 80 K and 64 K. The sample No. 3 showed the metallic behaviour up to 80 K and zero resistance at 53 K. While in the case of Sample No. 4, the $T_{c(on)}$ was observed at 108 K and $T_{c(off)}$ at 90 K. The results of resistance vs. temperature data of these samples have been summarized in the table 1 given below:

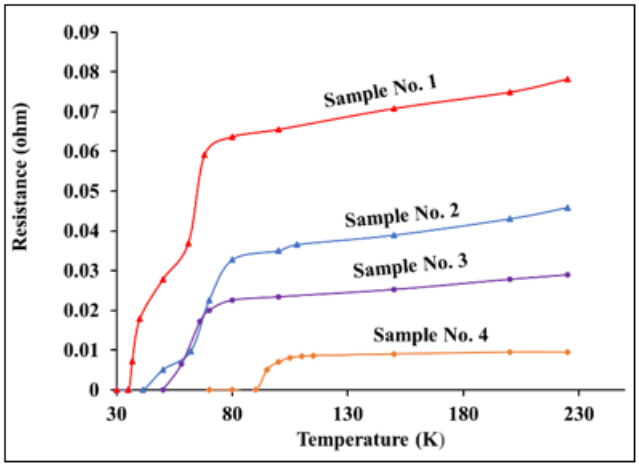

Figure 1: The resistance vs temperature characteristics of sample Nos. 1, 2, 3 & 4

Table 1: T_c Values of sample Nos. 1, 2, 3 and 4

Sample No.	$T_{c(on)}$ (K)	$T_{c(off)}$ (K)
1	70	35
2	108	41.4
3	80	53
4	108	90

All the samples were investigated by transmission electron microscopy and electron diffraction techniques to study the microstructural features. The lattice imaging technique was used to ascertain the presence of 2201, 2212 and 2223 superconducting phases in these samples.

The electron micrographs shown in figures. 2, depicts the microstructural features of sample No. 1. This electron micrograph depicts the high-resolution lattice image of an interesting region of sample No. 1. The lattice spacing between the lattice planes was found to 24.5 A°, which is very close to the c-parameter of 2201 superconducting phase.

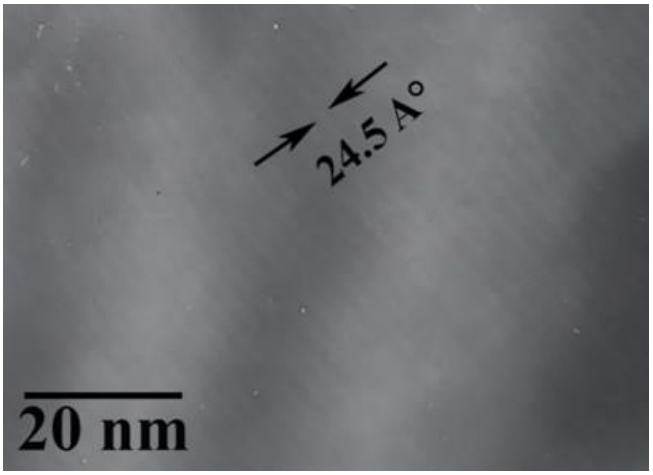

Figure 2: Lattice planes of 2201 phase observed in sample No.1

The microstructural features of sample No.2 are shown in figures 3(a) & 3(b). The electron micrograph shown in figure 3(a), depicts lattice planes of the superconducting phase formed in sample No. 2. The lattice spacing between the lattice planes was found to be 24.6 A° indicating the presence 2201 superconducting phase. The grain boundaries were also observed. One specimen of sample Nos. 2 was prepared by using the Dual Ion Milling machine. When the ion milled specimen was investigated by transmission electron microscope, it showed interesting features as shown in figure 3(b).

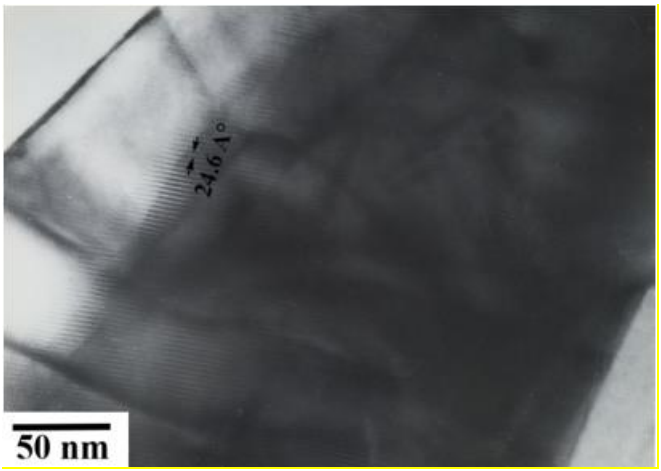

Figure 3 (a): Lattice planes of 2201 phase observed in sample No.2

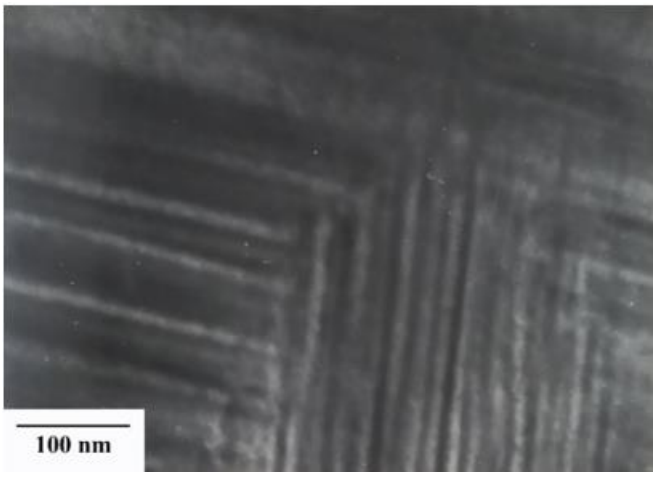

Figure 3 (b): Band Structure and Twinning observed in sample No.2

The microstructural features of sample No.3 are shown in figures 4(a) & 4(b). The micrograph shown in figure 4(a) depicts dislocations and twining in the specimen. The high-resolution electron micrograph of the sample No. 3 shown in figure 4 (b) clearly depicts the Lattice fringes. The micrograph contains two types of the lattice fringes of the unit cells having c-parameters of 24.5 A° and 12.15 A°. Apart from the lattice fringes, the grain boundaries were also observed in it. The lattice spacing of 24.5 A° belongs to the c-parameter of the unit cell of 2201 superconducting phase. While 12.15 A° is equal to c-parameter of the unreacted Ca_2CuO_3 phase. Figure 4(c) depicts the selected area diffraction pattern of same sample. The electron diffraction pattern of a region of this sample shown in figure 4(c) depicts the main reflection along with the satellite spots along b-axis indicating the incommensurately modulated structure [11] and five-fold symmetry along b-axis. This micrograph shows that the diffraction patterns was produced by two crystals / unit cells lying over one another at an angle of 32°.

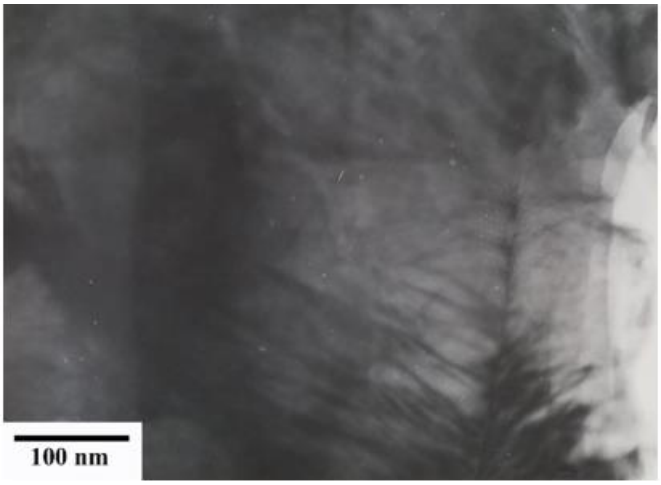

Figure 4 (a): Dislocations and Twinning observed in Sample No. 3

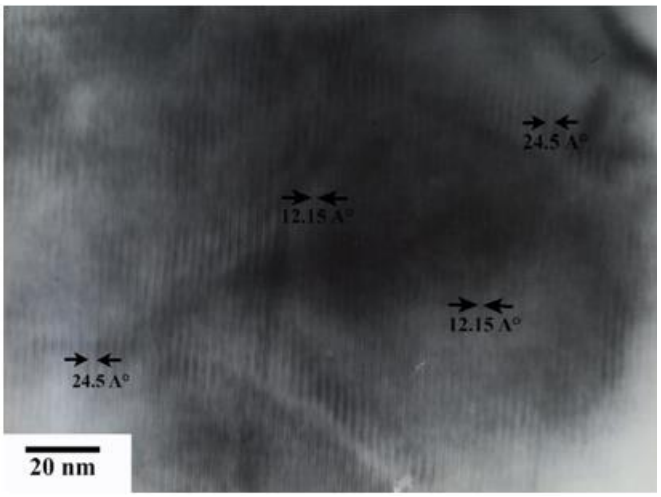

Figure 4 (b): Lattice fringes observed in Sample No. 3

Figure 4 (c): SAD Pattern observed in Sample No. 3

The electron micrograph shown in figure 5(a) depicts the HRTEM image of sample No. 4 while the micrograph shown in figure 5(b) depicts its selected area diffraction pattern. The high-resolution image of an interesting region of this sample shows the presence of brick like structure / band structure in the specimen, which is supposed to be formed due to the excessive formation of rotational Moire patterns. The separation between the rotational Moire fringes was observed to be 88.5 A° and 77.1 A°. The selected area diffraction pattern of some region is shown in figure 5(b). The diffraction pattern shows satellite spots indicating the incommensurately modulated structure and fivefold symmetry along b-axis.

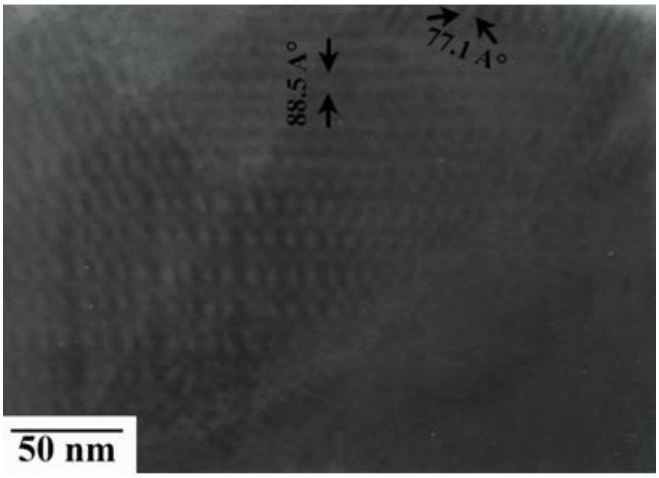

Figure 5 (a): Moire fringes observed in Sample No. 4

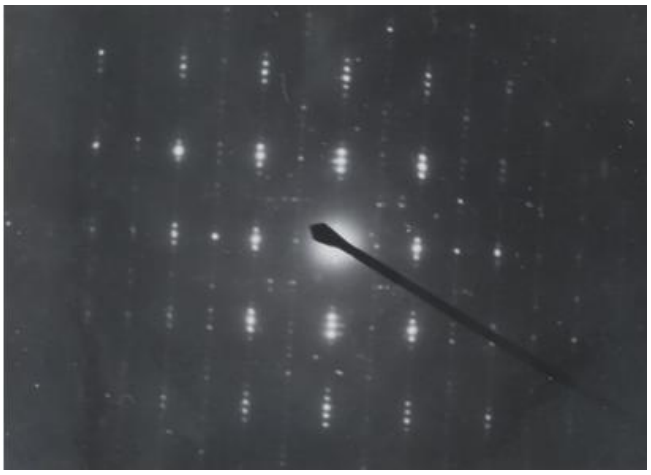

Figure 5 (b): Selected Area Diffraction Pattern of Sample No. 4

4. Discussions

From the T_c measurements, shown in Figure 1 as well as Table 1, sample Nos. 1 & 2, it is clear that the recalcination of sample No 2 and its sintering for a little longer time increases the T_c values to some extent. It is because, when the calcined material was reground to form a fine and homogeneous powder and re-calcined, it might have induced the favourable conditions for the growth of superconducting phases in turn the T_c values. The results of sample Nos. 2 and 3 indicate that although both the samples were sintered for the same duration, but sample No.3 which was partially melted after sintering, was found to show higher values of T_c. This may be due to the partial melting would have been helpful in proper diffusion of atoms to form the superconducting phases. While sample No. 4, which was doped and calcined at 830°C & sintered at 845°C showed $T_{c(off)}$ at a higher value than the undoped sample Nos. 1, 2 & 3 calcined at temperatures less than 830°C.

The analysis of the results of T_c measurements, indicated that the calcination at 830°C was helpful in enhancing the T_c values in Pb-doped 1112-compound of BSCCO superconductors. This is because the melting point of Bi_2O_3 is 820 °C. When the homogeneous mixture of the powders of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ 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. Also, some of the Bi-atoms may get evaporated during calcination at a temperature greater than its melting point. The vacancies thus created are occupied by the Pb-atoms. This could be the one of the probable reasons responsible to enhance the value of T_c.

This electron micrograph, shown in figures. 2, depicts the high-resolution lattice image of an interesting region of sample No. 1. The lattice spacing between the lattice planes was found to 24.5 A° which is nearly equal to the c-parameter of 2201 phase of BSSCO superconductors. The 2201 superconducting phase of BSCCO superconductors is considered to be very low T_c superconducting phase. Thus, by resolving the c-parameter of 2201 superconducting phase in BSCCO compounds by lattice imaging technique, it's presence was confirmed in Sample No. 1.

The electron micrograph shown in figure 3(a), depicts lattice planes of the superconducting phase formed in sample No. 2. The lattice spacing between the lattice planes was found to be 24.6 A° indicating the presence 2201 superconducting phase. The presence of 2201 superconducting phase was prominently observed in this sample. The presence of 2212 and 2223 phases could not be observed in this sample. It may be because the duration of calcination and sintering is not sufficient for the growth of 2212 and 2223 superconducting phases. The grain boundaries were also observed. One specimen of sample Nos. 2 was prepared by using the Dual Ion Milling machine, for HRTEM studies. The microstructural features of this sample are shown in figure 3(b). This specimen showed the banded structure and the twinning.

The micrograph shown in figure 4(a) depicts dislocations and twining in the sample No.3. The high-resolution electron micrograph of the sample No. 3 shown in figure 4 (b) clearly depicts the Lattice fringes. The micrograph contains two types of the lattice fringes of the unit cells having c-parameters of 24.5 A° and 12.15 A°. The lattice spacing of 24.5 A° belongs to the c-parameter of the unit cell of 2201 superconducting phase. While 12.15 A° is equal to c-parameter of the unreacted Ca_2CuO_3 phase. Although the partial melting of sample No.3 showed a little higher value of $T_{c(off)}$ in compaision to the $T_{c(off)}$ values of Sample No. 1 & 2, yet the. the presence of unreacted phase Ca_2CuO_3 may be responsible for creating the unfavourable conditions for the proper growth of 2212 & 2223 high T_c superconducting phases resulting in the microstructural instability. Apart from the lattice fringes, the grain boundaries were also observed in it.

The selected area diffraction pattern of a region of sample No. 3 shown in figure 4(c) depicts the main reflections along with the satellite spots along b-axis indicating the incommensurately modulated in structure. The formation of this diffraction pattern is due to the presence of two overlapping unit cells lying over one another at an angle of 32° between their respective axes.

The high-resolution image of an interesting region of sample No. 4, shown in figure 5(a), depicts the presence of brick like

structure / band structure, which is perhaps formed due to the excessive formation of rotational Moire patterns. The spacings between the rotational Moire fringes was observed to be 88.5 A° and 77.1 A°. The presence of Moire fringes having a spacing of 88.5 A° is formed due to the two unit cell of 2223 superconducting phase lying over one another with c-axes at an angle of 24° from one another. The presence of Moire fringes having a spacing of 77.1 A° is formed due to the two unit cell of 2212 superconducting phase lying over one another with their c-axes at an angle of 23° from one another.

The selected area diffraction pattern of some region of sample No. 4, shown in figure 5(b). shows satellite spots indicate the incommensurately modulated structure and fivefold symmetry along b-axis. The electron diffraction study of the samples revealed orthorhombic structure and the values of the a and b parameters of the unit cell were found to 5.4 A° and 27 A° respectively.

5. Conclusions

Samples of 1112 compounds of undoped & Pb-1112-BSSCO were prepared and characterized by DC Four Probe technique, lattice imaging, High Resolution Transmission Electron Microscopy and Electron Diffraction Techniques.

From the T_c measurements of sample Nos. 1 & 2, shown in Figure 1 as well as Table 1, it is clear that the recalcination of sample No 2 and its sintering for a little longer time increases the T_c values to some extent. The results of sample Nos. 2 and 3 indicate that although both the samples were sintered for the same duration, but sample No.3 which was partially melted after sintering, was found to show a little higher value of T_c. While sample No. 4, which was doped and calcined at 830°C & sintered at 845°C showed $T_{c(off)}$ at a higher value than the undoped sample Nos. 1, 2 & 3 calcined at temperatures less than 830°C. The analysis of the results of T_c measurements, indicated that the calcination at 830°C was helpful in enhancing the T_c values in Pb-doped 1112-compound of BSCCO superconductors.

The presence of lattice planes having spacing, approximately, 24.5 A° confirms the presence of 2201 superconducting phase in sample Nos. 1, 2 &3. Even the lattice planes having spacing 12.15 A° belonging to an unreacted Ca_2CuO_3 phase were also observed. A specimen prepared from sample No.2 by Dual Ion Milling machine for HRTEM studies showed the banded structure and the twinning. The dislocations and twining were also observed in sample No. 3. The selected area diffraction pattern of a region of sample No. 3 depicted the incommensurately modulated and the present of overlapping crystals with their axes rotated at angle of 32°.

The high-resolution image of an interesting region of sample No. 4, depicted the presence of brick like structure / band structure, which is supposed to be formed due to the excessive formation of rotational Moire patterns. The analysis of these rotational Moire patterns confirmed the presence of 2212 and 2223 high Tc superconducting Phases in Sample No. 4. The selected area diffraction pattern of sample No. 4, indicated the incommensurately modulated structure and fivefold symmetry along b-axis.

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