

## **SOLID STATE PHASE FORMATION IN THE Bi<sub>2</sub>O<sub>3</sub>-PbO-CaO SYSTEM**

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### **Abstract**

Following our previous research, this work is dedicated to the study of phase formation in the subsolidus domain of the Bi<sub>2</sub>O<sub>3</sub>-PbO-CaO system.

Former investigations performed by DTA/TGA and XRD have pointed out that under non-isothermal conditions only the formation of binary compounds occurs. Under such conditions these compounds could be non-equilibrium phases.

In order to establish the conditions of formation of equilibrium phases, a study of the Bi<sub>2</sub>O<sub>3</sub>-PbO-CaO system, in isothermal conditions, was carried out. The results obtained in isothermal conditions have confirmed the presence of Bi<sub>2</sub>O<sub>3</sub>-rich solid solutions and Ca<sub>2</sub>PbO<sub>4</sub> as main equilibrium phases. An attempt to represent the phase relations of the mentioned system at 700°C should be equally mentioned.

**Keywords:** Bi<sub>2</sub>O<sub>3</sub>-PbO-CaO system, DTA, solid-state reactions, X-ray diffraction

### **Introduction**

It is now well-known that the obtaining of superconducting materials in the Bi<sub>2</sub>O<sub>3</sub>-(Sr,Ca)O-CuO system is a very complex process which occurs by successive solid state reactions.

Former results [1] indicated that the reactivity of the components in systems containing Bi<sub>2</sub>O<sub>3</sub> and CaO is much higher than in systems containing CuO and SrO. In the meantime the presence of PbO enhances high-*T<sub>c</sub>* superconducting phase formation [2-10].

Our previous research [11], in non-isothermal conditions, has shown that when PbO and Bi<sub>2</sub>O<sub>3</sub> coexist with CaO, the first reaction which occurs is that between Bi<sub>2</sub>O<sub>3</sub> and PbO. On increasing the temperature, the so formed compound melts leading, in the presence of CaO, to the preferential formation of 2CaO·PbO<sub>2</sub>. The last compounds which are generated in the system result from the reaction between Bi<sub>2</sub>O<sub>3</sub> and CaO. The formation process occurs in several steps. Firstly, solid solutions with the molar ratio Bi<sub>2</sub>O<sub>3</sub>/CaO higher than in the initial mixture are obtained.

Subsequently, these react with the excess of  $\text{CaCO}_3$  leading to the formation of the stoichiometric compound  $4\text{CaO}\cdot 3\text{Bi}_2\text{O}_3$ .

Thus, in the considered system, the phase formation reactions are complex and the obtained products could be non-equilibrium ones.

This work aims an investigation of the conditions of formation of equilibrium phases in the  $\text{Bi}_2\text{O}_3$ - $\text{PbO}$ - $\text{CaO}$  system. An attempt to represent the phase relations of the mentioned system at  $700^\circ\text{C}$  was carried out.

## Experimental

### Preparation of mixtures

The raw materials were p.a. grade oxides and carbonates:  $\text{Bi}_2\text{O}_3$  (Carlo Erba),  $\text{CaCO}_3$  (Merck) and  $\text{PbO}$ -massicote (Fluka). The ternary oxide compositions were realised by a dry homogenization technique for one hour.

The initial mixtures were used as powdered samples for non-isothermal investigations.

For isothermal investigations, pellets, 10 mm diameter and 2 mm thickness, were prepared using a die press, by compaction at 30 MPa. The pellets were sintered for 10 h at the characteristic temperatures as shown by the DTA curves.

### Methods of analysis

DTA investigations of the studied mixtures were performed up to  $800^\circ\text{C}$ , in static air atmosphere with  $\alpha\text{-Al}_2\text{O}_3$  as reference at a heating rate of  $5^\circ\text{C min}^{-1}$ . A MOM Budapest type Paulik-Paulik-Erdey derivatograph OD-102 was used.

The thermal analysis data were completed with X-ray diffraction data in order to clarify the mechanism of phase formation in the studied system. A HZG 3 X ray dif

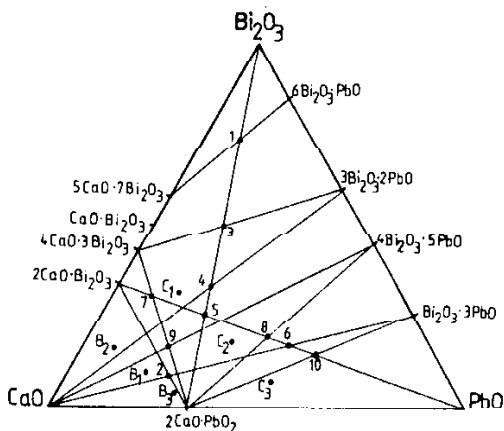


Fig. 1 The position of the investigated samples in the ternary system  $\text{Bi}_2\text{O}_3$ - $\text{PbO}$ - $\text{CaO}$

fractometer with CoK $\alpha$  radiation was used. The phases were identified according to the JCPDS files [12] and literature data [13, 14].

## Results and discussion

### *Non-isothermal treatments*

Previously [11], non-isothermal investigations on six compositions corresponding to the formulae 2CaO·(Pb<sub>1-x</sub>Bi<sub>x</sub>)O<sub>2+x</sub>, with  $x=0, 0.5$  and  $0.8$  and 5[(Bi<sub>1-y</sub>Pb<sub>y</sub>)<sub>2</sub>O<sub>3-y</sub>]-7CaO with  $y=0, 0.2$  and  $0.5$  were carried out. In this work, the sample number was extended with the compositions B<sub>3</sub> with  $x=0.8$  and C<sub>3</sub> with  $y=0.8$  and the compositions shown in Fig. 1, which are located at the intersection of the possible coordination lines between the binary compounds from the studied system.

Table 1 shows the molar composition of the investigated samples as well as the peak temperatures corresponding to the DTA curves, in the temperature range 400–800°C. Under 400°C, the samples do not exhibit characteristic thermal effects.

The thermal effects are concentrated around three temperature ranges. Except samples 1 and B<sub>3</sub> the low temperature effects are recorded close to 600°C. Most of the samples show thermal effects close to 700°C and in some cases thermal effects close to 800°C are recorded.

**Table 1** The molar composition and the DTA results for the investigated samples

Sample	Composition/mol%			Thermal effects (endo)/°C
	Bi <sub>2</sub> O <sub>3</sub>	PbO	CaO	
1	74.5	8.4	17.1	682, 795
3	50.0	16.8	33.2	605, 680, 710, 735 <sup>s</sup> , 758, 798 <sup>s</sup> , 800
4	33.3	22.5	44.1	590 <sup>s</sup> , 618, 680, 740
5	25.0	50.0	25.0	590 <sup>s</sup> , 615, 670 <sup>s</sup> , 700 <sup>s</sup> , 735
7	30.0	10.0	60.0	600, 660 <sup>s</sup> , 682 <sup>s</sup> , 740, 760, 790
9	16.6	20.4	63.0	575 <sup>s</sup> , 595, 715, 738 <sup>s</sup> , 788
2	8.2	25.0	66.8	570 <sup>s</sup> , 592 <sup>s</sup> , 640, 705, 740, 785
8	19.0	43.0	38.0	568, 620, 630, 698
6	16.5	50.0	33.5	590, 640, 658
10	14.0	57.0	29.0	570, 620, 640
B <sub>2</sub> <sup>*</sup>	15.4	7.7	76.9	595, 655 <sup>s</sup> , 675 <sup>s</sup> , 762, 780
B <sub>1</sub> <sup>*</sup>	9.1	18.2	72.7	570, 597 <sup>s</sup> , 622 <sup>s</sup> , 640, 700, 760, 780
B <sub>3</sub> <sup>*</sup>	3.4	27.6	69.0	678, 708, 722, 760, 780 <sup>s</sup>
C <sub>1</sub> <sup>*</sup>	30.8	15.4	53.8	580 <sup>s</sup> , 605, 668, 705 <sup>s</sup> , 735, 785
C <sub>2</sub> <sup>*</sup>	17.2	34.5	48.3	580, 630 <sup>s</sup> , 642, 687 <sup>s</sup> , 720, 765
C <sub>3</sub> <sup>*</sup>	62.0	50.0	43.8	590 <sup>s</sup> , 635 <sup>s</sup> , 658, 690

\* samples studied before [11]

<sup>s</sup> shoulder

**Table 2** Phases identified by X-ray diffraction in the samples themally treated under isothermal conditions (10 h)

Sample	Thermal treatment (10 h)		
	600°C	700°C	800°C
1	Bi <sub>2</sub> O <sub>3</sub> , 6Bi <sub>2</sub> O <sub>3</sub> ·PbO ss CaO·3Bi <sub>2</sub> O <sub>3</sub>	ss CaO·Bi <sub>2</sub> O <sub>3</sub>	ss CaO·3Bi <sub>2</sub> O <sub>3</sub>
3	6Bi <sub>2</sub> O <sub>3</sub> ·PbO, CaO·Bi <sub>2</sub> O <sub>3</sub> 5CaO·7Bi <sub>2</sub> O <sub>3</sub>	ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub> 33CaO·67(1/2Bi <sub>2</sub> O <sub>3</sub> ) <sup>1,131</sup>	ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub>
4	2CaO·PbO <sub>2</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub>	CaO·Bi <sub>2</sub> O <sub>3</sub> 2CaO·PbO <sub>2</sub>	4CaO·3Bi <sub>2</sub> O <sub>3</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub> 2CaO·PbO <sub>2</sub>
5	2CaO·PbO <sub>2</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> CaO·Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub>
7	4CaO·3Bi <sub>2</sub> O <sub>3</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub> 2CaO·PbO <sub>2</sub> , a	4CaO·3Bi <sub>2</sub> O <sub>3</sub> 2CaO·PbO <sub>2</sub>	4CaO·3Bi <sub>2</sub> O <sub>3</sub> 2CaO·PbO <sub>2</sub>
9	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub> , a	4CaO·3Bi <sub>2</sub> O <sub>3</sub> 2CaO·PbO <sub>2</sub>	4CaO·3Bi <sub>2</sub> O <sub>3</sub> 2CaO·PbO <sub>2</sub>
2	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub>
8	2CaO·PbO <sub>2</sub> 6Bi <sub>2</sub> O <sub>3</sub> ·PbO 4Bi <sub>2</sub> O <sub>3</sub> ·5PbO, a	2CaO·PbO <sub>2</sub> 4Bi <sub>2</sub> O <sub>3</sub> ·5PbO	2CaO·PbO <sub>2</sub>
6	2CaO·PbO <sub>2</sub> m	2CaO·PbO <sub>2</sub> 4Bi <sub>2</sub> O <sub>3</sub> ·5PbO, m	2CaO·PbO <sub>2</sub>
10	2CaO·PbO <sub>2</sub> m	2CaO·PbO <sub>2</sub> m	2CaO·PbO <sub>2</sub>
B <sub>2</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub> 2CaO·Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub>
B <sub>1</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub> CaCO <sub>3</sub> , a	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub>
B <sub>3</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub>
C <sub>1</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub>	2CaO·PbO <sub>2</sub> 4CaO·3Bi <sub>2</sub> O <sub>3</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub>
C <sub>2</sub>	2CaO·PbO <sub>2</sub>	2CaO·PbO <sub>2</sub>	2CaO·PbO <sub>2</sub> ss α <sub>1</sub> '-3CaO·4Bi <sub>2</sub> O <sub>3</sub>
C <sub>3</sub>	2CaO·PbO <sub>2</sub> m	2CaO·PbO <sub>2</sub> m	2CaO·PbO <sub>2</sub> m

m - mixture of Bi<sub>2</sub>O<sub>3</sub>·PbO phases; a - amorphous phase; ss - solid solution

Our previous investigation [11] showed that the low temperature effects (550–650°C) are due to the formation and melting of the compounds which result from the reaction between Bi<sub>2</sub>O<sub>3</sub> and PbO. The thermal effects around 700°C can be assigned to the formation of 2CaO·PbO<sub>2</sub>. As far as the thermal effects of high temperatures are concerned, these are due to the reaction between Bi<sub>2</sub>O<sub>3</sub> and CaO.

The complexity of the thermal analysis curves of the investigated ternary mixtures can be explained taking into account the complexity of the reactions in the binary systems: Bi<sub>2</sub>O<sub>3</sub>-PbO [15], Bi<sub>2</sub>O<sub>3</sub>-CaO [16] and CaO-PbO [17], which are components of the ternary system Bi<sub>2</sub>O<sub>3</sub>-PbO-CaO.

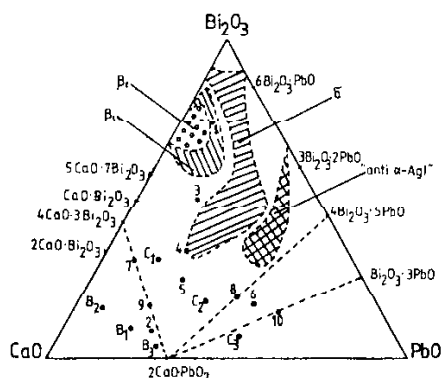
### *Isothermal treatments*

The phase composition of the samples thermally treated under isothermal conditions is presented in Table 2.

The analysis of the results obtained at 600°C shows a rather high number of components. Some samples exhibit a broad band in the X-ray diffractograms assigned to an amorphous phase, showing that under such conditions the reactions still occur, some of the identified phases being non-equilibrium ones.

The formation of a higher number of compounds at 600°C is determined by the mechanism of formation of binary compounds containing Bi<sub>2</sub>O<sub>3</sub>. In the Bi<sub>2</sub>O<sub>3</sub>-PbO system the first phase generated at low temperatures is 6Bi<sub>2</sub>O<sub>3</sub>·PbO. As far as the system Bi<sub>2</sub>O<sub>3</sub>-CaO is concerned, at low temperatures, compounds with a higher Bi<sub>2</sub>O<sub>3</sub> content than the equilibrium compounds are generated.

At 700°C the number of phases is lower. The obtained results agree with the literature data [18, 19] according to which in the field rich in Bi<sub>2</sub>O<sub>3</sub> of the system Bi<sub>2</sub>O<sub>3</sub>-PbO-CaO, solid solutions with the lower limit of existence of 40% Bi<sub>2</sub>O<sub>3</sub> are formed. In the field rich in CaO, the compounds 2CaO·PbO<sub>2</sub> and 4CaO·3Bi<sub>2</sub>O<sub>3</sub> were evidenced. In the field rich in PbO, 2CaO·PbO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>·PbO compounds were identified. In the average field of the ternary system 2CaO·PbO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>·CaO were found.



**Fig. 2** Phase relations in the Bi<sub>2</sub>O<sub>3</sub>-PbO-CaO system at 700°C (the fields of solid solutions are mentioned in [18])

The results obtained at 800°C do not differ significantly from those obtained at 700°C. In the samples thermally treated at 800°C the Bi:Pb compounds were not found, due to their melting.

An attempt to represent the phase relations in the Bi<sub>2</sub>O<sub>3</sub>-PbO-CaO system at 700°C led us to the diagram shown in Fig. 2.

## Conclusions

- Non-isothermal and isothermal investigations of the ternary system Bi<sub>2</sub>O<sub>3</sub>-PbO-CaO were carried out.

- The non-isothermal investigations confirmed the complexity of the solid state reactions that occur in the studied system.

- The isothermal investigations showed that binary compounds and solid solutions rich in Bi<sub>2</sub>O<sub>3</sub> are formed; no ternary compounds were identified in the ternary compositions.

- An attempt to record the phase equilibrium diagram of the Bi<sub>2</sub>O<sub>3</sub>-PbO-CaO system, at 700°C, was presented.

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