

# The Effect of Sintering Temperature in $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ Superconductors

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**Abstract** In this study, the effects of sintering temperature on the Bi-2223 phase formation and the influence of minor phases on the intergranular properties of Sb substituted Bi-2223 samples were investigated. The samples were prepared by solid-state reaction method with different sintering temperatures ranging from 800 to 855 °C. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and density measurements. We observed the optimal temperature of the Sb + Pb substituted Bi-2223 system as 845 °C.

**Keywords** Bi-based superconductors · Sintering temperature · Scanning electron microscopy · X-ray diffraction

## 1 Introduction

A tremendous amount of work on the Bi-2223 system has been carried out since its discovery [1]. In recent investigations on the high- $T_c$  superconducting ceramics, BSCCO system has received much attention because of its transition temperature and its high critical current density. Chemical doping, substitution, addition and diffusion with different elements at various amounts and adjusting the preparation condition play a very important role in high- $T_c$  superconductors [2]. It is well known that there are several phases in the BSCCO system. The composition of each phase is expressed by a general formula of  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$

( $n = 1, 2, 3$ ) and  $T_c$  of ~20, 95 and 110 K, respectively. The phases are called Bi-2201, Bi-2212 and Bi-2223 for  $n = 1, 2, 3$ , respectively [3]. In these series, Bi-2223 is the most attractive, because its superconducting transition temperature is the highest one,  $T_c$ , of about 110 K. System Bi–Sr–Ca–Cu–O contains non-toxic elements and its preparation is cheap, which makes it a very promising material for technical applications [4]. The Bi-2212 and Bi-2223 phases are important for technological applications; however, it is rather difficult to obtain them in an isolated form since the Bi-2212 phase grows prior to the Bi-2223 phase during synthesis [5].

Despite extensive studies, the mechanism of the high- $T_c$  superconductivity remains unclear. Dopant may play an important role in the properties of high-temperature superconducting materials. The influence of dopant materials like Al, La, Sb, Pb on the Bi-based superconductors has been reported by different authors [6]. In our previous work [7], we investigated the effects of Li substitution on the properties of high-temperature superconductor  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{Li}_x\text{O}_y$ . The X-ray diffraction indicated the formation of a large amount of Bi-(2223) phase along with a minor amount of Bi-(2212) phase. Maximal value of the volume percentage of high- $T_c$  (2223) phase was calculated to be 81 for the sample having Li content  $x = 0.20$ .

Many substitutions and dopings have also been used to improve formation and stability of the 2223 phase. Lead (Pb) is the most important doping element that influences the microstructure, phase composition and the related superconducting properties of the BSCCO system. The presence of Pb in the initial mixture, usually as PbO, favors the reaction kinetics of the 110 K (2223) phase. The lead (Pb) addition results in the creation of a superconductivity solid solution Bi-2223 by partial substitution of bismuth (Bi) and the optimal Pb content ( $x$ ) lies between 0.3 and 0.4 [6, 8].

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Partial replacement of Bi by Pb and Sb produces materials of extremely high phase purity, and antimony plays an important role in accelerating the formation of the phase with higher superconductive transition in the Bi-2223 system. The effect of the partial substitution of Bi by Sb, the nearest neighbor element in the same group as bismuth in the periodic table, on the superconductive characteristics of the Bi-based system was analyzed. The presence of antimony in the form of  $\text{Sb}_2\text{O}_3$  is believed to make the system more reactive, enhance the kinetics of the reaction and hence promote the high- $T_c$  phase [9]. The ionic radii of Bi, Pb and Sb are 1.03, 1.19 and 0.76 Å, respectively. Low-concentration of Sb ( $x \leq 0.2$ ) in  $\text{Bi}_{1.5}\text{Pb}_{0.5-x}\text{Sb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  system promotes the formation of high- $T_c$  phase (2223) [10].

In their study, Iqbal et al. [11] synthesized a series of antimony-doped bismuth (2223) superconducting materials with nominal composition  $\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{2-x}\text{Sb}_x\text{Ca}_2\text{Cu}_3\text{O}_y$  ( $x = 0.00, 0.02, 0.04, 0.05, 0.06, 0.08$  and  $0.15$ ) by simple solid-state reaction method. The effect of antimony on superconducting behavior has been investigated by X-ray diffraction (XRD) analysis. The maximal value of the volume percentage of high- $T_c$  (2223) phase was calculated to be 69.44 for the sample having Sb content  $x = 0.06$ .

Even though there are several reports about 2223 phase presented in the current literature, the choice of a suitable nominal composition is still a major problem in the sample preparation. It has been widely proved that the starting composition, several times of intermediate grinding, and a long time sintering have a strong influence on the final 2223 phase.

On the basis of the investigations carried out on  $\text{Bi}_{1.75}\text{Pb}_{0.35}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  samples sintered at different temperatures, Ibrahim et al. [12] concluded that, with increasing sintering temperature, the volume fraction of the Bi-2223 phase increases indicating a homogeneity enhancement. The 2223 phase was the dominant one among all of the investigated samples. The volume fraction of the Bi-2223 phase was found to be the highest, 87% with sintering temperature of 1133 K (860°C).

Kameli et al. [13] have studied the effect of sintering temperature on the weak link behavior of polycrystalline  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  superconductors with different intergranular coupling using the XRD technique. The XRD results show that by increasing sintering temperature up to 865°C, the Bi-2212 phase fraction decreases. It was also found that the Bi-2212 phase on the grain boundaries is likely to play the part of weak links and consequently reduces the intergranular coupling.

$\text{Bi}_{1.75}\text{Pb}_{0.35}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  compounds were synthesized successfully by solid-state reaction technique. The samples were sintered from 1123 K to 1143 K (850°C to 870°C) and the effect of sintering on the structural properties was investigated. The X-ray diffraction technique and scanning electron microscope measurements showed that there is nearly

single (2223) phase in the samples. From XRD data, it was seen that single (2223) phase could be formed without detectable impurity after the sample was sintered at 1123 K (850°C) for a long time (20 days) [14].

In their study, Pop et al. [15] investigated bulk samples with nominal composition  $(\text{Bi}_{1.8}\text{Pb}_{0.46})\text{Sr}_{1.88}\text{Ca}_2\text{Cu}_3\text{O}_y$ . The X-ray diffraction (XRD) analysis confirmed that the majority of peaks belong to the 2223 phase (phase content of 95%) with a few of peaks belonging to the 2212 phase in the sample sintered at 850°C for 150 hours.

Due to the role of the heat treatment condition in enhancing the homogeneity of the HTSC (published elsewhere), the aim of our work is to study the effect of sintering temperature on the excess conductivity of polycrystalline samples of  $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  composition. For this purpose, five samples with different sintering temperatures, 800–855°C, were prepared. We have studied the samples in terms of XRD, SEM and density measurements.

## 2 Experimental Procedure

Samples of nominal composition  $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  were prepared by the conventional solid-state reaction method. The starting powders were corresponding stoichiometric quantities of high purity (99.99%)  $\text{Bi}_2\text{O}_3$ , PbO,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , CuO and  $\text{Sb}_2\text{O}_3$ . The powders were weighed in necessary atomic ratios. The weighed powders were thoroughly mixed and ground by using a mortar and pestle and calcined at 800°C for 20 h in air. The powder mixture was again calcined at 820°C for 20 h in air after a second intermediate grinding. The final product after calcinations was ground once more. Then these powders were pressed under 450 MPa pressure using a press machine (Graseby Specac) to form them into pellets 13 mm in diameter and 1 to 1.5 mm thickness. The prepared pellets were finally sintered respectively at temperatures 800, 820, 840, 845, 855°C for 150 h each. The pellets, after sintering, were furnace-cooled to the room temperature. Samples with 800, 820, 840, 845, 855°C sintering temperature were labeled as A, B, C, D and E, respectively.

X-ray diffraction (XRD) patterns in the  $2\theta = 3\text{--}55^\circ$   $\text{CuK}\alpha$  range were obtained by using Phillips X'Pert Pro Diffractometer. Scanning electron microscopy (SEM) images were taken by using JSM-6060 JEOL microscope. The bulk densities were obtained from the bulk dimensions and an Archimedes water displacement technique.

## 3 Results and Discussion

The XRD patterns of all samples are presented in Fig. 1. The high- $T_c$ , low- $T_c$  and impurity phase peaks were iden-

**Fig. 1** XRD patterns of the samples **A, B, C, D,** and **E** with composition  $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$

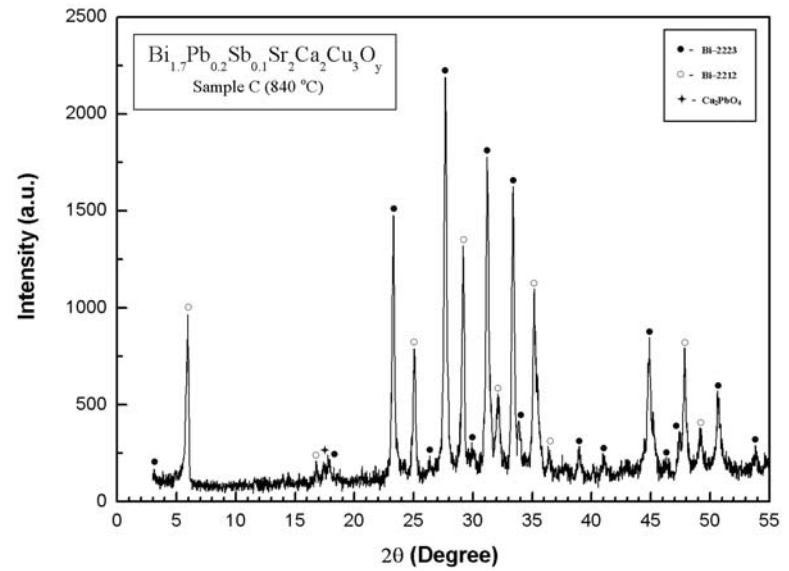
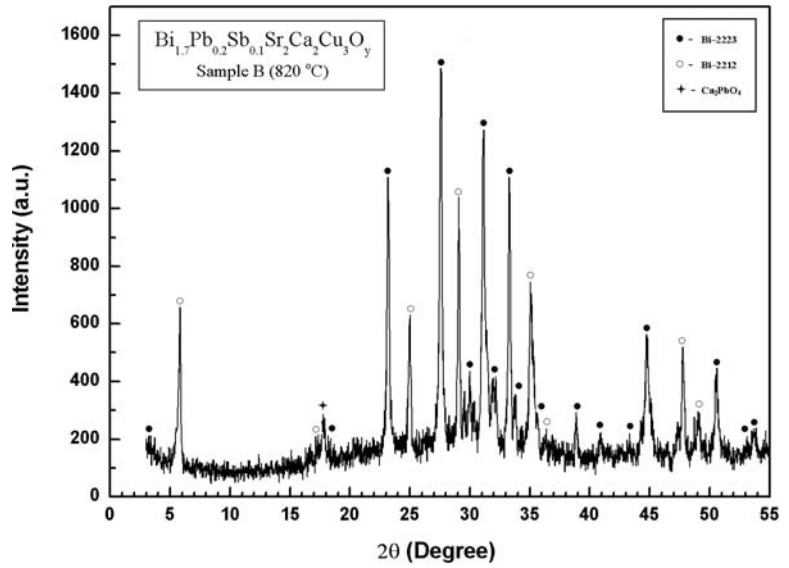
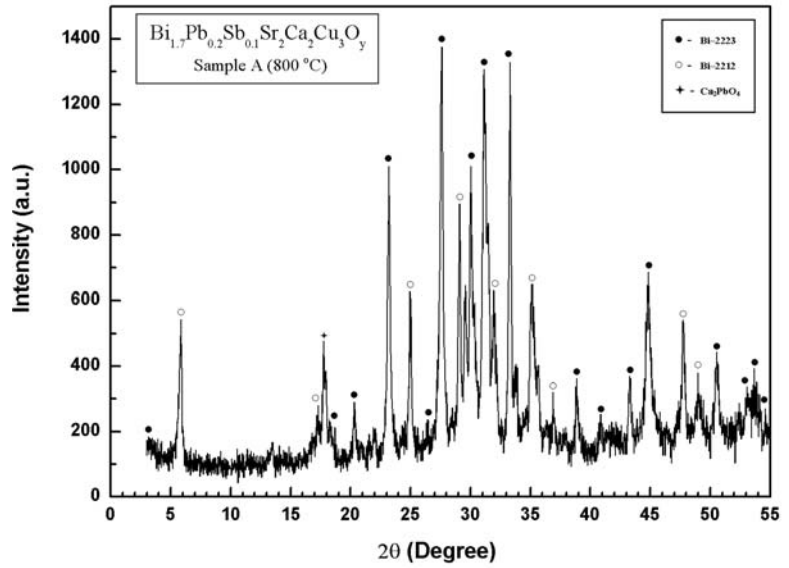
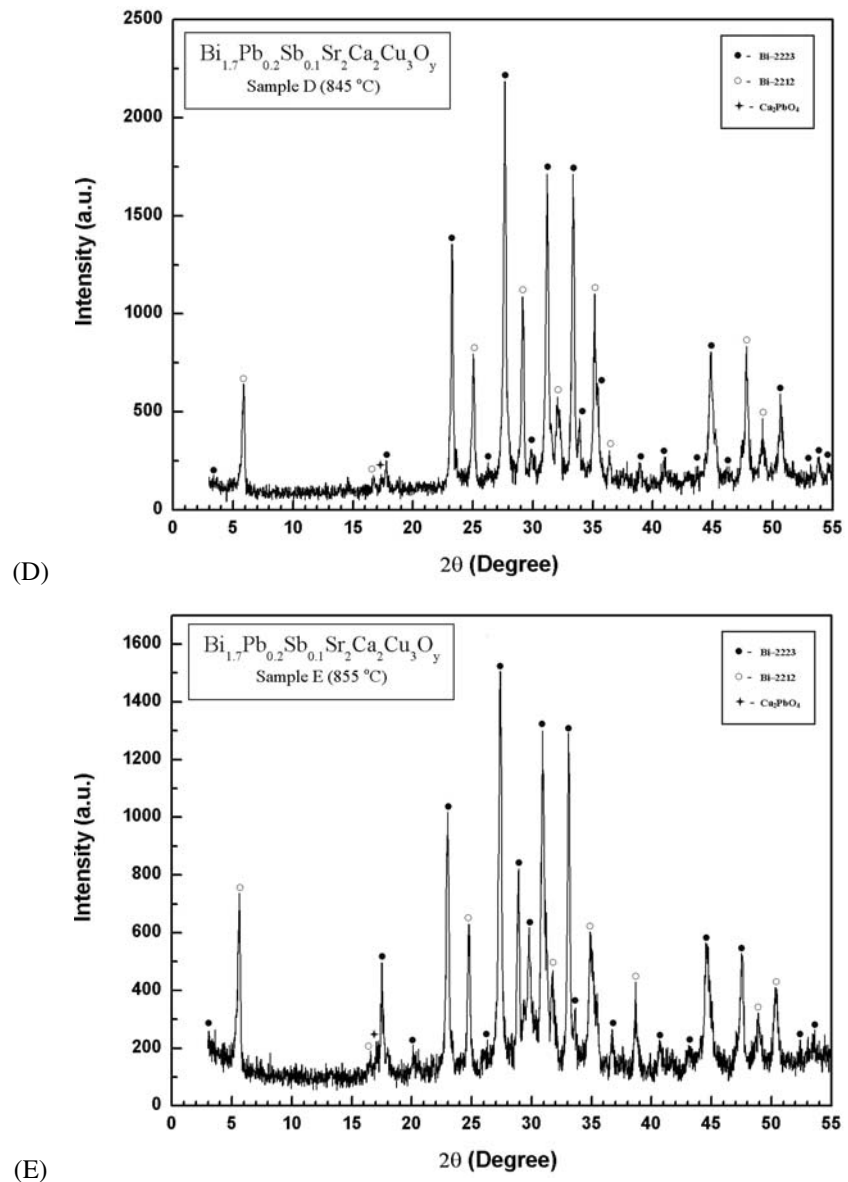


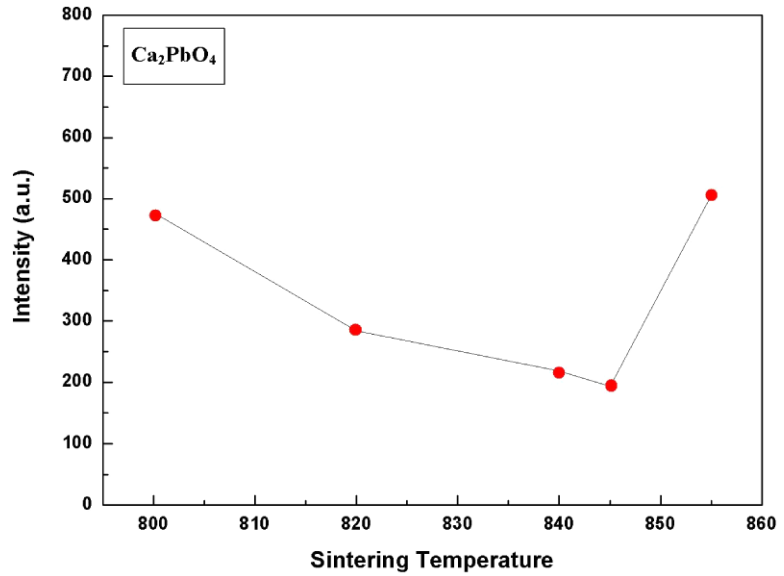
Fig. 1 (Continued)



tified by using the tables given by different researches. All the samples have a multiphase nature with high- $T_c$  and low- $T_c$  peaks. A Pb-rich phase with stoichiometry  $\text{Ca}_2\text{PbO}_4$  was found in all the samples. A weak characteristic impurity phase  $\text{Ca}_2\text{PbO}_4$  peak at  $2\theta = 17.8^\circ$  was identified in all the samples. It is clear that formation of  $\text{Ca}_2\text{PbO}_4$  will disturb Pb stoichiometry of the sample. This eventually will elevate the phase segregation from Bi-2223 to Bi-2212, which results in the appearance of higher 2212 phase peaks in XRD patterns. These stoichiometric changes have influence on the other structural properties, such as oxygen content, lattice parameters and grain connectivity, all of which are somehow interrelated. In the Pb-doped Bi-2223 superconductor, the lead ions are found to be unstable under oxidizing atmosphere and tend to segregate out of the 2223 matrix, forming a  $\text{Ca}_2\text{PbO}_4$ -like phase. The precipitation of this im-

purity not only has an obvious influence on the modulation structure and superconducting properties of the 2223 superconductor, but also causes the apparent oxygen content increase, which may result in some ambiguities on the effect of oxygen on the superconductivity. Therefore, it is believed that the relationship of oxygen content and superconductivity in the 2223 compound can only be correctly established when there is a clear understanding on the behavior of the lead ion [16]. It is observed in our study that  $\text{Ca}_2\text{PbO}_4$  peak intensity decreases as the sintering temperature increases. The variation of  $\text{Ca}_2\text{PbO}_4$  peak intensity with sintering temperature is shown in Fig. 2. It has the minimal value at  $845^\circ\text{C}$  and the maximal value at  $855^\circ\text{C}$ . These results are in agreement with those reported previously in literature. The decrease intensity of  $\text{Ca}_2\text{PbO}_4$  peak with increasing the temperature at a long enough sintering

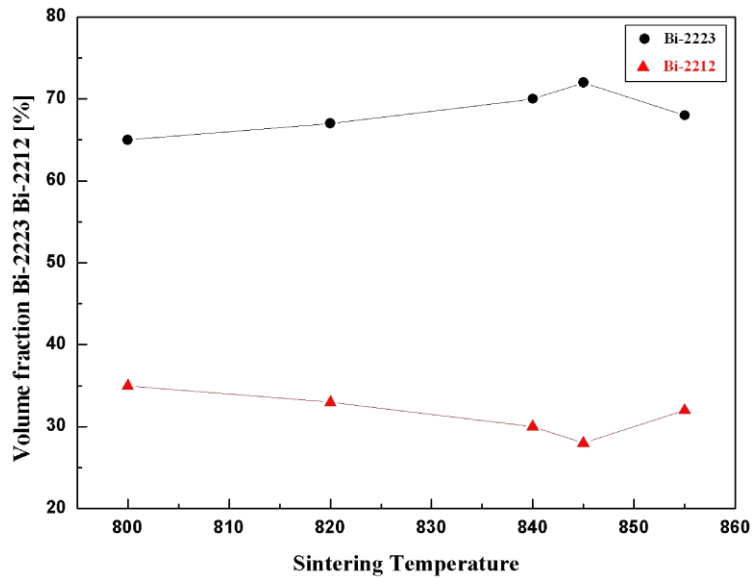
**Fig. 2** Variation of sintering temperature and intensity of  $\text{Ca}_2\text{PbO}_4$  impurity phase for all the samples

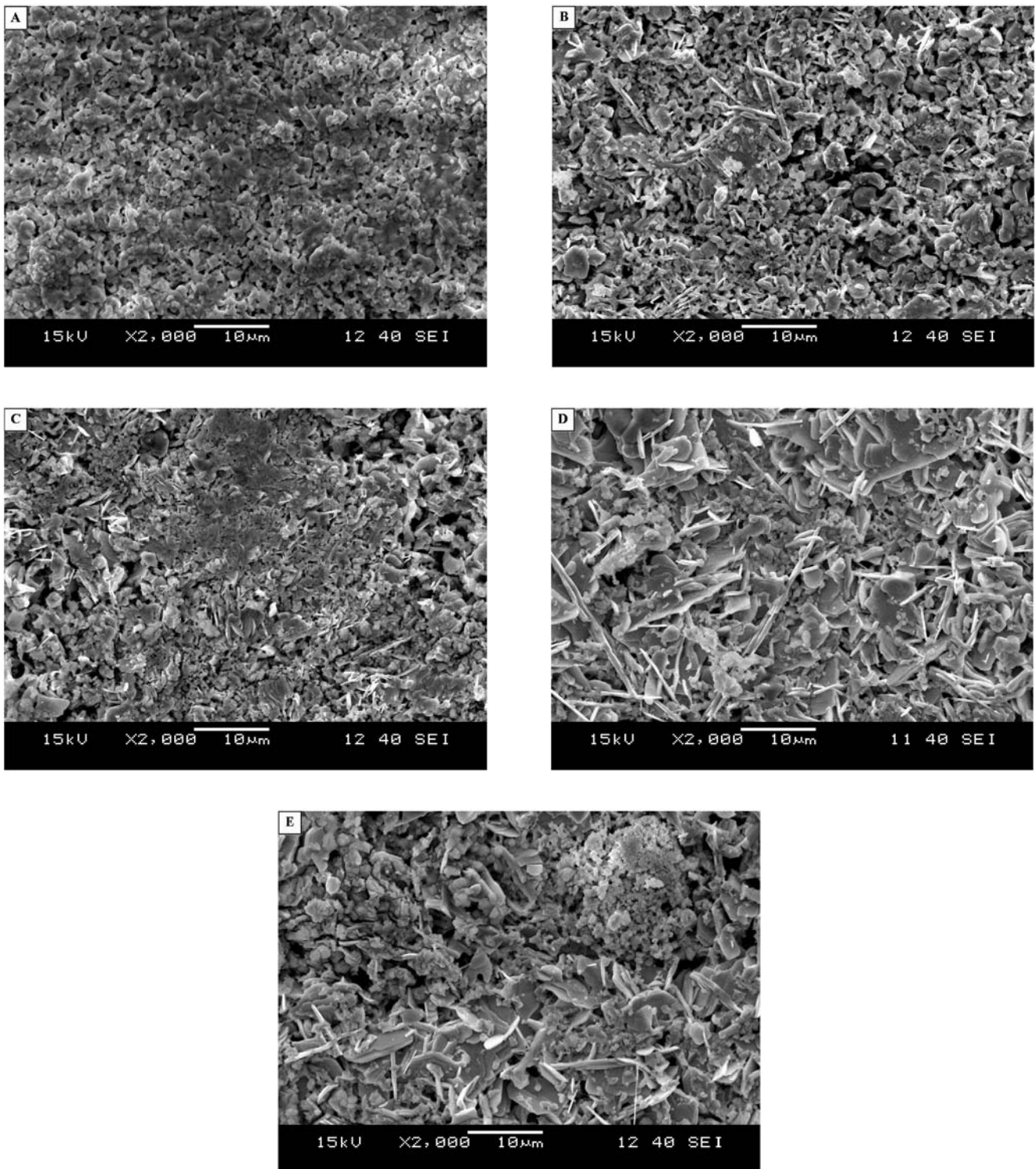


**Table 1** Percentage volume fraction of Bi-(2223) and Bi-(2212) phases in the sample  $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$

Sample	Sintering temperature (°C)	Volume fraction of phases formed (%)	
		Bi-2223 phase	Bi-2212 phase
A	800	65	35
B	820	67	33
C	840	70	30
D	845	72	28
E	855	68	32

**Fig. 3** Volume fraction of Bi-(2223) and Bi-(2212) phases determined from the X-ray diffraction patterns

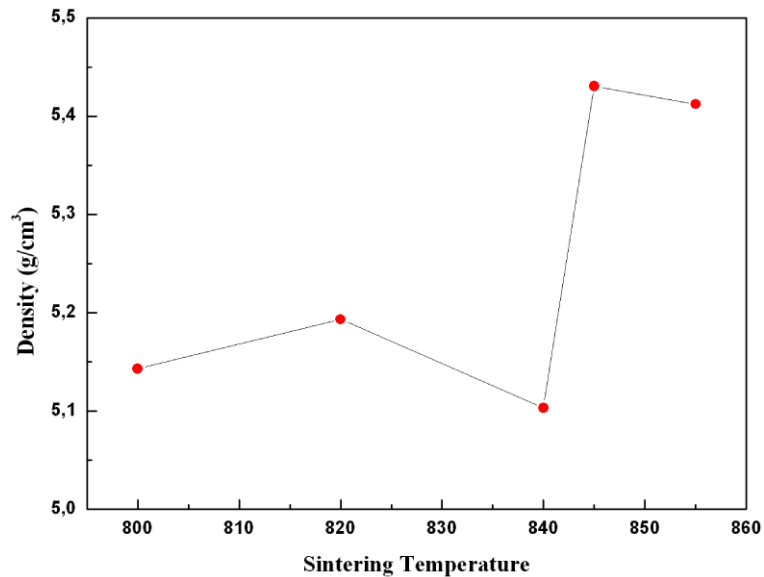




**Fig. 4** SEM micrograph of the samples A, B, C, D, E with composition  $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$



**Fig. 5** Sintering temperature dependence on the densities for all the samples



time and the same Pb content has been observed by several authors [17].

We have used all the peaks of Bi-2223 and Bi-2212 phases for the estimation of the volume fraction of the phases, namely

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

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

where I(2223) and I(2212) are the intensities of the diffraction lines for Bi-2223 and Bi-2212 phases respectively [18].

It can be seen from Table 1 that the Bi-2223 phase in D reaches the maximal value of 72%, which is the maximal volume formation when compared to the other samples. As seen in Table 1, samples with different sintering temperatures ranging from 800 to 855 °C contain 65, 70, 67, 72 and 68% of the 2223 phase, respectively. Volume fraction of Bi-2223 and Bi-2212 phases determined from the X-ray diffraction patterns is shown in Fig. 3. XRD results showed that the best sintering temperature is 845 °C, which has the highest volume fraction of Bi-2223, for Sb-doped samples in our study.

The microstructures of the top surfaces of all samples are shown in the SEM photographs taken at the same magnification (× 2000) in Fig. 4. The superconducting phases are not observed in the third sample with 800 °C sintering temperature. Pellet-like particular structure has started in A and B, and also a small amount of crystallization has started in B. There is grain structure in the second sample with 820 °C sintering temperature and there are spherical shaped grains in the structure. The grain size of the sample with 840 °C

sintering temperature is very small and there is melting in some parts. Crystallization is more in C with respect to B. Plate and spherical crystallization is observed. Plate structure is dominant in D and its dimensions are larger with respect to B. Plate structure is dominant; however, there is also a small amount of spherical structure. There is a small amount of pellet-like particulars, which are not crystallized and grain dimensions are not homogeneous. There are plate-like structures in the sample with 845 °C sintering temperature; on the other hand, there are still impurity phases. The sample has more uniform surface with a dense alignment of grains. Grain dimensions are larger. There are plate-like structures and melting in some parts as well, in the last sample with 855 °C sintering temperature. The melting might have prevented the crystallization. There are also impurity phases. Crystal dimensions are larger in E with respect to D.

Sintering temperature dependence on the densities for all the samples is shown in Fig. 5. The theoretical density of Bi<sub>1.6</sub>Cu<sub>0.4</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> was obtained as 6.313 g/cm<sup>3</sup> from the lattice parameters [19]. The density calculated from the lattice structure was reported as 6.2 g/cm<sup>3</sup> for Sb and Pb-doped BSCCO ceramics. The bulk densities of Pb-doped BSCCO pellets were evaluated by using a theoretical density of 6.45 g/cm<sup>3</sup>. Another work reported that samples have mass density 6.3–6.5 g/cm<sup>3</sup> for the Bi-based high-temperature superconducting phases [20]. Our results from A to E are 5.1431, 5.1934, 5.1032, 5.4304, 5.4323, respectively. As shown in the density results, the sample D has a high density value and low porosity. Since the sample D with sintering temperature of 845 °C has the highest density, the highest critical temperature and the lowest Ca<sub>2</sub>PbO<sub>4</sub> phase, 845 °C can be taken as the optimal temperature.

#### 4 Conclusions

The samples with nominal composition  $\text{Bi}_{1.7}\text{Pb}_{0.2}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  were prepared by the solid-state reaction method. The samples were sintered from 800 °C to 855 °C and the effect of sintering temperature on the structural properties was investigated. Based on the results of our investigation of Bi-2223 ceramic superconductors, the following conclusions can be drawn:

The result of XRD indicates that the optimal sintering temperature is about 845 °C, which is the highest density value and the highest volume fraction of Bi-2223 phase. Moreover, the XRD results show that by increasing sintering temperature up to 845 °C, the Bi-2212 phase fraction decreases.

SEM results indicate that the surface morphology of the sample is bettered with increasing sintering temperature up to 845 °C. This result is supported by XRD and density measurements of the sample.

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