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Synthesis of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ via sol-gel method using different acetate-derived precursors

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Sol-gel method have been used to convert metal carbonates, oxides and nitrates into corresponding acetate precursors for gel formation. About 90% volume of high T_C superconducting phase (2223) has been obtained for oxide-carbonate system. This value is comparable to that obtained from pure acetates (91% volume). However, the nitrates-'derived sample has a high-T_C phase of 88% due to poor conversion of nitrates to acetates as observed by the infrared spectra. The dominance of high-T_C phase was observed in all systems as evidenced in the single step transition of R-T curves. Hence the percentage of the high-T_C phase dictates the value of $T_C(R=0)$ as 104 K, 103 K and 99 K, for oxide-carbonate, pure metal acetates and nitrates system respectively.

1. Introduction

The solid state reaction, as conventional route, has been widely and routinely adopted for the processing of ceramic superconductors [1–3]. There are two major problems associated with this process; the high porosity and poor homogeneity of the sintered sample, which affect the superconducting property [4]. One of the solution is to employ starting powders having submicron-sized particles so as to improve the solid state reaction during sintering. The sol-gel method is a well known technique employed to produce particles of submicron in size and the resulting powders are more homogeneous so as to enhance reaction during heat treatment [5]. Sheen *et al*. [6] reported that via this method, calcination and sintering temperature could be lowered and the heat-treatment time could be shortened. Metal acetates precursors are commonly used in sol-gel process for the preparation of superconducting ceramics [7–9].

However, metal acetates are quite expensive as compared to other conventional materials such as carbonates, oxides and nitrates that are commonly used in solid state reactions. Conversion of these materials to metal acetate precursors can reduce the costs of pure acetates required in the preparation of superconducting ceramics. The present paper describes the sol-gel procedures to derive the acetate precursors from these conventional chemicals such as oxides, carbonates and nitrates. Structural and electrical properties of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ superconducting ceramic produced by this method will be discussed.

2. Experimental procedures

The superconducting oxide of Bi-Pb-Sr-Ca-Cu-O system was prepared via sol-gel process by

i) using pure metal acetate of $Bi(CH_3COO)_3$, $Pb(CH_3COO)_2{\cdot}H_2O$, $Ca(CH_3COO)_2{\cdot}3H_2O$, $Sr(CH_3COO)_2$ and $Cu(CH_3COO)_2$ having purity of 99.0% as precursors,
ii) converting metal oxides, Bi_2O_3, PbO, and carbonates of $CaCO_3$ or $SrCO_3$ of purity 99.99% into respective metal acetates precursors,
iii) converting all metal nitrates, $Bi_2(NO_3)_3$, $Pb(NO_3)_2$, $Ca(NO_3)_2{\cdot}4H_2O$, $Sr(NO_3)_2$, $Cu(NO_3)_2{\cdot}6H_2)O$, (reagent grade purity 99%) into respective metal acetates precursors,

In all cases the individual chemicals were weighed in the stoichiometric molar ratio of Bi : Pb : Sr : Ca : Cu = 1.5 : 0.5 : 2.0 : 2.0 : 3.0, so as to give ultimate composition of the superconductor. Each inorganic precursor (oxides, carbonates or nitrates as the case may be) was dissolved in acetic acid to convert them into corresponding acetate as shown in Fig. 1. The solutions were stirred for 6 h and dried in the oven at 80° C overnight. The dried samples were subjected to IR spectrum to examine the acetate formation. Pure and converted acetates were dissolved separately in acetic acid and mixed to hydrolyse and polycondense the solutions for 6 hours at room temperature using motorised stirring so as to maintain the pH value at 5.5. The use of

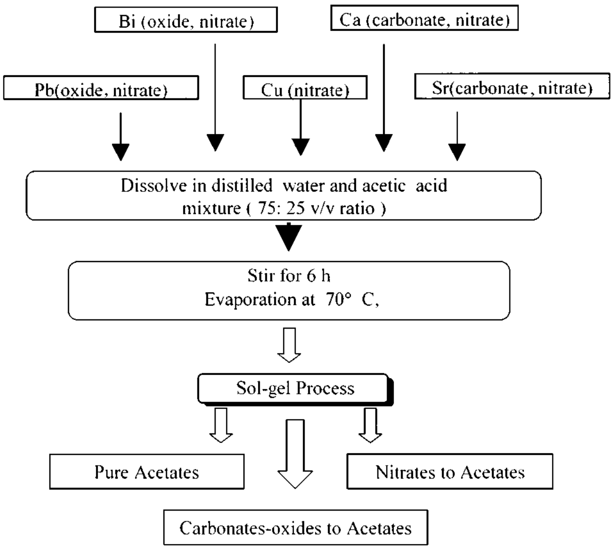


Figure 1 Flow chart for the preparation of gel from oxide-carbonate and nitrates system.

acetic acid avoids the formation of a colloidal gel and promotes that of a polymeric gel. Hence there is no necessity of performing the experiment in very dry atmosphere since the essential role of the acetic acid is to diminish the hydrolysis rate. By heating the hydrolysed solutions for 35 hours at 80° C transformed the solution into a transparent gel due to slow evaporation. The wet gel thus formed was examined by thermogravimetric analysis (TGA). Further heating of the wet gel at 150, 180, 240 °C for 3, 2 and one hour respectively converted the gel into solid bloating powders. The powders were then dried in the furnace for 3 h at 250° C followed by calcination at 800 °C for 12 h. The ceramic powders thus obtained were pelletized into disks of 1 cm and 2 cm in diameter and thickness respectively. The pellets were placed in a tube furnace and sintered in air at 855° C for 150 h at a heating rate of 2° C per minute. Identification of the crystalline phases existing in the samples was done by using SIEMEN X-ray machine with Cu-K_α radiation. Lattice parameters a, b and c were determined from the x-ray intensity peak using standard least square fitting and an interpolation technique. The microstructure of the samples was observed by scanning electron microscopy (SEM) using JOEL JSM 4600. Four-point probe technique was used to measure the samples electrical resistance using dc current of 20 mA.

3. Results and discussion

The infrared spectra of dried samples of converted acetates are shown in Fig. 2, where lead oxide, strontium carbonate and copper nitrate as example, were completely converted into corresponding acetate. The IR peaks that correspond to the acetate bonds appeared at wave number 617, 1021, 1051, 1342 and 1419 cm^{-1} [10].

Fig. 3, shows the thermogravimetric (TG) curves of gel obtained from different starting materials, heated to 1000° C with heating rate of 10° C per minute. Thermal analysis is used to provide information on the temperatures at which volatile matter is lost from the gel and the key temperature at which the decomposition is complete [11]. The curves show that the initial weight loss of ~70% occurs between 220 to 250° C. In this range the gel was in soft mode and bloats shape, the bloating may be attributed to decomposition of organic acids and further loss of water [12]. On further heating there was a slight weight loss ~7% at 500° C which could be due to the decomposition of carbonates. Beyond this temperature no significant weight loss were observed.

The temperature variations of the resistance of the sintered samples obtained from three sets of starting materials are as shown in Fig. 4. Samples prepared from nitrates and pure acetates showed metallic behaviour above 107 K and became fully superconducting ($R = 0$) at 99 K and 103 K respectively. However, sample prepared from carbonates and oxide as starting materials showed metallic behaviour above 113 K and became resistantless ($R = 0$) at 104 K. By extrapolating the R-T curves, the normalized residual resistance of samples prepared from nitrate-derived acetate was found to be the highest. This correlates with the degree of purity of the starting materials used. Fig. 5 shows the differential resistance of the three samples. Sharp peak with narrower transition width has been observed for the sample obtained from oxide-carbonate system as compared to that of the samples prepared from pure

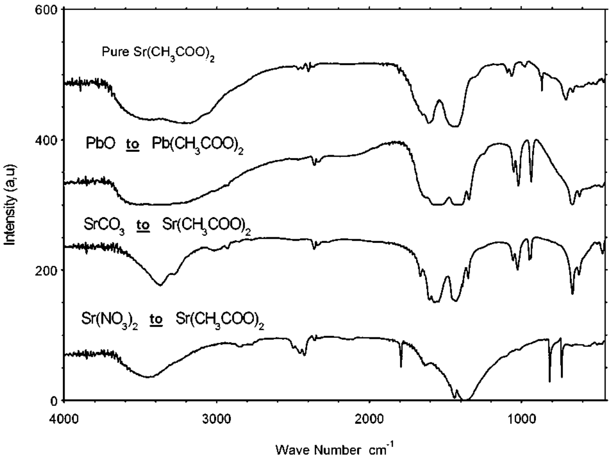


Figure 2 Infrared spectra of the converted acetates.

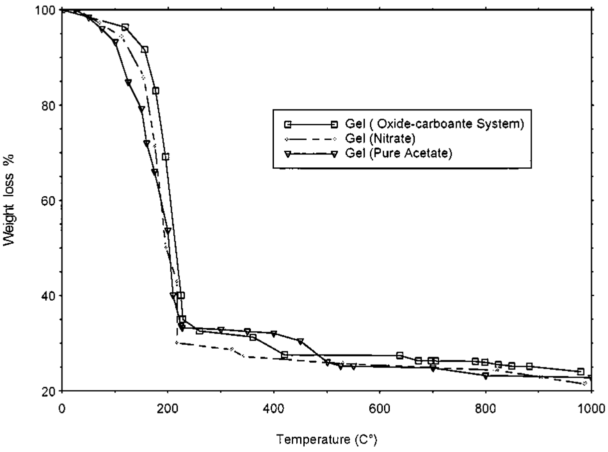


Figure 3 TGA curves for the heated gel.

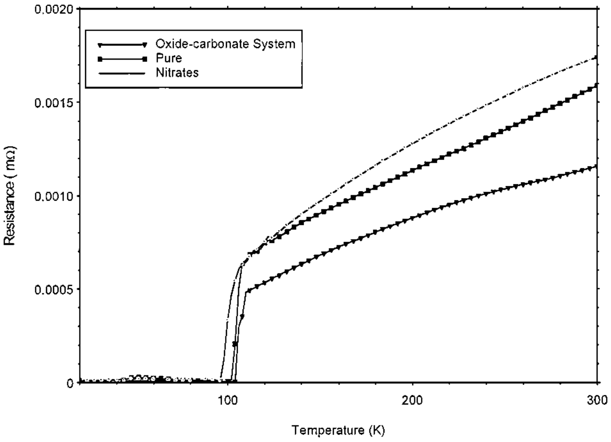


Figure 4 Temperature dependent of resistance of sintered sample.

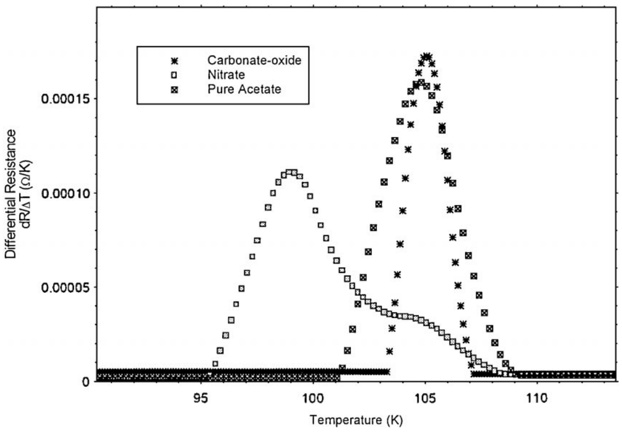


Figure 5 Differential resistance curves for sintered samples.

acetates and nitrates precursor. The quality of the sintered samples can be deduced from these curves. The narrower transition width shows that the grains of the sintered samples were strongly coupled. Ac susceptibility measurements will be carried out to investigate the nature of grains coupling and will be reported elsewhere. The high purity (99.99%) of the starting oxide and carbonate powders contributes to the formation of well-linked grains and high $T_C(R = 0)$.

From the x-ray diffraction analysis, all samples are mainly dominated by high T_C 2223 phase as shown in Fig. 6, since most of the peaks matched with the patterns of the high T_C phase obtained in the handbook of Chemistry of Superconductor Materials [13]. From the Miller indices lattice parameters a, b and c were calculated by assuming that the unit cell is tetragonal and the values are summarized in Table I. These values are comparable to that obtained by other workers [14, 15]. The c axis for nitrate-derived sample is longer and hence affects its superconducting properties. The diffraction patterns for nitrate sample exhibited some

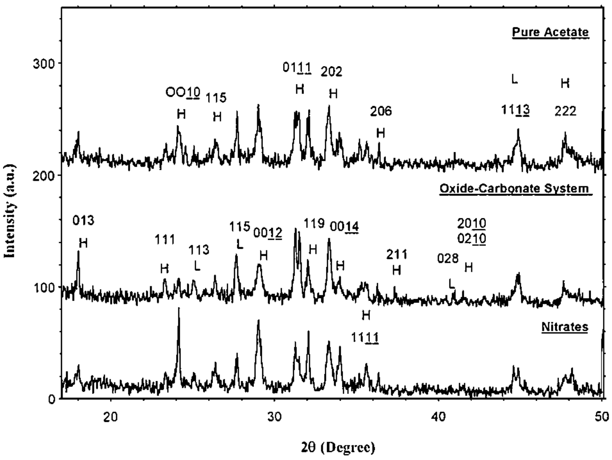
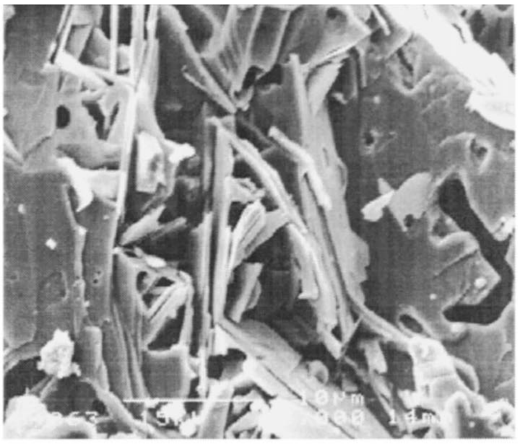
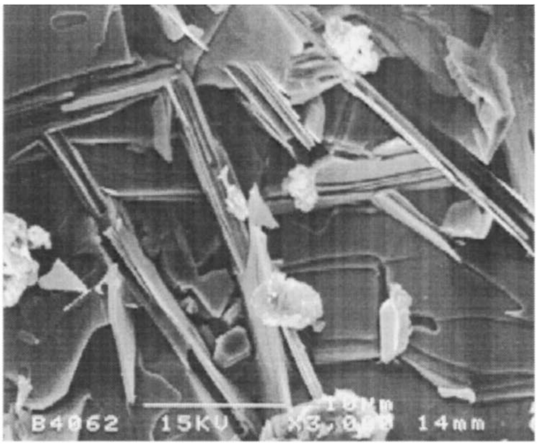


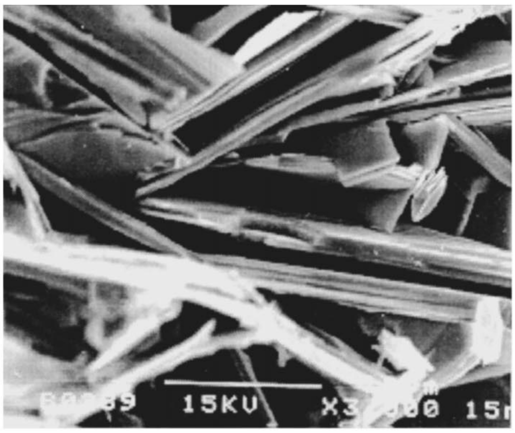
Figure 6 X-ray diffraction patterns of sintered samples.



Oxide-carbonate system



Nitrates



Pure Acetates

Figure 7 SEM photographs of sintered samples.

TABLE I Lattice parameters and volume fraction of 2223 phase

Sample	a Å	b Å	c Å	Phase	Volume %
Pure acetates	5.369	5.377	36.722	2223	(90%)
Oxide-carbonates	5.372	5.375	36.786	2223	(91%)
Nitrates	5.372	5.371	37.198	2223	(88%)

degree of orientation in the H $(11l)$ and H $(00l)$ planes as compared to other samples. The volume fraction of 2223 phase in all the samples was calculated by using Equation 1.

$$V(2223) = \frac{\Sigma I(2223)}{\Sigma I(2223) + \Sigma I(2212)}, \qquad (1)$$

where total intensity of the peaks of 2223 phase were compared to the summation of the intensities of all the peaks for $2\theta = 15–50^\circ$. The results are shown in Table I. The nitrate-derived acetate sample has the lowest percentage of high phase and this is consistent with the extrapolated data of the normalized residual resistance.

Fig. 7 shows the microstructure of the sintered samples of the three systems. Flaky plate-like grains with random distribution are common features in all the systems. The thickness of the plates is between 1 to 2 μm. The size of the plates is much bigger in the sample derived from pure acetates. There is some degree of compactness and texturing, resulting from compacting of nano-sized particles derived from sol-gel process, in the nitrates-derived acetate samples. This observation correlates with the x-ray analysis described earlier.

4. Conclusion

In summary, it has been shown that besides pure metal acetate precursors, metal carbonates, oxides and nitrates could also be converted into corresponding acetate precursors for gel formation. About 90% volume of high T_C superconducting phase (2223) has been obtained for pure acetates. This value is comparable to that obtained from oxide-carbonate system (91% volume). However, the nitrates-derived sample has a high-T_C phase of 88% due to poor conversion of nitrates to acetates as observed by the infrared spectra. The dominance of high-T_C phase occurred in all systems as evidenced in the single step transition of R-T curves. The $T_C(R=0)$ for oxide-carbonate system, pure metal acetates, and nitrates system are 104 K, 103 K and 99 K, respectively showing that the percentage of the high-T_C phase dictates the value of $T_C(R=0)$.

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