

Electrical, Structural and Morphological Properties of Sb-Doped Bi-Based Superconductors

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Abstract

In this paper, samples of antimony doped Bi-based superconductor with stoichiometric composition $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Ca}_3\text{O}_{10}$ were prepared by a solid state reaction method. The effect of sintering time on the superconducting properties was studied; all samples were sintered in air at 850°C for different sintering time (80, 100, 120, 140, and 160) h. X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements were performed for determination of the crystal structure and surface morphology of samples, respectively. All samples showed an orthorhombic structure with two phases, high- T_c phase (2223) and low- T_c phase (2212) in addition to an impure phase. It has been observed that the critical temperature and the high- T_c phase increases and appears to be the dominant phase when the sintering time is increased to 140 h, while with increasing sintering time to 160 h, both T_c and the high phase started to decrease. (SEM) results show that increasing sintering time enhances the growing of superconducting phase unidirectional and suppresses the high phase intrusion which leads to the production of nearly single Bi-2223 phase with higher T_c .

Keywords

(Bi, Pb) Superconductors, Sb Substitution, Sintering Time

1. Introduction

Among high- T_c superconductors, Bi-2223 compound with the superconducting critical temperature $T_c \approx 110$ K is one of the promising candidates for practical applications, such as power transmission cables, flexible wire or tape carrying high density of current at liquid nitrogen temperature [1] [2]. It is now well known that the Bi-

based system has layered structure and according to their compositions, it has three different phases: Bi-(2201), Bi-(2212), and Bi-(2223) [3] [4]. The Bi-2223 phase seems to dominate in all the three systems in spite of the fact that single-phase formation is very difficult. However, it has been reported that Pb doping at Bi-sites promotes the formation of single Bi-2223 phase and leads to higher T_c values by inducing a partially melted liquid phase, which eases the diffusion of elements that improve the connectivity between regions of the 2223 structure, and promotes the formation of a Bi-2223 nearly single-phase sample. On the other hand, it increases their critical current density [5] [6].

The superconducting properties of BiSrCaCuO compounds can be controlled by the addition or substitution of impurity atoms with different ionic radius and different bonding characters that produces atomic level crystal defects, lattice strains, non-superconducting inclusions and other structural defects. These inhomogeneties can improve T_c . For successful results different receipts can be found in the literature [7]-[10]. Partial replacement of Bi by Pb ($x \leq 0.3$) and Sb ($y \leq 0.2$) doping produces materials of high T_c phase purity [11], with Antimony playing an important role in accelerating the formation of the phase with higher superconductive transition in the Bi-system.

The role of Antimony appeared to be the enhancement of low- T_c to high T_c phase reaction beyond that achievable by lead incorporation alone [12]. The enhancement of $T_c(0)$ by Sb-content in $\text{Bi}_{1.7}\text{Tl}_{0.3-x}\text{Sb}_x\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ system is also reported by Iqbal *et al.* [13]. The presence of antimony, as Sb_2O_3 , is believed to make the system more reactive, enhances the kinetics of the reaction and hence promotes the high- T_c phase [14]. Antimony addition has been stated to be effective in preventing Pb from evaporating during calcinations, and produces stabilization in the formation of Bi-2223 phase [12] [15] [16]. This work is aimed to investigate the sintering time effect on the superconducting properties of $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Ca}_3\text{O}_{10}$ compound.

2. Materials and Methods

$\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Ca}_3\text{O}_{10}$ samples were prepared by a standard solid state reaction method. The stoichiometric amounts of high purity powders (99.999%) of Bi_2O_3 , Pb_3O_4 , Sb_2O_3 , $\text{Sr}(\text{NO}_3)_2$, CaO, and CuO were used as starting materials. The powders of precursor were mixed together by using agate mortar. The mixture homogenization takes place by adding a sufficient quantity of 2-propanol to form a paste during the process of grinding for about 1 h. The mixture was grounded to a fine powder and then calcined in air by using a tube furnace at 800°C for 30 h with a rate of $2^\circ\text{C}/\text{min}$. The mixture then pressed into pellets by using hydraulic press type (SPECAC) under pressure of 0.7 GPa. Five sets of samples were sintered at 850°C for 80, 100, 120, 140, and 160 h in order to study the effect of sintering time on the superconducting properties of the prepared samples. In this work all samples were subjected to gross structural characterization by X-ray diffraction (XRD) (Philips, with CuKalpha source). A computer program was used to calculate the lattice parameters, based on Cohen's least square method. Resistance-temperature data were obtained by using four point probe DC method at temperature range (77 - 300) K to determine the critical temperature (T_c). Scanning electron microscopy (SEM) was performed by (JEOL JSEM-5910).

3. Results and Discussion

The X-ray diffraction analysis was performed for all samples as shown in **Figure 1**. The results of $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Ca}_3\text{O}_{10}$ samples sintered for different periods of time (80, 100, 120, 140, and 160) h indicate that all samples have an orthorhombic structure with two phases; high- T_c phase (2223) and low- T_c phase (2212), in addition to a small amount of impurity phases of $\text{Sr}_2\text{Ca}_2\text{Cu}_7\text{O}$ in all samples at $2\theta = 36.8^\circ$ [17]. The occurrence of all those non-superconducting impurity phases will lead to a reduction of the T_c for all samples. The appearance of more than two phases could be related to the stacking faults along the c-axis. The intensity and peak position of reflections are in good agreement with the values reported in the literature. Also, it is clear that the relative intensity and peak positions vary slightly with increasing sintering time, which causes a change in the lattice constant of the sample. This result indicates that all samples were mainly consisting of (2212) and (2223) phases. Although the impurity phase of $\text{Sr}_2\text{Ca}_2\text{Cu}_7\text{O}$ peak at $2\theta = 36.8^\circ$ looks slightly higher in the samples sintered for 140 h, the (2223) phase being the dominant one as shown in **Table 1**. The peaks belonging to the (2223) phase were indexed with respect to an orthorhombic unit cell. Also, similar results were obtained by Saleh [18]. Increasing sintering time may well enhance crystallinity and the peaks to be sharper. The most intense peak pattern of samples belongs to the high- T_c phase, which also indicates an increase in the volume fraction of the 2223

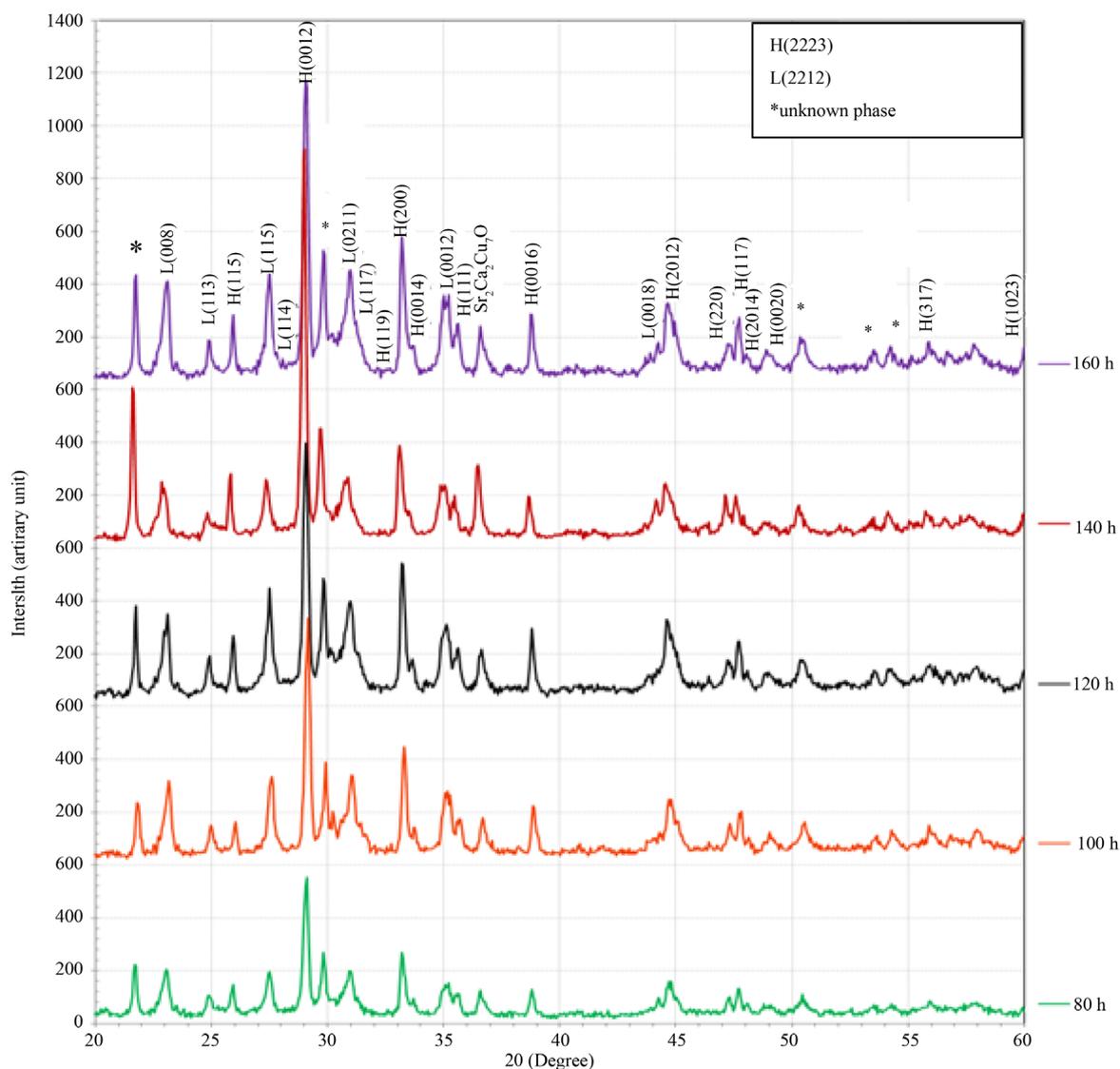


Figure 1. XRD patterns of $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ sintered for (80, 100, 120, 140 and 160) h.

Table 1. Lattice parameter, volume of the unit cell, critical temperature and percentage volume fraction of Bi-(2223) and Bi-(2212) phases in $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ samples at different sintering time.

t_s (h)	a(Å)	b(Å)	c(Å)	V(Å) ³	c/a	T_c	Volume fraction of phases formed (%)	
							Bi-2223 phase	Bi-2212 phase
80	5.391	5.418	37.081	1.083	6.878	<77	56.1	43.9
100	5.389	5.394	37.120	1.079	6.888	<77	56.7	43.3
120	5.388	5.387	37.139	1.078	6.892	84	62.1	37.9
140	5.387	5.417	37.148	1.084	6.895	110	82.6	17.4
160	5.390	5.397	37.091	1.078	6.881	<77	64.2	35.8

phase, and this leads to an increase in the T_c value. Such result was also obtained by Kocabas [19].

We have used all the peaks of Bi-(2223) and Bi-(2212) phases for the estimation of the volume fraction of the phases using the following formulas [20]:

$$\text{Bi-(2223)\%} = \frac{\sum I(2223)}{\sum I(2223) + \sum I(2212) + \sum I_{\text{other}}} \times 100 \quad (1)$$

$$\text{Bi-(2212)\%} = \frac{\sum I(2212)}{\sum I(2223) + \sum I(2212) + \sum I_{\text{other}}} \times 100 \quad (2)$$

where: $I(2223)$, $I(2212)$ and I_{other} are the intensities of Bi-2223 and Bi-2212 and other phases respectively. The volume fractions of the phases and lattice parameters a , b , c and c/a for all samples are given in **Table 1**. This Table indicates that an increase of the sintering time from 120 to 140 h. change the structural parameters. The deformation in the c -axis adjusts the amount of charge transfer from Bi-O layer to Cu-O layer sheet will tend to improve the critical temperature T_c . Increasing sintering time resulted in an increase in the volume fraction of Bi-2223 phase to 82.6% for the sample sintered for 140 h. Also, a decrease in the peaks intensities of the 2212 phase was obtained. On the other hand, a decrease in the volume fraction of the high phase and the critical temperature T_c was obtained with increasing sintering time to 160 h.

The percent volume fraction of the 2223 and 2212 phases as a function of sintering temperature were calculated from the XRD patterns of the $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Ca}_3\text{O}_{10}$ samples and are shown in **Figure 2**.

The electrical resistivity versus temperature plots at different sintering time is shown in **Figure 3**. All samples show that the resistivity decreases linearly with temperature in the normal state. Furthermore, all samples displayed a metallic character above onset temperature. It can be observed from the plots that prolonged sintering time up to a certain maximum time could improve the critical temperature (T_c) of stoichiometry composition. It is clear that the transition temperature increases from 84 K to 110 K with the increase of the sintering time from

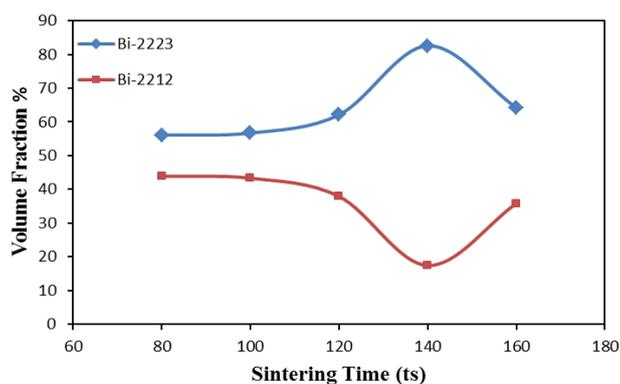


Figure 2. The volume fraction of Bi-(2223) and Bi-(2212) phases in $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Ca}_3\text{O}_{10}$ samples at different sintering time.

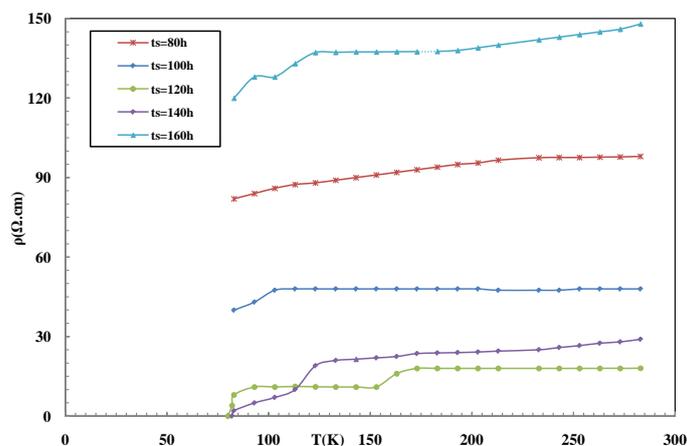


Figure 3. Temperature dependence of resistivity for $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Ca}_3\text{O}_{10}$ sintered for (80, 100, 120, 140 and 160) h.

120 to 140 h, which is related to the increasing of (2223) phase volume fraction. The increase in the T_c value is mainly due to the strong link and increasing of the contact areas between grains, which have higher alignment along the c-axis as inferred from both XRD and SEM analyses. Such result was also obtained by Mizauno *et al.* [21]. They suggested that long sintering time will give a chance to insert extra layers of Cu-O₂ and Ca planes into the perovskite layers of the low- T_c phase. Furthermore, it seems that the Sb is replaced in the Pb site in the sample structure, and the role of Pb is very important in the stability and in the enhanced percentage of Bi-2223 phase. This result is confirmed by Shoushtari *et al.* [22]. On the other hand, when the samples sintered for 160 h the resistivity decreases slowly (as it behaves like a superconductor) but does not become zero, even at the boiling point of liquid nitrogen. The reduction of the critical temperature can be due to either the crack formation as a result of excessive mechanical deformation or due to amorphous phase formation during the sintering process.

The surface morphology for the prepared samples is shown in Figures 4(a)-(e). The grains of all samples are randomly plate-like grains and their size is found to increase with increasing sintering time. The occurrence of

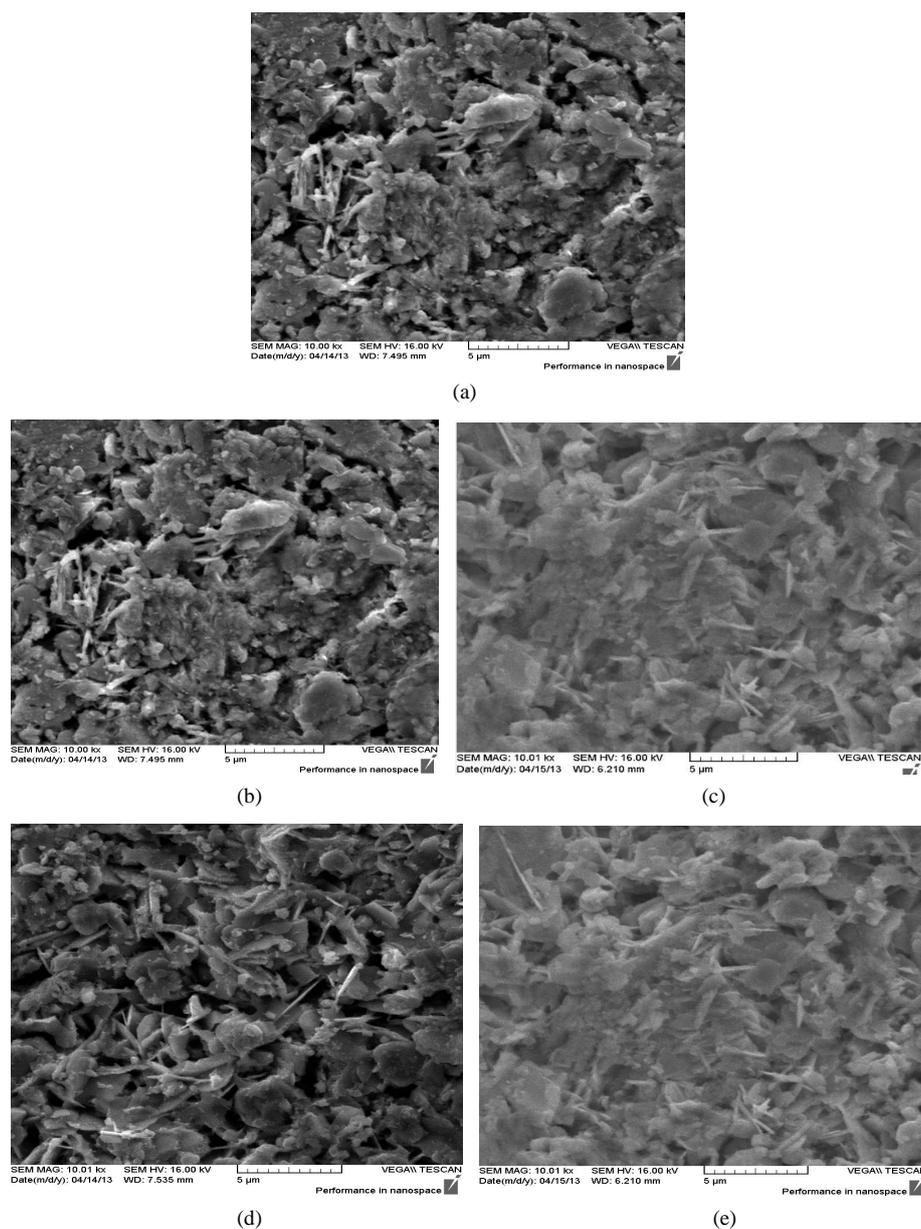


Figure 4. SEM images for Bi_{1.7}Pb_{0.2}Sb_{0.1}Sr₂Ca₂Ca₃O₁₀ samples with different sintering time: (a) 80 h; (b) 100 h; (c) 120 h; (d) 140 h; (e) 160 h.

grains with plate-like structure is a signature of the Bi-2223 phase formation from the Bi-2212 matrix mostly due to the prolonged sintering process [23]. Samples sintered for 80 and 100 h show a small amount of sphere-like grains, which could be due to the $\text{Sr}_2\text{Ca}_2\text{Cu}_7\text{O}$ solid particles that are randomly distributed over the phase plates [24]. Obviously, it can be noticed that the surface morphology of the sample sintered for 140 h reveals that it is more homogenous and have more pronounced alignment of its crystallites with c-axis. In addition, the plate-like grains were aligned to make denser and conductive sample. Such result was mentioned by Govea-Alcaide *et al.* [25]. Also, from **Figure 4(e)** a presence of bright areas with a small amounts of grains can be observed due to a possible melting of the synthesized material during the sintering process. It can be seen that the increase of sintering time to more than 140 h leads to the formation of a liquid phase that acts as insulating layers around the superconductor grains, which increases the resistance of grain boundaries and leads to a decrease in the transition temperature T_c as indicated by Guilmeau *et al.* [26].

4. Conclusion

The effect of sintering time on the phase formation and superconducting properties were investigated. Results revealed that prolonged sintering time up to a certain maximum time could improve the critical temperature of stoichiometry composition and increase the high- T_c (2223) phase. A remarkable increase in the critical temperature from 84 to 110 K was obtained with increasing sintering temperature from 120 to 140 h. Our results also show that samples sintered for 140 h had the highest critical temperature $T_c = 110$ K and highest volume fraction of Bi(Pb)-(2223) high- T_c phase 82.6%. On the other hand, increasing sintering temperature to 160 h decreases the critical temperature and the volume fraction of the high T_c phase.

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