A COMPARATIVE STUDY OF EDTA-GEL DERIVED BSCCO AND Pb-BSCCO SYSTEMS BY THERMOANALYTICAL AND X-RAY DIFFRACTION TECHNIQUES

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Superconducting phases in the BSCCO and Pb-BSCCO systems have been produced by ethylenediaminetetraacetic acid (EDTA) gel derived route using nitrates of metal salts. Thermal decomposition and formation of various phases of gel and calcined powder of both BSCCO and Pb-BSCCO have been investigated by thermoanalytical and XRD techniques. It has been observed that Pb-containing system shows high volume of high T_c phase as compared to Pb-free system at the same sintering temperature. Thermal behavior (TG) indicates that sample doped with Pb decomposed in a series of steps when compared with Pb-free sample, which decomposed in a single step. The effect of Pb is shown to lower the sintering temperature (845°C) of formation of high T_c phase (2223). However, in the Pb-free sample the high T_c phase produced at higher temperature (860°C).

Keywords: *BSCCO system, high T_c phase (2223), Pb-BSCCO system, Pb-doped sample (P4), Pb-free sample (P0), phase 2212, superconducting phases, thermoanalytical study, XRD pattern*

Introduction

Recently many researchers have reported that sol–gel technique is successful route for the production of superconducting phases along with their characterization by thermal and spectroscopic techniques [1–4]. The copper oxide-containing superconductor (Ba–Ca–Cu–O) with a critical temperature 30 K was discovered by Bednorz and Muller [5] in 1986. This was followed by the discovery of another copper containing superconductor, Y–Ba–Cu–O (YBCO), by Wu *et al.* [6] with a superconducting transition of 90 K. The later discovery of high T_c (above 100 K) phase in the system Bi–Sr–Ca–Cu–O (BSCCO) has led to further studies on this material. This system was discovered by Maeda *et al.* [7]. This system has the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ [8], where n=1 to 3. The phases exist in this system are 2201 (n=1, T_c=20 K), 2212 (n=2, T_c=80 K) and 2223 (n=3, T_c=110 K). The high temperature material (BSCCO) belongs to class of rare earth free superconductors as compared to YBCO. The advantages of BSCCO material over the YBCO system, stem from the presence of phases exhibiting superconducting properties at 80 and 110 K and also from the processing point of view because BSCCO does not contain Ba, thus, eliminating difficulties associated with the decarbonation of $BaCO_3$ starting material. The BSCCO system offers the opportunity of glass formation so that glass-ceramic processing techniques can be used to form crystallize materials into desired products. However, it is unfortunate that a major problem exists with the BSCCO system in the formation of 2223 single phase material.

Presently much attention is being paid to the preparation of the pure 2223 phase with an attempt to increase the volume-fraction of the 2223 phase in possible industrial materials. By increasing the volume-fraction of this phase, it is anticipated that the optimum superconducting properties may be obtained in Bi-based superconductors. Many attempts have been made to increase the volume-fraction of 2223 phase [9, 10], however, it seems that the most effective way to increase the volume-fraction of 2223 phase is the partial replacement of Bi by Pb [11, 12].

The purpose of the present studies was to produce BSCCO and Pb-BSCCO systems and to compare the volume-fraction of 2223 phase in both systems. Ethylenediaminetetraacetic acid (EDTA) gel has been used to produce the superconducting material with the starting compositions, $Bi_{2-x}Pb_xSr_2Ca_2Cu_4O_y$ where x=0 and 4. EDTA-gel processing is more effective method than other gel processing routes, because EDTA have a great ability to chelate metal cations and form very stable and soluble complexes [1–14]. The material produced at different stages was characterized by thermal analyzer and X-ray diffraction (XRD).

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Experimental

High purity (99.9%) compounds of Bi, Pb, Sr, Ca and Cu of Analar grade were employed as starting materials. The required amounts of each nitrate were dissolved in distilled water separately. In case of bismuth nitrate, which did not dissolved easily in water, some nitric acid was added in order to prevent $Bi(OH)_2NO_3$ formation and to obtain a clear solution of Bi-nitrate. The individual nitrate solutions were mixed together and the desired EDTA solution was gradually added to the final solution. Some ammonia was added to maintain the pH between 5 and 6. The mixed solution was concentrated using a rotatory evaporator, which was maintained at 75±5°C under vacuum until a viscous liquid was obtained. The liquid was placed in an evaporating dish and was left in vacuum oven at 70±5°C for 20 to 24 h in order to produce the dried precursor, which was brittle, porous and glass like. The gel was heated at different temperature to produce the oxide powder and finally powder was sintered to obtain the desired superconducting material. The thermal stability of the precursor and its decomposition products were studied by Seiko Simultaneous Thermal Analyzer (STA-409). X-ray diffraction analyzer of gel, oxide powder and sintered powder was carried out using CuK_{α} radiation and a Philips diffractometer with a voltage of 40 kV and a current of 20 mA.

Results and discussion

Characterization of precursor and oxide powder

Figures 1a and b shows XRD patterns of the samples P0 (Pb-free) and P4 (doped with Pb). The basic gel for the sample P0 was amorphous but contained a significant amount of NH_4NO_3 as a crystalline phase. However, small amount of NH_4NO_3 precipitated during the processing of P4 sample (Fig. 1b). In the present study, the P0 sample, (BSCCO), required a large amount of nitric acid to dissolve the Bi-nitrate and ammonia to adjust the pH as compared to P4 sample (Pb-BSCCO). The P4 sample required lower amount of both nitric acid and ammonia because Pb was doped on the Bi-site. Hence, large amount of NH_4NO_3 precipitated during the processing of P0 sample (BSCCO).

Figures 2a and b shows the TG/DTA curves for the EDTA precursors, $Bi_2Sr_2Ca_2Cu_4O_x$ (BSCCO, sample P0) and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_4O_x$ (Pb-BSCCO, sample P4). The TG curve Fig. 2a of P0, revealed that after the initial loss of water, a single sharp mass loss occurred and the precursor decomposed almost completely at 260°C (DTA curve) with a major mass loss. The breaking up of the organic complex, volatilization of NH_4NO_3, elimination of nitrate ions and free EDTA,
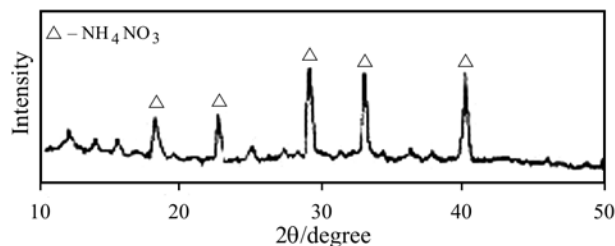

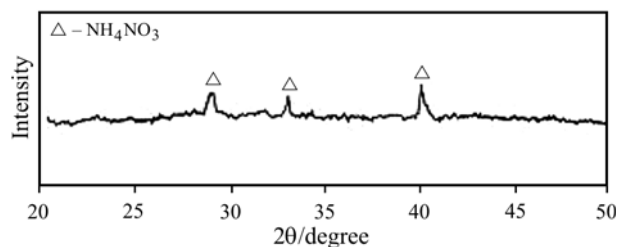**Fig. 1a** X-ray diffraction pattern of sample P0 (Pb-free)

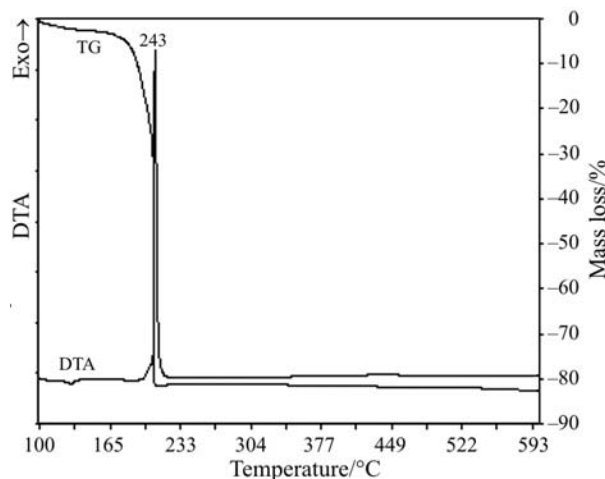**Fig. 1b** X-ray diffraction pattern of sample P4 (doped with Pb)
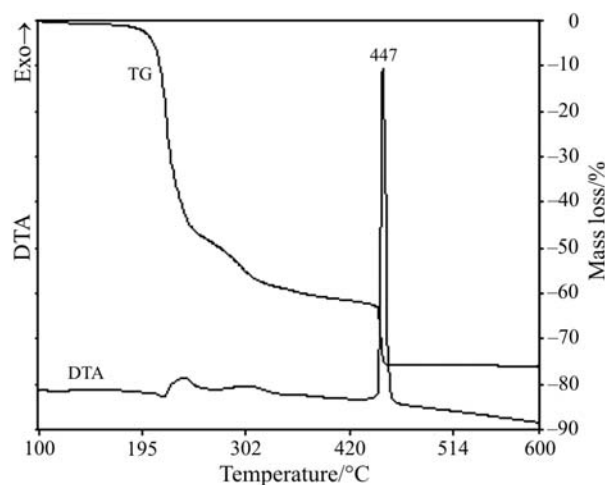

Fig. 2a TG/DTA curves for sample P0

Fig. 2b TG/DTA curves for sample P4

contributed to this stage. Figure 2b illustrates the TG curve for the sample P4. It follows from the TG curve that sample doped with Pb decomposed in a series of stages when compared with Pb-free samples (P0, Fig. 2a). The first (I) stage (between 180 to 240°C) shows a sharp mass loss of precursor. This sudden decomposition is due to NH_4NO_3, which had formed as indicated by XRD (Fig. 1b). This stage is almost equivalent to sample P0. The second (II) stage (between 240 to 440°C) highlights a further mass loss of precursor, which refers to decomposition of carbonates. The final (III) stage (between 440 to 470°C) is associated with a large exothermic peak that may be attributed to the decomposition of $Pb(NO_3)_2$ [15]

$$[Pb(NO_3)_2] \rightarrow [2PbO + O_{2(g)} + 4NO_{2(g)}] \qquad (I)$$
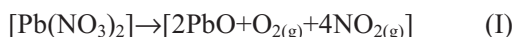
and stabilization of the phases from the amorphous precursor. It is revealed from these results that the presence of NH_4NO_3 as a crystalline phase in both the precursors (P0 and P4) does not cause any problem of chemical inhomogeneity or agglomeration in the superconducting material as it did not involve any of the metal ions required in the final product.

Figures 3a and b gives the XRD patterns for the product obtained by heating the precursors (P0 and P4) at 800°C. For sample P0 (Fig. 3a), the characteristic peaks of the 2212 phase appeared at 'd' spacing of 15.30 Å. The peaks of 2201, CuO and Ca_2CuO_3 phases, were also observed in the oxide powder. For sample P4, it is evident from the XRD patterns (Fig. 3b) that the 2212 phase is dominant in this sample as compared to
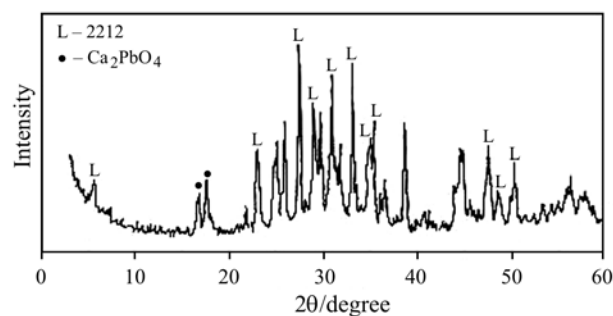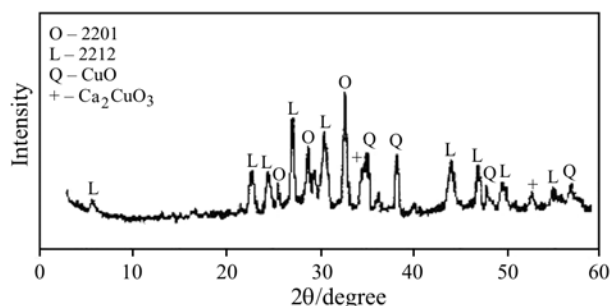
P0. The thermal analysis (TG/DTA) was also conducted for both the samples (P0 and P4) to find out the optimum sintering temperature. For sample P0, it can be seen from Fig. 4a that there are two endothermic peaks at temperatures of 867 and 874°C. Hatano *et al*. [16] observed two endothermic peaks in their DTA data at 870 and 880°C for BSCCO sample. Figure 4a also reveals the onset of the first peak at 845°C and that of the second at 870°C. The first peak was the largest endothermic of the two and was coincident with the largest mass loss trace as shown in TG curve. The second endothermic at 870°C in the DTA curve occurred due to the decomposition reaction of the superconducting phases. For sample P4, Fig. 4b shows two endothermic peaks at temperatures of 855 and 870°C, which are at lower temperatures when compared to those of sample P0. The first endothermic peak, which occurred at temperature between 835 and 865°C, is associated with the partial melting point. The second endothermic peak occurred at temperatures between 865 and 885°C. According to
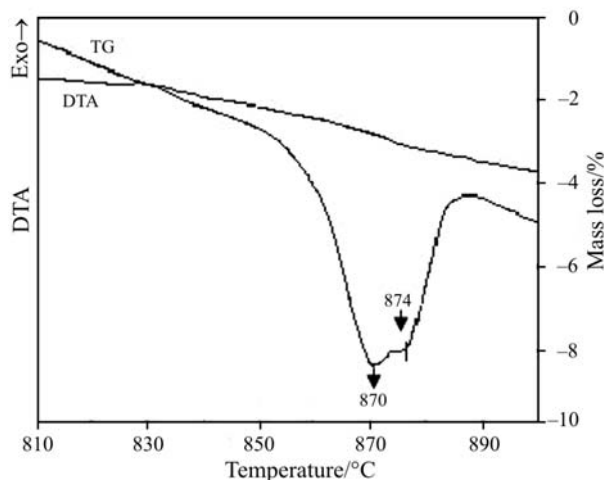

Fig. 4a TG/DTA curves for sample P0 calcined at 800°C

Fig. 3a X-ray diffraction pattern of sample P0 calcined at 800°C

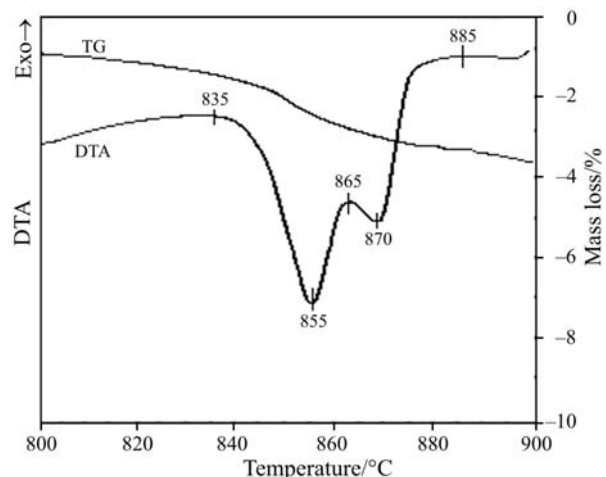**Fig. 3b** X-ray diffraction pattern of sample P4 calcined at 800°C

Fig. 4b TG/DTA curves for sample P4 calcined at 800°C

Wong-N.G *et al.* [17], 870°C is the decomposition temperature of the 2212 phase which disintegrates into $Bi_2Sr_2CuO_x$ (2201) and other Ca and Cu compounds and so it implies that the second endothermic peak is linked with this decomposition. The DTA data indicates that with the doping of Pb, the partial melting of the material decreases as compared to Pb-free sample P0.

Characterization of sintered products

It has been observed that the optimum sintering temperature for the formation of the superconducting phases in the BSCCO and Pb-BSCCO system occurred over the range from T_x to T_z as indicated in Figs 4a and b. For sample P0 (Pb-free), Fig. 4a (DTA curve) revealed that the temperature, T_x, which is the effective onset of the peak, started at 845°C, the peak temperature T_y, fell to 867°C and the temperature at which the endothermicity completed was 870°C (T_z). For sample P4 (Fig. 4b), DTA curve shows that the T_x, T_y and T_z lie at 835, 855 and 865°C, respectively. In order to observe the superconducting phases present in both the samples (P0 and P4), pellets were processed and sintered at 845°C for different time intervals (60 to 120 h). The sintered pellets were then powdered and characterized using X-ray diffraction (XRD). Figures 5a and b illustrates XRD pattern for the samples P0 and P4 sintered at 845°C for 60 and 120 h.

From Fig. 5a it follows that the major phase in the sintered sample, P0, is the 2212. It is anticipated that the stronger peaks from the 2212 phase in the sintered material occurred as compared to powdered sample because of grain growth and enhanced crystallization of this phase during the sintering process. Phase 2223 was not observed in the sample P0 sintered at 845°C in the time interval 60→120 h. Figure 5b gives the XRD pattern of the sample P4 sintered at 845°C for 60 and 120 h. The 2223 phase, which had appeared in small amount after 60 h increased with further heat treatment time 120 h. It is evident that the volume-fraction of the 2223 phase increases with time since its mechanism of production is a diffusional time-depended process. The phases observed in powdered and sintered (at 845°C for 120 h) samples of P0 (Pb-free) and P4 (Pb-doped) are given in Table 1.

From the Table 1, it follows that the major phase in the sintered sample (P0), is the 2212. There is no change in the basic XRD patterns in the powdered and sintered products, other than the peak of CuO was reduced in the sintered material and Ca_2CuO_3 increased. It is believed that the stronger peaks from the 2212 phase in the sintered material occurred because of grain growth and enhanced crystallization of this phase during the sintering process. There is no change in the phase by sintering the material at higher tempera-
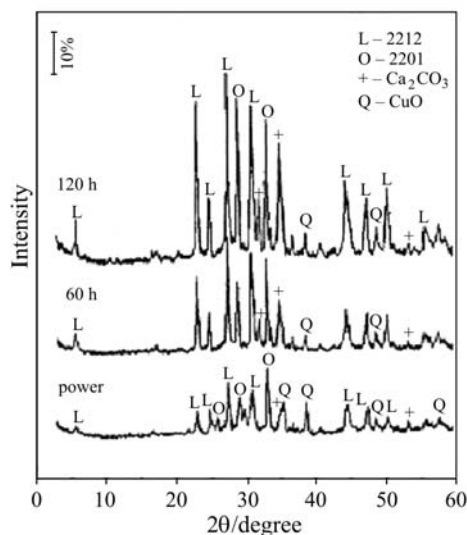

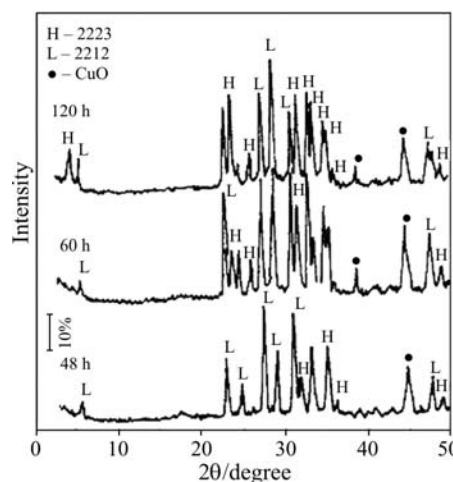**Fig. 5a** X-ray diffraction pattern of sample P0 calcined at 800°C

Fig. 5b X-ray diffraction pattern of sample P4 calcined at 800°C

Table 1 Phases observed in P0 and P4 samples

Sample no.	Samples		Phases			
P0	powder (800°C)	2201	2212		CuO	Ca_2CuO_3
P4	powder (800°C)	2201	2212		CuO	Ca_2CuO_3 Ca_2PbO_4
P0	sintered 845°C/120 h	2201	2212 (strong peaks)		CuO	Ca_2CuO_3
P4	sintered 845°C/120 h	2201	2212, 2223		CuO (small)	

ture 845°C. This can be explained from the DTA curve (Fig. 4a) where it is evident that there is no peak in the temperature range 800–845°C.

This also confirms the stability of the 2212 phase in the BSCCO material. The only difference in XRD patterns of P0 and P4 powdered samples is the appearance of the Ca_2PbO_4 in the latter. It has been noticed by Chen *et al*. [18] that the presence of Ca_2PbO_4 accelerates the formation of 2223 phase at higher temperature. They noted that Ca_2PbO_4 produced a lead-rich liquid phase and CaO above 822°C. The CaO reacts with CuO to form Ca_2CuO_3 which then speeds up the formation of the 2223 phase when Ca_2CuO_3 reacts with 2212 phase.

$$2(2212)+2CuO+Ca_2CuO_3\rightarrow2(2223) \qquad (II)$$

It can be seen in the case of sample P4 that the formation of a large amount of the 2212 phase in the powdered sample facilitates the formation of the 2223 phase at high temperature (845°C). It has been observed that the 2212 phase is a stable compound and it takes a very long time to produce high amount of the 2223 phase. The 2223 phase has a long periodic structure. In general, long periodic structures are more difficult to synthesis. In summary, the XRD results of samples show that the formation of the 2223 phase depends on the prior formation of the 2212 phase, sintering time and the liquid phase which is formed above 822°C as this facilitates the process of diffusion. So it can be epitomized that a partial substitution of Pb for Bi in the BSCCO system is effective apparently in promoting the formation of the 2223 phase at lower temperature (845°C) and also in enhancing the volume-fraction of the 2223 phase.

Conclusions

- Large amount of NH_4NO_3 was observed in P0 sample as compared to P4. The presence of NH_4NO_3 did not affect the synthesis of final product.
- EDTA-gel of Pb-free sample decomposed in single step, however, Pb-doped sample degraded in a series of steps, which shows the stability of Pb-doped sample.
- The phase 2212 was dominated in powdered sample of P4 as compared to P0.
- By Pb-doping, the exothermic peaks (DTA) of powdered sample shifted toward lower temperature and became more sharp than Pb-free sample.
- The difference between P0 and P4 powdered samples is the appearance of $CaPbO_4$ in P4.
- The formation of 2223 phase in sintered sample depends upon the prior formation (in powdered sample) of 2212 phase.
- XRD patterns of both sintered samples (P0, P4) revealed that P4 contained the large volume of high

T_c phase at the same sintering temperature and duration, because the powdered sample of P4 had large volume of 2212 phase as compared to P0.

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