

Microstructural Development of Superconducting Phases in Pb-BSCCO System Derived from Sol-Gel Technique

¹AMMAD HUSSAIN QURESHI*, ¹NAZAR HUSSAIN, ¹SHAHID KHAN DURRANI,
¹HASSAN WAQAS AND ²MUHAMMAD ARSHAD

¹Materials Division, Directorate of Technology, PINSTECH, Islamabad, Pakistan.

²Chemistry Division, Directorate of Science, PINSTECH, Islamabad, Pakistan.

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Summary: Sol-gel processing technique has been utilized to produce the gel of Pb-BSCCO system ($\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$, where $x = 0.2, 0.4, \text{ and } 0.8$, are the mole fraction of Pb substituted against Bi). The gel samples were subsequently heated to 800 °C for 2 h to obtain the powders which were then pressed and sintered at 845 °C for 60 h. The morphologies in the Pb-BSCCO gel, powder and sintered products were observed with scanning electron microscope (SEM) and optical microscope. The plate-like growths of the superconducting phases are evident from the SEM micrographs. The optical micrographs of sintered samples showed that the samples containing 0.2 and 0.8 mole fraction of Pb mainly consisted of dark grey and white regions, while sample having 0.4 mole fraction of Pb comprised of dark grey, light grey, and white regions. The different regions were analyzed by using energy dispersive X-rays (EDX) analyzer attached with SEM. The results revealed that the dark grey regions in all the samples represented the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ (2212) phase whereas, light grey regions in sample ($x = 0.4$) constituted the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ (2223) phase. The white regions in all samples depicted the presence of CuO. The best result in term of larger fraction of superconducting phase (2223) has been observed in sample containing 0.4 mole fraction of Pb.

Introduction

In 1911 the Dutch physicist, Heike Kamerlingh Onnes, discovered that the dc Resistivity of mercury suddenly drops to zero whenever the sample is cooled below 4.2 K, the boiling point of liquid helium. He named the new phenomena-superconductivity [1]. In the years to follow it was discovered that many other metallic elements exhibit superconductivity at very low temperature. In late 1986, Bednorze and Muller discovered superconductivity in cuprate oxides. More precisely, they found evidence for superconductivity at about 30 K in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ceramics [2]. In February 1987, Wu *et al.*, discovered superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramics. Its T_c was about 90 K [3]. This was the existence of superconductivity with a critical temperature above that of liquid nitrogen which is a much cheaper coolant than the liquid helium. Only a year later $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ and $\text{Hg}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ cuprate oxides were discovered with $T_c \sim 110$ K, 120 K and 134 K, respectively [4]. Thus, a new class of materials, copper oxide ceramics with a layered perovskite structure had rapidly arisen. The system $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ (BSCCO) has the general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$, where $n = 1$ to 3. The phases exist in this system are $\text{Bi}_2\text{Sr}_2\text{Cu}_3\text{O}_{6+y}$ 2201 ($n = 1$, $T_c = 20$ K), $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+y}$ (2212) ($n = 2$, $T_c = 80$ K) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ (2223) ($n = 3$,

$T_c = 110$ K). In the recent year, strong effort has been devoted to enhance the volume fraction of the phase 2223 in the BSCCO system by using different synthesis techniques. From the processing point of view, it has been reported [5-7] that the sol-gel technique obviates several cycles of firing and grinding of oxides or carbonates, which are required in conventional treatment. Ethylenediamine-tetraacetic acid (EDTA)-gel processing is more effective method than other gel processing routes, because EDTA has a great ability to chelate metal cations and form very stable and soluble complexes [8-17]. The (Bi, Pb)-2223 phase formation strongly depends on parameters such as sintering temperature, thermal processing time, synthesis atmosphere, precursor compositions, and doping or substitution of various cations and anions [18-20].

This work is a continuation of the studies on BSCCO and Pb-BSCCO systems [15, 21-23] in which we have reported systematic investigations on complex formation, thermal decomposition, phase analyses, and transition temperature. The primary objective of the current research work was to explore the microstructural features of sol-gel derived Pb-BSCCO system and to correlate the results of phase

*To whom all correspondence should be addressed.

analyses obtained by EDX with the XRD results [15]. Although XRD is a basic tool for phase analysis but the current research work results revealed that the EDX analyses can also be employed as an alternative route to confirm the presences of desired phases (2201, 2212, 2223) and compositions in superconducting materials.

Results and Discussion

XRD results of samples P2, P4 and P8 calcined at 800 °C and sintered at 845 °C for 60 h have already been represented [15]. The phases observed by XRD of these samples are presented in Table-1.

Microscopy of Gel

Scanning electron micrographs, Figs. 1a-c, show the appearance of dried gel pieces of samples P2, P4 and P8, which indicated the glass type morphology. The morphologies of dried gel were same regardless of the change of composition.

Table-1: Phases observed by XRD in Oxide powders and sintered pellets of P2, P4, and P8 [15].

| Sample | Phases observed by XRD | |
|--------|--|---|
| | Heated at 800 °C (Oxide Powder) | Sintered at 845°C for 60 h |
| P2 | 2212, 2201, CuO, Ca ₂ PbO ₄ , Ca ₂ CuO ₃ | 2201, 2212, 2223 (small), CuO, Ca ₂ CuO ₃ |
| P4 | 2212, Ca ₂ PbO ₄ | 2201, 2212, 2223, CuO |
| P8 | 2212, Ca ₂ PbO ₄ | 2201, 2212, CuO, Ca ₂ PbO ₄ |

Microscopy of Powders

The gel was firstly heated to 300 and then to 800 to avoid the burning of the gel. After heating the gel at 800 °C, the material converted into the crystalline form as shown in Figs. 2a-c. The SEM study reveals that the powders still have some porous structure but agglomeration on crystallisation is clear from the figure. It is evident that the powders are in micron size (range 5-20 μm). Ball milling was conducted in breaking down of the agglomeration and further reduction in the particle size (2-5 μm).

Microscopy of Sintered Pellets

The green pellets of samples P2, P4, and P8, were sintered at 845°C for 60 h. The temperature 845°C was selected from the study of thermal decomposition behaviour of Pb-BSCCO system conducted previously

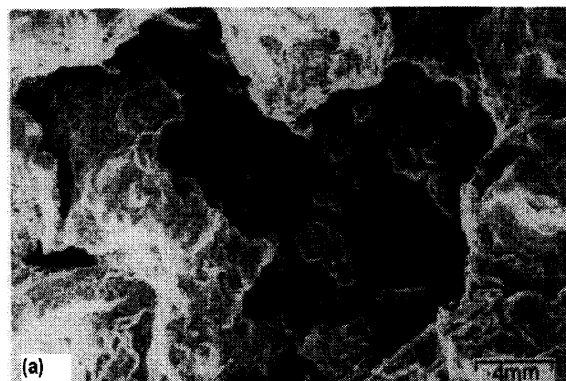


Fig. 1a-c: Gel morphologies of specimens (a) P2, (b) P4 and (c) P8.

[15]. The sintered pellets were fractured from the centre and analyzed under scanning electron microscope (SEM). Figs. 3a-c shows the morphologies of different phases in all the samples. The plate-like growths of the phases (2212, 2223) are evident. The SEM structure of sample P4 was found very similar to micrographs given by Chen *et al.* [24] and Sahin *et al.* [25]. As Scanning electron microscopy also offered a qualitative means to measure the average thickness of the superconducting layer. Therefore the super-

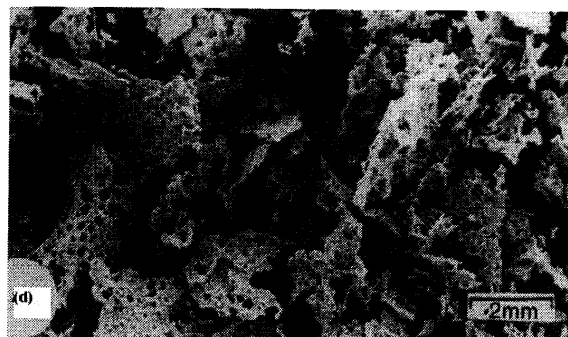


Fig. 2a-c: Powder morphologies of specimens calcined at 800 °C (a) P2, (b) P4 and (c) P8.

conducting layers in all samples were measured in the range 1-3 microns thick, with a variation of 10 microns across the full length of the samples (Figs 3a-c).

Energy Dispersive X-Rays (EDX) Analysis of Sintered Pellets

Figs. 4a-c show optical micrographs of the samples P2, P4 and P8 sintered at 845 °C. It can be seen that there are different coloured regions, present in each micrograph. The micrograph of samples P2, and P8

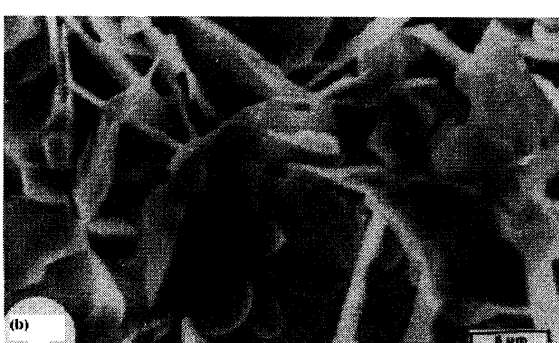
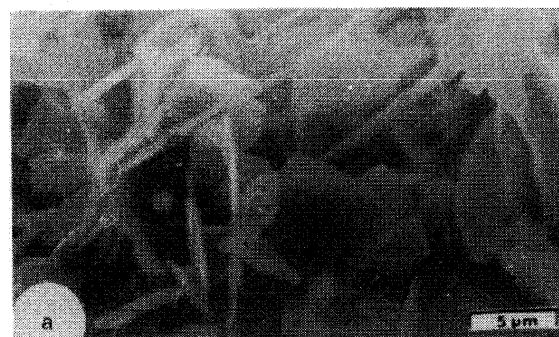


Fig. 3a-c: SEM of fractured surfaces of specimens sintered at 845 °C for 60 h (a) P2 (b) P4 and (c) P8.

mainly consist of dark grey, and white regions, marked with A and C, respectively, while sample P4 consists of dark grey, light grey, and white regions mark with A, B and C. These polished specimens were used for phase analysis. The dark grey region (A) in all the samples is the 2212 phase according to EDX analysis as given in Table-2. The light grey region (B) in sample P4 showed the composition of the 2223 phase. Whereas, the white regions in all the samples showed the presence of CuO.

The microanalysis data as given in Table-2 depict that Pb has substituted Bi in the structure. It can

Table-2: EDX analysis (atomic %) of samples P2, P4, and P8 sintered at 845 °C for 60 h.

| Sample | Bi | Pb | Sr | Ca | Cu |
|-----------|------|-----|------|-------|-------|
| P2 (2212) | 23.1 | 5.8 | 28.1 | 14.5 | 28.5 |
| | 24.1 | 4.8 | 27.8 | 14.10 | 29.20 |
| | 24 | 4.6 | 27.9 | 14.30 | 29.10 |
| P4 (2212) | 23.1 | 5.5 | 27.9 | 14.60 | 28.80 |
| | 25 | 4.5 | 28.4 | 13.90 | 28.10 |
| | 25.1 | 4.6 | 27.6 | 13.80 | 28.90 |
| P4 (2223) | 23.5 | 4.6 | 29.4 | 14.10 | 28.30 |
| | 24.5 | 4.6 | 28 | 14.50 | 28.40 |
| | 18.7 | 4.2 | 23.8 | 21 | 32.3 |
| P8 (2212) | 19.3 | 4.4 | 22.8 | 21.9 | 31.6 |
| | 18.5 | 4.5 | 22.4 | 20.8 | 33.8 |
| | 24.3 | 3.5 | 28.5 | 14.8 | 28.9 |
| | 25.9 | 2.5 | 28.6 | 15 | 28.1 |
| | 25.8 | 2.8 | 28.1 | 14.6 | 28.8 |

be seen that the substitution of Pb for Bi decreases with increasing Pb contents in base composition. The results showed that the solubility limit of Pb in the 2212 phase was around to be of 10-25 atomic % and for the 2223 phase (sample P4) was 22-25 atomic % of the total Bi-concentration. These analyses show that for higher Pb contents in the starting composition, the Pb content in the phases does not increase. The upper limit of Pb seems to be 25% of the total Bi-concentration.

The weight relationships among reacting chemical species *i.e.*, empirical formulae (number of atoms per unit cell) of the samples were calculated using chemical stoichiometry method [26] and tabulated in Table-3. It is revealed from the Table-3 and Fig. 4a-c that the dark grey regions in all the samples (P2, P4, and P8) is the 2212 phase while the light grey region in sample P4 (P4-2 in Table-3) indicated the 2223 phase, however, white region in all the samples showed the presence of CuO. The P4-I and P4-II in Table-3 represented the 2212, and 2223 phases in sample P4.

Comparison of Sintered Pellets of P2, P4 and P8

In sample with higher concentration of Pb (P8) the small volume fraction of 2223 phase was observed at 845 °C. The higher volume fraction of 2223 phase with higher concentrations of Pb found to be difficult due to the formation of excessive quantities of the Ca_2PbO_4 [15] which effectively trap Ca required to build the large amount of 2212 phase at 800 °C and The 2223 phase in small quantity was

Table-3: EDX analysis (molar ratios) of samples P2, P4, and P8 sintered at 845 °C for 60 h.

| Sample | Composition (mole ratios) | | | | | Oxide Formulae | Phase |
|--------|---------------------------|--------------|--------------|--------------|--------------|---|-------|
| | Bi_2O_3 | PbO | SrO | CaO | CuO | | |
| P2 | 0.055 | 0.03 | 0.075 | 0.059 | 0.098 | $\text{Bi}_{1.46}\text{Pb}_{0.79}\text{Sr}_{2.4}\text{Ca}_{1.2}\text{Cu}_{2.3}\text{O}_{8.095y}$ | 2212 |
| P4-I | 0.073 | 0.028 | 0.108 | 0.056 | 0.105 | $\text{Bi}_{1.97}\text{Pb}_{0.64}\text{Sr}_{2.4}\text{Ca}_{1.2}\text{Cu}_{2.3}\text{O}_{8.115y}$ | 2212 |
| P4-II | 0.085 | 0.0414 | 0.155 | 0.161 | 0.206 | $\text{Bi}_{1.09}\text{Pb}_{0.53}\text{Sr}_{1.99}\text{Ca}_{2.08}\text{Cu}_{2.65}\text{O}_{8.735y}$ | 2223 |
| P8 | 0.086 | 0.044 | 0.176 | 0.208 | 0.229 | $\text{Bi}_{0.96}\text{Pb}_{0.49}\text{Sr}_{1.97}\text{Ca}_{1.33}\text{Cu}_{2.2}\text{O}_{8.515y}$ | 2212 |

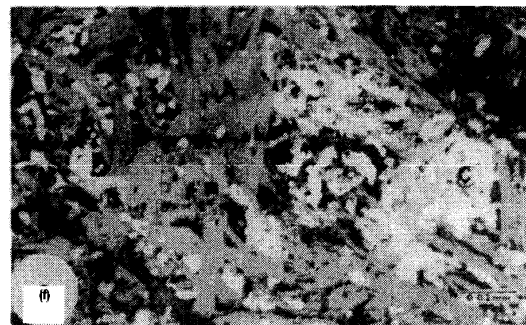
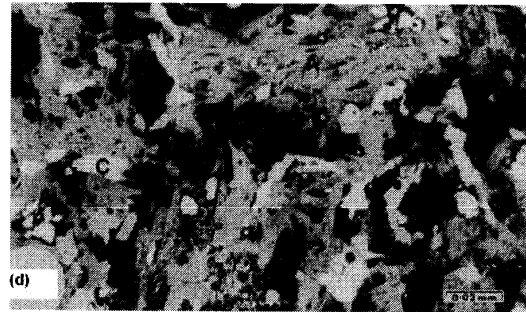
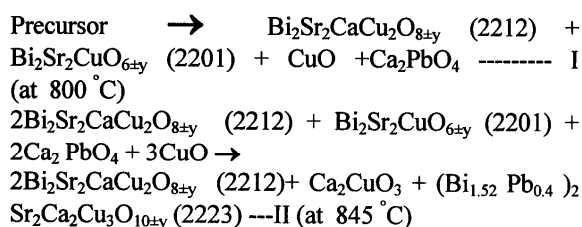


Fig. 4a-c: Optical micrograph of fractured surfaces of specimens sintered at 845 °C for 60 h (a) P2 (b) P4 and (c) P8.

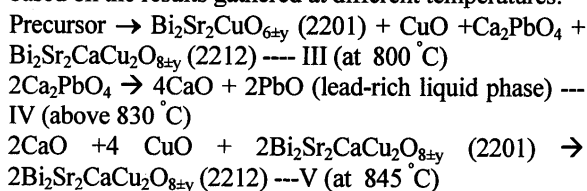
observed in sample P2 when sintered at 845 °C for 60 h. (Table-1), which confirmed that this temperature is not high enough to produce the large volume fraction of 2223 phase. It has been observed [27] that with very low concentration of Pb, the sample required sintering

at or above 860 °C or at the temperature of the endothermic peak [28] for a longer period to produce a high volume-fraction of the 2223 phase.

A higher volume-fraction of 2223 phase was observed in the sample P4. The chemical reaction occurred in the Pb-BSCCO system is the formation of Ca_2PbO_4 phase at 550°C [29]. This means that most of the Ca was taken up by Ca_2PbO_4 . However, as soon as Ca was released from the Ca_2PbO_4 on partial fusion, the formation of the 2212 phase was initiated. The Ca_2PbO_4 produces a lead-rich liquid phase and CaO [30] above 822°C. Within the lead-rich phase, rate of interdiffusion increased among the 2212 phase, Ca_2CuO_3 and CuO beyond the solid-state reaction. It is anticipated that the Pb ions incorporated in the liquid phase possibly enhance the diffusibility of Ca and Cu into the 2212 phase and act as efficient nucleation and growth sites for the formation of the 2223 phase. Hence, it is assumed that in the sample P4 at 845°C, the presence of moderate amounts of Ca_2PbO_4 [15] enhanced the rate of formation of the 2223 phase as it decomposes at a lower temperature to form a liquid phase, thus, acting as a flux and accelerating the transportation of the constituents required to form the 2223 phase. The following reaction mechanisms (I & II) explains the results obtained in the temperature range 800-845 °C for the sample P4:



result in the production of 2201 as the major phase. Hence, for P8 it seems that the first stage of reaction at higher temperature (845 °C/60 h) is the formation of the 2212 phase. On the time scale of the experiments carried out in these studies, it appears that the newly-produced 2212 phase does not stand any chance for further reaction to give the 2223 phase in P8 sample. The following reaction mechanisms (III, IV & V) are based on the results gathered at different temperatures:



These results indicate that Pb concentration in the starting composition should be optimised to prevent the formation of a huge amount of Ca_2PbO_4 in the oxide powder at 800 °C since it binds two metals, *i.e.*, Ca and Pb, which are considered necessary components for building 2212 phase at 800 °C and 2223 at higher temperatures.

The transition temperatures of the superconducting phases of the samples P2, P4, and P8 sintered at 845 °C for 60 h have already been presented [31]. In the sample P4 the transition temperature of the 2223 phase was observed at 110 K. The transition temperature for samples P2 and P8 was in the range 80-85 K because these contained high volume fraction of 2212 phase.

Experimental

Samples with nominal composition $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ (Pb-BSCCO), where $x = 0.2, 0.4$ and 0.8 mole fraction of Pb substituted against Bi, were prepared and designated as P2 ($x = 0.2$), P4 ($x = 0.4$) and P8 ($x = 0.8$). These samples were prepared from nitrate salts (A. R. grade) of Bi, Pb, Sr, Ca and CuO of at least 99.9% purity. The individual nitrate solutions were mixed together and the desired EDTA solution was gradually added (mole ratio nitrate ions: EDTA 1:1.2). The resultant solution was concentrated through a rotary evaporator, which was maintained at 80 °C under vacuum until a viscous liquid was obtained. The liquid was placed in an evaporating dish and was left in a vacuum oven at 80 °C for 24 h in order to produce the dried gel (precursor). The dried precursor was calcined at 300 °C for 2 h. Further calcination was performed at 800 °C for 2 h to obtain powders which were then pressed into pellets of approximately 1.3 cm diameter and 2 mm thickness. The pellets were sintered at 845 °C for 60 h. The morphologies of gels, powders and sintered products were viewed with scanning electron microscope (SEM). The sintered specimens were polished and examined using a Nikon optical microscope. The microanalysis of the phases present on the polished surfaces was carried out using energy dispersive X-rays (EDX) attached with SEM.

Conclusions

Sol-gel processing technique was successfully employed to produce the superconducting phases. The micrographs of sintered samples P2 & P8 mainly consisted of low T_c (2212)

superconducting phases and CuO, whereas P4 also contained high T_c phase (2223). The best result in term of large-fraction of 2223 phase was observed in the sample P4. All these studies (microscopy and EDX) have confirmed the results obtained by XRD in the previous investigation [15]. These results revealed that EDX analyses can also be employed as alternative route to investigate and to confirm the presences of desired phases (2201, 2212, 2223) and their compositions in superconducting materials.

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