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THE FORMATION OF SUPERCONDUCTING OXIDE PHASES IN THE (Bi,Pb)–Sr–Ca–Cu–O SYSTEM

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Abstract

The crystallization mechanism of superconducting phases in the (Bi,Pb)–Sr–Ca–Cu–O system was determined on the basis of the results of DTA, DTG and TG studies, supplemented by X-ray examination of ceramic powders obtained by the sol-gel method.

It has been demonstrated that the factor determining the formation of superconducting phases: $Bi_2Sr_2CaCu_2O_x$ (low-T_c) and $Bi_2Sr_2Ca_2Cu_3O_x$ (high-T_c) is the kinetics of reaction of calcium and strontium carbonates with molten $CuBi_2O_4$. As a result of the reaction of the bimetallic compound $CuBi_2O_4$ with $SrCO_3$ in the liquid phase the compound $Bi_2Sr_2CuO_6$ is formed. This compound, reacting with calcium and copper oxides, yields superconducting phases: the low-T_c and the high-T_c phase. It has been also observed that an increase in the volume fraction of high-T_c phase in powder subjected to thermal treatment takes place probably due to the repeated disproportionation of low-T_c phase and its repeated synthesis from $Bi_2Sr_2CuO_6$, CuO and CaO.

Keywords: HTS (High Temperature Superconductors), (Bi,Pb)–Sr–Ca–Cu–O system, $Bi_2Sr_2Ca_2Cu_3O_x$ (high-T_c), $Bi_2Sr_2CaCu_2O_x$ (low-T_c)

Introduction

High Temperature Superconduction in the oxide system (Bi,Pb)–Sr–Ca–Cu–O (BPSCCO) is connected with the occurrence in this system of two superconducting phases, i.e. the high-T_c-'2223' and the low-T_c-'2212' phases at the transition temperature 110 and 85 K, respectively [1].

Numerous studies dealing with the preparation and investigation of this group of superconductors point to serious difficulties in developing the preparation technique of single-phase materials with superconducting properties at the highest temperature, i.e. $T_c = 110$ K. Physico-chemical investigations of superconductors in the above system [2, 3] have shown that the nucleation of high-T_c phases is very complex due to the occurrence of a liquid phase having varying stoichiometry depending on the conditions of thermal treatment. In the reaction mixture in addition to the superconducting phases: $Bi_2Sr_2Ca_2Cu_3O_x$-'2223', $Bi_2Sr_2CaCu_2O_x$-'2212', there appear also intermediate solid phases

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which are nonstoichiometric in both oxide and cation sublattice. Understanding of the mechanism of the superconducting phases formation should enable better control of phase transitions, accompanying the formation of the above HTS (High Temperature Superconductor) phases during thermal treatment in order to obtain superconducting materials of most advantageous low temperature electric and magnetic parameters.

The aim of the present study was to propose a reaction mechanism of the superconducting phases formation during calcination of powders obtained by a sol–gel method on the basis of thermogravimetric and X-ray investigations.

Experimental

The synthesis of powders in the system (Bi,Pb)–Sr–Ca–Cu–O (BPSCCO) was carried out by a sol–gel method. The principle of this method, described in elsewhere [4, 5], consisted in the formation of stable complexes of metal cations from the above system in a water solution, using ethylenediaminetetraacetic acid (H-EDTA), and next, in the vacuum dehydration at the temperatures 60–80°C with the formation of a gel amorphous precursor. After pyrolysis of the gel in oxygen at 520°C for 1.5 h, the obtained powders were subjected to calcination in air, in the temperature range 770–830°C (770, 800 and 830°C) for 12 h. The phase composition of powders obtained as a result of pyrolysis and calcination was examined by differential thermal analysis (DTA), thermogravimetric analysis (TG) and differential thermogravimetry analysis (DTG), as well as X-ray diffraction (XRD). The X-ray diffraction method was also used to estimate the volume fraction of the high-T_c phase in HTS powders according to the procedure proposed by Onoda and Yamamoto [6].

Results and discussion

Figure 1 shows the DTA, DTG and TG curves obtained on heating the organometallic gel precursor in the range 20–600°C. It follows from the DTA curve (Fig. 1) that the decomposition of gel taking place at temperatures 200–250°C is exothermic. The distinct exothermic peak, recorded for this temperature range, is made up to three thermal effects observed at the heating rate 2 deg·min^{-1}. The following reactions are attributed to these effects [7, 8]:

1) rearrangement of complex compounds,

2) formation of intermediate products with conjugated double bonds,

3) decomposition of single organometallic compounds into bismuth and copper oxides, as well as into calcium, strontium and lead nitrates.

Successive two exothermic peaks were observed in the temperature range 430–470°C. The first one is ascribed to the formation of $CaCO_3$, while the

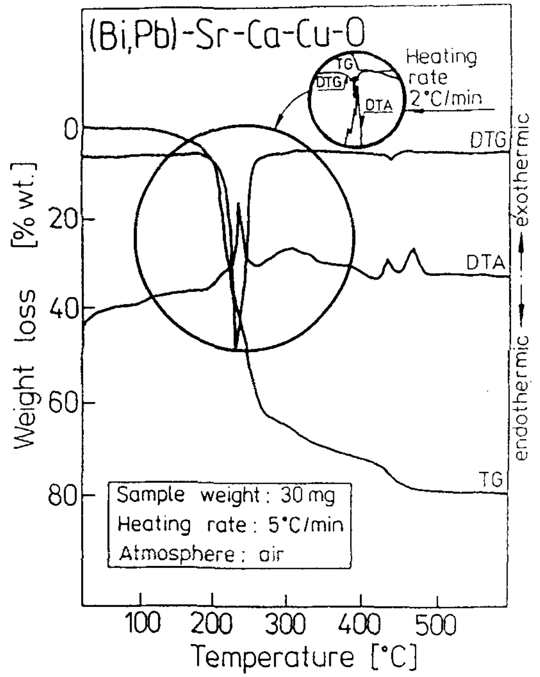

Fig. 1 DTA, DTG and TG curves for a (Bi,Pb)–Sr–Ca–Cu–O amorphous gel precursor after dewatering in vacuum at 60–80°C

other is the result of the formation of $SrCO_3$, PbO and reoxidation of the remaining part of CO into CO_2 in air. The total loss of mass was 80%, out of which as much as 63% occurred in the temperature range 200–250°C.

X-ray investigations of phase composition of the powder obtained after pyrolysis of a gel precursor at 520°C in oxygen for 1.5 h, revealed the presence of the following phases: Bi_2O_3, CuO, $SrCO_3$, $CaCO_3$ and $CuBi_2O_4$. In the course of further chemical reaction at higher temperatures, the above identified carbonates and oxides, form HTS compounds: $Bi_2Sr_2Ca_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_x$. The formation of these compounds in the examined powder mixtures depends on the decomposition rate of calcium and strontium carbonates. Due to high thermodynamic stability of the above carbonate compounds, their decomposition is slow. In order to estimate the temperature range of the decomposition of calcium and strontium carbonates and the solidification of the superconducting phases further thermogravimetric investigations were carried out with BPSCCO powders obtained after gel pyrolysis in oxygen at 520°C for 1.5 h and after calcination in air at 800°C for 12 h. The results are shown in Figs 2 and 3, and Tables 1 and 2 respectively. From the DTA and TG curves, shown in Fig. 2, it follows that the decomposition of the BPSCCO powder pro-

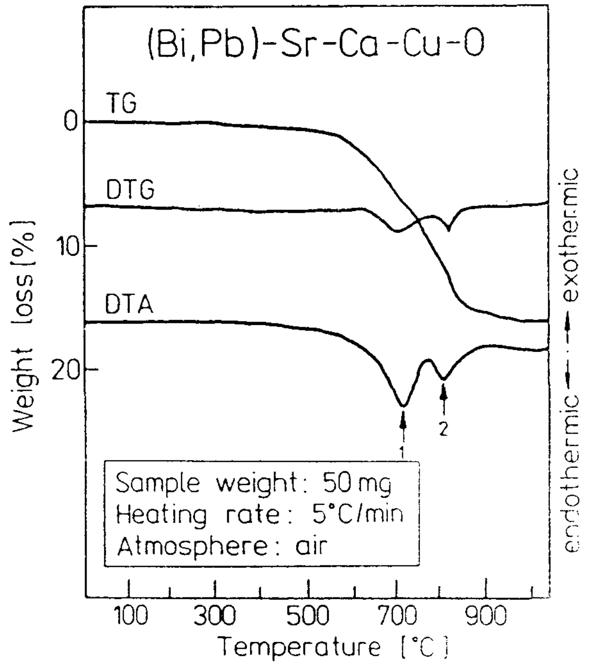

Fig. 2 DTA, DTG and TG curves for a (Bi,Pb)–Sr–Ca–Cu–O powder after pyrolysis of the gel precursor at 530°C in oxygen during 1.5 h

ceeds in two stages. During the first stage of the $CaCO_3$ decomposition (Table 1), a monotonous weight loss (by 8.3%) is observed starting from the temperature 550°C up to 780°C. At the second stage, in the temperature range 780–860°C, a weight loss by about 5% is observed on the TG curve, which is attributed to the decomposition of $SrCO_3$ into CO_2 and SrO (Table 1). The total weight loss due to thermal decomposition of carbonates was 14.8%, which represents about 98% of the theoretical one.

Table 1 Peak assignment for DTA profile of decomposed powder BPSCCO

Process	Peak	Thermal effects / °C	
		Endo	Exo
$CaCO_3 \rightleftarrows CaO+CO_2$	1	710 (broad)	–
$SrCO_3 \rightleftarrows SrO+CO_2$	2	800 (broad)	–

The course of DTA curve, shown in Fig. 3, for the powder obtained after the calcination in air at 800°C for 12 h shows the presence of four peaks associated exclusively with endothermic effects. These effects are accompanied by definite

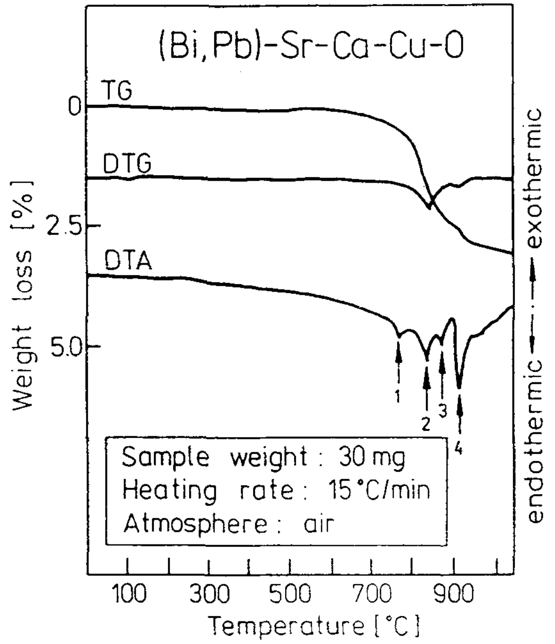

Fig. 3 DTA, DTG and TG curves for a (Bi,Pb)-Sr-Ca-Cu-O powder after calcination at 800°C in air during 12 h

physico-chemical processes, listed in Table 2 together with the corresponding temperatures ranges of their occurrence: the first of them, observed in the range 730–760°C corresponds to the polymorphous transition of Bi_2O_3 $\alpha \rightarrow \gamma$ [9]. The two successive endothermic effects, i.e. in the range 805–815°C and 850–860°C are ascribed to the melting of Bi_2O_3 and $CuBi_2O_4$, respectively [10]. The occurrence of the highest endothermic peak in the range 880–910°C is probably associated with the formation of a liquid phase due to melting of low-T_c phase $Bi_2Sr_2Ca_2Cu_3O_x$ [11].

Basing on the above thermogravimetric investigations (Figs 2 and 3) it can be concluded that the factor determining the formation of superconducting

Table 2 Peak assignment for DTA profile of decomposed powder BPSCCO

Process	Peak	Thermal effects / °C	
		Endo	Exo
α-$Bi_2O_3 \rightarrow \gamma$-$Bi_2O_3$	1	760	–
Bi_2O_3 melting	2	830	–
$CuBi_2O_4$ melting	3	865	–
$Bi_2Sr_2CaCu_2O_x$ melting	4	905	–

phases is the kinetics of reaction of calcium and strontium carbonates with molten $CuBi_2O_4$. Considering the fact that the results of these investigations were obtained under dynamic conditions (at constant heating rate) (Fig. 2), it is assumed that prolonged calcination at constant temperature would enable the decomposition of carbonate bonds at lower temperature, and, consequently, the determination phase transition sequence leading to the formation of superconducting phases in the system (Bi,Pb)–Sr–Ca–Cu–O.

In connection with the above observation, BPSCCO powders, obtained after calcination at: 770, 800 and 830°C for 12 h in air, were subjected to X-ray examinations. Figure 4 shows the X-ray diffraction patterns of the analysed powders, and Table 3 lists the results of the percentage of the high-T_c phase in powders obtained after calcination in air in the temperature range 770–830°C for 12 h. From the diffraction patterns (Fig. 4) it follows that all BPSCCO pow-

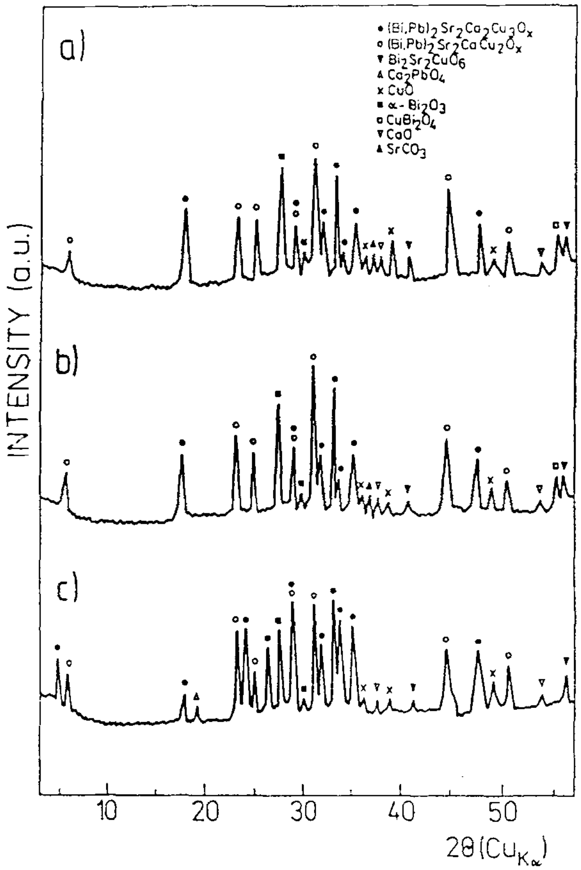

Fig. 4 X-ray diffraction patterns of the (Bi,Pb)–Sr–Ca–Cu–O powder after calcination in air for 12 h at: a) 770, b) 800 and c) 830°C

ders contain two superconducting phases, i.e. the low-T_c and the high-T_c one. In case of powder calcinated at the lowest temperature, i.e. 770°C, the low-T_c phase $Bi_2Sr_2CaCu_2O_x$, was the dominating are. Other phases $Bi_2Sr_2Ca_2Cu_3O_x$ (high-T_c), $Bi_2Sr_2CuO_x$, Bi_2CuO_4, and the oxides from incomplete reaction: α-Bi_2O, CuO, CaO and $SrCO_3$ were also observed. The intensity of reflexes derived from these phases decreases with increasing calcination temperature (Figs 4b and c). The intensity of reflexes attributed to the superconducting high temperature phase increases with increasing temperature of thermal treatment (Figs 4b and c). The calculation of volume fraction of this phase, presented in Table 3, confirms this tendency. It has been found that the highest volume fraction of high-T_c phase, equal to 43% was obtained in powder calcinated at 830°C.

Table 3 Volume fractions of the superconducting high-T_c phase in BPSCCO powders after calcination in the range 770–830°C for 12 h in air

	Calcination temperature / °C		
	770	800	830
Volume fraction of the high-T_c phase / %	8	17	43

As mentioned in the Introduction, the chemical reactions taking place during thermal treatment of powders in the (Bi,Pb)–Sr–Ca–Cu–O system, when the nuclei of superconducting a phase are formed, are very complex. This observation is based on the results of thermogravimetric (Figs 1, 2, 3) and X-ray (Fig. 4) studies, which may be helpful in formulating a plausible mechanism of formation of superconducting compounds: $Bi_2Sr_2CaCu_2O_x$ (low-T_c) and $Bi_2Sr_2Ca_2Cu_3O_x$ (high-T_c). In the powder obtained after pyrolysis of the gel precursor the presence of a bimetallic compound $CuBi_2O_4$ was observed. This compound formed above 500°C, reacts with strontium carbonate above 800°C according to the equation:

$$CuBi_2O_4 + 2SrCO_3 \rightarrow Bi_2Sr_2CuO_6 + 2CO_2 \qquad (1)$$

which leads to the formation of $Bi_2Sr_2CuO_6$. The progress of this reaction is consistent with the results of other researchers [10]. Thermogravimetric investigations have revealed the presence of a small endothermic effect in the temperature range 850–860°C on the DTA curve (Fig. 3), which accounts for melting of $CuBi_2O_4$. Thus one can assume that the reaction (1) proceeds with the participation of a liquid phase. On the other hand, calcium oxide identified in the powder calcinated at 770°C (Fig. 4a), together with $Bi_2Sr_2CuO_6$ and copper oxide, may lead to the formation of a high-T_c phase ($Bi_2Sr_2Ca_2Cu_3O_x$) according to the following reaction

$$Bi_2Sr_2CuO_6 + 2CaO + 2CuO \rightarrow Bi_2Sr_2Ca_2Cu_3O_x + CuO \qquad (2)$$

The X-ray patterns of the analysed samples (Fig. 4) indicate the presence of $Bi_2Sr_2CuO_6$ and of the low-T_c phase: $Bi_2Sr_2CaCu_2O_x$, in addition to the superconducting high-T_c phase $Bi_2Sr_2Ca_2Cu_3O_x$, it can be suggested, in agreement other the authors [10], that the formation of the high-T_c phase is preceded by the formation of the low-T_c phase:

$$Bi_2Sr_2CuO_6 + CaO + CuO \rightarrow Bi_2Sr_2CaCu_2O_x \tag{3}$$

$Bi_2Sr_2CaCu_2O_x$, undergoes subsequently a disproportionation reaction [12]:

$$2Bi_2Sr_2CaCu_2O_x \rightarrow Bi_2Sr_2Ca_2Cu_3O_x+Bi_2Sr_2CuO_6 \tag{4}$$

leading to the formation of a high-T_c superconducting phase. $Bi_2Sr_2CuO_x$, resulting from reaction (4), at sufficient amounts of copper and calcium oxides, in the presence of a liquid phase enriched in lead oxide, causes again the formation of the low-T_c phase ($Bi_2Sr_2CaCu_2O_x$). The latter undergoes disproportionation (4), to yield the high-T_c phase ($Bi_2Sr_2Ca_2Cu_3O_x$). The increase in volume fraction of high-T_c phase in BPSCCO powders subjected to calcination at 830°C, estimated on the basis of X-ray diffraction patterns (Fig. 4, Table 3), is probably due to a repeated cycle of the reaction according to Eqs (3) and (4). This hypothesis is in agreement with the results reported by other authors [12].

To summarize these considerations, it should be emphasized that the proposed cycle of chemical reactions leading to the formation of superconducting high-T_c and low-T_c phases represents only one of many possible mechanisms. However, from among the numerous models [2, 3] describing the formation of superconducting phases ($Bi_2Sr_2CaCu_2O_x$ and $Bi_2Sr_2Ca_2Cu_3O_x$), the mechanism described in the present paper appears to be the most justified one on account of the absence of other phases such as: Ca_2CuO_3 or Bi_2CuO_4, which may also participate in the crystallization process of the superconducting phases.

Conclusions

The results presented in the paper allow to formulate the following conclusions:

1) The kinetics of reaction of calcium and strontium carbonates with molten $CuBi_2O_4$ is the factor determining the formation of superconducting phases: $Bi_2Sr_2CaCu_2O_x$ and $Bi_2Sr_2Ca_2Cu_3O_x$.

2) An intermediate product obtained during the formation of the above superconducting phases is $Bi_2Sr_2CuO_6$. This compound precipitates within the liquid phase formed as a result of melting of the bimetallic compound $CuBi_2O_4$ at 865°C.

3) The increase in volume fraction of the high-T_c phase takes place probably due to repeated disproportionation of the low-T_c phase and its repeated synthesis from the phases; $Bi_2Sr_2CuO_6$, CuO and CaO.

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Zusammenfassung — Auf der Grundlage der Ergebnisse von DTA-, DTG- und TG-Untersuchungen, ergänzt durch Röntgendiffraktionsuntersuchungen an mittels der Sol-Gel-Methode hergestellten keramischen Pulvern wurde der Kristallisationsmechanismus von supraleitenden Phasen im (Bi,Pb)–Sr–Ca–Cu–O–System bestimmt.
Es wurde gezeigt, daß der Faktor, der die Bildung der supraleitenden Phasen $Bi_2Sr_2CaCu_2O_x$ (Nieder-T_c) und $Bi_2Sr_2Ca_2Cu_3O_x$ (Hoch-T_c) die Kinetik der Reaktion von Calcium- und Strontiumkarbonaten mit geschmolzenem $CuBi_2O_4$ ist. Im Ergebnis der Reaktion der bimetallischen Verbindung $CuBi_2O_4$ mit $SrCO_3$ in der flüssigen Phase wird die Verbindung $Bi_2Sr_2CuO_6$ gebildet. Nach Reaktion mit Calcium- und Kupferoxiden liefert diese Verbindung supraleitende Phasen: eine Nieder-T_c und eine Hoch-T_c Phase. Weiter wurde beobachtet, daß durch thermische Behandlung ein Anstieg des Volumenanteiles der Hoch-T_c-Phase erfolgt, wahrscheinlich wegen der wiederholten Disproportionierung der Nieder-T_c-Phase und dessen wiederholter Synthese aus $Bi_2Sr_2CuO_6$, CuO und CaO.