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THERMOANALYTICAL STUDY OF THE FORMATION OF COMPOUNDS IN THE PbO-MO (*M* = Ca, Sr, Ca+ Sr) SYSTEM

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In order to clarify the effect of PbO addition on the formation steps of the superconducting phases in the system Bi_2O_3–SrO–CaO–CuO, a study of solid-state reactions under non-isothermal conditions, in the PbO–MO (M = Ca, Sr, Ca + Sr) system has been carried out.

Results suggest that the reactivity of the components in the system containing PbO and CaO is much higher than in the system containing SrO. The Ca_2PbO_4 compound is formed first even in the system where M = Ca + Sr. It is confirmed that Ca_2PbO_4 formation represents one of the first steps in obtaining the high-T_c phases in Bi-based systems containing PbO.

Keywords: PbO-MO system, solid-solid reactions

Introduction

The presence of PbO is well known to enhance high-T_c superconducting phase formation, in the Bi_2O_3–SrO–CaO–CuO system and, at the same time, modifies the steps of defined compound formation [1–5].

In order to clarify the role that Pb plays in the above-mentioned phenomena, phase diagram studies in the ternary PbO–CaO–SrO system have been carried out [6], from which formation of the Ca_2PbO_4 compound, as well as that of the $SrPbO_3$ and Sr_2PbO_4 compounds, was established together with the existence of a continuous solid solution between them. It should also be noted that a $CaPbO_3$ compound has been synthesized by dehydration of $CaPb(OH)_6$ at 100 atm. of O_2 and 420°C [7].

The present paper describes investigations into a number of solid-phase reactions under non-isothermal conditions, carried out to clarify formation of defined compounds in the PbO–MO (M = Ca, Sr, Ca + Sr) systems, as well as the role they play in the formation mechanism of superconducting phases in the Bi_2O_3–SrO–CaO–CuO system.

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Experimental

Preparation of mixtures

The investigated compositions are given by the following mole ratios: PbO:MO (M = Ca, Sr, Ca + Sr) = 1:1 and 1:2. The raw materials were Analar p.a. grade oxides and carbonates: PbO, $CaCO_3$ and $SrCO_3$. The mixtures studied were prepared by a dry homogenization technique.

Methods and analysis

DTA and TG analyses of the mixtures were performed up to 1000°C in air, with Al_2O_3 as reference the heating rate was 10 deg/min. An OD–102 Derivatograph was used.

X-ray diffraction analyses were carried out on samples resulting from non-isothermal DTA/TG runs up to 600°, 700°, 800°, 850° and 1000°C. A HZG-3 Diffractometer utilizing CuK_α radiation was used.

Results and discussion

DTA/TG curves for the studied compositions are presented in Figs 1 and 2. Experimental and theoretical weight losses corresponding to the reactions between the components are presented in Table 1.

Table 1 TG data for the PbO–MO (M = Ca, Sr, Ca + Sr) systems

Temperature / °C	1:1		1:2	
	Molar ratio			
	Weight loss / %		Weight loss / %	
	Experimental	Calculated	Experimental	Calculated
PbO – CaO system				
500 – 850	11.82	13.61	17.27	20.79
PbO – SrO system				
500 – 860	3.18		3.125	
860 – 920	1.59		1.875	
920 – 1010	3.86		5.625	
500 – 1010	8.63	11.87	10.625	16.98
PbO – (Ca, Sr)O system				
500 – 800	5.45		8.13	
800 – 1010	6.59		9.06	
500 – 1010	12.04	12.68	17.19	18.69

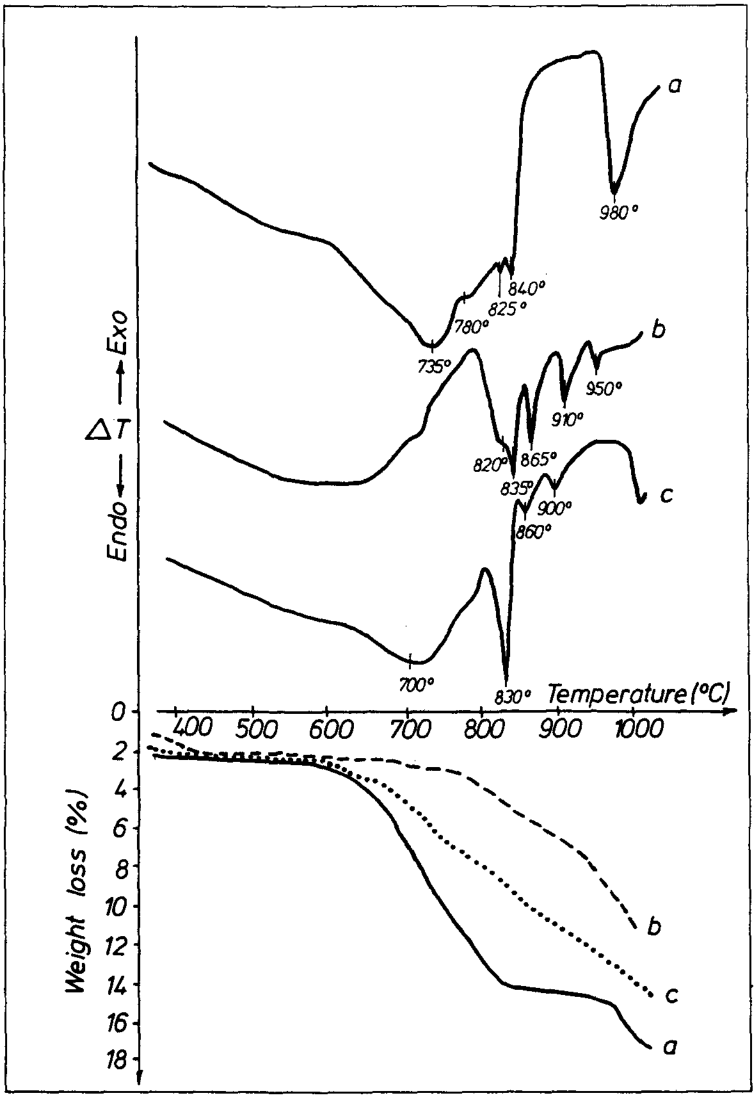

Fig. 1 DTA/TG curves of the mixtures in PbO–MO systems with molar ratio 1:1 (a. M = Ca, b. M = Sr, c. M = Ca + Sr)

X-ray diffraction data are presented in Fig. 3.

The phase composition of the analysed samples will be far removed from the equilibrium composition at any given temperatures, but it is indicative of the reaction rates of the initial compounds.

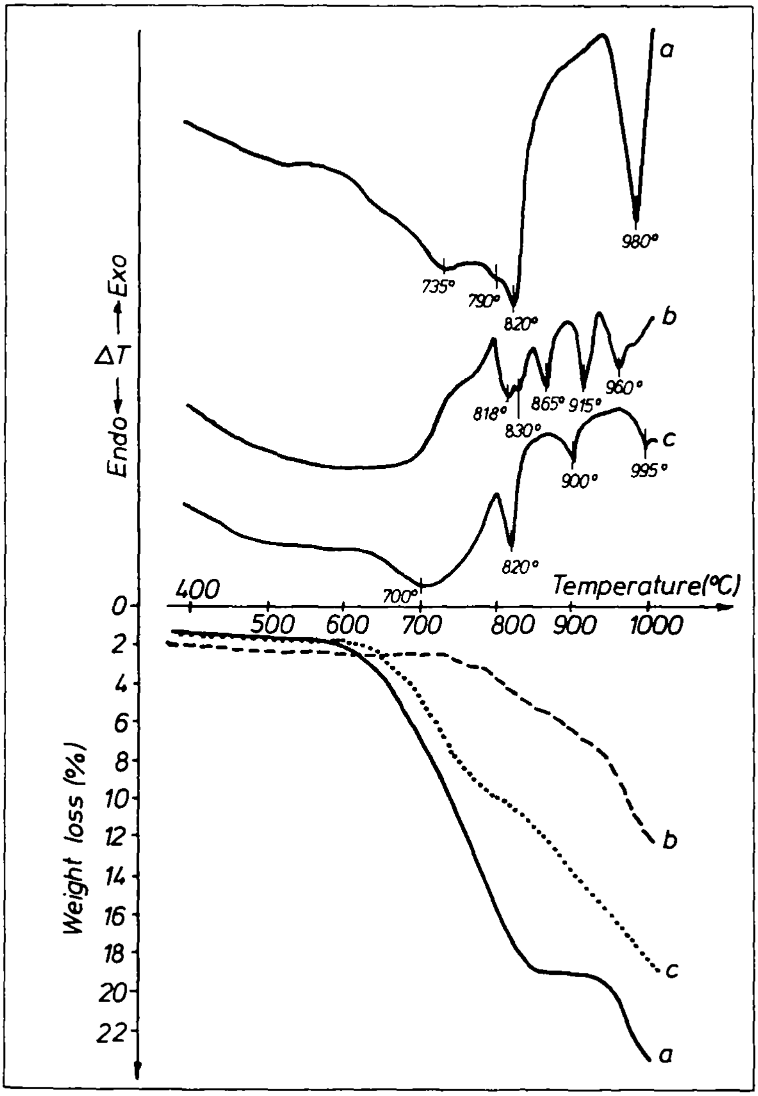

Fig. 2 DTA/TG curves of the mixtures in PbO–MO systems with molar ratio 1:2 (a. *M* = Ca, b. *M* = Sr, c. *M* = Ca + Sr)

PbO–CaO *system*

DTA/TG curves for both 1:1 and 1:2 compositions (Figs 1a and 2a) show that the reaction of PbO with $CaCO_3$ starts at about 550°C. The reaction takes place in one step and is finished at about 850°C.

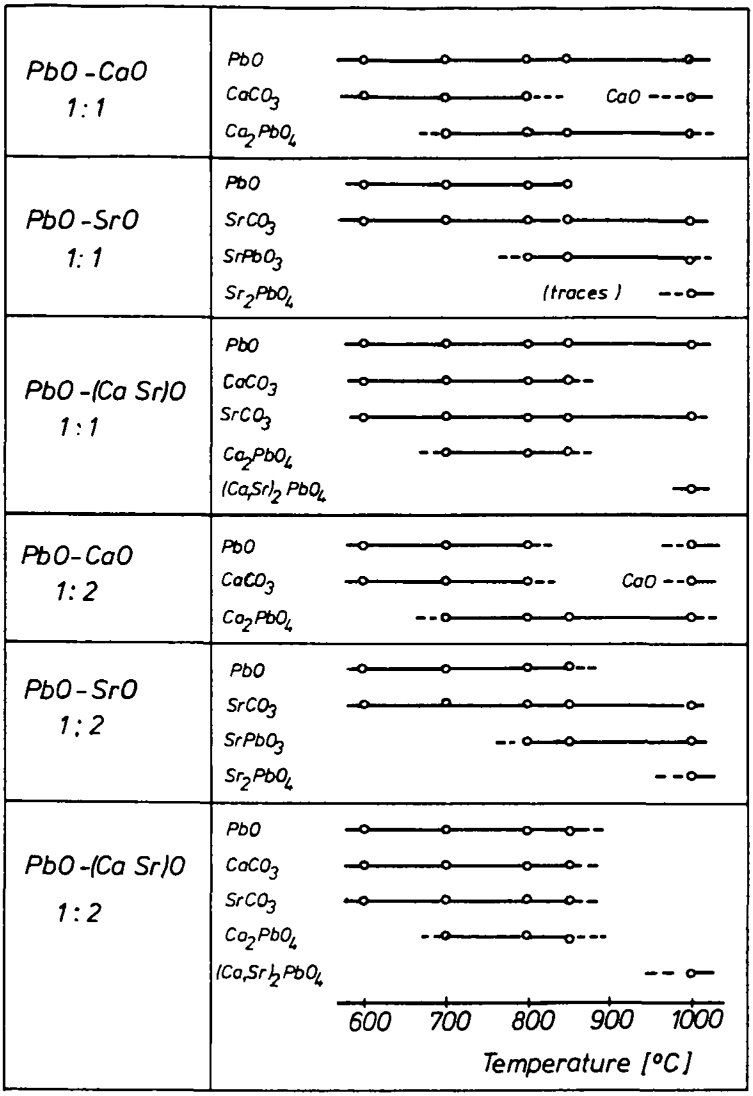

Fig. 3 Phase composition *vs.* temperature in the PbO–MO systems (M = Ca, Sr, Ca + Sr)

The phase composition of the samples resulting from thermal analysis under non-isothermal conditions, as shown in Fig. 3, indicates that the only compound obtained in the system (beginning at 700°C) for both molar ratios under study is Ca_2PbO_4. All the $CaCO_3$ decomposed and reacted with PbO, forming very well crystallized Ca_2PbO_4.

Experimental weight losses are lower than the calculated values (Table 1). This can be attributed to the oxidation of PbO to PbO_2 during Ca_2PbO_4 formation. The DTA curves show a strong endothermic effect at 980°C, because of the incongruent melting of Ca_2PbO_4. This endothermic effect is accompanied by a weight loss attributed to the reduction of PbO_2 (resulting from Ca_2PbO_4 decomposition) to PbO. (The possibility of some PbO evaporation from the melt is not excluded.) This observation is confirmed by the X-ray diffraction results, which indicate, at 1000°C CaO and PbO, as well as Ca_2PbO_4.

PbO–SrO *system*

DTA/TG curves for both 1:1 and 1:2 compositions are presented in Figs 1b and 2b. The reaction of PbO and $SrCO_3$ starts at higher temperature (about 700°C) and the decomposition of $SrCO_3$ is not complete at 1000°C. This decomposition takes place in several steps, accompanied by the corresponding endo-thermic effects. The difference between observed and calculated weight loss is higher than in the first case. This is in good agreement with the incomplete decomposition of $SrCO_3$.

Thermal analysis results are confirmed by X-ray determinations. In both cases $SrCO_3$ is identified up to 1000°C. The first reaction compound is always $SrPbO_3$, this beginning to crystallize at 800°C. In the sample with 1:2 molar ratio, Sr_2PbO_4 is identified at 1000°C only. Its formation takes place in two steps. The first-formed compound, $SrPbO_3$, reacts at higher temperatures with the excess $SrCO_3$, forming the Sr_2PbO_4 compound.

PbO–(Ca, Sr)O *system*

DTA/TG curves for both 1:1 and 1:2 compositions are presented in Figs 1c and 2c. In this case one can note the sum of the effects recorded for the binary oxide systems.

Reaction of PbO with the carbonates starts below 600°C (as in the PbO–CaO system), but is not finished until 1000°C (as in the PbO–SrO system). The first compound to appear, in both compositions, is Ca_2PbO_4 (Fig. 3). The presence of $SrCO_3$ leads to a slower $CaCO_3$ decomposition, which exists to above 850°C, unlike the PbO–CaO system, where all the $CaCO_3$ has been consumed at this temperature during the formation of Ca_2PbO_4.

However, the presence of Ca_2PbO_4 hinders $SrPbO_3$ formation, inducing – at 1000°C – the direct formation of the solid solution having the $(Ca_{1-x}Sr_x)_2PbO_4$ composition. For the 1:2 composition mixture, formation of the solid $(Ca, Sr)_2PbO_4$ solution is complete, with the whole of the $SrCO_3$ being consumed.

Conclusions

DTA/TG and X-ray diffraction determinations suggest that, under non-isothermal conditions, the reactivity of components in the system containing PbO and CaO is much higher than in the PbO and SrO system.

In the PbO–CaO system, regardless of the initial ratio of the components, the Ca_2PbO_4 compound is the only one formed.

In the PbO–SrO system, whatever the initial ratio of the components, $SrPbO_3$ is formed first, and this reacts at higher temperatures with excess $SrCO_3$, to form the Sr_2PbO_4 compound.

In the complex PbO–(Ca, Sr)O system, for both compositions Ca_2PbO_4 is formed first. This compound hinders $SrPbO_3$ formation and induces direct generation of the $(Ca_{1-x}Sr_x)_2PbO_4$ solid-solution.

As the Ca_2PbO_4 compound is formed first, even in the system where M = Ca+Sr, it is confirmed that the formation of this compound represents one of the first steps in the production of the high-T_c phases in Bi-based systems containing PbO.

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Zusammenfassung — Zur Klärung des Einflusses von PbO-Zusatz bei der Bildung supra-leitender Phasen im System Bi_2O_3–SrO–CaO–CuO wurden unter nichtisothermen Bedingungen Feststoffreaktionen im System PbO–MO (M=Ca, Sr, Ca+Sr) untersucht.

Die Resultate zeigen, daß die Reaktivität der Komponenten in Systemen mit PbO und CaO viel höher liegt als in Systemen mit SrO. In den Systemen mit M =Ca+Sr wird zuerst die Verbindung Ca_2PbO_4 gebildet. Es wurde festgestellt, daß die Bildung von Ca_2PbO_4 einer der ersten Schritte ist, um in PbO-haltigen Systemen auf Bi-Basis die Hoch-T_c-Phasen zu erhalten.