Sol–Gel preparation of nonstoichiometric Bi,Pb–2223 superconductors

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Department of General and Inorganic Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania A simple aqueous sol–gel synthesis technique has been applied to prepare nonstoichiometric (B $i_{1.75}Pb_{0.25}$)Sr₂Ca₂Cu₃O_x, (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca₂Cu₃O_x, (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.05}Cu_{3.05}O_x and (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.55}Cu_{3.05}O_x and (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.55}Cu_{3.55}O_x (Bi,Pb–2223) oxides. The formation of Bi,Pb–2223 phases depending on the synthesis conditions (duration of annealing, stoichiometry of metals) has been estimated. The synthesized products were characterized by powder X-ray diffraction analysis (XRD) and magnetic susceptibility measurements. It was demonstrated, that the investigated synthesis conditions have an impact on the phase purity and superconducting properties of Bi,Pb–2223 phase.

Key words: superconductors, Bi, Pb-2223, sol-gel synthesis

INTRODUCTION

Bi-based compounds are considered to be the most promising material for the application of high- T_c superconductors. Since the discovery of bismuth oxide superconductors by Michel et al. [1] with critical transition temperature of superconductivity (T_c) at about 20 K for Bi₂Sr₂CuO₆₊₈, many studies have been carried out by elemental substitutions in order to increase T_c and improve other superconducting properties of this system [2–6]. The introduction of calcium to this system produced a new family of these ceramic materials [7–9]. The general formula for these compounds is given by Bi₂Sr₂Ca_{n-1}Cu_nO_{2n+4} with n = 1, 2, 3 and are commonly called the Bi–2201 ($T_c = 20$ K), Bi–2212 ($T_c = 80$ K) and Bi–2223 ($T_c = 110$ K) phases, respectively.

In Bi-based superconducting systems, variations in hole concentration of the CuO₂ planes can be achieved by cationic substitution of the divalent Ca/Sr by trivalent rare earth elements, or substitution of trivalent bismuth by lead, or using nonstoichiometric amounts of Ca or Cu [2, 10]. Syntheses of Bi, Pb-2223 phases have been reported for different compositions, starting materials, and methods [10-12]. Intermediate products and reaction pathways are usually not well known until Bi,Pb-2223 develops at the expense of Bi-2201, Bi-2212 and cuprates. Highest T_c values expected for Sr-rich Bi,Pb-2223 phases and phases obtained under reducing sintering atmospheres [13, 14]. Moreover, the substitution of Pb for Bi stabilizes the Bi-based superconductors; even these phases have the stoichiometric compositions [15-18]. For example, recently the Bi,Pb-2223 phase has been synthesized through the synthesis route, in which the reactivity was controlled by a NO₂ atmosphere through the formation of nitrate precursors [19]. It was demonstrated that the formation of oxide nitrates as intermediate products guarantees a reliable and rather reproducible standard procedure for the preparation of Bi,Pb–2223.

The main purpose of this work is to provide a novel sol–gel method for the preparation of high purity and homogeneity high– T_c superconducting Bi,Pb–2223 phase. Also, we investigated the influence of stoichiometry and synthesis conditions on the phase puriy of Bi,Pb–2223 samples obtained by the sol–gel method.

EXPERIMENTAL

The Bi,Pb-2223 samples were prepared from four types of precursors having different molar ratios of metals. The synthesis of these compounds with different nominal composition (Bi, 75Pb, 25)Sr,C $a_2Cu_3O_x$, $(Bi_{18}Pb_{03})Sr_{187}Ca_2Cu_3O_x$, $(Bi_{18}Pb_{033})Sr_{187}Ca_{205}Cu_{305}O_x$ and (Bi18Pb033)Sr187Ca25Cu35Ox has been performed by a simple sol-gel method using aqueous mixtures of corresponding metal acetates and tartaric acid as a chelating agent. First of all, bismuth acetate and lead acetate in the desired proportions were separately treated with an aqueous solution of nitric acid (50 ml 0.1 M HNO₂), mixed together and stirred for 1 h at 55-60 °C. Secondly, strontium acetate mixed with an aqueous solution of nitric acid was added, and the obtained solution was stirred for the next 1 h at the same temperature. Then calcium acetate and copper acetate aqueous solutions were added. After stirring for 1h, the complexing agent was added into the above solution (an aqueous solution of tartaric acid $(n_{(tartaric acid)}/n_{(Cu)} = 0.45)$ dissolved in 25ml H₂O). After stirring for 1 h, the resulting solution was slowly evaporated at 70 °C. The viscous liquid began to set into a Bi-Pb-Sr-Ca-Cu-O acetate-nitrate-tartrate gel with colour change from light blue to blue. The obtained gels were dried at 100 °C in an ordinary furnace. The gel samples were ground in an agate mortar, placed into corundum crucibles and pre-heated in air for 2 h at ~400 °C and calcined for 10 h at 650 °C. The additional annealing process was carried out at 850 °C for 3, 24, and 72 h in air atmosphere.

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The XRD patterns in the range of 2θ from 20 to 50° were recorded on a STADI-P (STOE, Darmstadt) transmission diffractometer with Cu-K α_1 radiation. The diamagnetic susceptibility was determined with a Lake Shore 7000 AC susceptometer.

RESULTS AND DISCUSSION

In Fig. 1 the XRD patterns of the (Bi_{1.75}Pb_{0.25})Sr₂Ca₂Cu₃O_x superconducting oxides prepared at slightly different conditions are presented. As seen, the X-ray diffraction pattern of the Bi,Pb–2223 sample synthesized for 3 h at 850 °C shows that an almost single phase (Bi_{1.75}Pb_{0.25})Sr₂Ca₂Cu₃O_x compound is formed. Evidently, all single lines may be indexed and only few unindexed lines can be observed. The diffraction lines observed at 20 \approx 26°, 32°, 36° and 40° are attributable to the Bi–2212 phase. A minor amount of SrO and CuO phases could be also determined from the XRD pattern. However, we failed to attribute the diffraction line observed at 20 \approx 32.5° to any related crystalline phase.

Fig. 1. X-ray diffraction patterns of superconducting (Bi_{1.75}Pb_{0.25})Sr₂Ca₂Cu₃O_x oxides: (a) insertion from Powder Diffraction Data (PDF No [42–450]) and sol–gel derived after annealing at 850 °C for (b) 3 h, (c) 24 h and (d) 72 h. The crystalline side phases are marked: B_{1.6}Pb_{0.4}Sr_{1.81}CaCu₂O_{8.71} (PDF No [80–2029]) (x), Bi_{0.96}Pb_{0.24}SrCaCu_{1.6} O_{5+x} (PDF No [46–393]) (+), SrO (PDF No [6–520] (•), CuO (PDF No [44–706]) (¹), Bi₂Sr₂CuO_x (PDF No [39–283] (≤) and unindexed phases (¹)



Surprisingly, in the case of $(Bi_{1.75}Pb_{0.25})Sr_2Ca_2Cu_3O_x$ superconductor, the intensity of the Bi–2212 peak at $2\theta \approx 26^{\circ}$ increased strongly with increasing annealing time from 3 to 24 h (see Fig. 1 b). Moreover, the additional impurity peaks at $2\theta \approx$ 46° and 48° attributable to the Bi₂Sr₂CuO_x phase appeared in the XRD pattern. Finally, with further increasing annealing time up to 72 h, the intensities of impurity peaks became less intensive except that of Bi–2212 phase.

Fig. 2 shows the XRD patterns of slightly nonstoichiometric Bi,Pb–2223 phase ($(Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_2Cu_3O_x$) prepared using different annealing time. As seen, the XRD patterns presented in Figs. 1 and 2 are very similar. Therefore, we can conclude that the formation of Bi,Pb–2223 phase occurs in the same manner when the molar ratio of metals Bi:Pb:Sr = 1.75:0.25:2.00 or Bi: Pb:Sr = 1.8:0.33:1.87 was used. The only difference observed in the case of $(Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_2Cu_3O_x$ was that the formation of side $Bi_5Sr_2CuO_x$ phase started already after 24 h of annealing.

Fig. 2. X-ray diffraction patterns of superconducting $(Bi_{1,8}Pb_{0,33})Sr_{1,87}Ca_2Cu_3O_x$ oxides: (a) insertion from Powder Diffraction Data (PDF No [42–50]) and sol–gel derived after annealing at 850 °C for (b) 3 h, (c) 24 h and (d) 72 h. The crystalline side phases are marked: $B_{1,6}Pb_{0,4}Sr_{1,81}CaCu_2O_{8,71}$ (PDF No [80-2029]) (x), $Bi_{0,96}Pb_{0,24}SrCaCu_{1,6}O_{5+x}$ (PDF No [46–393]) (+), Sr0 (PDF No [6–520] (•), Cu0 (PDF No [44–706]) (¹¹), $Bi_2Sr_2CuO_x$ (PDF No [39–283] (\leq) and unindexed phases (¹)



The next step was to synthesize Bi,Pb–2223 compounds having nonstoichiometric amounts of Ca and Cu at the same time keeping a constant molar ratio of bismuth, lead and strontium (Bi:Pb:Sr = 1.8:0.33:1.87). The X-ray diffraction patterns of two nonstoichiometric compounds ($(Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.05}Cu_{3.05}O_x$ and $(Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.5}Cu_{3.5}O_x$) prepared using different duration of preparation are presented in Figs. 3 and 4, respectively. As seen, the intensities of reflections attributable to the side phases increased considerably in both cases. Moreover additional peaks at around $2\theta \approx 27^{\circ}$ and 44° attributable to the Bi₃O₃ and CaO phas-

Fig. 3. X-ray diffraction patterns of superconducting $(Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.05}Cu_{3.05}O_x$ oxides: (a) insertion from Powder Diffraction Data (PDF No [42–450]) and sol-gel derived after annealing at 850 °C for (b) 3 h, (c) 24 h and (d) 72 h. The crystalline side phases are marked: B_{1.6} Pb_{0.4}Sr_{1.81}CaCu_0_{8.71} (PDF No [80-2029]) (x), Bi_{0.96}Pb_{0.24}SrCaCu_{1.0}O_{5+x} (PDF No [46–393]) (+), Sr0 (PDF No [6-520] (•), Cu0 (PDF No [44–706]) (¹), Bi_2Sr_CuO_x (PDF No [39–283] (≤), Bi_2O_3 (PDF No [18–244]) (v), CaO (PDF No [28-775]) (œ) and unindexed phases (¹)





Fig. 4. X-ray diffraction patterns of superconducting $(Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.5}Cu_{3.5}O_x$ oxides: (a) insertion from Powder Diffraction Data (PDF No [42–450]) and sol–gel derived after annealing at 850 °C for (b) 3 h, (c) 24 h and (d) 72 h. The crystalline side phases are marked: $B_{1.6}Pb_{0.4}Sr_{1.81}CaCu_{0.871}$ (PDF No [80-2029]) (x), $Bi_{0.96}Pb_{0.24}SrCaCu_{1.}$ ${}_{*}O_{5+x}$ (PDF No [46–393]) (+), SrO (PDF No [6-520] (•), CuO (PDF No [44–706]) (¹¹), $Bi_{2}Sr_{2}CuO_{x}$ (PDF No [39–283] (\leq), $Bi_{2}O_{3}$ (PDF No [18–244]) (v), CaO (PDF No [28–775]) (œ) and unindexed phases (¹)

es, respectively, appeared in the XRD patterns. Consequently, we can conclude that changing the stoichiometry of Ca and Cu does not promote the formation of high-purity Bi,Pb–2223 phase. On the contrary, the amount of impurity phases in the case of non-stoichiometric amount of calcium and copper, $((Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.05}Cu_{3.05}O_x)$ and $(Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.5}Cu_{3.5}O_x)$, increases during the preparation of Bi,Pb–2223 superconductors.

Fig. 5 shows the resistivity versus temperature on as-prepared ($Bi_{1.75}Pb_{0.25}$) $Sr_2Ca_2Cu_3O_x$ and ($Bi_{1.8}Pb_{0.33}$) $Sr_{1.87}Ca_2Cu_3O_x$ samples. As seen, both specimens were found to be superconducting having T_c (onset) = 108 K (for ($Bi_{1.75}Pb_{0.25}$) $Sr_2Ca_2Cu_3$ O_x) and T_c (onset) = 110 K (for ($Bi_{1.8}Pb_{0.33}$) $Sr_{1.87}Ca_2Cu_3O_x$). The obtained values of the critical temperature of superconductivity for the sol-gel derived Bi,Pb-2223 superconductors are in good agreement with literature data. Interestingly, the calcium and copper nonstoichiometric Bi,Pb-2223 specimens were nonsuperconducting anymore (Fig. 6). The susceptibilities were very small. In the case of ($Bi_{1.8}Pb_{0.33}$) $Sr_{1.87}Ca_{2.5}Cu_{3.5}O_x$, down to about



Fig. 5. Magnetic susceptibility measurements of $(Bi_{1.75}Pb_{0.25})Sr_2Ca_2Cu_3O_x$ (1) and $(Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_2Cu_3O_x$ (2) oxides



Fig. 6. Magnetic susceptibility measurements of $(Bi_{1,8}Pb_{0.33})Sr_{1,87}Ca_{2.05}Cu_{3.05}O_x(1)$ and $(Bi_{1,8}Pb_{0.33})Sr_{1,87}Ca_{2.05}Cu_{3.05}O_x(2)$ oxides

70 K the susceptibility is nearly temperature-independent, initially suggesting diamagnetism [20]. However, below 70 K the susceptibility increases slightly, which might be attributed to the magnetism of bismuth atoms. In the case of $(Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.0} {}_{5}Cu_{3.05}O_{x}$, the susceptibility exhibits paramagnetic behaviour.

CONCLUSIONS

In this study, the sol-gel synthesis and characterization of bismuth-type (Bi,Pb-2223) superconducting oxides have been reported. The formation of Bi,Pb-2223 phases depending on the duration of annealing and stoichiometry of metals has been estimated. The sol-gel synthesized mixed-metal oxides ((Bi175P $b_{_{0,25}})Sr_{_{2}}Ca_{_{2}}Cu_{_{3}}O_{_{x}}, (Bi_{_{1.8}}Pb_{_{0,33}})Sr_{_{1.87}}Ca_{_{2}}Cu_{_{3}}O_{_{x}}, (Bi_{_{1.8}}Pb_{_{0,33}})Sr_{_{1.87}}Ca_{_{2.05}}$ $Cu_{3.05}O_x$ and $(Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.5}Cu_{3.5}O_x)$ were characterized by powder X-ray diffraction analysis (XRD) and magnetic susceptibility measurements. The X-ray diffraction patterns of (Bi, 75P b_{0.25})Sr₂Ca₂Cu₃O_x and (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca₂Cu₃O_x samples showed that the sol-gel synthesis route gave almost single phase Bi,Pb-2223 compounds. However, the amount of impurity phases in the case of calcium and copper nonstoichiometric compounds $((Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.05}Cu_{3.05}O_x \text{ and } (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.5}Cu_{3.5}O_x)$ increased considerably. Both (Bi175Pb025)Sr2Ca2Cu3Ox and (Bi18 Pb_{0.33})Sr_{1.87}Ca₂Cu₃O_y samples were found to be superconducting having T_c (onset) = 108 K and T_c (onset) = 110 K, respectively. The calcium and copper nonstoichiometric Bi,Pb-2223 specimens were non-superconducting.

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NESTECHIOMETRINIŲ BI,PB-2223 SUPERLAIDININKŲ SINTEZĖ ZOLIŲ-GELIŲ METODU

Santrauka

Šiame darbe zolių–gelių metodu sintetinti nestechiometriniai Bi klasės superlaidininkai ((Bi_{1.75}Pb_{0.25})Sr₂Ca₂Cu₃O_x, (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca₂Cu₃O_x, (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.05}Cu_{3.05}O_x ir (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.5}Cu_{3.5}O_x (Bi,Pb–2223)). Gauti junginiai apibūdinti remiantis rentgeno spindulių difrakcinės analizės bei magnetinių savybių tyrimo rezultatais. Nustatyta, kad Bi,Pb–2223 fazės susidarymas priklauso ir nuo kaitinimo 850°C temperatūroje trukmės, ir nuo metalų stechiometrijos. Parodyta, kad (Bi_{1.75}Pb_{0.25})Sr₂Ca₂Cu₃O_x oksido krizinė superlaidumo temperatūra (T_c) yra lygi 108 K, o (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca₂Cu₃O_x – 110 K. Be to, nustatyta, kad kalcio ir vario nestechiometriniai junginiai ((Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.05}Cu_{3.05}O_x ir (Bi_{1.8}Pb_{0.33})Sr_{1.87}Ca_{2.5}Cu_{3.5}O_x) yra nesuperlaidūs.