PHASE FORMATION AND THERMAL STABILITY OF THE COMPOUNDS IN THE Bi$_2$O$_3$–PbO SYSTEM

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Abstract

The scientific interest for the Bi$_2$O$_3$–PbO system has increased due to the importance of the PbO in the high-T_c superconducting phase formation in the Bi$_2$O$_3$–SrO–CaO–CuO system. Also Bi$_2$O$_3$–PbO system contains compounds with some specific semiconductor and dielectric properties and Bi$_2$O$_3$–based solid solutions are well known as high oxygen ion conductors.

Previously, several low melting defined compounds have been identified in the system: 6Bi$_2$O$_3$·PbO; 3Bi$_2$O$_3$·2PbO; 4Bi$_2$O$_3$·5PbO; 4Bi$_2$O$_3$·6PbO and Bi$_2$O$_3$·3PbO.

This work deals with the phase formation and thermal stability of these compounds. Under non-isothermal conditions, in all mixtures regardless of the Bi$_2$O$_3$/PbO ratio, the compound 6Bi$_2$O$_3$·PbO is preferentially formed, followed by the compound 4Bi$_2$O$_3$·5PbO. The formation of the compound 4Bi$_2$O$_3$·6PbO was not confirmed while the formation of the compound Bi$_2$O$_3$·3PbO occurs through a complex mechanism which includes an intermediate step in which a solid solution with the litharge structure was identified. Under isothermal conditions in the same temperature range the tendency to form the stoichiometric compounds increases. All compounds form, decompose and melt at temperatures between 530–780°C.

Keywords: Bi$_2$O$_3$–PbO system, DTA–TG, X-ray diffraction

Introduction

The interest in the phase diagram of the binary system Bi$_2$O$_3$–PbO is due to the fact that it contains compounds with some specific semiconductor and dielectric properties [1–3] and Bi$_2$O$_3$–based solid solutions are well known as high oxygen ion conductors over a wide temperature range [4–7]; in addition PbO is frequently used as an additive to enhance high-T_c superconducting phase formation in the system Bi$_2$O$_3$–SrO–CaO–CuO.

The phase diagram of the Bi$_2$O$_3$–PbO system was established by Boivin *et al.* [8, 9] who pointed out the existence of the following 5 compounds: 6Bi$_2$O$_3$·PbO; 3Bi$_2$O$_3$·2PbO; 4Bi$_2$O$_3$·5PbO; 3Bi$_2$O$_3$·7PbO and Bi$_2$O$_3$·3PbO. Further investigations carried out by Biefeld and White [10] confirm the existence of the compounds 6Bi$_2$O$_3$·PbO; 3Bi$_2$O$_3$·2PbO; 4Bi$_2$O$_3$·5PbO and Bi$_2$O$_3$·3PbO, but not the existence of 3Bi$_2$O$_3$·7PbO. While Vihreva *et al.* [11] indicate as well as the existence of the compound 4Bi$_2$O$_3$·5PbO as well as that of 4Bi$_2$O$_3$·6PbO, other authors [12] show the existence of two polymorphic forms for the compound 4Bi$_2$O$_3$·5PbO.

All the papers confirm the formation of all the defined compounds at low temperatures; they are characterized by a low temperature range of thermal stability.

Fig. 1 The phase diagram of the Bi₂O₃–PbO system [10]

Figure 1 shows the phase diagram of the system Bi₂O₃–PbO as given by Biefeld and White [10].

In a previous study [13] the competition between PbO and Bi₂O₃ in the reaction with CaO, when these three oxides coexist, has been investigated. It has been shown that the first reaction which occurs is that between Bi₂O₃ and PbO leading, in the presence of CaO, to the preferential formation of Ca_2PbO_4.

Taking into account the literature data and following our previous studies [14, 15], this paper is dedicated to the investigation of the formation of the compounds in the binary system Bi₂O₃–PbO. As these compounds are low temperature intermediates in the Bi-based system, the thermal stability of these compounds was also investigated.

Experimental

Preparation of mixtures

The initial oxide compositions (mol%) of the investigated samples are listed in Table 1.

The raw materials were p.a. grade oxides: Bi₂O₃ (Carlo Erba) and PbO-litharge (Fluka). The analysed mixtures were prepared by a dry homogenization technique.

Table 1 Starting oxide composition of the investigated samples (mol%)

Sample	Formula	Bi_2O_3	PbO
6:1	$6Bi_2O_3 \cdot PbO$	85.71	14.29
3:2	$3Bi_2O_3 \cdot 2PbO$	60.00	40.00
4:5	$4Bi_2O_3 \cdot 5PbO$	44.44	55.56
4:6	$4Bi_2O_3 \cdot 6PbO$	40.00	60.00
1:3	$Bi_2O_3 \cdot 3PbO$	25.00	75.00

Methods of analysis

DTA and TG investigations of the mixtures were performed up to 800°C, in static air atmosphere at a heating rate of 3 K min⁻¹. A MOM Budapest type Paulik-Paulik-Erdey derivatograph OD-102 was used. Pellets, 10 mm diameter and 2 mm thickness, were prepared using a die press, and were sintered for 1 h at characteristic temperatures as shown by the DTA curves.

In order to characterize the phase composition of the samples, X-ray diffraction analyses were carried out both on samples resulting from non-isothermal treatments, under DTA-TG conditions, up to different temperatures and on samples resulting from isothermal treatments. A HZG-3 X-ray diffractometer with CoK_α radiation was used. Phases were identified according to the JCPDS card file [16] and literature data [10, 11].

Results and discussion

Non-isothermal treatments

Figure 2 shows the DTA and TG curves of the mixtures corresponding to the formation of the binary compounds, in the temperature range 400–800°C. The assignment of the recorded thermal effects is listed in Table 2.

In all cases the formation, decomposition and melting of the investigated compounds occurred in the 530–780°C temperature range. For all the investigated samples, at 530°C, an overlap of weak endothermic effects accompanied by weight loss could be noticed. This could be assigned to the reduction of Pb_3O_4 generated by the oxidation of the PbO introduced into the mixtures, simultaneously with the formation of some nonequilibrium compounds.

The assignment of the thermal effects recorded at temperatures higher than 530°C, shown in Table 2, is in good agreement with the phase diagram established by Biefeld and White [10].

The phase composition of all the samples thermally treated under non-isothermal conditions is presented in Table 3. This has been obtained for two temperatures of thermal treatment considered characteristic for the formation of the compounds in the investigated system. The X-ray diffraction data confirmed the assignment of the thermal effects from the DTA curves.
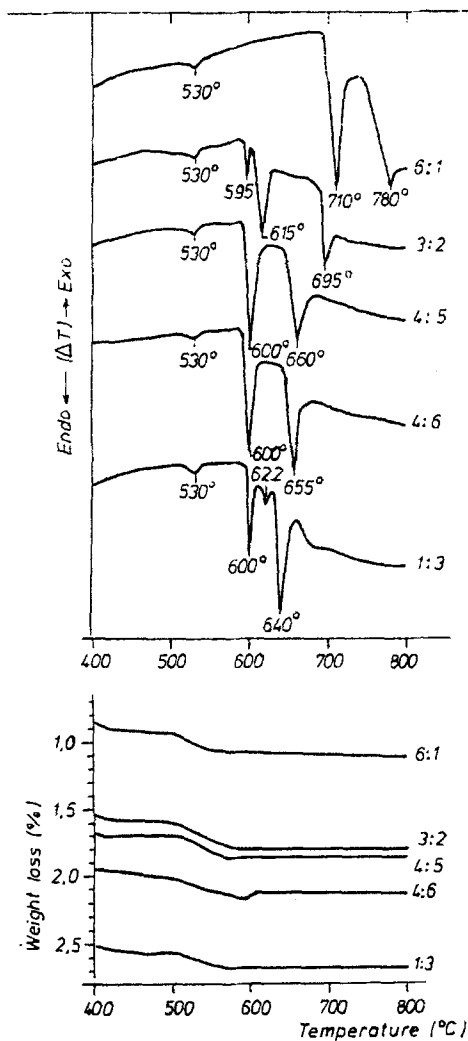
Fig. 2 DTA–TG curves of all the investigated binary composition

In all the cases at 550°C the compound $6Bi_2O_3 \cdot PbO$ was identified. Thus this was an intermediate phase for all the investigated mixtures no matter what the initial composition was, even in the mixture 1:3 in which PbO exceeds. Except the 6:1 mixture, at 550°C, in all the other mixtures the compound $4Bi_2O_3 \cdot 5PbO$ was also identified. Thus under non-isothermal conditions, at 550°C, for all compositions a mixture of phases was present.

At 600°C, in all mixtures (except the mixtures 3:2 and 1:3), single phases were obtained. For the mixtures 6:1 and 4:5 the stoichiometric compounds were formed. The compound $4Bi_2O_3 \cdot 5PbO$ was identified both in 4:5 and 4:6 mixtures. In the 4:6

Table 2 DTA-TG results for the investigated compositions

Sample	Starting composition	T_{range}/°C	Thermal effects (endo)	Mass variation/%	Assignment
6:1	6Bi$_2$O$_3$·PbO	400–550	530	−0.25	6Bi$_2$O$_3$·PbO formation
		550–800	710		6Bi$_2$O$_3$·PbO decomposition
			780		melting
3:2	3Bi$_2$O$_3$·2PbO	400–550	530	−0.26	mixture of phases formation
		550–800	595		3Bi$_2$O$_3$·2PbO formation
			615		3Bi$_2$O$_3$·2PbO decomposition
			695		melting
4:5	4Bi$_2$O$_3$·5PbO	400–550	530	−0.18	mixture of phases formation
		550–800	600		4Bi$_2$O$_3$·5PbO formation
			660		melting
4:6	4Bi$_2$O$_3$·6PbO	400–550	530	−0.21	mixture of phase formation
		550–800	600	+0.04	4Bi$_2$O$_3$·5PbO formation and PbO oxidation
			655		melting
1:3	Bi$_2$O$_3$·3PbO	400–550	530	−0.16	mixture of phases formation
		550–800	600		Bi$_2$O$_3$·3PbO formation
			622		Bi$_2$O$_3$·3PbO decomposition
			640		melting

Table 3 Phases identified by X-ray diffraction in the samples thermally treated under non-iso-thermal conditions

Sample	Thermal treatment	
	550°C	600°C
6:1	6Bi$_2$O$_3$·PbO; X*	6Bi$_2$O$_3$·PbO
3:2	6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO 3Bi$_2$O$_3$·2PbO	6Bi$_2$O$_3$·PbO 4Bi$_2$O$_3$·5PbO
4:5	6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO 3Bi$_2$O$_3$·2PbO	4Bi$_2$O$_3$·5PbO
4:6	6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO 3Bi$_2$O$_3$·2PbO	4Bi$_2$O$_3$·5PbO
1:3	6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO Bi$_2$O$_3$·3PbO; PbO (massicote)	solid solution with litharge stucture; Bi$_2$O$_3$·3PbO

*X-Bi$_2$O$_3$-based solid solution with CaF$_2$ type cubic structure

Table 4 Phases identified by X-ray diffraction in the samples thermally treated under isothermal conditions (1 h)

Sample	Thermal treatment			
	510°C	550°C	600°C	620°C
6:1		6Bi$_2$O$_3$·PbO; X*	6Bi$_2$O$_3$·PbO; X*	6Bi$_2$O$_3$·PbO
3:2		6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO; 3Bi$_2$O$_3$·2PbO	6Bi$_2$O$_3$·PbO; 3Bi$_2$O$_3$·2PbO	6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO; 3Bi$_2$O$_3$·2PbO
4:5	6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO; Pb$_3$O$_4$	6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO; Pb$_3$O$_4$	4Bi$_2$O$_3$·5PbO	4Bi$_2$O$_3$·5PbO
4:6	6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO; Pb$_3$O$_4$	6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO; Pb$_3$O$_4$	4Bi$_2$O$_3$·5PbO	4Bi$_2$O$_3$·5PbO
1:3		6Bi$_2$O$_3$·PbO; 4Bi$_2$O$_3$·5PbO; Pb$_3$O$_4$	Bi$_2$O$_3$·3PbO	Bi$_2$O$_3$·3PbO

*X-Bi$_2$O$_3$-based solid solution with CaF$_2$ type cubic structure
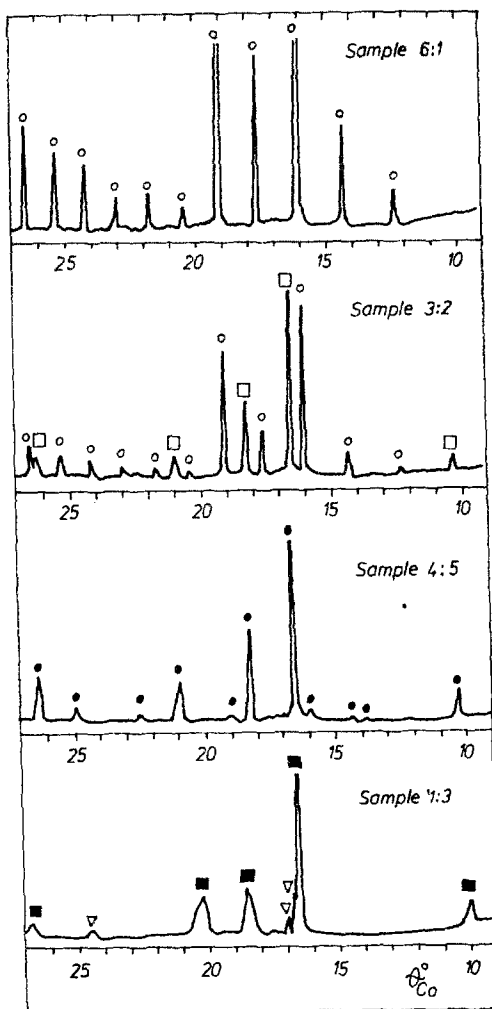
Fig. 3 X-ray diffraction data for some representative samples: 6:1, 3:2, 4:5 and 1:3, thermally treated under non-isothermal conditions up to 600°C (o 6Bi₂O₃·PbO; • 4Bi₂O₃·5PbO; ∇ Bi₂O₃·3PbO; ■ solid solution with litharge structure)

mixture the PbO excess oxidized and led to a small weight increase noticed in the TG curve (Fig. 1). In the mixture 1:3 a solid solution with the litharge structure was observed.

The identification of a mixture of 6Bi₂O₃·PbO and 4Bi₂O₃·5PbO compounds in the mixture 3:2 could be accounted for by the low temperature range of thermal stability of the compound 3Bi₂O₃·2PbO (575–610°C). Through slow cooling, the sample 3:2 decomposed into 6Bi₂O₃·PbO and 4Bi₂O₃·5PbO.

As shown in Fig. 3, the X-ray diffraction results have established that in all the investigated compositions well crystallized compounds have been obtained, indicating the high reactivity of the oxides in the system.

Isothermal treatments

The results of X-ray diffraction for the isothermally treated samples are listed in Table 4.

The samples 4:5 and 4:6 isothermally treated at 510°C exhibited a phase mixture in which the compound Pb_3O_4 was identified.

At 550°C, in all compositions, a mixture of phases was present in agreement with the non-isothermal treatment results. For the mixtures rich in PbO the compound Pb_3O_4 was still identified.

At 600°C, in most cases, defined compounds according to the initial molar ratio were obtained. However, one has to mention that for the composition 4:6 the structure of the compound 4:5 was identified and for the composition 3:2 a mixture of phases was present which could be explained by the low temperature range of the thermal stability of this compound. Similar behaviour was recorded at 620°C.

Conclusions

DTA–TG and X-ray diffraction investigations have been performed on the system Bi_2O_3–PbO both under non-isothermal and isothermal conditions.

Under non-isothermal conditions:

– the first compound which is formed is $6Bi_2O_3 \cdot PbO$, no matter what the composition of the initial mixture was, which is followed by the compound $4Bi_2O_3 \cdot 5PbO$;

– for the starting composition 4:6 the X-ray diffraction pattern corresponding to the compound $4Bi_2O_3 \cdot 5PbO$ was obtained;

– the compound $3Bi_2O_3 \cdot 2PbO$ has not been obtained as a pure phase, due to its low temperature range of thermal stability;

– the formation of the compound $Bi_2O_3 \cdot 3PbO$ occurs through a complex mechanism which includes an intermediate step in which a solid solution with litharge structure was identified.

Under isothermal conditions for the same temperature range, the trend to form stoichiometric compounds increases. All compounds form, decompose and melt at temperatures between 530–780°C.

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