Research Article

Investigation of Structural Formation of Starting Composition 2245 in the Bi-Pb-Sr-Ca-Cu-O System Superconductors

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Structural formation of $\text{Bi}_{1.65}\text{Pb}_{0.35}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_y$ (2245 phase) superconducting compound was investigated by preparing the sample in a new matrix route. The phases formed at different intervals of heat treatment are monitored by X-ray diffraction studies. Bi-2212 phase was found to be the predominant phase till 20 hours of sintering at 850°C after which Bi-2223 phase was found to be the major phase. Traces of Ca_2PbO_4 were also noticed along with 2212 and 2223 phases. For the first time, the highest T_C onset of 127 K with maximum superconducting volume fraction was observed for the sample sintered at 850°C for 30 hours in this preparation. Further sintering is found to deteriorate the T_C onset value of the sample. There was no signature of the formation of 2234 or 2245 phase in this synthesis.

1. Introduction

The bismuth system superconductors are generally represented by the formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ with critical temperature (T_C) values around 10 K, 80 K, and 110 K for $n = 1, 2$, and 3, respectively [1, 2]. Among the above, $n = 2$ member, namely, $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ (2212), is found to be the most stable one. Preparation of $n = 3$ member, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223), as a single phase is extremely difficult because of the intergrowth of low T_C 2212 phase with 2223 phase. Many research groups have tried to synthesize 2223 compound as a single phase [3–8]. The addition of lead to the superconducting Bi-Sr-Ca-Cu-O compounds leading to the formation of 2223 phase has been reported by Wang et al. [5]. Shi et al. [6] have tried to synthesize 2223 phase by heating an off stoichiometric starting composition with excess Ca and Cu. Sastry et al. [7] have tried the matrix method to obtain a single phase 2223 compound with a T_C 120 K. Though there were many attempts made to synthesize $n = 4$ (2234) and $n = 5$ (2245) members [9, 10], no conclusive evidence is available on the structure and T_C values of the above phases.

In this paper we report the results of our attempt to synthesize the 2245 phase by solid state reaction method.

2. Materials and Methods

The sample $\text{Bi}_{1.65}\text{Pb}_{0.35}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_y$ was prepared by solid state reaction method as the combinations of two matrices M_1 and M_2 ($M_1 = \text{Bi}_{1.65}\text{Pb}_{0.35}\text{Sr}_2\text{Cu}_3\text{O}_x$ and $M_2 = 2\text{Ca}_2\text{CuO}_3$). High purity (99.9%) Bi_2O_3 , PbO , SrCO_3 , CaCO_3 , and CuO powders were used as starting materials. The powders with the molar ratio of $[\text{Bi}]:[\text{Pb}]:[\text{Sr}]:[\text{Cu}] = 1.65:0.35:2:3$ (matrix M_1) and $[\text{Ca}]:[\text{Cu}] = 4:2$ (matrix M_2) were separately prepared by thoroughly mixing the components for about an hour using an agate mortar and pestle. The final mixtures in powder form were kept in two alumina crucibles and calcined at 810°C for 16 hours in a tubular furnace. The calcined powders were reground and pressed into pellets of about 10 mm in diameter and 2 to 3 mm in thickness under a pressure of 5 tons/cm². These pellets of matrices M_1 and M_2 were sintered at 835°C for 40 hours with two intermediate grindings and pelletisation and then furnace

FIGURE 1: Temperature profile of the tubular furnace.

cooled to room temperature. One pellet of each sample was used for experimental measurements such as X-ray diffraction (XRD), SEM, and EDAX.

The two matrix samples M_1 and M_2 were mixed stoichiometrically into M_{12} sample of composition $\text{Bi}_{1.65}\text{Pb}_{0.35}\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_y$. The samples were well ground and mixed thoroughly into a fine powder. It is pressed into pellets of 10 mm diameter and 2 to 3 mm thick. These pellets were kept in a crucible and pulled along the axis of the tubular furnace at the rate of 1 cm per minute. The constant temperature region of the furnace was maintained at 900°C and it took about 40 minutes to pull the samples from one end to the other end of the furnace. The temperature profile along the axis of the tubular furnace is shown in Figure 1. Though a slight melting was observed on the surface of the pellets, all the pellets could be separated. These pellets were further sintered in air at 850°C for varying durations of 5 hours, 10 hours, and 15 hours, removing one pellet at the end of each interval after furnace cooling. The remaining pellets were ground, repelletised, and sintered at 850°C and one pellet each was removed as before at the end of total of 20 hours, 25 hours, 30 hours, and 40 hours, respectively. The removed pellets were labelled as M_{12} (A, B, C, D, E, F, and G), respectively. For comparison, one more sample of the same composition was prepared by the usual solid state reaction route in which all the constituent compounds are mixed initially and calcined at 810°C for 20 hours, followed by sintering at 835°C for 45 hours with one intermediate grinding and pelletisation. This sample is labelled as P 2245.

One part of each pellet was cut, powdered, and used for X-ray diffraction, scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDAX) measurements. Another piece of the pellet was used for T_C measurement. The T_C of the sample was determined by self-inductance method. A Colpitts oscillator and a frequency counter along with a liquid nitrogen cryostat were used for the purpose. The temperature of the sample was recorded using a calibrated chromel-alumel thermocouple with an accuracy of $\pm 1^\circ\text{C}$. The T_C of the samples were also confirmed by resistance measurement using the conventional four-probe method.

FIGURE 2: X-ray diffractogram of matrices M_1 and M_2 .

3. Results and Discussion

The X-ray diffraction patterns of the matrices M_1 and M_2 are shown in Figure 2. The XRD of matrix M_1 indicates almost a single phase compound and is indexed in an orthorhombic cell with cell parameters $a = 5.387 \text{ \AA}$, $b = 5.301 \text{ \AA}$, and $c = 24.574 \text{ \AA}$. The XRD pattern is similar to the one obtained by Sinclair et al. [11]. Two peaks of unreacted CuO were also identified in the XRD pattern of M_1 . All the peaks in the XRD pattern of matrix M_2 (except one small peak at $2\theta = 38.74^\circ$ due to CuO) were indexed in an orthorhombic cell with cell parameters $a = 12.247 \text{ \AA}$, $b = 3.780 \text{ \AA}$, and $c = 3.259 \text{ \AA}$. This pattern is similar to that of pure Ca_2CuO_3 compound identified with the ICDD XRD file (34-0282) as reported by Breuer et al. [12].

The XRD pattern of samples M_{12} (A, B, C, and D) is indicated in Figure 3. The XRD pattern shows that majority of the peaks belong to 2212 phase (marked as L). Three peaks of Ca_2PbO_4 at $2\theta = 17.62^\circ$, 31.06° , and 32.08° have also been identified in B, C, and D patterns. It can be noted that peaks due to 2223 phase (marked as H) gradually develop as the duration of heat treatment is increased. The analysis of XRD pattern of the samples M_{12} (E, F, and G) (Figure 4) has shown an increase in cell parameter values and has been indexed in a tetragonal structure with $a \approx b \approx 5.4 \text{ \AA}$ and $c \approx 37.2 \text{ \AA}$. These peaks are due to the 2223 phase which has formed when the duration of heat treatment exceeded 20 hours at 850°C . Figure 5 shows the XRD pattern of the sample P2245. Except for three peaks at $2\theta = 17.62^\circ$, 31.06° , and 32.08° of Ca_2PbO_4 all peaks are identified with that of 2223 phase. The lattice parameters of all the samples calculated from XRD data are given in Table 1.

The scanning electron microscope (SEM) images and superimposed EDAX spectra of samples M_1 and M_2 are represented in Figure 6. The EDAX spectra are in conformity with the atomic weight percentage of constituent elements as per the stoichiometry. As evident, SEM images reveal a granular and porous surface. The average grain size is

TABLE 1: Heating profile and results of X-ray diffraction analysis of samples.

Sample name	History of heat treatment		a Å	b Å	c Å	Cell volume ($\times 10^{-30}$) m ³	Grain size (in nm)
	Temperature (°C)	Duration (hours)					
M ₁	835	42	5.387	5.301	24.574	701.747	40.116
M ₂	835	42	12.247	3.780	3.259	150.871	74.570
M ₁₂ A	850	5	5.393	5.421	30.788	900.200	61.139
M ₁₂ B	850	10	5.389	5.395	30.767	894.580	75.690
M ₁₂ C	850	15	5.392	5.365	30.874	893.198	61.137
M ₁₂ D	850	20	5.401	5.391	30.775	896.255	72.250
M ₁₂ E	850	25	5.404	5.396	37.253	1086.570	63.580
M ₁₂ F	850	30	5.398	5.402	37.220	1085.335	58.870
M ₁₂ G	850	40	5.390	5.415	37.216	1086.217	44.170
P 2245	835	45	5.423	5.407	37.003	1085.008	68.814

FIGURE 3: X-ray diffractogram of samples M₁₂ (A, B, C, and D). FIGURE 4: X-ray diffractogram of samples M₁₂ (D, E, F, and G).

calculated from XRD data using Scherrer formula, $t = 0.89\lambda / B \cos \theta_B$, where t is the grain size, λ is the wavelength of the X-rays, θ_B is the Bragg angle, and B is the full width at half maximum (FWHM). SEM images of samples M₁₂ (E, F,

and G) and P 2245 are indicated in Figure 7. The variation of average grain size with duration of heating is shown in Figure 8. The mean value of grain size is found to be about 60 nm.

H-2223

L-2212

FIGURE 5: X-ray diffractogram of sample P 2245.

M_1 M_2 FIGURE 6: SEM and EDAX images of the samples M_1 and M_2 .

The normalised frequency (f/f_{RT} , where f_{RT} is room temperature frequency) of Colpitts oscillator versus temperature plots of the samples after different durations of heat treatment is represented in Figure 9. The normalised resistance (R/R_{RT} , where R_{RT} is the resistance at room temperature) versus temperature graph of selected samples is shown in Figure 10. Table 2 shows the T_C values and identified phases in the prepared samples. The superconducting signature is observed in the sample only after 15 hours of sintering at 850°C. The volume fraction of the superconducting phase gradually increases with increase in the duration of heat

treatment which is evident from the steeper transitions (Figure 9, M_{12} C and D). The major phase present in the sample after 20 hours of heating is 2212 phase. The sample heated for 25 hours at 850°C shows a two-step transition, one around 125 K (2223 phase) and another at around 105 K (2212 phase). The corresponding XRD pattern (Figure 4, M_{12} E) confirms this observation. The maximum value of T_C onset (127 K) was observed for the sample heated for 30 hours (Figure 9, M_{12} F). The sample heated for 40 hours shows the T_C onset at 125 K but the volume fraction of the superconducting phase has decreased drastically which is

FIGURE 7: SEM images of the samples M₁₂ (E, F, and G) and P 2245.TABLE 2: T_C values and identified phases in the samples.

Sample	Sintering at 850°C (hours)	Phases identified from XRD	Colpitts oscillator		Four-probe	
			T_C onset (K)	T_C (K)	T_C onset (K)	T_C zero (K)
M ₁₂ A	5	2212, 2223, Ca ₂ PbO ₄				
M ₁₂ B	10	2212, 2223, Ca ₂ PbO ₄				
M ₁₂ C	15	2212, 2223, Ca ₂ PbO ₄	110	—	—	—
M ₁₂ D	20	2212, 2223, Ca ₂ PbO ₄	120	—	—	—
M ₁₂ E	25	2223, 2212, Ca ₂ PbO ₄	124	107	125, 111	95
M ₁₂ F	30	2223, 2212, Ca ₂ PbO ₄	127	110	127, 115	105
M ₁₂ G	40	2223, 2212, Ca ₂ PbO ₄ , Bi ₂ O ₃	122	100	121	105
P 2245	45	2223, 2212	119	100	120	100

FIGURE 8: Grain size versus duration of heating.

FIGURE 9: Normalised frequencies versus temperature curves of samples.

evident from the relatively smaller change in frequency. The XRD pattern of this sample (Figure 4, $M_{12}G$) also shows two peaks at $2\theta = 27.8^\circ$ and 28.1° , respectively, which are identified with that of Bi_2O_3 . Therefore, it is inferred that prolonged heating up to 40 hours has resulted in some Bi_2O_3 coming out of the structure and hence the decrease in volume fraction of the superconducting phase. The T_C values measured by four-probe method also shows similar values which are tabulated in Table 2.

The T_C value of cuprate superconductors is known to vary with oxygen stoichiometry and is found to be a maximum for an optimum value of oxygen content. This can be manifested in terms of partial change of the valence state of copper from Cu^{2+} to Cu^{3+} in the Bi system superconductors [13–16].

FIGURE 10: Normalised resistance versus temperature curves of the selected samples.

4. Conclusions

We synthesised $Bi_{1.65}Pb_{0.35}Sr_2Ca_4Cu_5O_y$ superconductor by the matrix method with a new sintering cycle. The sample was initially heated at a comparatively high temperature of $900^\circ C$ for a short duration followed by sintering at $850^\circ C$ for different durations. The formation of the different phases as a function of duration of heat treatment was monitored. The X-ray diffraction analysis of the prepared samples revealed the presence of predominantly 2212 phase when sintered at $850^\circ C$ for 20 hours. Further sintering at the same temperature for 25 hours, 30 hours, and 40 hours, respectively, resulted in the formation of the 2223 phase as the major component. But after 40 hours of sintering, Bi_2O_3 was noticed to be coming out of the structure. The highest T_C onset value (127 K) with maximum superconducting volume fraction was found for the sample sintered at $850^\circ C$ for 30 hours. The presence of Ca_2PbO_4 is noticed in all samples which are preheated at $900^\circ C$. No traces of 2234 or 2245 phase were noticed under the above preparation conditions.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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