International Journal of Science and Research (IJSR)
ISSN: 2319-7064
SJIF (2022): 7.942

Investigation of Atom Diffusivity and Phase Formation in Bi-System Superconductors

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Abstract: ***The samples of $Bi_1Sr_1Ca_1Cu_2O_x$ and $Bi(Pb)_1Sr_1Ca_1Cu_2O_x$ superconductorswere prepared by solid state reaction technique. The studies showed that the formation of 2223 - high T_c phase, 2212 - low T_c phase and 1112 phase etc. took place in the final product obtained after calcination and sintering. The electrical resistance versus temperature characteristics of these samples showed that although the prolonged sintering was found to enhance the T_c values, yet it could not be helpful in obtaining the single phased material. Scanning Electron Microscopic (SEM) studies of these samples depicted different kinds of surface morphological features and confirmed the presence of various phases.***

Keywords: Surface Morphology, Elemental Analysis, Stoichiometric Composition, Calcination, Sintering

1. Introduction

The study of Bi-System superconductors has been carried out by several workers [1-12]. The Bi-system superconductors were found to consist three superconducting phases namely 2201 phase, 2212 phase and 2223 phase. The highest value of T_c up to 120 K has been reported [8] in the samples of BSCCO system prepared under very well controlled conditions, while the Pb-doped samples of Bi-System superconductors showed T_c values at 125 K [9]. In the present paper, the results obtained from the studies of the of $Bi_1Sr_1Ca_1Cu_2O_x$ and $Bi(Pb)_1Sr_1Ca_1Cu_2O_x$ superconducting materials prepared by using solid state reaction technique and investigating these samples by using DC Four Probe Technique, Scanning Electron Microscopy (SEM) and Energy dispersive X-ray spectrometer (EDS) have been discussed. The main objective of the study was to study the diffusivity of atoms into the structure of high T_c and low T_c phases of $Bi_1Sr_1Ca_1Cu_2O_x$ and $Bi(Pb)_1Sr_1Ca_1Cu_2O_x$ superconducting samples.

2. Materials and Methods

The solid state reaction technique was used to prepare the samples of undoped as well as Pb-doped 1112 compounds of Bi- system of superconductors. The undoped samples of 1112 compound of Bi- system of superconductors were prepared by taking the powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO in the starting nominal ratio Bi:Sr:Ca:Cu::1:1:1:2. These powders were mixed and ground an agate pestle and mortar to get a homogeneous mixture. The homogeneous mixture was calcined twice at 800 °C for 6 hrs. with intermediate grinding and then cooled to room temperature. The resulting mixture was reground and pelletized. These pellets were sintered at 850 °C for 3 hrs. in air and then cooled to 500 °C at acooling rate of 1 °C/min. The pellets were annealed at 500 °C for 5 hrs. After annealing the pellets were cooled to room temperature and were named as sample No. 1**.**

Pb-doped samples of 1112 superconductors were prepared by mixing the powders of Bi_2O_3, PbO, $SrCo_3$, $CaCO_3$, and CuO in the starting nominal stoichiometric ratio Bi:Pb:Sr:Ca:Cu::0.7:0.3:1:1:2. These powders were mixed and ground in an agate pestle and mortar to form a fine and homogeneous powder. The powder was calcined at 830 °C for 48 hrs. with intermediate grinding. After cooling the resulting powder was reground to make a fine homgeneous mixture and then this mixture was pellettized. These pellets were divided into three parts.The pellets of the first part were sintered at 845 °C for 288 hrs. and later cooled to room temperature at a cooling rate of 2 °C/min. These pellets were named as sample No. 2. Similarly the pellets of second part were sintered at 845 °C for 312 hrs. & cooled to room temperature at a coling rate of 2 °C/min. and were named as sample No. 3. While the pellets of third part were sintered at 845 °C for 408 hrs. these pellets were cooled to room temperature at a coling rate of 2 °C/min. and named as sample No. 4.

3. Results

The variation of resistance with temperature of these samples has been studied with DC four probe method to determine the T_c values. The resistance versus temperature curves of these samples are shown in fig. 1.

The resistance versus temperature curve of sample No. 1 showed the metallic behaviour from room temperature to 70 K. This sample showed the superconducting behaviour below 70 K and the zero resistance was observed at 50 K. The resistance versus temperature curve of sample No. 2 showed the behaviour as that of a metal from room temperature to 90 K. It showed the superconducting nature below 90 K and zero resistance was observed at 71 K. The resistance versus temperature curve of sample No. 3 showed the behaviour similar to a semiconducting material between room temperature and 93 K. It showed the superconducting properties below 93 K and zero resistance was observed at 73 K. This sample showed higher values of resistancecompared to other samples. The resistance versus temperature curve of sample No. 4 showed the metallic behaviour between room temperature and 105 K. It showed the superconducting properties below 105 K and zero resistance was observed at 90 K.

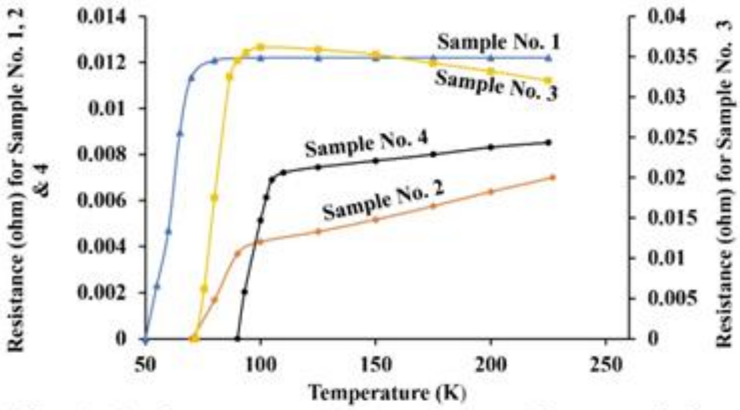

Fig. 1: Resistance vs. Temperature Characteristics of Sample Nos. 1, 2, 3 & 4

The T_c values of sample No. 1, 2, 3 and 4 obtained form the resistance versus temperature curves of these samples are summarized in the table given below:

Sample No.	$T_{C(on)}$ (K)	$T_{C(off)}$ (K)
1	70	50
2	90	71
3	93	73
4	105	90

The surface morphological investigations of these samples were carried out by Scanning Electron Microscopy (SEM) and the elemental analysis at a number of regions of these samples. showing various morphological features, was carried out by Energy Dispersive X-ray Spectrometer attached with SEM. The electron micrograph depicting the surface morphological features of sample No. 1 is shown in fig. 2(a).

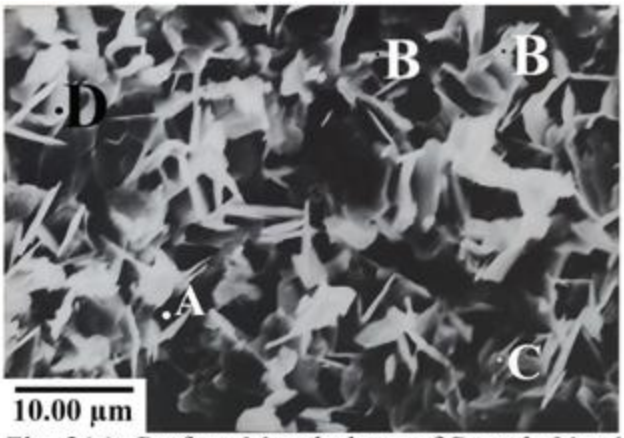

Fig. 2(a): Surface Morphology of Sample No. 1

The micrograph basically depicts various types of morphological features. The composition at various regions marked as A, B, C and D is given below:

Table 1: Composition at various regions of Sample No. 1

Region Marked as	Bi	Sr	Ca	Cu
A	1.00	3.42	2.19	28.47
B	0.95	1.10	1.00	1.96
C	1.00	1.20	1.09	2.96
D	2.01	2.03	0.99	2.05

It can be seen from the table 1 that the black region marked as 'A' was found to have excessive copper and rich in strontium also. The rod like morphology marked as 'B' was found to possess 1112 composition with a little excess of strontium while the region marked as 'C', showed strontium rich 1113 composition. While the region as 'D' was found to possess the 2212 - low T_c superconducting phase.

The surface morphological features of sample No. 2 are shown in fig. 2(b). The composition at various regions marked as A, B, C and D is given below:

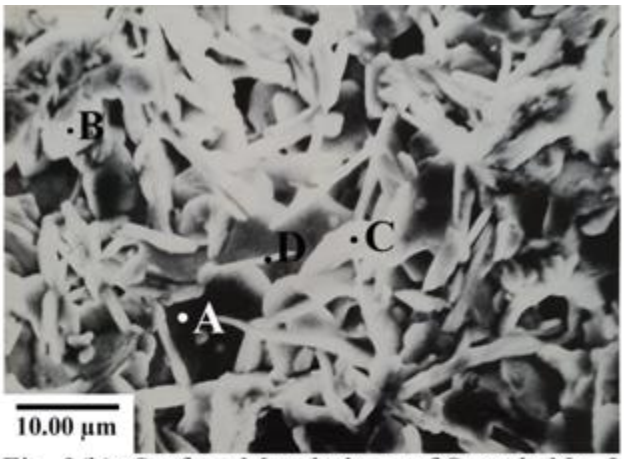

Fig. 2(b): Surface Morphology of Sample No. 2

Table 2: Composition at various regions of Sample No. 2

Region Marked as	Bi(Pb)	Sr	Ca	Cu
A	1.40	1.12	1.11	18.61
B	1.00	1.15	1.00	2.05
C	1.96	2.01	0.98	2.06
D	2.00	2.00	1.99	2.95

It can be seen from the table 2 that various phases were formed in the sintered material. The region marked as 'A' represents Cu rich phase and the region marked as 'B' is to found to possess 1112 composition. The region marked as 'C' depicts the 2212 low T_c phase, while the region marked as 'D' was found to contain 2223 high T_c phase.

The surface morphological features of sample No. 3 are shown in fig. 2(c). The composition at various regions marked as A, B, C and D is given below:

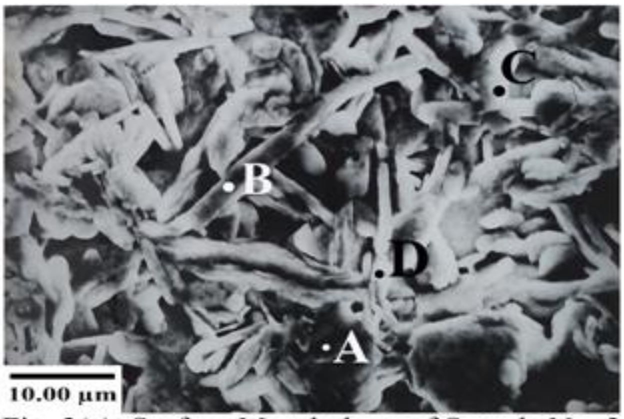

Fig. 2(c): Surface Morphology of Sample No. 3

Table 3: Composition at various regions of Sample No. 3

Region Marked as	Bi(Pb)	Sr	Ca	Cu
A	-----	0.89	1.14	8.06
B	1.00	0.92	0.96	2.14
C	1.01	0.95	1.00	3.02
D	2.00	2.05	2.01	3.06

It can be seen from the table that various phases were formed in the sintered material. The region marked as 'A' showed the completed absence of Bi(Pb) and was found to be rich in Cu. While the region marked as 'B' showed 1112 composition. The region marked as 'C' represented 1113 phase and the region marked as 'D' is to found to possess 2223 high T_c phase.

The surface morphological features of sample No. 4 are shown in fig. 2(d). The composition at various regions marked as A, B, C and D is given below:

Table 4: Composition at various regions of Sample No. 4

Region Marked as	Bi(Pb)	Sr	Ca	Cu
A	1.00	1.00	0.09	13.16
B	1.00	0.97	0.91	2.03
C	2.00	2.00	1.00	2.00
D	2.00	1.98	2.02	2.98

It can be seen from the table that various phases were formed in the sintered material. The region marked as 'A' was found to be rich in Cu, while the region marked as 'B' was found to represent the 1112 phase. The region marked as 'C' depicts 2212 low T_c phase, and the region marked as 'D' is to found to possess 2223 high T_c phase.

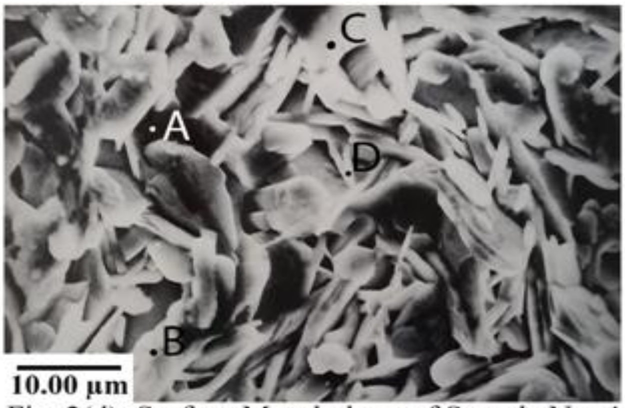

Fig. 2(d): Surface Morphology of Sample No. 4

4. Discussions

Sample No. 1 showed the superconducting behaviour below 70 K and the zero resistance was observed at 50 K. This indicate that a small sintering period of 3 hrs. is enough to start the nucleation of superconducting phases in the sample. But for the further development of these superconducting phase, the samples need to be sintered for more time.

All the samples studied and being discussed here, showed the behaviour as that of a metal or a semiconductor between the room temperature and crtical transition temperature $T_{c(on)}$.These samples showed the superconducting behaviour below $T_{c(on)}$. The samples numbered 2 and 3 did not show much variation in the T_c values, even sample No. 3 was sintered for 24 hrs. more than that of Sample No. 2. It has been observed from the study of the variation of resistance versus temperature characteristics, shown in figure 1, of these samples, that sample No. 4, sintered for 408 hrs., showed the higher value of $T_c$in comparision to samples numbered 1, 2 and 3.

Sample No. 1 showed a number of morphological features as shown in figure 2(a). As observed from the elemental analysis at the morphological features that the elemental composition at each feature is not same. It is indicative of the nucleation of various phases in this sample. This sample did not show higher values of T_c, due to lack of the proper growth high T_c phase in this sample. It can be concluded that the sintering time of 3 hrs. is just not sufficient for the development and growth of high $T_c$phase in this sample. A large area of the sample was found to possess excessive Copper and also rich in strontium. This is indicative that the diffusion of the atoms, in the desired ratio, into the structure of high $T_c$superconducting phases did not take place. Although there are many other factors, such as calcination time, calcination temperature, sintering time, sintering temperature, cooling mode, rate of cooling, annealing time and temperature etc., which are supposed to be responsible for the proper growth of the desired high T_c phase.The doping of Pb into 1112 compound of Bi-system of superconductors was also found to enhance and stabilize the growth of high T_c phase.With a view to study the diffusion of atoms, in desired ratio, into the structure of high T_c superconducting phases, the sample Nos. 2, 3 and 4 were doped with Pb to enhance the growth of high T_c. These samples were also sintered for longer period to study the further growth of high T_c phase, in turn the diffusion of the atoms of Bi, Pb, Sr, Ca and Cu into the structure of high T_c phases forming the unit cells of 2212 and 2223 superconducting phases. The SEM and EDS investigations of these samples indicated that every sample contains regions with excessive copper. In sample No. 3, the complete absence of Bi(Sr) was observed at some regions, while several regions of sample No. 2 were found to possess excessive Copper, Bi(Pb), Sr and Ca and sample No. 4 was found to deficient in Ca. These results indicate that the diffusion of atoms Bi, Pb, Sr, Ca, and Cu into the structure of high T_c superconducting phase, in proper ratio, is lacking in these sample. Even the prolonged period of sintering could not be completely helpful in controlling the proper diffusion of atoms for the growth 2223 high T_c

phase.Although the longer period of sintering changed the morphological features, but still more than one type of morphological features was observed. Elemental analysis of these samples confirmed the presence of various phases in these samples. Thus, just by sintering the material for longer periods is neither helpful in getting the single-phased material i.e., properly grown 2223 high T_c phase nor helping in the helping in the proper diffusion of atoms in the structure of 2212 or 2223 – superconducting phases.

5. Conclusions

In the case of sample No. 1, it was observed that a small sintering period of 3 hrs. is enough to start the nucleation of vaious phases. But this time period is not sufficient for the furthur growth of high T_c superconducting phase.For this to achieve the sample should be sintered for more time.It has been observed from the study of the variation of resistance versus temperature characteristics, shown in figure 1, of these samples, that sample No. 4, sintered for 408 hrs., showed the higher value of $T_c$in comparision to samples numbered 1, 2 and 3.

The elemental analysis at different morphological features indicated that the nucleation of various phases took place in all the samples. Several local areas of these sample were found to possess excessive Copper, Strontium Bi(Pb), and Calcium. While some regions of these samples, in particular Sample No. 3 were found to be rich in Copper with the complete absence of Bi(Pb). Also, some regions of sample No. 4 were found to be Copper rich and highly deficient in Calcium. This is indicative that the diffusion of the atoms of Bi, Pb, Sr, Ca, and Cu in the desired ratio for the formation and development of high T_c phase could not take place. The prolonged period of sintering could not be completely helpful in controlling the proper diffusion of atoms for the growth 2223 high T_c phase. Although the longer period of sintering changed the morphological features, but still more than one type of morphological features was observed. Different morphological features were found to consist different elemental compositions.

Acknowledgement

The author has carried out this work at the Electron Microscope Section, National Physical Laboratory, New Delhi (India). The author wishes to thank the National Physical Laboratory and late Dr. S. K. Sharma for providing the technical support for carrying out this research work.

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