Sintering Time Effect on the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ High Temperature Superconductors

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Abstract

The sintering time effects on the structure properties of two distinct phases of $Bi_2Sr_2Ca_{n-1}Cu_nO_x$, namely, Bi-2223 and Bi-2212 phases prepared by the solid state reaction method, are investigated. The microstructures of the samples are examined by X-ray diffractometer (XRD) as well as by Scanning Electron Microscopy (SEM). The volume fractions of the phases Bi-2223 and Bi-2212 are calculated in the bulk samples. It is observed that the c-lattice parameters increase from 30.9855Å to 31.7649Å for Bi-2212 phase whereas for the Bi-2223 phase it increases from 37.4131Å to 38.9023Å with the increasing sintering time. Meanwhile, the a-lattice parameters increase from 5.3032Å to 5.3272Å for Bi-2223 phase with the increasing sintering time. In effect, the SEM analyses of the samples indicate that the respective microstructure improves with the increasing sintering time.

1. Introduction

The Oxide superconductors are commonly used in various technological applications nowadays. These applications require the bulk materials to have the properties almost the same as those of a single crystal one. However, it is not possible to obtain such desired properties in real life. Nevertheless, it is possible to achieve remarkable results regarding the crystal structure since the sample preparation procedures for these materials in general has significant affect the bulk properties superconductor. The Sintering time is also an important factor for the bulk high temperature superconductors (HTSs). Among high-T_c superconductors, $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ (BSCCO) ceramics have attracted popular interest because both Bi-2223 ($n= 3$, $T_c= 110$ K), Bi-2212($n= 2$, $T_c= 85$ K) and Bi-2201 ($n = 1$, $T_c= 10$ K) have considerable potential for practical use as a result of its high critical temperature (T_c,) [1-3]. The principal difficulty in the crystal growth of the BSCCO superconductors comes from their complex chemical composition and the layered structure. There are various ceramics examined in broad ranges of metal and oxygen stoichiometry, which include superconducting compositions. The production of such samples, consisting of the Bi2223 and Bi2212 phases have revealed that it is not a simple task because of the large number of the variables involved in the process.

The HTSs are basically composite ceramic materials, for which the presence of secondary phases leads to a weak connectivity between grains, and this currently constitutes a major limiting factor for prospective technological applications. Moreover, the grain orientation has long known to have an important effect on the transport properties of the HTSs. To improve the superconducting properties, it is necessary to increase the grain alignment and minimize the

amount of secondary phases, for which the optimization of the processing parameters and heat treatment conditions are more crucial. To obtain a well-textured material, many different conditions have been applied in the relevant methods, such as the film technology, and the wire and tape fabrication by the powder-in-tube technique. Long sintering time is a different constraint in the production of the well-textured superconductors. In spite of its lower critical temperature (T_c), the Bi-2212 phase has received considerably more attention than the Bi-2223 phase because it is easier to prepare in a single-phase form. The Bi-2212 phase is thermodynamically stable within a wide temperature range, and in contrast to the Bi-2223 phase which possesses a narrower crystallization field [4–6]. Heat treatment is a crucial factor for the development of superconducting phases and several studies concerning the temperature and the time annealing conditions have been made in order to optimize the superconducting properties and as well as to accelerate the transformation kinetics of the HTS phases [7–9].

In this work, the effect of the sintering time on the Bi-2223 and Bi-2212 phase formation and the influence of this on the structural properties of these phases are investigated with x-ray diffraction and SEM analysis. The X-ray diffraction has been taken using a Bruker AXS D8 diffractometer and Leo 440 Scanning Microscope has been used in taking SEM micrographs.

2. Experimental Procedure

The studied samples were prepared by weighing appropriate amounts of high purity starting powders of Bi_2O_3, PbO, $SrCO_3$, CaO, and CuO and then using these powders with liquid ammonium nitrate to obtain a chemically homogeneous mixture**.** The powders were then regrinded, and subsequently heated at about 700, 700, 750, 780°C for 10min, 30min, 180min, 1200 min, respectively. Aim of the calcinations and the regrinding procedure is to obtain pure materials. The samples were calcined for various temperatures 700, 700, 750 and 780°C to purify the unexpected oxides and others.

After the calcinations, the resulting powders are mixed using a mortar machine and then pressed into pellets under a pressure of 250 MPa atmospheric pressure. These pellets are placed into a furnace at room temperature and sintered at 700°C in oxygen for 15, 60, 85 and 130 h. Then they are directly taken to room temperature. This procedure so far is called quenching that is well-known in the literature. We named the samples as S15, S60, S85 and S130 referring to 15, 60, 85 and 130 h sintered BSCCO samples, respectively. The calcination and sintering processes are depıcted in Fig. 1 (a-d) and Fig. 2(a-d), respectively.

Results and discussion

Before X-ray diffraction (XRD) patterns of BSCCO sample sintered at 700°C and directly taken to room temperature for 15, 60, 85 and 130 h shown in Fig. 3(a–d), respectively. For S1 sample the sintering time is 15h. In spite of the fact that at the time the crystallization of the matrix had begun, it was observed that it is not possible to identify the phase using diffraction peaks.

From Fig. 3 (b-d) one can observe that the diffraction patterns consist of low-T_c (Bi-2212) and high-T_c (Bi-2223) superconducting phases.

Fig. 4 shows that the increasing of the sintering time come out the Bi-2212 phase is the dominant in the mixture. The amount of the friction of the Bi-2212 phase is ranging from 36.5946% to 53.9780% in the volume of the superconductor matrix. Besides, the amount of the friction of the Bi-2223 phase is ranging from 63.4053% to 46.0220% in the volume of the superconductor mixture. This implies that the selection of the sintering procedure improve the Bi-2212 phase in the matrix. By making use of the above percentage values for calculating the volume, it was observed that, for Bi-2223, the peaks of (002) and (0010) with 2θ=4.7° and 24.04°, and for Bi-2212 at (002) and (008) with 2θ=5.7° and 23.22°, respectively [10-12]. The volume fraction of the Bi-2223 and Bi-2212 phases in the samples were evaluated the relative intensities of the X-ray diffraction peaks by making use of using the following expression [13, 14];

$$Bi\text{-}2223\ (\%) = \{\Sigma I_{(2223)} / [\Sigma I_{(2223)} + I_{(2212)}]\} \times 100$$

$$Bi\text{-}2212\ (\%) = \{\Sigma I_{(2212)} / [\Sigma I_{(2223)} + I_{(2212)}]\} \times 100 \quad (1)$$

The relative volume fractions of the Bi-2223 and Bi-2212 phases were determined from the peak intensities of the same particular diffraction patterns. It is observed that Bi-2223 phase decreases and Bi-2212 phase increases with increasing sintering time. From the above results, it is inferred that, as the main result of this research, the sintering time has the positive effect of decomposing the structure of high-T_c phase and enhancing the low-T_c phase creation, as well.

In BSCCO superconductors, there are several phases, such as the transition temperatures of three superconducting phases are known, in particular T_c~20 K (Bi-2201), T_c~90 K (Bi-2212) and T_c~110 K (Bi-2223) [15]. The microstructure of any of these three phases typically consists of platelets having their crystallographic *c*-axis perpendicular to the longitudinal plane. Although the significant results in the fabrication of BSCCO thick films and tapes have been obtained [16–18], the further improvements are required in order to render these compounds suitable for large-scale applications. Hence, it is crucial to fully understand the mechanisms that lead to a highly textured microstructure.

A method of making a dominant phase Bi-2212 oxide superconductor, to get in at least 60-90 vol % of the oxide superconductor, the precursor must be selected such that it can be converted into Bi-2212. Because of the Bi-2212 phase melts incongruently, the phase change begins at ~825°C [19] and some investigators reported that it begins at 800°C [20,21], at 820°C [22], where in the sintering at a temperature less than the melting temperature between to about 700°C and 820°C. Under the preconditions are selected to decompose remaining secondary phases at the oxide superconducting grain boundary or within the oxide superconductor grain and to convert the secondary phases into the Bi-2212 phase. One of the aims of this work is to obtain the dominant Bi-2212 phase rather than Bi-2223 phase.

Fig. 5 shows the change of the *c*-lattice parameter with the sintering time for Bi-2212 and Bi-2223 phases. The Bi-2223 phase is formed in the matrix for the sample for S1 as can be deduced in Fig. 5. In Bi-2223 phase, the *c*- lattice parameter value is found to be 37.413 Å and this is lowest value, but for S4 sample, the *c*- lattice parameter value is found to be 38.3900 Å which is the highest value.

The Bi-2212 phase is created in the matrix for the sample S1 as can be seen in the Fig.5. In Bi-2212 phase, the *c*-lattice parameter value is found to be 30.9855 Å and this is lowest value, but for S4 sample, the *c*- lattice parameter value is found to be 31.7540 Å which is highest value. These samples have been increases the *c*-lattice parameter with changing the sintering time with Bi-2212 and Bi-2223 phases. This indicates that the increasing sintering time is effected, growing direction of the samples. For the samples, the optimum growing was observed to correspond to the sintering time that is nearly equal that of S3 and S4.

Bi-2223 phase, the *a*- lattice parameter value is 5.3032 Å and is lowest value, but for S4 sample, the *a*- lattice parameter value is 5.3270 Å and is highest value (as can be seen in Figure 6). Therefore, under these conditions, the good and the lowest time may be the one for the sample S3. The lattice parameters are calculated by taking all the tetragonal structure into account. The calculated *a* and *c* lattice parameters of the Bi-2223 and Bi-2212 phases are listed in table 1.

These results show the sintering time effect on the low-T_c (2212) phase become to dominant phase in the structure with increasing time. Because the long sintering time changed the dominant phase to Bi-2212 in the initial of the process, the previous dominant phase was Bi-2223 in the matrix. But eventually, the Bi-2212 phase becomes dominant phase in the matrix. This enables one to recover the matrix phase via temperature conditions and long sintering time.

3. Microstructure Characterization

Fig. 7 shows that the SEM images of the four superconducting ceramics. Its main features are typical of this kind of ceramics whereas Fig. 7-a. displays the micrograph of the dominant phase of the Bi-2223. A homogeneous sample, although some co-workers reported that the needle shaped grains appear, have some plate-like shaped grains population, with a mean size of 5 μm and low connectivity between grains. In addition, because of the method used, that the ammoniums nitrate, the grain packing is of low density. The microanalysis study shows the presence of Bi-2212 second phase composed of grains within the matrix.

Representative microstructures of the annealed BSCCO grown presented in fig. 7(a-d), respectively. Although the different growth conditions lead to distinct morphologies, S2, S3 and S4 samples exhibiting as main matrix phase a composition close to Bi-2212. However, these Bi-2212 superconducting crystals much more aligned and randomly orientated in the BSCCO matrix. These crystals are immersed in a superconducting matrix that becomes 2212 homogeneous after heat treatment (in figure 1(b, c, d)).

As can be seen, the microstructures of the samples under study are clearly different. It is interesting to note that the microstructures of the all sample are completely different but they had plate-like, partially textured grains.

4. Conclusions

Polycrystals have generally many phases in the matrix and HTSs are polycrystalline structure. The phases affect several conditions such as produce method, nominal conditions, calcinations, regrinding, long sintering time conditions. The sintering conditions are playing important role to obtain high amount of the Bi-2212 phase in the matrix. The long sintering time effects on the structural properties the one can draw are listed below;

X-ray diffraction analyses show that the Bi-2212 (low-T_c) phase in the matrix has dominant phase at the long time sintering for the sample S4. Lattice parameters change nearly linear with the effect of the sintering time increasing. c-lattice parameter is increasing with increasing sintering time for the Bi-2212 phase and the same time Bi-2223 phase. Nevertheless, the amount of Bi-2223 phases is not changed appreciably compared to the initial values. However, the amount of Bi-2212 phase changes considerably with compared the initial value. This implies that the volume fraction of the phases in the matrix may change from Bi-2223 phase to the Bi-2212 phase.

1 The Scanning electron microscopy examination shows that the grain sizes of the samples decrease with the increases of the sintering time. The microstructures of the samples are distinctly different. It is interesting to note that the microstructures of the all sample are completely different but they had plate-like, partially textured grains.

2 As a result of mentioned above, it is concluded that the main purpose of the polycrystalline materials is to obtain high percentage and dominant phase growth in the matrix. In this work, it showed that the Bi-2212 phase can be grown in short sintering time, highly important to manufacturing [23-24] and applications [25-28].
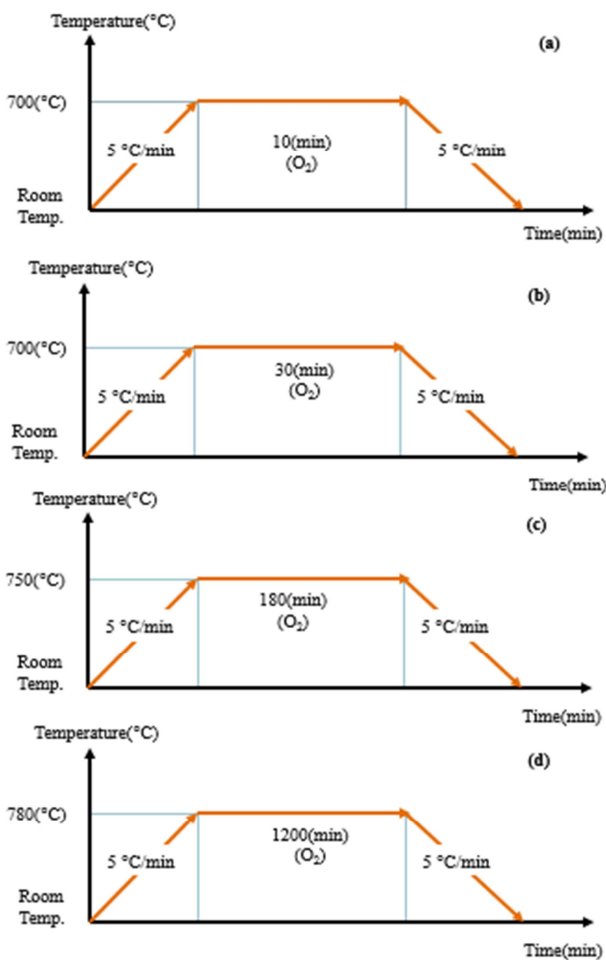
Acknowledgements

Figure Captions

Fig. 1. (a-d) shows the calcinations procedure of S15, S60, S85 and S130, respectively.
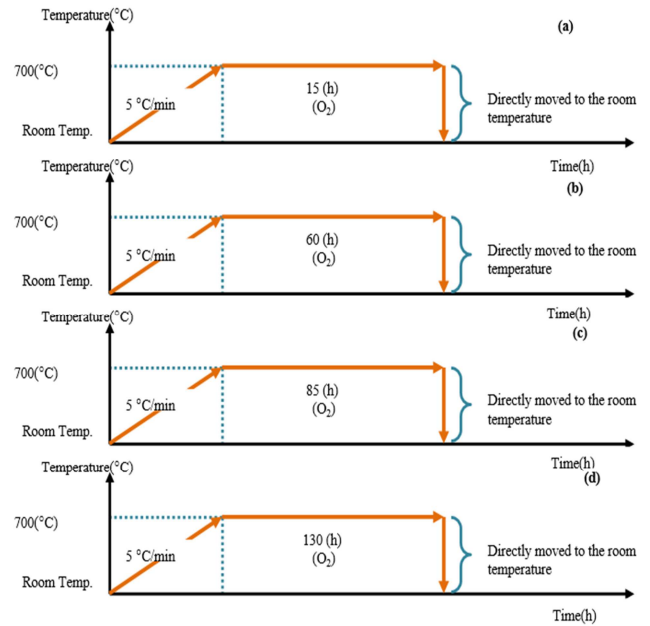

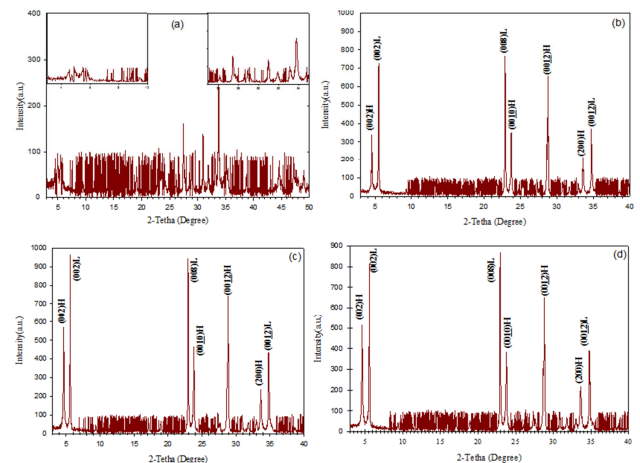**Fig. 2.** (a-d) shows the sintering procedure of S15, S60, S85 and S130, respectively.

Fig. 3. (a-d) shows the room temperature XRD patterns of S15, S60, S85 and S130 sintered BSCCO samples, respectively.
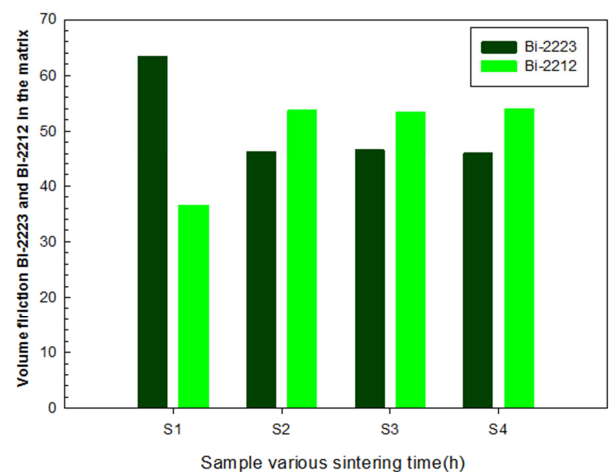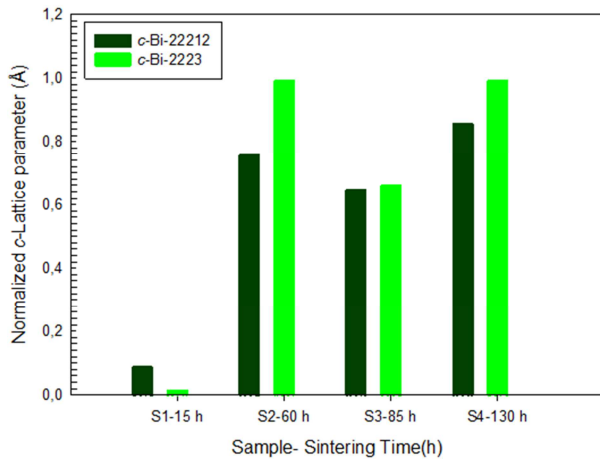

Fig. 4. shows that the volume friction of Bi-2223 and Bi-2212 phases in the superconducting mixture.

Table 1. List of the *a* and *c* lattice parameters.

Sample	*c* (Å) lattice parameter		*a* (Å) lattice parameter
	Bi-2212	*Bi-2223*	*Bi-2223*
S1	30.9855	37.4131	5.3032
S2	31.6540	38.3900	5.3270
S3	31.5430	38.0580	5.3170
S4	31.7540	38.3900	5.3270

Fig. 5. Shows that *c*-lattice parameter change the sintering time with Bi-2212 and Bi-2223 phases.
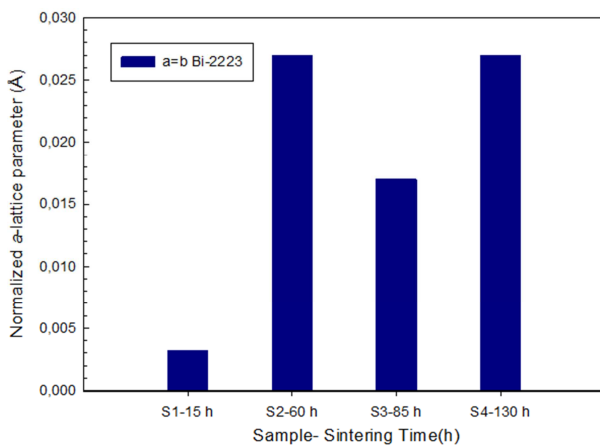
Fig. 6. Shows that *a*-lattice parameter versus the sintering time.
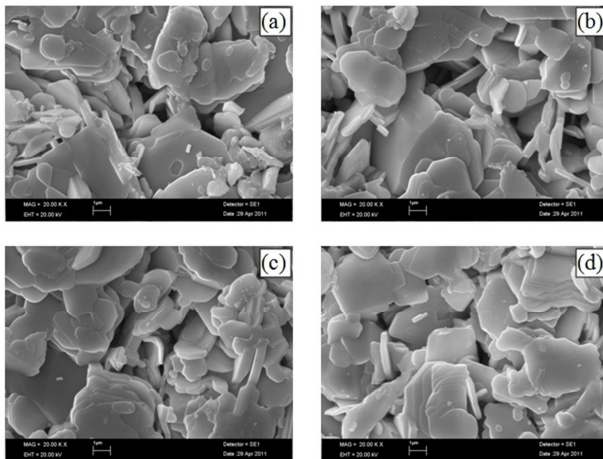
Fig. 7. Displays the rate of formation of Bi-2223 and Bi-2212 phases with respect to effect of the sintering time on the BSCCO samples.

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