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Importance of Avrami Index in the processing of bismuth based high temperature superconductors

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ABSTRACT

It is well known that processing of Bismuth based high T_c perovskites is difficult and often results in only multiphase systems. Innumerous reports on parameters like annealing temperature, annealing time, selection of right combination of elements and addition of dopants like Pb are available since a long time and still the synthesis of single phase High T_c is not an easy task in contrast to the synthesis of Yitrium based cuprates. Here we report for the first time, how the knowledge of Avrami Index (dimensionality of crystal growth) provides critical insight in selecting the right mixture of Lead doped Bismuth cuprates for forming a highly single phase and high T_c compound through glassy precursor route.

1. Introduction

Among the new high T_c superconductor families, only bismuth-based composition could be prepared in glassy form due to glass forming ability of the materials such as Bi, Ca and Sr [2]. Glass ceramic method [3,4,7,18], for the fabrication of the high T_c superconductors in PBSCCO (Bi–Pb–Sr–Ca–Cu–O) system has been studied by a number of research groups. This method provides homogenous and dense products compared to the conventional solid-state reaction technique. Bi-2223 has the highest transition temperature among the Bi cuprate family of superconductors. It however has a sluggish rate of formation and a very narrow range of temperature stability [7]. In Bismuth perovskites the addition of Pb at the cost of Bi increases the volume fraction of 2223 [1]. However, prolonged sintering is found to be required for obtaining single high T_c phase, still the phase purity is found to be evasive. Besides the sintering temperature and time, the activation energy and dimensionality of crystal growth play an important role in obtaining single phase Bi high temperature superconductors. Since glassy materials are in meta-stable state, it will be crystallized with time and temperature change. An understanding of crystallization kinetics and crystallization mechanism is obviously very important for the optimization of processing parameters required for the preparation of high T_c superconductors prepared through glassy route. In this context, here an attempt has been made to synthesis a Pb based BSCCO system with varying Cu and Ca contents in the general formula $Bi_{1.6}Pb_{0.4}Sr_2Ca_{n-1}Cu_nO_x$ $n = 2$, 2.5, 4 by melt quenching technique and co-relate the Avrami Index, the activation energy of crystallization with Ca to Cu ratio to superconducting grain formation so as to optimize the sintering conditions of PBSCCO compositions during their synthesis.

2. Experimental details

The preparation of glass–ceramic samples and experimental specifications are as per Ref. [11]. Commercial high-grade powders (99.999%) of Bi_2O_3, $CaCO_3$, $SrCO_3$, CuO and PbO are used. $CaCO_3$ and $SrCO_3$ has been heated using microwave to 373 K for a short duration as it is hydrophilic, to ensure the exact amount of Ca and Sr, which plays a major role in superconductivity of PBSCCO system. Nominal composition of $Bi_{1.6}Pb_{0.4}Sr_2Cu_nCa_{n-1}O_w$, where $n = 2$, 2.5, 4 are obtained $n = 3$ has not been selected as it was studied by many groups. For simplicity $n = 2$ has been assigned the name *B*1, *B*2 for 2.5 and *B*3 for $n = 4$. The raw powders were mixed in an agate mortar for 2 h and the batches were melted in an open alumina crucible in an electrically heated high temperature-melting furnace at 1403 K for half an hour. Processing temperature is selected in such a way to reduce, the vaporization of volatile substances like Bismuth and Lead. The furnace has been calibrated to an accuracy of ±2 K. The melt is then splash quenched by pouring onto a cold steel plate. The rapidly quenched glass samples have been analyzed by using XRD. These compositions are powdered and palletized at a pressure of 2 ton per square cm and sintered for 24 h at a temperature of 1093 K. Again, compositions *B*1 and *B*2 sintered at 1093 K, mixed in equal proportion to get the right stoichiometry of high temperature phase and palletized at the same pressure, named as *B*4. Again *B*3 and *B*4 sintered at 1103 K for 24 h and 48 h and their structural, vibrational and electrical properties have been evaluated.

3. Results and discussion

The three PBSCCO compounds synthesized through glassy precursor route mentioned above are indicated as *B*1, *B*2 and *B*3.

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Table 1
EDX analysis of the quenched samples at 1403 K.

Composition	Bismuth (wt.%)		Lead (wt.%)		Strontium (wt.%)		Calcium (wt.%)		Copper (wt.%)	
	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
*B*3	28.93	39.62 ± 1.84	7.17	7.04 ± 1.52	15.163	19.27 ± 0.88	10.4	6.86 ± 0.45	21.99	23.66 ± 1.69
*B*2	35.11	28.34 ± 1.56	8.703	5.12 ± 1.30	18.402	14.59 ± 0.73	6.31	4.36 ± 0.35	16.68	11.10 ± 1.23
*B*1	37.81	56.42 ± 2.28	9.37	12.88 ± 1.90	19.81	31.62 ± 1.09	4.531	6.52 ± 0.49	14.37	23.39 ± 1.77

Glassy nature of the first two compositions are confirmed by the XRD. In the case of third sample *B*3, two types of microstructures noticed, glassy and crystalline. EDX analysis showed in Table 1 reveals the chemical content deviations for Bismuth and Calcium. For *B*2 the entire elements have shown a decrease in its weight percentage. It could seen that for *B*1 and *B*3 during glass formation Bismuth concentration rises, compensating for the Calcium loss and Copper content becomes slightly higher than the nominal values, due to the compensation from the other elements during the melt quenching process [4]. It may be due to the occupation of Sr site or Ca site by Pb atoms even though the doping has been done at Bi site due to the relative ionic size of Pb in comparison with Ca or Sr. It is our experience through Reitveld analysis that the Pb doped is at the calcium site. Reitveld analysis has been done only for the final composition sintered at 48 h. The refinement has been done for scale factor, thermal parameters, wave parameters, lattice parameters and atomic positions. Taking into account the solid solution of the members of the homologous series, the chemical composition can be expressed more precisely with formula $Bi_{2+x+z}Sr_{2-x-y}Ca_{n-1-z+y}Cu_{n-y}O_{4+2n+z}$ showing that a. Bi substitutes for Sr and Ca b. Sr substitutes for Ca and vice versa c. Cu is slightly deficient and oxygen in excess [4].

Glassy behavior of the precursor glass is further investigated through DSC by heating the samples through different heating rates 5 K/min, 10 K/min, 15 K/min and 20 K/min. Fig. 1a shows the DSC thermo gram for $n = 2, 2.5, 4$ heated in Argon atmosphere at a heating rate of 10 K/min. The reduction in the glass transition temperature may be due to the relative increase of Bismuth, which is a good glass-forming agent. The DSC traces of all the composition showed an endothermic activity between 400 °C and 450 °C. Shift

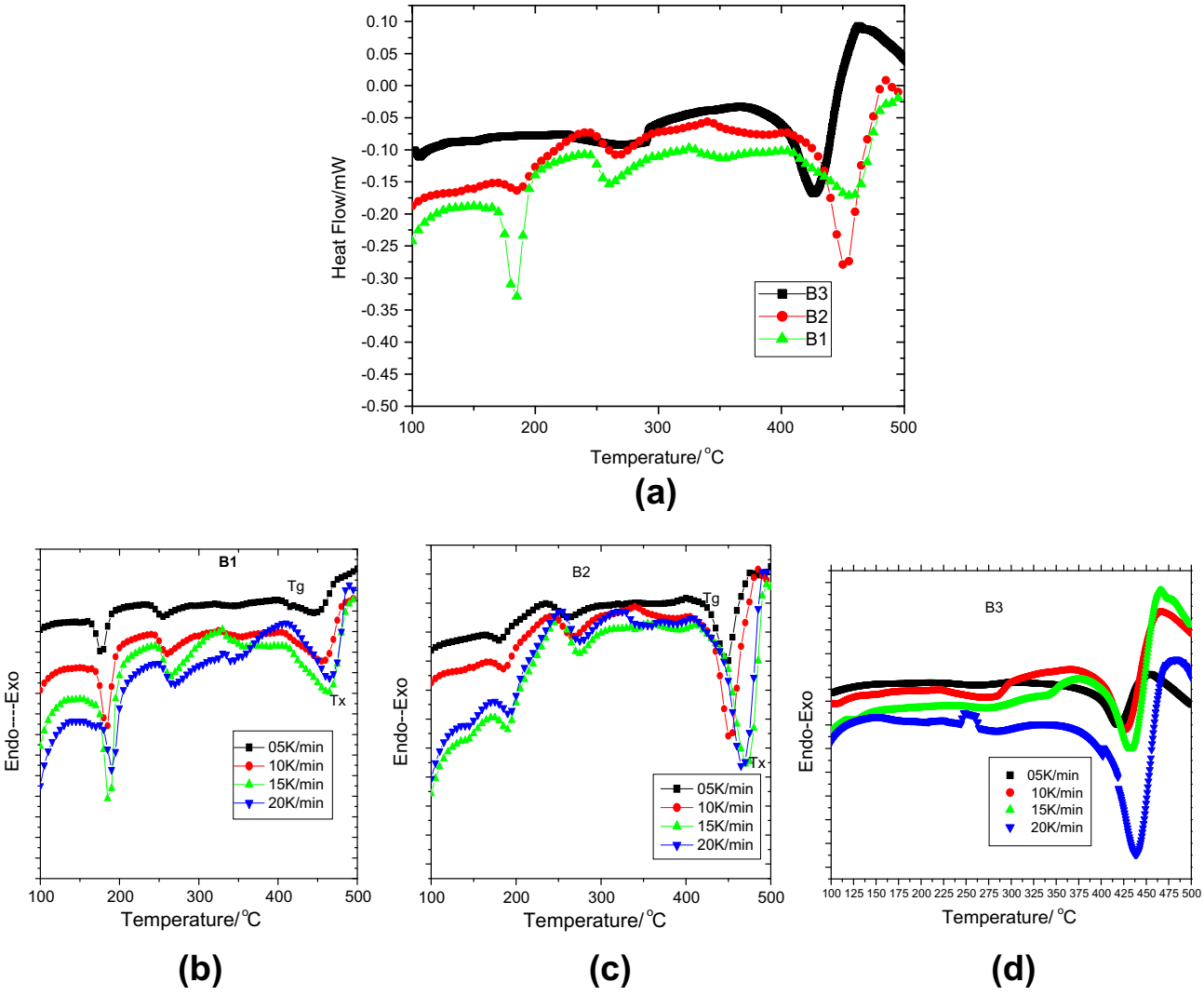

Fig. 1. (a) DSC thermo grams of different compositions at a heating rate of 10 K/min and for *B*1, *B*2 and *B*3 for different heating rates (b) *B*1 (c) *B*2 and (d) *B*3. As found from the graph, the glass transition temperature T_g and crystallization temperature T_x shifted to the lower temperature region with the increase of Ca and Cu.