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High-T_c phase obtained in the Pb/Sb doped Bi–Sr–Ca–Cu–O system

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Abstract

Partial replacement of Bi by Pb and Sb produces materials of high-T_c pure phase, with antimony playing an important role in accelerating the formation of the phase with the higher superconductive transition in the Bi–Sr–Ca–Cu–O system. The influence of the antimony precursors on the superconducting phases mechanism formation was examined. Using a solid state reaction route, two nominal compositions $Bi_{1.6}Pb_{0.3}Sb_{0.1}Sr_2Ca_2Cu_3Oy$ and $Bi_{1.6}Pb_{0.4}Sb_{0.1}Sr_2Ca_2Cu_4Oy$ were investigated. The sources of antimony were Sb_2O_3, αSb_2O_4 and a prepared mixture $Bi_{1.9}Sb_{0.1}O_x$. The mechanism formation of the phases upon annealing was investigated using X-ray diffraction and simultaneous thermal analysis. Electrical properties of the obtained materials were evaluated. The presence of the antimony ions determined a higher reactivity of the system as well as the promotion of the superconducting high-T_c phase enhancement.

Keywords: Antimony precursor; Bi–Pb–Sb–Sr–Ca–Cu–O system; Superconductors

1. Introduction

Partial replacement of Bi by Pb and Sb produces materials of extremely high phase purity, with antimony playing an important role in accelerating the formation of the phase with higher superconductive transition in the Bi–Sr–Ca–Cu–O system.[1,2] The effect of the partial substitution of Bi by Sb, the nearest neighbor element in the same group as bismuth in the periodic table, on the superconductive characteristics of the Bi-based system was analysed.[3–7] Initial attempts of Sb doping in small amounts ($<10\%$) from a stoichiometric starting composition showed T_c^{on} as high as 135 K.[8] However the value of T_c^{on} was dependent on the annealing temperature. The X-ray diffraction (XRD) pattern presented peaks that have never been observed for a non-doped or Pb-doped Bi system.[5,9] Improvement in T_c was attributed to the structural disorder, such as incommensuration or some additional electronic reasons associated with the addition of Sb. Later, there were few reports on the partial substitution of Bi by Sb and Pb simultaneously.[10,11] Independent of the different proportions of Pb and Sb or different cooling procedures, the resultant material was a multi-phase system. The XRD investigations showed in most reports the presence of a new phase observed earlier in Sb-doped Bi system, with its characteristic peaks near $2\theta = 30°$ and other peaks of low intensity or the systematic shift of the peaks of 2223 phase.[12,13]

Although the addition of Sb along with Pb in Bi systems seems to enhance the formation of the high-T_c phase and/or the formation of a 'new phase' there are controversial aspects that remain unsolved. The role of Sb in the high temperature superconductivity, the effect of the presence of the new phase on the superconducting behavior of the Bi–Pb system still remain unclear and further investigations are necessary.

An attempt to clarify some of the above aspects is made in this report, using different precursors as sources for Sb. The fact that the formation temperatures of the superconducting phases obtained in the Bi–Sr–Ca–Cu–O system (low and high-T_c phase) exceeds the polymorph transition temperature $\alpha Bi_2O_3 \rightarrow \delta Bi_2O_3$ (735 °C) suggests that the use of high temperature or metastable polymorph forms of Bi_2O_3 as a starting material will shorten the sintering time.

2. Experimental

Two nominal compositions $Bi_{1.6}Pb_{0.3}Sb_{0.1}Sr_2Ca_2Cu_3O_y$-label 1 and $Bi_{1.6}Pb_{0.4}Sb_{0.1}Sr_2Ca_2Cu_4O_y$-label 2

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were investigated. The samples were prepared by the conventional solid state reaction of Bi_2O_3, PbO, $CaCO_3$, $SrCO_3$ and CuO of high purity (99.99%), in air. The antimony was introduced in the system as Sb_2O_3 (label A), αSb_2O_4 (label B)[prepared as $Sb_2O_3 + 1/2O_2$ (600 °C/5 h)$\rightarrow \alpha Sb_2O_4$] and a solid solution with the nominal composition $Bi_{1.9}Sb_{0.1}O_x$ (label C), prepared by annealing treatment of the αBi_2O_3 and Sb_2O_3 stoichiometric mixture[14] [450 °C/5 h + 820 °C/20 h]. The main phase identified in the sample was tetragonal (Fig. 1) with lattice parameters of $a = 10.927$ Å and $c = 5.623$ Å, SG: P(−)4b2(117) associated with the metastable βBi_2O_3 phase (JCPDS 29-0236).

The mixtures were precalcined (800°/10 h), mixed, die pressed and annealed at 855 °C for 30 h. The resulting product was ground and pressed again and supplementary annealed for 30 h at 855 °C.

Thermal analysis (DTA/TG) was performed with a MOM-OD 102 derivatograph, in non-isothermal conditions, in air. More detailed thermal analysis was realized in a Stanton thermobalance, with sensibility of 0.1 mg. The structure of the obtained materials was determined by XRD. The XRD patterns were recorded with a standard D5000 Siemens Diffractometer θ–2θ equipped with a graphite monochromatized using CuK_α radiation ($\lambda = 1.5405$ Å) operating at 40 mA and 40 kV. The powder morphology was determined by scanning electron microscopy (SEM) with a scanning microscope Zeiss DSM 942 equipped with a Link Energy Dispersive X-ray system. The standard four point technique was used to determine the resistance–temperature (R–T) characteristics of the superconducting phases in the samples.

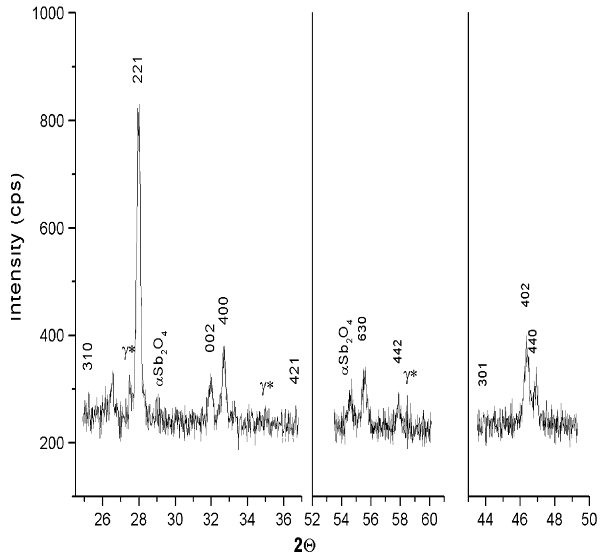

Fig. 1. XRD pattern of the mixture $Bi_{1.9}Sb_{0.1}O_x$ after 20 h annealing treatment at 820 °C (γ^*–γBi_2O_3 phase).

3. Results and discussion

The thermal behavior of the powder mixtures was examined and the thermal analysis (DTA/TG) results are presented in Fig. 2. A different curve profile for samples C1 and C2 can be observed. A small endothermic event occurs at around 860–870 °C. Chen et al.[7] indicated that this DTA peak (endothermic on the heating) has been identified as corresponding to the formation of the 110 K phase. A DTA peak is common to all curves at 820 °C, endothermic event that may be assigned to a melting process of δBi_2O_3; this process may be responsible for the acceleration of the diffusion and enhancement of the mass transfer, which helps also the densification of the sample-pellet. The TG curves generally show the main events corresponding to decarbonation process. In the case of samples A1 and A2 (precursor Sb_2O_3) the process started at around 550 °C, being almost complete at 1000 °C.

The XRD patterns of the sintered samples are presented in Fig. 3 (series 1) and Fig. 4 (series 2). All samples were multi-phase, the main components being the low-T_c (90 K) and the high-T_c (110 K) phases. It has been observed that irrespective of the precursors always existed a group of sharp and intense peaks around $2\theta = 30°$. For both series the high-T_c phase increased

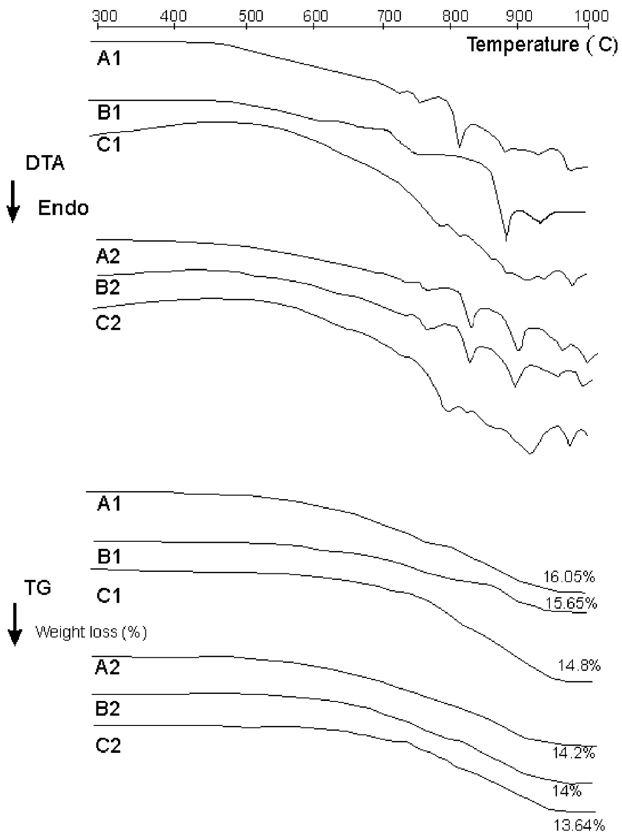

Fig. 2. DTA/TG curves of the starting mixture $Bi_{1.6}Pb_{0.3}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ (A1, B1, C1) and $Bi_{1.6}Pb_{0.4}Sb_{0.1}Sr_2Ca_2Cu_4O_y$ (A2, B2, C2).

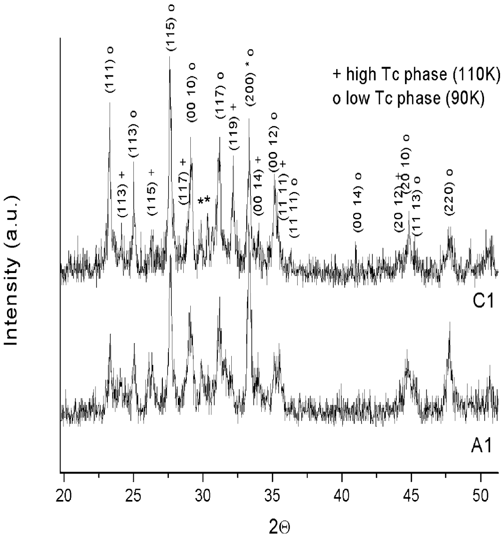

Fig. 3. XRD powder patterns of the sintered compositions $Bi_{1.6}Pb_{0.3}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ (A1, C1) at 855 °C/30 h.

Fig. 5. The SEM micrograph showing the morphology of the powders of composition $Bi_{1.6}Pb_{0.3}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ (C1).

when the precursor was the tetragonal solid solution (C1 and C2). The cell parameters were smaller especially on b and c direction for high T_c phase (ex. in the case of sample C2 $a=5.416$ Å, $b=5.398$ Å, and $c=37.126$ Å) and increased on c direction for low T_c phase (ex. $a=5.412$ Å, $b=5.396$ Å and $c=30.742$ Å) than those reported in the JPCDS files, confirming the substitution of the Bi^{3+} ions by the smaller ions Sb^{3+}. Also a systematical shift of the peaks to higher angles was observed. Quantitatively, the high-T_c phase is well represented also in the samples C1 and C2 (see $2\theta=4$–$6°$ Fig. 4). Some reflections could not be identified (noted *). The role of antimony appears to be the enhancement of the low $T_c \rightarrow$ high T_c phase reaction rate beyond that achievable by lead incorporation alone. While additional peaks in the XRD pattern suggest the formation of a separate antimony-containing phase, some degree of Sb incorporation into the superconducting structure seem to be necessary in order to affect the high T_c phase formation rate.

Microstructure examination using SEM showed the mica-like characteristic structure of bismuth-containing superconductors. The well-formed crystals are illustrated in Fig. 5, for the case of sample C1.

The presence of the two superconducting phases was confirmed by the R–T characteristics shown in Fig. 6. The beginning of the superconducting transition was

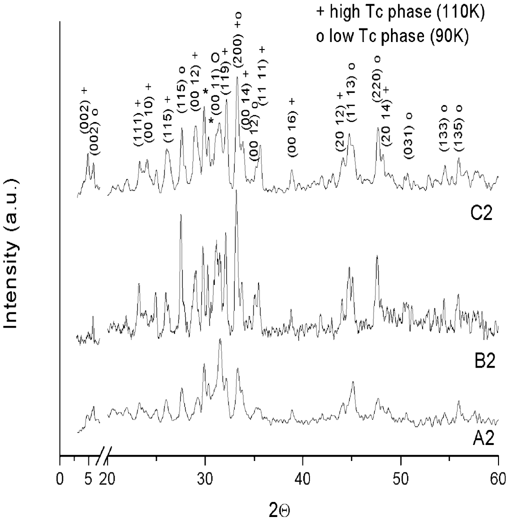

Fig. 4. XRD powder patterns of the sintered compositions $Bi_{1.6}Pb_{0.4}Sb_{0.1}Sr_2Ca_2Cu_4O_y$ (A2,B2, C2) at 855 °C/30 h.

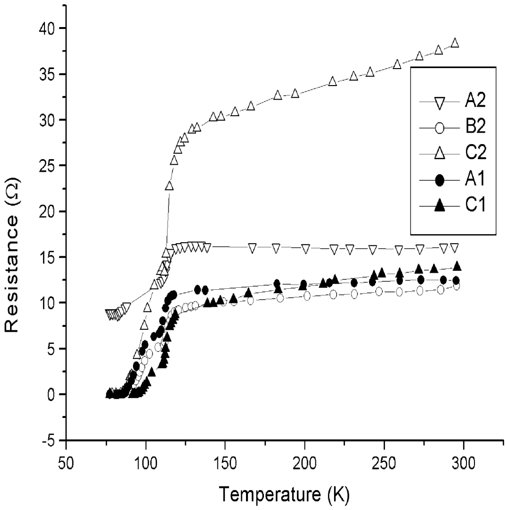

Fig. 6. Temperature dependence of the electrical resistance for compositions $Bi_{1.6}Pb_{0.3}Sb_{0.1}Sr_2Ca_2Cu_3Oy$ (A1, C1) and $Bi_{1.6}Pb_{0.4}Sb_{0.1}Sr_2Ca_2Cu_4Oy$ (A2, B2, C2) after sintering 855 °C/30 h.

observed around 115 K for all the samples confirming the existence of high-T_c phase. An inflection on the *R* (*T*) curves at 106 K can be observed, attributed to the superconducting 2212 phase and microstructure disorder. Supplementary treatments are indicated to minimize this effect.

4. Conclusions

The influence of the antimony precursors on the mechanism formation of the superconducting phases was examined. The presence of antimony, as Sb_2O_3, made the system more reactive and enhanced the kinetic of reaction (especially decarbonation), as well as the promotion of the high-T_c phase. For both ranges of compositions the best results were obtained when a tetragonal solid solution with the nominal composition $Bi_{1.9}Sb_{0.1}O_x$ was used. This precursor can be suitable also for other application such as ionic conductors.

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