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Microstructural Investigations & Compositional Analysis of Undoped and Pb-Doped 1112-Compounds of BSCCO System

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Abstract: ***Undoped and Pb-doped superconducting 1112-compounds of Bi-system were prepared by solid state reaction technique. The electrical resistance versus temperature characteristics of these samples showed that the partial melting of the material was helpful in enhancing the T_c values. The doping of 1112-compound of Bi-Sr-Ca-Cu-O system with Pb, showed further higher values of $T_{c\,(on)}$ and $T_{c\,(off)}$. The elemental analysis of these of these samples, carried out by EDS, confirmed the presence of 2223, 2212 and 2201 phases in these samples. SEM studies of these samples depicted different kinds of surface morphological features indicating the presence of various phases. The studies indicated that although the initial stoichiometric composition taken was 1112, yet the nucleation of various phases such as high T_c phase (2223), low T_c phase (2212) and 2201 phase etc. took place and the final product, contained various phases. Microstructural investigations of these samples were carried out to study the lattice parameters, grain boundaries, twin boundaries and Moire patterns etc. High resolution images having lattice spacing 24.5 A° and 30.8 Aº were observed.***

Keywords: Energy Dispersive X-ray Spectrometer, High Resolution Electron Microscopy, Microstructure, Moire fringes, Surface Morphology

1. Introduction

Since the discovery of High T_c superconducting phase in Bi-Sr-Ca-Cu-O system by Maeda et al [1], the extensive research work has been carried out in this area by several researchers [2-12]. The compounds of BSCCO system were generally found to consist three superconducting phases; very low T_c phase (2201), low T_c phase (2212) and high T_c phase (2223). The value of T_c up to 120 K has been reported [3] in the samples of BSCCO system prepared under well controlled conditions. It has been reported [4] that partial substitution of Bi by Pb is effective in increasing the volume fraction of high T_c phase in BSCCO system. In Pb-doped BSCCO superconductors the zero resistance has been achieved at 125K by Huang et al [5].

In the present paper the author has reported the results of the micro structural investigations and compositional analysis of the process of nucleation of high T_c super conducting 2223 phase to understand its growth process in undoped and Pb-doped 1112-compound of BSCCO system.

2. Experimental

The samples of undoped and Pb-doped 1112 compounds of Bi-system were prepared by using solid state reaction technique. The nominal stoichiometric composition, for Sample Nos. 1 & 2 was taken in the ratio Bi: Sr: Ca: Cu: 1: 1: 1: 2. The powders of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO were mixed with cation molar ratios, in the stoichiometric proportion of 1112. The mixture was thoroughly mixed for 3 hours to form a homogeneous mixture. The homogeneous mixture was put in alumina boats and was calcined at 800 ^oC for 13 hrs. in an electric furnace. After the mixture was calcined at 800 ^oC for 13 hrs., the furnace was switched off and the material was cooled to room temperature inside the furnace. After the material was cooled to room temperature, the alumina boats were taken out of the furnace and the mixture was reground for 3 hours, to form a fine and homogeneous powder. Several pellets were prepared from this powder using the stainless-steel die and hydraulic press machine.

Some of these pellets were then put in alumina boats & were sintered at 850^{o}C for 2 hrs. in air. After sintering the pellets were cooled to 500^{o}C at a cooling rate of 1^{o}C/min. These pellets were then annealed at 500^{o}C for 6 hrs., and later cooled to room temperature at a cooling rate of 1^{o}C/min. These pellets were named as Sample No. 1.

The remaining pellets were sintered at 850 ^{o}C for 5 hrs. in air were and were then partially melted at 900 ^{o}C for one minute. The partially melted pellets were cooled to 500 ^{o}C at a cooling rate of cooling of 1^{o}C/min. These pellets were then annealed at 500^{o}C for 6 hrs. and later cooled to room temperature at a cooling rate of 1^{o}C/min. These pellets were named as Sample No. 2.

A Pb-doped sample having the stoichiometric composition, Bi: Pb: Sr: Ca: Cu: : 0.7: 0.3: 1: 1: 2 was also prepared. The powders of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO were mixed with cation molar ratios, in the stoichiometric proportion Bi: Pb: Sr: Ca: Cu: : 0.7: 0.3: 1: 1: 2. The mixture was thoroughly mixed for 3 hours to form a homogeneous mixture. The homogeneous mixture was put in alumina boats and was calcined at 830 ^{o}C for 24 hrs. in an electric furnace with intermediate grinding. After the calcination the mixture of the mixture was over, the furnace was switched off and mixture was allowed to cool to room temperature inside the furnace. After the material was cooled, alumina boats were taken out of the furnace and the mixture was pulverized for 3 hours to form a fine and homogeneous powder. Pellets were prepared from this powder using a stainless-steel die and hydraulic press. These pellets were

later sintered at 845°C for 432 hrs. in air. After sintering the pellets were cooled to 500 °C at a coolingrate of 1 °C/min. These pellets were then annealed at 500 °C for 6 hrs. and later cooled to room temperature at a cooling rate of 1 °C/min. These pellets were named as Sample No. 3.

The resistance vs. temperature characteristics of sample Nos. 1, 2 & 3 were carried out by DC four probe techniques. The temperature was varied from room temperature to low temperatures using liquid helium / nitrogen bath. The surface morphological studies and the elemental analysis of these samples, in pelletized form, were carried out by using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectrometer (EDS). To study the microstructure of these samples, the pellets of sample Nos. 1, 2 & 3 were again pulverized and fine powders of sample Nos. 1, 2 & 3 were prepared. The fine powders of these samples were sprinkled on to the carbon / formvar coated copper grids. These copper grids were then investigated by using Transmission Electron Microscope (TEM) to study the microstructure of these samples.

3. Results

The variation of resistance with temperature of these samples was carried out at low temperatures by dc four probe technique. The resistance versus temperature characteristics of these samples is shown in figures 1. The resistance versus temperature curve of sample No. 1 showed drops in resistance at temperatures 70 K and 45 K with $T_{c\ (off)}$ at 35 K, indicating the predominance of low T_c Phases. The resistance versus temperature measurements of sample No. 2 showed a sharp drop of resistance at 82 K and $T_{c\ (off)}$ at 52.5 °C as depicted in figure 1. It was observed that sample No. 2, which has been partially melted, showed higher values of $T_{c\ (on)}$ and $T_{c\ (off)}$ as compared to that of Sample No. 1. From the resistance versus temperature curve of sample No. 3, the Pb-doped 1112 compound, the onset of transition temperature $T_{c\ (on)}$ was observed at 108 K and zero resistance, $T_{c\ (off)}$ at 90 K. The onset at 108 K indicates the presence of high T_c superconducting phase.

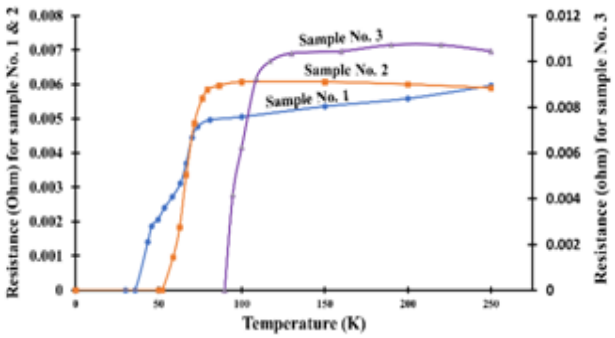

Figure 1: Temperature dependence of Resistances of sample Nos. 1, 2 & 3

The Scanning Electron Micrograph, depicting the surface morphology of sample No. 1, is shown in fig. 2. The elemental analysis was carried out at several regions showing different morphological features. The results of elemental analysis, carried out by Energy Dispersive X-ray Spectrometer (EDS), at different regions marked as A, B, C, D and E of this sample are summarized in the table 1.

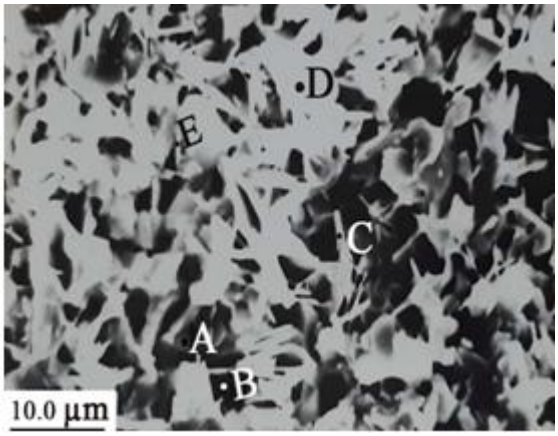

Figure 2: Depicts the surface morphology of Sample No. 1

Table 1

Region marked as	Bi	Sr	Ca	Cu
A	1.95	2.01	---	1.05
B	1.00	1.50	0.90	5.00
C	1.00	1.10	0.50	1.10
D	1.00	1.00	1.00	2.00
E	2.03	2.00	1.98	3.06

As shown in the table 1, the region marked A is deficient in Ca and has a composition equivalent to 2201. The region marked B is rich in copper, while the region marked C has composition close to 2212 phase (the low T_c Phase). The composition of the region marked D was found to 1112. The presence of 2223 phase could be estimated in the region marked E.

The SEM and EDS investigations of this sample showed the existence of a few small grains consisting of 2223 phase but bigger grains having 2223 phase could not be observed. These experiments confirmed that although the samples Bi-Sr-Ca-CuO system were prepared by solid state reaction with starting stoichiometric composition 1112, yet the nucleation of high T_c phase 2223 took place.

The SEM micrograph depicting a number of surface morphological features of sample No. 2 is shown in figure 3. The results of EDS investigation of this sample at different regions A, B, C, D, E and F as marked in the micrograph are summarized in the table 2. The EDS analysis shows that the grains marked A are Bi deficient and rich in Ca and Cu. The region marked B is rich in Cu, while the region marked C is rich in Ca and Cu. The region marked D represents the 1112 phase. The region marked E is mainly Cu dominated and Bi deficient with a little concentration of Sr and Ca. The presence of 2223 high T_c superconducting phase was observed in the region marked F of sample No. 2.

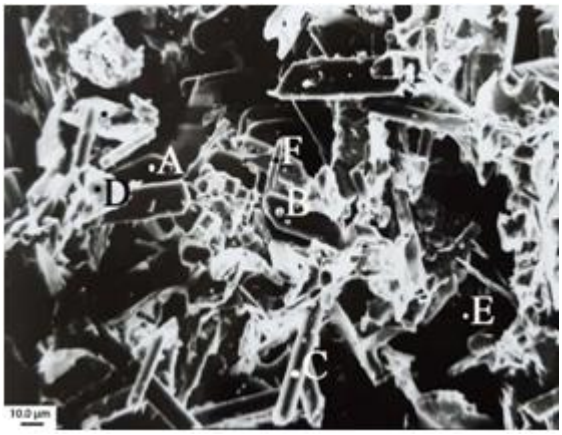

Figure 3: Depicts the surface morphology of Sample No. 2

Table 2

Region marked as	Bi	Sr	Ca	Cu
A	---	1.32	8.18	5.03
B	1.00	1.08	1.04	31.30
C	1.00	2.29	8.01	4.46
D	1.00	1.01	0.99	2.01
E	---	0.68	0.38	33.40
F	1.98	2.00	1.99	3.01

The SEM micrograph depicting the surface morphology of sample No. 3 is shown in figure 4. The results of EDS investigation on different regions of this sample, having various morphological features marked as A, B, C, and D are summarized in the table 3.

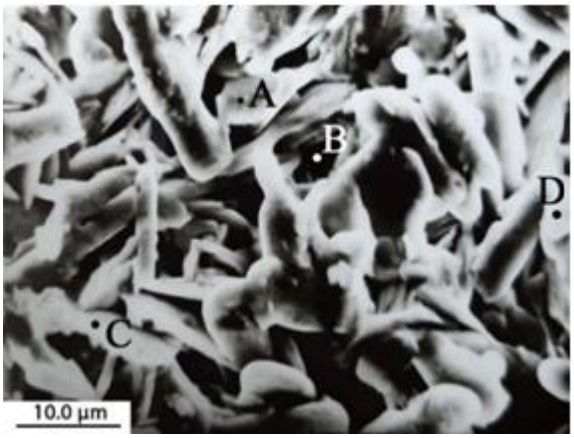

Figure 4: Depicts the surface morphology of Sample No. 3

Table 3

Region marked as	Bi	Sr	Ca	Cu
A	1.90	1.90	1.00	2.01
B	1.00	1.10	1.12	19.51
C	2.00	2.09	1.98	3.10
D	2.01	1.96	1.13	2.17

The EDS analysis of sample No. 3 indicates that the regions marked A and D possess 2212 phase while the region marked C possesses 2223 phase. The region B represents the region having excess of Cu. As revealed from these results, this sample shows the formation of mainly two phases 2212 and 2223.

The Transmission Electron Microscopy and Electron Diffraction studies of sample 3 depicted the rotational Moire pattern, grain boundaries and twin boundaries, as shown in figures5 & 6. The electron diffraction pattern of the same region is shown in figure 7. It is observed that the formation of this diffraction pattern takes place due to the two overlapping crystals having their ‘a’ or ‘b’ axis lying at some angle from one another. In this case, the angle measured between the ‘a’ or ‘b’ axis of the overlapping crystals was found to be 54°.

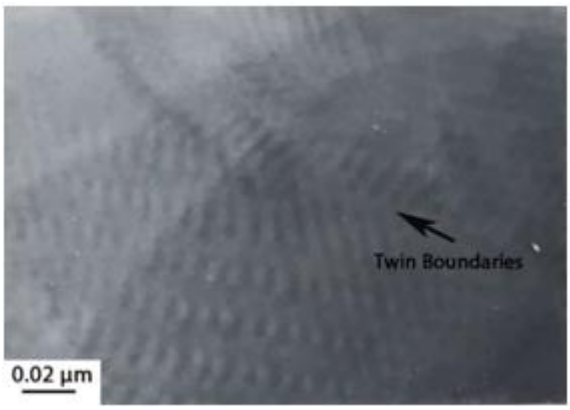

Figure 5: Depicts the Rotational Moire Pattern and the intergrowth of various phases

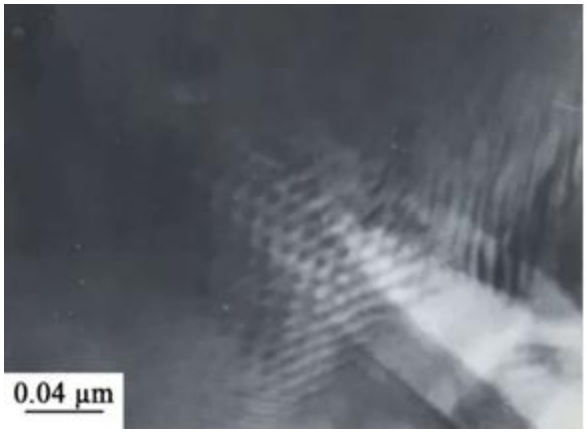

Figure 6: Depicts the Rotational Moire Pattern and grain boundaries

The high-resolution electron micrograph depicted in figure 8 also shows the presence of parallel Moire pattern. The formation of parallel Moire pattern confirmed presence of two or more overlapping crystals having different lattice parameters. This indicates the formation of various superconducting phases, in turn, the intergrowth of superconducting phase in the sample. The electron micrograph shown in fig. 9 also shows the formation of rotational as well as parallel Moire Patterns. This micrograph also shows the lattice images having the lattice spacing of 24.5 A° and 30.8 A°. The lattice spacing of 24.5 A° is close to the c-parameter of the unit cell of 2201 superconducting phase while the lattice parameter of 30.8 A° is equal to the c-parameter of the unit cell of 2212 superconducting phase. The diffraction pattern of the same region of the specimen is shown in figure 10. The diffraction of the beam was along [001] indicating the modulated structure along ‘b’ parameter. After indexing the diffraction pattern, the ‘a’ parameter of the superconducting phases 2201 or 2212 was found to be 5.409 A°.

Figure 7: Depicts the Electron Diffraction Pattern from overlapping crystals

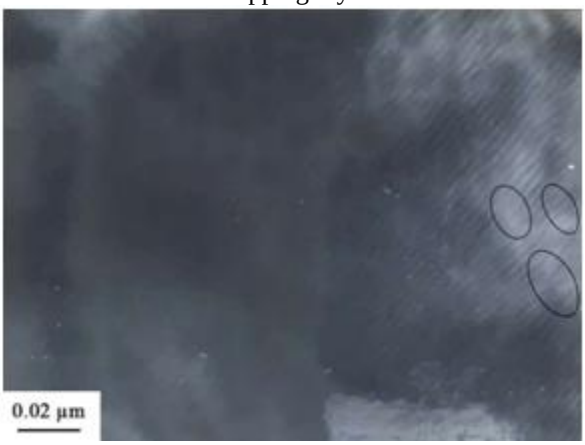

Figure 8: Depicts Moire Fringes

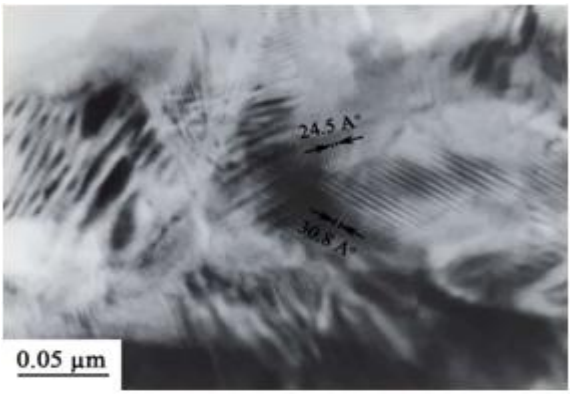

Figure 9: Depicts the microstructural features of Sample No. 3

Figure 10: Depict the electron Diffraction pattern of Sample No. 3

4. Discussion

It was observed from the R-T measurements of these samples that sample No. 3 showed the T_c values higher than that of sample Nos. 1 & 2. This is due to (i) Pb doping and (ii) the calcination at 830 °C. The SEM and EDS analysis of these samples confirmed the presence of 2223 high T_c phase in all the samples prepared with starting with the starting stoichiometric compositions 1112. The results of sample No. 1 & 2 indicate that the formation of nuclei of 2223 phase takes place, but the further growth of these nuclei does not take place. It may be because of the conditions not being conducive for the growth of high T_c phase and also the rate of diffusion of atoms in the proper proportion under these conditions does not take place. Although the partial melting, in the case of Sample No. 2, was found to enhance the T_c values, indicating that the partial melting during sintering process play an important role in the formation of high T_c phase. The addition of Pb in the compound of Bi-system and its calcination at 830 °C helps in the nucleation of 2223 high T_c phase a little faster and its growth in the case of material prepared with the starting stoichiometric composition 1112. The enhanced nucleation and growth of high T_c phase in the samples calcined at 830 °C may be because, the melting of Bi_2O_3 takes place at 820 ^oC, which permits a solid liquid diffusion reaction thereby promoting rapid nucleation of high T_c phase. Also, the similarities in size Pb & Bi, although theirvalencesare different, the Bi atoms may get replaced by Pb atoms into the structure, causing a stability of the lattice. The formation of phases, other than 2223 high T_c phase, could be envisaged due to the different rate of diffusion of suitable ions/atoms during solid state reaction process and depends upon a number of factors such as the homogeneity of the mixed powder, temperature and period of calcination and sintering, cooling rate etc.

As observed in TEM observations of sample No. 3, the presence of parallel and rotational Moire patterns due to the overlapping crystals suggests the intergrowth of various phases and also the formulation of the modulated structure. The high-resolution lattice images with different spacing and grain boundaries observed at most of the regions of the specimen are also indicative of the intergrowth of different phases. The lattice spacing of 30.8 A^o, as was observed in the high-resolution images of this specimen, confirmed the presence of the 2212 phase of Bi-System. The diffraction pattern also confirmed the presence of two crystals lying over one another at angle of 54^o. The satellite spots along b-axis indicated modulation in along b-axis.

5. Conclusions

The surface morphological, elemental analysis and microstructural investigations carried out on undoped and Pb-doped 1112 compounds of Bi-system led to the conclusion that the nucleation of various phases such as 2223, 1112, 2212 and 2201took place. Further growth of different phases depends upon the calcination, sintering and cooling conditions adopted for the preparation of these compounds. The study has revealed that in the materials calcined at 800 °C and sintered at 850 ^oC, the nucleation and the rate of growth of high T_c phase is seriously affected as the diffusion of right type of atoms under these conditions is

not adequate for their growth. The partial melting of the samples was found to enhance the values of $T_{c\ (on)}$, $T_{c\ (off)}$, played an important role in the formation of high T_c phase. Pb-doped samples of Bi-compounds shows higher values of $T_{c\ (on)}$ and $T_{c\ (off)}$ as compared undoped samples of Bi-compounds.

The microstructural investigations of sample No. 3, Pb-doped 1112 compound of Bi-system, was found to consist the modulated structure, intergrowth of various phases, Moire pattern, two crystals lying one over another at angle of 54^o, lattice fringes having spacing 24.5 A^o & 30.8 A^o, grain boundaries and modulation in along b-axis.

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