Ba$_2$Ca$_2$Cu$_3$O$_x$ PRECURSOR EFFECTS ON SYNTHESIS OF (Hg,Pb)Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ SUPERCONDUCTOR

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Abstract

The influence of Ba$_2$Ca$_2$Cu$_3$O$_x$ precursor on the synthesis and properties of (Hg,Pb)Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ has been examined. Fine homogeneous Hg-free precursor powder of Ba$_2$Ca$_2$Cu$_3$O$_x$ of desirable phase composition was prepared by sol-gel method using EDTA acid as a complexing agent. A reproducible superconducting sample of Hg$_{0.8}$Pb$_{0.2}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ with fine-grained, dense microstructure, composed predominantly of (Hg,Pb)-1223 phase and with advantageous magnetic properties, was synthesized by high pressure crystallization in mercury environment of well-calcined Ba$_2$Ca$_2$Cu$_3$O$_x$ precursor.

Keywords: high-temperature superconductors, mercury based HTS, microstructure, sol-gel method, thermal decomposition

Introduction

HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ (Hg-1223), belonging to the Hg-based high temperature superconductors family with highest critical temperature, T_c over 150 K under high pressure [1], has been extensively investigated as an interesting material for application in the modern microelectronics field [2, 3]. The typical preparation method of Hg-1223 superconductor comprises a two-step process: synthesis of Ba$_2$Ca$_2$Cu$_3$O$_x$ precursor followed by annealing of this powder with Hg vapour. The key problem in the synthesis of HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ ceramics is the preparation of Ba$_2$Ca$_2$Cu$_3$O$_x$ precursors with appropriate physico-chemical properties [4–7]. A systematic study of the precursor role in the formation mechanism of Hg-1223 samples under high pressure has shown that HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ compound crystallizes as a result of converting of HgCaO$_2$ and HgBa$_2$CaCu$_2$O$_x$ phases through the intercalation process of Ba–Cu–O and Ca–Cu–O [5–7]. Thus the mixing level of the cations Ca and Cu in the starting precursor strongly affects the formation rate of the Hg-1223 phase and the increase of its volume fraction. Moreover, the precursor in which Ca-ions reacted well with other ions

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should be insensitive to moist air. The existence of large CaO grains in the incompletely reacted precursor $Ba_2Ca_2Cu_3O_x$, obtained by a solid-state reaction technique, may require the increase of synthesis temperature or prolongation of synthesis time, and then the impurities may appear. In this respect the sol-gel method using EDTA acid as a complexing agent (versenate gel processes) appears to be promising.

In the present paper, the preparation of the Hg-free precursor powder of $Ba_2Ca_2Cu_3O_x$ by the versenate gel processes has been presented and the main emphasis is given to the study of the precursor effects on the synthesis and physicochemical properties of $Hg_{0.8}Pb_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ superconductors obtained by the high-pressure gas method.

Experimental procedure

The synthesis of a precursor with $Ba_2Ca_2Cu_3O_x$ composition was carried out by the sol-gel method using EDTA acid as a complexing agent. The aqueous solutions of 0.5 N, prepared by dissolving the analytical purity reagents of $Ba(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ in distilled water, were mixed in appropriate cation-proportions Ba:Ca:Cu=2:2:3 together with a 0.1 mol EDTA acid (ethylene-diamine-tetra-acetic) added for every equivalent mole of cations. Constant pH=7.5 was maintained by dropwise addition of ammonia. A clear blue mixture was then vacuum evaporated at 60–80°C to make an amorphous versenate gel. The viscous gel was pyrolysed in oxygen at 450°C for 1.5 h and the resulting precursor powder was calcined in air at 800–900°C for 10–24 h. After thermal treatment fine-grained agglomerated micropowders with soft aggregates, about 0.5–3 μm, were obtained. The prepared $Ba_2Ca_2Cu_3O_x$ precursor was then mixed in a dry box with HgO and PbO to get the initial composition of $Hg_{0.8}Pb_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$, and sintered in pellet form at the temperature of 1067±1°C for 10 min in argon containing 20% of oxygen under 10 kbar pressure. After sintering the samples were annealed at 840°C for 2 h and afterwards cooled at a rate 10°C min^{-1}. The sintering and the following annealing of $Hg_{0.8}Pb_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ polycrystalline samples were performed by high-pressure gas method using the devices set-up constructed at the High Pressure Research Center 'Unipress' Warsaw. The construction of the high pressure instruments and the crystallization experiment have been described in detail elsewhere [4].

To monitor the decomposition and crystallization processes on heating a Hg-free mercury precursor, the simultaneous thermal analysis using DTA and TG techniques (STA-SDT 2960 TA-Instruments), as well as X-ray diffraction (Seifert-FPM XRD 7) were applied. The scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDX) analysis was used to study the microstructure and chemistry of the samples. Low temperature magnetic measurements of the HTS materials were carried out by the standard mutual inductance bridge with the amplitude of ac magnetic field 280 mOe.

Results and discussion

The most severe limitation to the development of the versenate gel processes used in the present work for the processing of $Ba_2Ca_2Cu_3O_x$ precursor is removing the volatile components, such as CO_2, nitrogen oxides, carbon oxides and water vapor, which may contaminate the very reactive native oxides and lead to formation of stable $BaCO_3$ and $CaCO_3$, which impede full reaction of the components. In order to determine the temperature range for the progress of the physicochemical phenomena, accompanying the formation of the desired chemical phases, as well as the optimal calcination conditions of the precursor, the thermal analysis using DTA and TG technique has been applied.
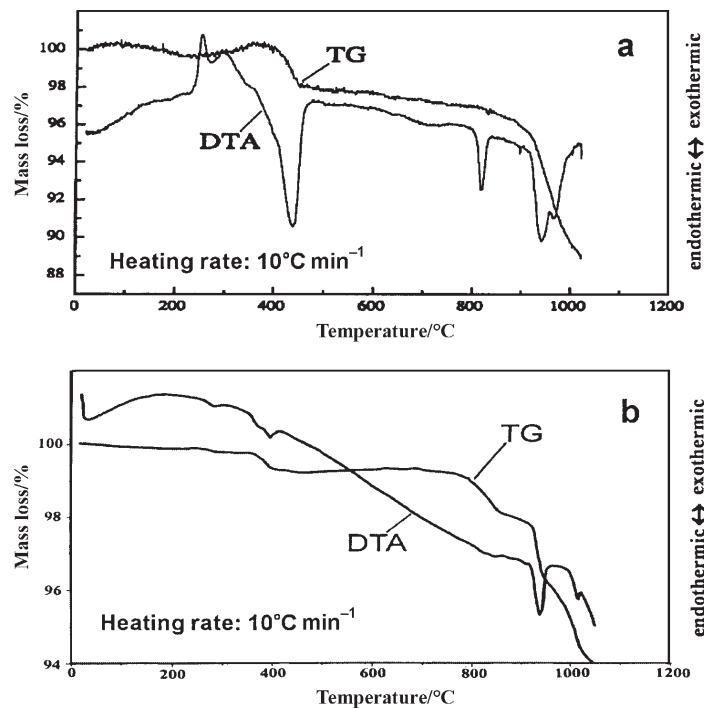
Fig. 1 DTA and TG curves for the Ba–Ca–Cu–O precursor after: a – pyrolysis at 450°C for 1.5 h in oxygen and b – calcination at 900°C for 24 h in air

Figures 1a and b show the DTA and TG curves for the Ba–Ca–Cu–O precursor obtained after gel pyrolysis at 450°C for 1.5 h in oxygen and after calcination at 900°C for 24 h in air, respectively. The DTA/TG analysis of the precursor was studied up to 1050°C in flowing air, using a heating rate of 10°C min⁻¹. DTA results in Fig. 1a have revealed that the pyrolysed precursor undergoes exothermal decomposition reaction at 220–320°C. These two effects are due to the combustion reactions of

the organic residues from the gel components to the form of barium and calcium carbonates and copper oxide. At higher temperatures the presence of three peaks, associated exclusively with the endothermic effects was observed. The first one occurs at around 445°C and is attributed to the decomposition of the remaining precipitates of barium nitrate in the pyrolysed precursor according to the reaction (1):

$$Ba(NO_3)_2 + CO_2 \rightarrow BaCO_3 + N_2O_5 \qquad (1)$$
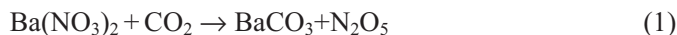
The two successive distinct endothermic effects appeared at 820 and 940°C, respectively. To identify them, additional DTA analysis has been made on powder obtained after calcination at 900°C for 24 h. According to the DTA curve, in Fig. 1b, the endothermic peak at 820°C almost disappears, suggesting an irreversible reaction at this temperature, while the other endothermic effect at 940°C occurs at the same temperature as that on the DTA curve for the pyrolysed precursor (Fig. 1a).

To elucidate the origin of these effects, the X-ray diffraction analysis of Ba–Ca–Cu–O precursor powders subjected to thermal treatment at various temperatures and times was performed. X-ray analysis has shown that the pyrolysed precursor has a multi-phase composition and the following phases are present: $BaCO_3$, CaO, CuO, Ba_3CuO_4, $Ba(NO_3)_2$. After calcination of the precursor at 800°C in air the dominant compounds crystallizing from the previous phases were $BaCuO_2$, $Ba_2Cu_3O_5$, CaO and CuO, while for calcined precursor at 840°C for 10 h the $BaCuO_2$, Ca_2CuO_3 and CaO phases were identified. Further higher-temperature calcination at 900°C leads to the formation of only two phases of $BaCuO_2$ and Ca_2CuO_3 as shown in Fig. 2. The existence of only $BaCuO_2$ and Ca_2CuO_3 phases at 900°C well-calcined precursor powder with Ba:Ca:Cu=2:2:3 cation ratio is in good agreement with the phase diagram analysis of the Ba–Ca–Cu–O system. It should be noted from TG data, shown in Fig. 1b, that such a properly calcined $Ba_2Ca_2Cu_3O_x$ precursor is insensitive to H_2O/CO_2 contamination. This precursor gains less than 0.3% mass after it has been stored for 3 months in air at room temperature.
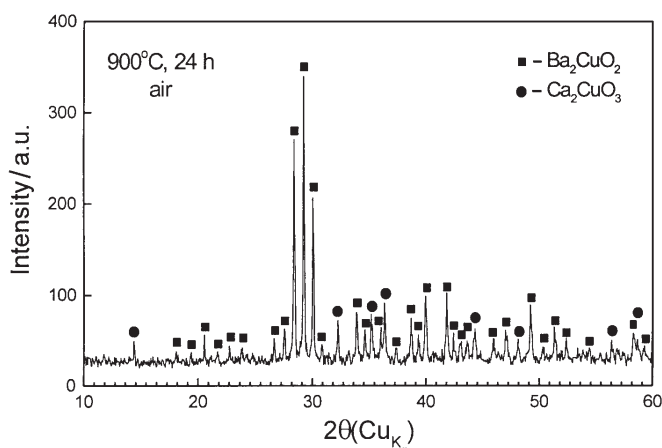
**Fig. 2** X-ray diffraction pattern of $Ba_2Ca_2Cu_3O_x$ precursor powder after calcination at 900°C for 24 h in air

Basing on the results of the thermal analysis and XRD investigation it may be suggested, in agreement with the literature data [6], that at temperature of about 820°C the formation of $BaCuO_2$ and Ca_2CuO_3 phases occurs, due to the two reactions, (2) and (3):

$$Ba_2Cu_3O_5 + 2CaO \rightarrow 2BaCuO_2 + Ca_2CuO_3 \qquad (2)$$

$$CuO + 2CaO \rightarrow Ca_2CuO_3 \qquad (3)$$
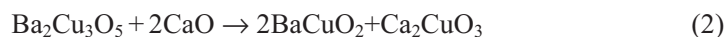
as the result of the fully converting process of CaO into Ca_2CuO_3 compound (Fig. 1b), which is stable from 1035 up to 200°C according to the phase-diagram of the CuO–CaO system [8]. The next distinct effect at 940°C is associated with the formation of a liquid phase due to incongruent melting of $BaCuO_2$, as it is confirmed by the XRD diffraction analysis and the documented literature data [6, 8, 9]. The combination of DTA and X-ray results shows that the lowest calcination temperature should be 900°C to avoid the undesirable phases, and to get only $BaCuO_2$ and Ca_2CuO_3 phases.

To verify the properties of the prepared $Ba_2Ca_2Cu_3O_x$ precursors, the synthesis of $(Hg,Pb)Ba_2Ca_2Cu_3O_{8+\delta}$ polycrystalline superconducting samples has been performed by high pressure gas method in mercury environment at the same conditions, i.e. 1067°C, 10 min, using precursors calcined at 800, 840 and 900°C, respectively. The X-ray diffraction studies has shown that the synthesized $(Hg,Pb)Ba_2Ca_2Cu_3O_{8+\delta}$ bulk sample from the 900°C calcined precursor is composed of two superconducting phases, i.e. the high-T_c (1223) and low-T_c (1212) with the predominance of the peaks assigned to the Hg-1223 phase in an orthorhombic cell. The lattice parameter a: 5.426, b: 5.421 and c: 15.448 Å obtained for the (Hg,Pb)-1223 phase was comparable with the previously reported values [10]. Moreover, the occurrence of other peaks with a small intensity attributed to the secondary phases of $BaCuO_2$, $CaHgO_2$, $CaCu_2O_3$, $BaPbO_3$ and CuO was also identified. The most intensive peaks for CaO phase were not observed in the diffractogram. Since CaO may hydrolyze in air to form $Ca(OH)_2$, we also checked for peaks of this compound [11], however these
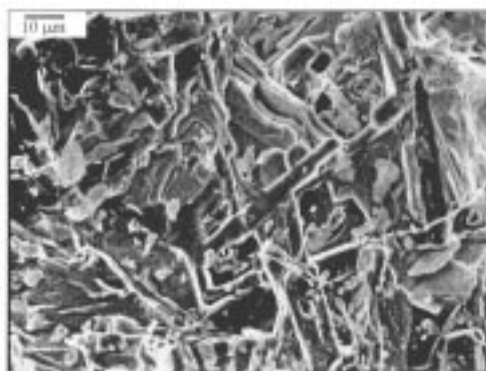

Fig. 3 SEM microphotograph of a fracture section of $Hg_{0.8}Pb_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ superconductor obtained by high-pressure gas method at 1067°C for 10 min

peaks could not be observed. The CaO content, although visible in scanning electron microscopy in the form of very fine particles, is thus too small or appearing in amorphous form to be detected in X-ray diffraction. Contrary to phase composition of $(Hg,Pb)Ba_2Ca_2Cu_3O_{8+\delta}$ prepared from the 900°C calcined precursor, the superconducting (Hg,Pb)–Ba–Ca–Cu–O samples, obtained by sintering of 840 and 800°C calcined precursors, respectively, in mercury vapor, exhibited a large amount of secondary phases such as: $BaCuO_2$, $CaHgO_2$, $CaCu_2O_3$, CaO, CuO with (Hg,Pb)-1223 and (Hg,Pb)-1212 as minority phases.

The morphology of a $Hg_{0.8}Pb_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ superconducting sample prepared from 900°C calcined precursor is presented in Fig. 3. The well-crystallized grains of a highly compact sample revealed plate-like grains with the greatest dimensions between 10 and 30 μm and the thickness of about 0.5–3 μm. The results of semi-quantitative elemental analyses by EDX for the plate-like crystals yielded average ratios of Hg:Pb:Ba:Ca:Cu of about 0.78:0.24:2.0:1.84:2.67, approximately in agreement with the overall composition of the superconductor. The determined average content of Ca and Cu was smaller than that for the stoichiometric (Hg,Pb)-1223 phase, probably due to the coexistence of a small amount of intergrowth of (Hg-1212+Hg-1223)-type phase, as observed in a Hg-1223 sample by transmission electron microscopy [12].

The magnetic susceptibility measurements of the dispersive part χ' as a function of temperature for $Hg_{0.8}Pb_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ sample, shown in Fig. 4a, confirmed the
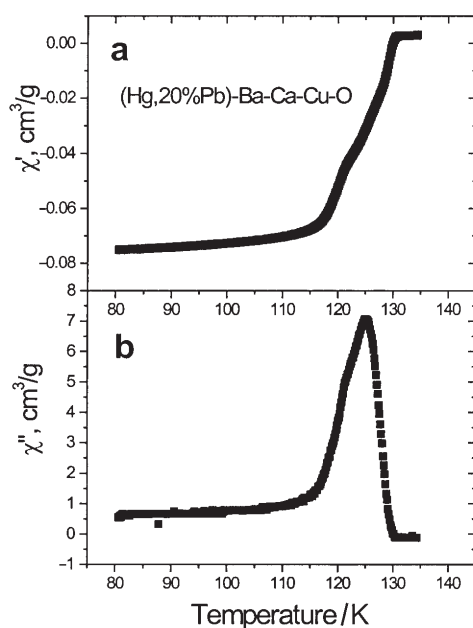
Fig. 4 Magnetic susceptibility of dispersive part χ' and absorptive part χ'' as a function of temperature of $Hg_{0.8}Pb_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ sample obtained by high pressure gas method at 1067°C for 10 min

superconducting properties appearing at the transition temperature $T_{c\chi'}$ =129.2 K in a narrow temperature range of ΔT_c=6.5 K. The narrow range of phase transition in connection with the high value of magnetic susceptibility χ'_{80K} can be attributed to the small porosity of the sample. From the course of the absorptive part dependence $\chi''=f(T)$ (Fig. 4b) it follows that the energy absorption of a variable magnetic field occurs in a narrow temperature range of 117–130 K. This confirms the small thickness distribution and the size distribution of microregions in intergranular links, which contain a small amount of the not completely reacted alien phases, thus enabling to obtain high magnetic transport properties of the synthesized superconductors.

Conclusions

1. Fine homogenous Hg-free precursor powder of $Ba_2Ca_2Cu_3O_x$ of desirable chemical and phase composition was successfully obtained by the sol-gel method based on complexion of metal cations by EDTA acid (versenate gel processes).
2. Polycrystalline dense samples of $Hg_{0.8}Pb_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ superconductors have been obtained by thermal treatment of well-calcined $Ba_2Ca_2Cu_3O_x$ precursor (900°C, 24 h, air) in the mercury vapor environment using high-pressure gas method. High-pressure crystallization from the batch of the starting composition $Hg_{0.8}Pb_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ resulted in formation of crystal aggregates composed mainly of single crystals of (Hg,Pb)-1223 phase (T_c=129.2 K, ΔT_c=6.5 K) in the form of plate-like crystallites containing a small amount of secondary phases.

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