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IMPACT OF Pb SUBSTITUTION ON THE FORMATION OF HIGH T_c SUPERCONDUCTING PHASE IN BSCCO SYSTEM DERIVED THROUGH SOL–GEL PROCESS

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Sol–gel process was employed to synthesize the Pb–BSCCO system having general composition $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10-\delta}$, where x=0.2, 0.4 and 0.8. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), dilatometry and vibrating sample magnetometer (VSM) were employed to study the materials produced at different stages. Two-stage heating firstly at 300 and then 800°C was adopted in order to avoid the burning of the materials and formation of carbonates. The carbonate formation was avoided by heating the materials firstly at 300°C for 2 h and without intermediate cooling moved to the furnace having temperature 800°C and hold for 2 h. The sintering behaviour of samples was studied by dilatometry and the results revealed that the sample having x=0.4 was stabled up to a temperature of 700°C while samples having x=0.2 and 0.8 to a temperature of 625°C. The maximum shrinkage was observed at 850°C in all the samples. On the basis of dilatometry results, the samples were sintered at 845°C for 60 h to observe the superconducting phases. The highest volume fraction of high superconducting phase (2223) was noticed in the sample containing x=0.4 having onset T_c=110 K.

Keywords: *dilatometry, FTIR study, high T_c phase, Pb–BSCCO system, pH effect, sol–gel technique, superconducting phases, VSM, XRD study*

Introduction

The development of high T_c superconductors is one of the most active field in scientific research. One of such ceramic system, which has shown promise, is BiSrCaCuO (BSCCO). Many communications have appeared on its importance and the parameters governing its synthesis. Many research efforts have been directed at improving the properties of BSCCO. It is evident that partial replacement of bismuth by lead (Pb) leads to enhance of superconducting properties such as J_c, T_c and mechanical properties [1–10]. The understanding of the other relevant parameters including structural stability, nature of charge carriers, the effect of carrier concentration on the superconducting properties of the system, thermal stabilities, etc. is drawing much attention and pertinent findings have been published [11–21].

Powder processing (sol–gel) by pyrolysis of amorphous organic precursor [22] or without organic acid aid [23] makes use of mixing appropriate amount of ions, usually in the form of metallic salts such as nitrates or chlorides, and a polyfunctional hydroxy acid, e.g., citric acid [24–26] or ethylenediaminetetraacetic (EDTA) acid [27–29]. The sol–gel method involves chelating of cations with polyfunctional hydroxy acids such as citric acid and EDTA and polyesterification of excess polyfunctional acid with a polymorphic alcohol such as ethylene glycol or glycerol [30–34]. The dehydration of the resulting solution renders gel and then the amorphous precursor. The homogeneity of the aqueous solution of salts is preserved in the amorphous precursor and possibly retained in the final solid oxide product. There are number of factors which need to be considered in a sol–gel process such as solvent, temperature, precursors, catalysts, additives, mechanical agitation and pH. The pH of initial aqueous solution is one of the most important factors affects the hydrolysis and condensation reactions. Acidic conditions favour hydrolysis, which means that fully or nearly fully hydrolyzed species are formed before condensation begins. Under acidic conditions there is a low crosslink density which yields a denser final product when gel collapses. Basic conditions favour condensation reactions; therefore, condensation begins before hydrolysis is complete. The pH also affects the isoelectric point and stability of the solution. Ammonium hydroxide is introduced into the precursor solution to aid pH adjustment and dissolution of metal salts [35, 36]. After gelation, calcination plays important role in improving the processing characteristics in operations such as grinding, compaction and sintering, because the calcination products are aggregates of

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small crystallites. In addition, the release of volatile matter during calcination minimizes internal shrinkage in later processing steps that can lead to the development of internal stresses and eventually crushing and warping [37]. To obtain a dense solid, the calcined powder requires to be pressed and subsequently sintered using either solid–solid or liquid phase diffusion processes.

The current work deals with the importance of pH and Pb substitutions on the fabrication of Pb–BSCCO system. As pH of initial aqueous solution is vital to complex formation and dissolution of metal salts, it was thought germane to examine its effect on the present system. In the present study pH=6 was chosen to be best for complex formation. EDTA does not dissolve in water at low pH=1 or 2 [38], so the pH had to be raised by the addition of NH_4OH solution and on the basis of preparing solution it was observed that pH=6 was more suitable to allow the organic acid to form organometallic complexes. It also constitutes a part of our ongoing studies on BSCCO and Pb–BSCCO and the results are based on the techniques previously applied [39–41].

Experimental

The superconducting oxides were prepared using sol–gel technique. The high purity Bi, Sr, Ca, Pb and Cu nitrates and EDTA were acquired from Aldrich to obtain the $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10-\delta}$, where x=0.2, 0.4 and 0.8. The samples were designated as P2 (x=0.2), P4 (x=0.4) and P8 (x=0.8). For the production of gel, primary solution is prepared by dissolving metal nitrates in deionised water. $Bi(NO_3)_3$ does not dissolve in water therefore the addition of HNO_3 is required to dissolve bismuth nitrate. For each batch, a sufficient amount of organic acid (EDTA) was added for requisite complexation. EDTA does not dissolve in water at low pH=1 or 2 [38], so the pH=6 was attained by the addition of NH_4OH solution. A pH=6 was used to allow the organic acid to form organometallic complexes. The primary solution was converted into an amorphous gel using a rotary evaporator in a water bath at approximately 70°C and applying vacuum of a few torr. At this point it was poured into a Pyrex dish, placed in a vacuum oven and left for at least 12 h at 80°C and 10^{-1} torr. The precursor was dehydrated and highly porous form with either glassy or foamy appearance resulted. The gel was converted into powder form by heating at 300 followed by 800°C each for 2 h in air. The pellets were produced by pressing the powder in press and then sintered at 845°C for different duration of time.

The investigation of complex, carbonates and powder formation was carried out by Perkin Elmer 2000 FTIR spectrometer, which operates in the range of 450–6500 cm^{-1}. The powders at each stage, precursor, calcined and sintered products were characterized by X-ray diffraction (XRD) using a Philips diffractometer coupled to a printing recorder and a computer with software for print-outs. The analyses were carried out at 40 kV and 20 mA. CuK_α, λ=1.5418 Å was used as the X-ray source. The calcined powders of samples P2, P4 and P8 were pressed into cylindrical pellets of 3 mm diameter and length 3–4 mm and heated to a temperature of 850°C with heating rate of 3°C min^{-1} in air in dilatometer. The superconducting transition temperatures were measured employing a vibrating sample magnetometer (VSM)-3001 from Oxford Instruments. The experiments in VSM were carried out at 100 Oe usually between 40 and 100 K using liquid helium. Readings were taken in 5 K steps with a settling time of 30 s, to give the sample the chance to reach equilibrium temperature.

Results and discussion

FTIR spectrum

FTIR spectrum of the EDTA–gel of samples P2, P4 and P8 in the region of 4500–600 cm^{-1} are shown in Figs 1a–c. FTIR spectrums provide information about the basic characteristics of the molecules, nature of atoms, their spatial arrangement and chemical linkage forces. The gel was water soluble that indicated the weakly bonded structure of the gel. Broad absorption peaks in the range of 3500–3000 cm^{-1} (marked at 3200 cm^{-1}) corresponded to stretching vibration of intermolecular hydrogen band (O–H). Peaks at 2400, 1400, 1150, 925, 725 and 650 were due to NO^{3-} ions present in all EDTA–gel samples, which indicated that most of the ions were consumed to produce the NH_4NO_3 precipitates in the precursor. This precipitation did not affect the chemical homogeneity or agglomeration in superconducting materials because no metal ion contributed in reaction. The peak at about 1750 cm^{-1} is due to the vibration of carbonyl group [C=O] and characteristic absorption band due to carboxylate ion [–COO–] is present at 1600 cm^{-1} which confirms the complex formation in Pb–BSCCO system [42–44].

Figures 1d–f show the FTIR spectrum of the powder from the samples P2, P4 and P8 after heating at 300°C. The peaks for the NO_3 ions as well as the carboxylic ion had disappeared. A new band due to stretching vibration of the CO_3^{2-} appeared at 1460 cm^{-1}. Other peaks, which appeared and can be attributed to carbonates and metal oxide [44], are given in Table 1. In order to avoid any carbonate formation, the complex gels were heated continuously without intermediate cooling from 300 to 800°C for 2 h because the carbonates are formed by exother-

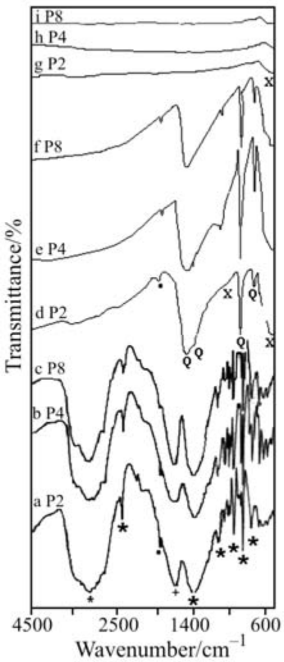

Fig. 1 FTIR spectrums of samples P2, P4 and P8; a–c – EDTA gel, d–f – samples heated at 300°C and g–i – samples heated at 800°C

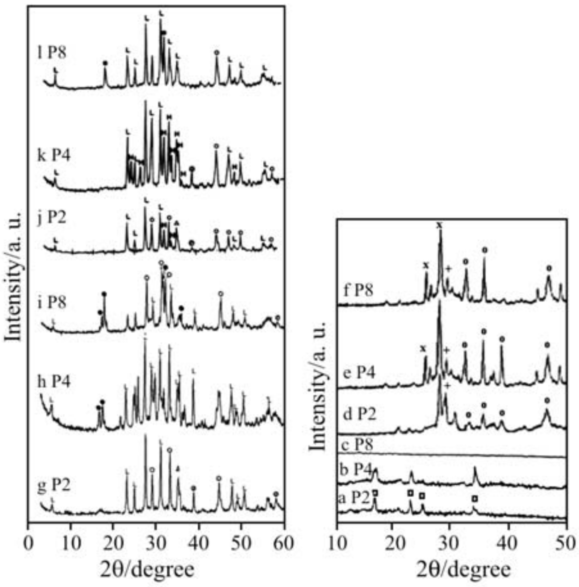

Fig. 2 XRD patterns of samples P2, P4 and P8; a–c – EDTA gel, d–f – samples heated at 300°C, g–i – samples heated at 800°C and j–l – sintered at 845°C for 60 h

mic reaction in the temperature range of 250 to 500°C [45–47]. No carbonates peaks were appeared (Figs 1g–i) in the precursor samples of P2, P4 and P8 heated at 800°C, which revealed that oxide powder is free of carbonates. The absorption bands observed in EDTA gel, at 300 and 800°C are summarized in Table 1.

X-ray diffraction and dilatometry

Figures 2a–i show an XRD patterns of gel, precursor heated at 300 and 800°C and powder pellets sintered at 845°C. The basic gels were amorphous, however due to the addition of ammonia in the samples having x=0.2 and 0.4 (P2, P4), the peaks of NH_4NO_3 were observed. The detailed discussion is already given previously [41]. In XRD patterns (Figs 2d–f) the formation of the CuO, Bi_2O_3, $SrCO_3$ and $CaCO_3$ phases were seen in the samples of P2, P4 and P8 when the samples were heated at 300°C, due to the partial decomposition and oxidation. As discussed before that carbonates are formed in the temperature range of 250 to 500°C [45–47]. Therefore, controlled decomposition of the gel would be carried out to suppress the formation of carbonates of constituent species, since these carbonates give possible segregation and non homogeneity in the final oxide powder. These results are also supported the FTIR findings.

The peaks of carbonate phase were not found in the XRD patterns of samples P2, P4 and P8 when heated up to 800 directly from 300°C (Figs 2g–i). The phases observed in the samples heated at 800°C are

Table 1 Maxima of absorption bands in the IR spectra for EDTA gel and precursors heated at 300 and 800°C

EDTA gel		Precursor/300°C		Precursor/800°C	
Wavenumber/cm^{-1}	Assignment (ions)	Wavenumber/cm^{-1}	Assignment (ions)	Wavenumber/cm^{-1}	Assignment (ions)
3200	O–H	–	–	–	–
2400	NO_3^-	–	–	–	–
1750	C=O	1750	carbonyl	–	
1600	–COO–	1460	carbonate	–	–
1400	NO_3^-	1380	carbonate	–	–
1150	NO_3^-	1075	metal oxide	–	
925	NO_3^-	850	carbonate	–	–
650	NO_3^-	–	–	–	–
–	–	–	–	500–517	metal oxide

Table 2 Phases identified in samples P2, P4 and P8 at different temperatures

Specimens	Phases		
	300°C (2 h)	800°C (2 h)	845°C (60 h)
P2	CuO, Bi_2O_3, $SrCO_3$, $CaCO_3$	2212, 2201, CuO, Ca_2PbO_4, Ca_2CuO_3	2201, 2212, 2223 (small), CuO, Ca_2CuO_3
P4	CuO, Bi_2O_3, $SrCO_3$, $CaCO_3$	2212, Ca_2PbO_4	2201, 2212, 2223, CuO
P8	CuO, Bi_2O_3, $SrCO_3$, $CaCO_3$	2212, Ca_2PbO_4	2201, 2212, CuO, Ca_2PbO_4

given in Table 2. In P2 sample the phase Ca_2PbO_4 was not observed, however, intermediate and higher amount of this phase was noticed in P4 and P8, respectively. As discussed previously [41] that large amount of Ca_2PbO_4 in the oxide powder at 800°C hinders the formation of 2212 phase because this phase (Ca_2PbO_4) took two metal species i.e. Ca and Pb.

Before final sintering of the powder pellets, its shrinkage behaviour has been studied by dilatometry. The cylindrical pellets of calcined powders of samples P2, P4 and P8 were heated at temperature of 850°C in the dilatometer. Figure 3 shows the shrinkage of the samples as a function of temperature. There is no change in the length of samples P2 and P8 up to a temperature of 625°C; however, in case of P4 the sample is stabled up to a temperature of 700°C. As discussed in the XRD results, the sample P4 contained the highest level of the 2212 phase as compared to P2 and P8, which started to shrink at a lower temperature because these samples also contained other low temperature phases in larger amount. A large shrinkage occurred in P2 and P8 as a result of sintering between 625 to 850°C. However, in the sample P4 this event was occurred in the range 700 to 850°C. At 850°C for P2 and P4 and at 845°C for P8 these samples can be seen to shrink drastically. On the basis of dilatometry results, the pellets of the powder were pressed and sintered at 845°C for 60 h in order to observe the formation of superconducting phases.

Figures 2j–l show the X-ray diffraction patterns of the samples P2, P4 and P8 sintered at 845°C for 60 h and phases obtained are given in Table 2. The small amount of 2223 phase was observed in sample P2 and negligible amount in P8. It has been observed [48, 49] that for lower concentration of Pb i.e. P2, the sample was required to be sintered at or above 860°C or at the temperature of the endothermic peak. In sample P8 a few peaks of Ca_2PbO_4 were observed even after heating at 845°C, possibly because of the large amount of this phase present in the oxide powder. Hence for P8 it seems that the first stage of reaction at higher temperature has to be the formation of the 2212 phase. In the time scale of the experiments carried out in these studies it appears that the newly produced 2212 phase in P8 does not have chance for further reaction to give the 2223 phase.

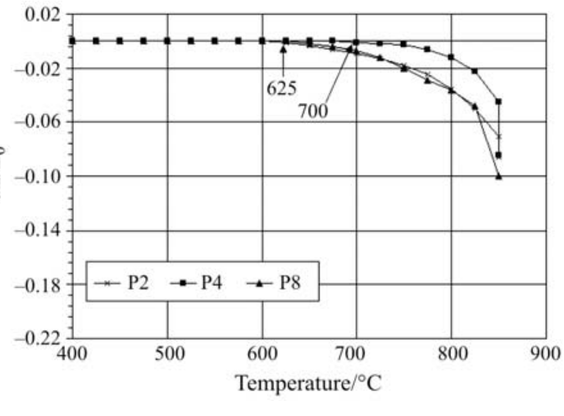

Fig. 3 Dilatometery curve for the precursors of P2, P4 and P8 calcined at 800°C

A higher volume fraction of the 2223 phase was observed in the sample P4. The Ca_2PbO_4 produces a lead-rich liquid phase and CaO above 822°C [50]. Within the lead-rich phase the rate of inter-diffusion among the 2212 phase, Ca_2CuO_3 and CuO can be increased beyond the solid-state reaction and as a result the formation of the 2223 phase is started.

Superconductivity

The presence of the superconducting phases in the samples P2, P4 and P8 sintered at 845°C for 60 h were also confirmed by magnetic measurements (Figs 4a–c). There are low superconducting phases present along with 2223 phase with T_c onset at 110 K in sample P2 (Fig. 4a). This sample mainly consists of low temperature superconducting phases. In the sample P4, the diamagnetic susceptibilities between 110–72, 72–32 and 32–5 K are attributed to the 2223, 2212 and 2201 phases respectively (Fig. 4b). This result shows the existence of low superconducting phases along the high T_c superconducting phases in the sample P4, which also supports the XRD results. The susceptibility data of sample P8 (Fig. 4c) also shows the existence of low temperature superconducting phases along with 2212 phase with T_c onset at 68 K.

It is shown that substitution of (x=0.4) Pb in the starting compositions $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10-\delta}$ having a maximum fraction of the $Bi_{1.09}Pb_{0.53}Sr_{1.97}Ca_{2.08}Cu_{2.65}O_{8.73+\xi}$ (2223) phase after 60 h at a sintering temperature of 845°C.

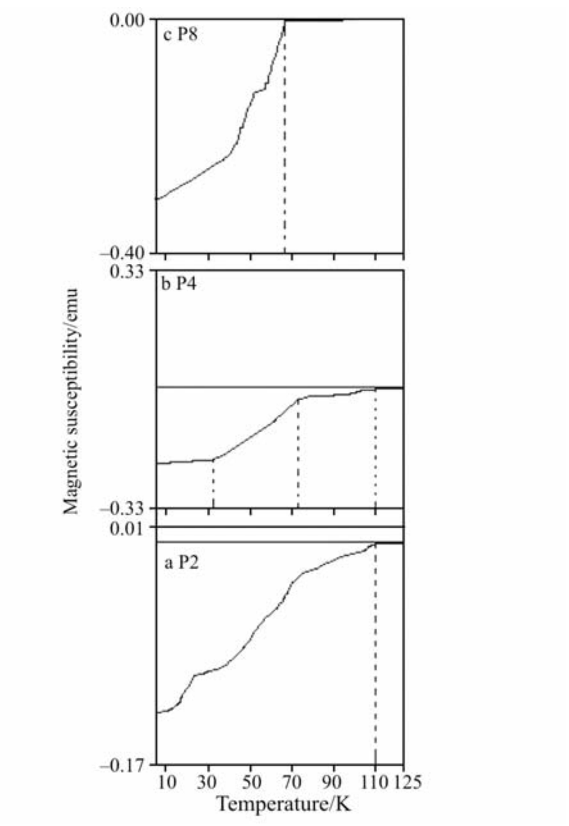

Fig. 4 Magnetic susceptibility behaviour of samples a – P2, b – P4 and c – P8 sintered at 845°C for 60 h

Conclusions

- Sol–gel process was successfully employed to synthesize the Pb–BSCCO system.
- Two stages heating was introduced, firstly at 300°C for 2 h and without intermediate cooling heated to 800°C, in order to avoid the burning of materials and formation of carbonates because these carbonates hinder the formation of superconducting phases.
- No change in the length of samples P2 and P8 up to a temperature of 625°C, however, in case of P4 the sample is stabled up to a temperature of 700°C and maximum shrinkage was observed at temperature of 850°C.
- The VSM results revealed that the sample P4 having both low (2212) and high (2223) T_c phases with the diamagnetic susceptibilities in the range 72–32 and 110–72 K, respectively.
- The study inferred that formation of 2223 phase involves a complex dissolution–diffusion precipitation mechanism.

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