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Thermoanalytical study of compound formation in the Bi_2O_3–PbO–CaO system[☆]

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Abstract

Previous studies concerning the formation of compounds in binary systems of the type Bi_2O_3–MO and PbO–MO (M–Ca, Sr and Ca + Sr) have shown that the reactions which occur with the highest rate are those between Bi_2O_3 and CaO and between PbO and CaO. This work deals with the competition betweeen PbO and Bi_2O_3 in reaction with CaO, when the three above mentioned oxides coexist.

DTA–TG analysis performed under non-isothermal conditions and X-ray diffraction determinations have shown that the first reaction which occurs is that between Bi_2O_3 and PbO. On increasing the temperature, the compound between Bi_2O_3 and PbO melts, leading in the presence of CaO, to the preferential formation of $2CaO \cdot PbO_2$.

Under non-isothermal conditions, up to 1173 K, in the ternary compositions investigated, the compound $3Bi_2O_3 \cdot 4CaO$ is also formed.

Keywords: Bi_2O_3–PbO–CaO system; DTA–TG; Ternary oxide mixtures; X-ray diffraction

1. Introduction

It is well known that the obtaining of Bi_2O_3-based superconducting materials by solid phase reactions requires successive thermal treatments at various temperatures

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(from 973 K to close to melting point) for a long time (days). This process is complex and may include intermediate non-equilibrium compounds.

In previous work [1] we carried out a non-isothermal study of phase formation in some binary and pseudobinary compounds in the system Bi_2O_3–(Sr, Ca)O–CuO as well as for the 4334 composition. The results indicated that the reactivity of components in systems containing Bi_2O_3 and CaO is much higher than in systems containing CuO and SrO.

In the meantime the presence of PbO is well known to enhance high-T_c superconducting phase formation in the system Bi_2O_3–SrO–CaO–CuO and, at the same time, modifies the steps of formation of the defined compounds [2–7].

This work deals with the study of the competition between PbO and Bi_2O_3 in reaction with CaO, when the three oxides mentioned above coexist.

2. Experimental

2.1. Preparation of mixtures

We started with compositions corresponding to the formation of the following binary compounds: $4Bi_2O_3 \cdot 6PbO$, $2CaO \cdot PbO_2$ and $5Bi_2O_3 \cdot 7CaO$ (a recent study has revised the composition of $5Bi_2O_3 \cdot 7CaO$ to $3Bi_2O_3 \cdot 4CaO$ and its crystal structure was reported in Ref. [8]).

In the composition corresponding to the formation of compound, $2CaO \cdot PbO_2$ part of Pb has been substituted by Bi and in the $5Bi_2O_3 \cdot 7CaO$ composition, part of Bi has been substituted by Pb. General formulae for the studied compositions are:

$2CaO \cdot (Pb_{1-x}Bi_x)O_{2+x}$ where $x = 0$, 0.5 and 0.8, and

$5\{(Bi_{1-y}Pb_y)_2O_{3-y}\} \cdot 7CaO$ where $y = 0$, 0.2 and 0.5.

The starting oxide compositions (mol. %) are presented in Table 1.

The binary compositions have been selected taking into account that the corresponding compounds are the most likely to be formed in the complex mixtures used in order to obtain Bi-based superconducting phases.

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

Sample	Formula	PbO	CaO	Bi_2O_3
A	$4Bi_2O_3 \cdot 6PbO$	60.00	–	40.00
B	$2CaO \cdot PbO$	33.33	66.66	–
B1	$2CaO \cdot (Pb_{0.5}Bi_{0.5})O_{2.5}$	18.18	72.72	9.09
B2	$2CaO \cdot (Pb_{0.2}Bi_{0.8})O_{2.8}$	7.69	76.92	15.38
C	$5Bi_2O_3 \cdot 7CaO$	–	58.33	41.66
C1	$5[(Bi_{0.8}Pb_{0.2})_2O_{2.8}] \cdot 7CaO$	15.38	53.84	30.77
C2	$5[(Bi_{0.5}Pb_{0.5})_2O_{2.5}] \cdot 7CaO$	34.48	48.27	17.24

The dopant contents were chosen according to the fact that in the mixtures used for obtaining the Bi-based superconductors, Bi_2O_3 exceeds PbO. The optimum substitution of Pb for Bi is generally 0.2–0.5 moles [2–7].

The raw materials were p.a. grade oxides and carbonates: Bi_2O_3 (Carlo Erba), PbO–massicote (Fluka) and $CaCO_3$ (Merck). The mixtures analysed were prepared by a dry homogenization technique.

2.2. *Methods of analysis*

DTA and TG analysis of the mixtures were performed up to 1173 K in air with Al_2O_3 as reference, at a heating rate of 2.7 K min^{-1}. An OD-102 Paulik–Paulik–Erdey type derivatograph was used.

X-ray diffractograms have been recorded for samples resulting from non-isothermal treatment under DTA–TGA conditions, up to different temperatures. A HZG-3 diffractometer with the $Co_{K\alpha}$ radiation was used.

3. Results

3.1. *Binary mixtures*

Fig. 1 presents the DTA–TGA curves of mixtures corresponding to binary compound formation in the 673–1173 K range. Preliminary studies have shown below 673 K the reaction between components does not occur.

In order to clarify the binary compound formation the DTA–TGA results were supplemented by X-ray diffraction analysis for phase recognition. The results are presented in Fig. 2 and Table 2 (the phase composition presented in Table 2 corresponds to samples thermally treated up to the temperatures at the end of each temperature range).

3.1.1. Bi_2O_3–PbO *system*

The DTA curve of the mixture corresponding to $4Bi_2O_3\cdot 6PbO$ formation shows three small endothermic effects at 773 K, 798 K and 823 K, followed by two more pronounced endothermic effects at 866 K and 923 K. According to literature data, the last two peaks can be assigned to formation of the mentioned compound and melting, respectively [9].

As DTA–TGA curves show, $4Bi_2O_3\cdot 6PbO$ formation is a complex process, with an endothermic resultant.

The X-ray diffraction pattern of the $4Bi_2O_3\cdot 6PbO$ mixture thermally treated up to 853 K in good agreement with literature data [9] confirming the complete formation of the mentioned compound. Bi_2O_3 and PbO were not identified (Fig. 2a).

3.1.2. PbO–CaO *system*

The DTA curve of the mixture corresponding to the formation of $2CaO\cdot PbO_2$ exhibits two endothermic effects at 978 K and 1008 K, accompanied by a weight loss in

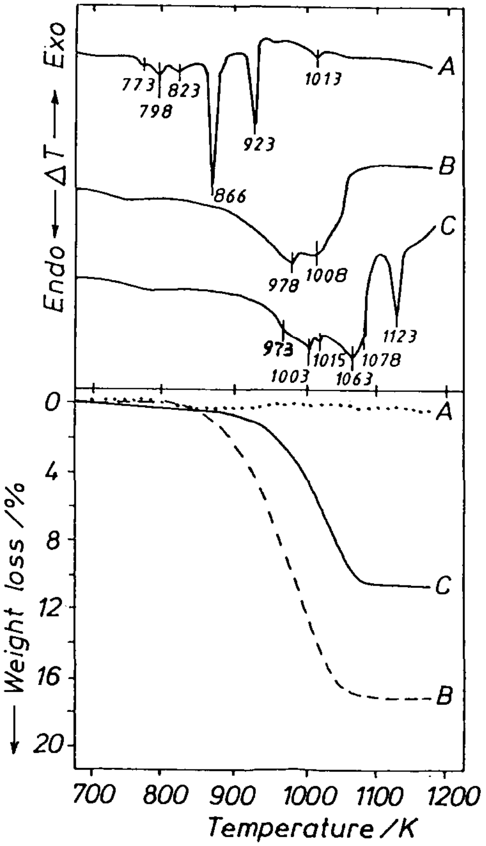

Fig. 1. DTA–TGA curves of the binary compositions: A–$4Bi_2O_3 \cdot 6PbO$, B – $2CaO \cdot PbO_2$, C – $5Bi_2O_3 \cdot 7CaO$

the 803–1073 K range. The recorded effects may be assigned to reaction between PbO and $CaCO_3$, leading to formation of $2CaO \cdot PbO_2$. As the formation of $2CaO \cdot PbO_2$ takes place simultaneously with $CaCO_3$ decarbonation, the last process being stronger than the former, the result is an overall endothermic effect.

The TG curve indicates complete decarbonation of $CaCO_3$ up to 1073 K. Experimental weight loss (17.19%) is lower than the calculated value (20.88%). This could be attributed to oxidation of PbO to PbO_2, during formation of $2CaO \cdot PbO_2$, as has been already mentioned [10].

The phase composition of the samples resulting from thermal analysis up to 853 K under non-isothermal conditions indicates the incomplete formation of $2CaO \cdot PbO_2$, $CaCO_3$ and PbO, being also identified in high quantity (Fig. 2b). At higher temperatures (as shown in Table 2) the only compound obtained in the system is $2CaO \cdot PbO_2$. All the $CaCO_3$ decomposed and reacted with PbO, generating very well crystallized $2CaO \cdot PbO_2$.

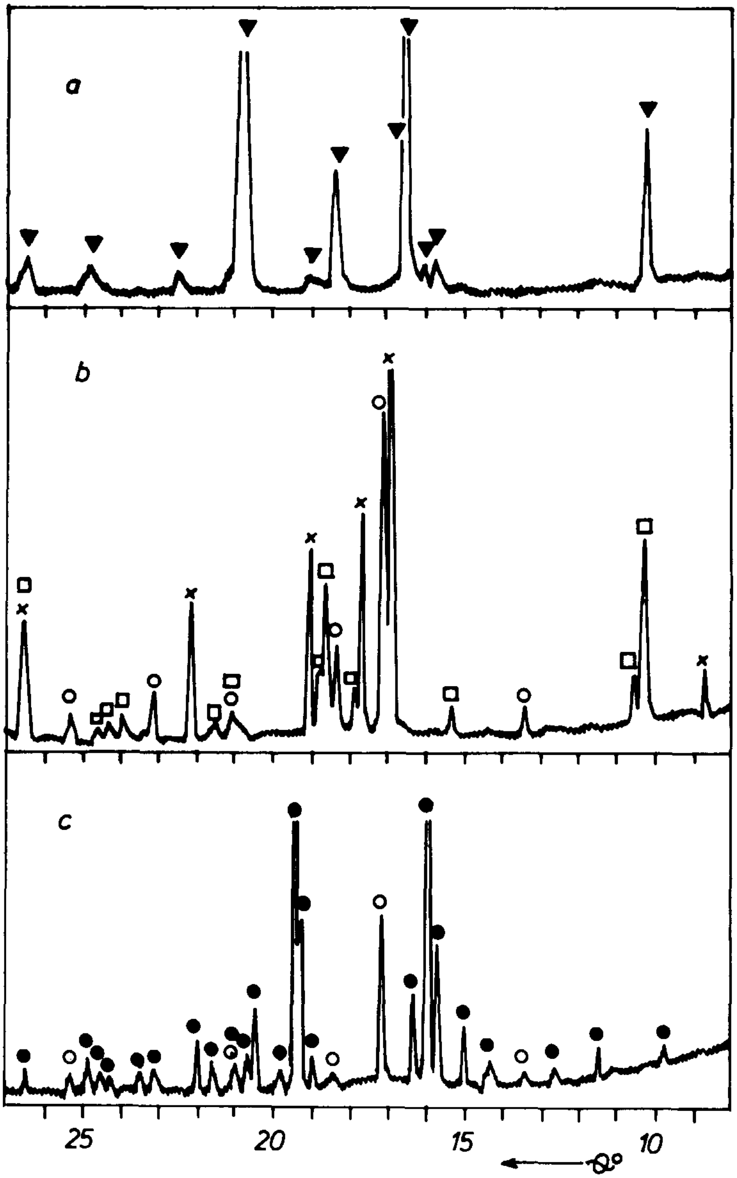

Fig. 2. X-ray powder diffraction for samples A (a), B (b) and C (c) thermally treated to 853 K. ○ - $CaCO_3$, × - PbO massicote, ● - Bi_2O_3 Δ - $3Bi_2O_3 \cdot 2PbO$, ▼ - $4Bi_2O_3 \cdot 6PbO$, □ - $2CaO \cdot PbO_2$.

3.1.3. Bi_2O_3–CaO *system*

The DTA curve of the $5Bi_2O_3 \cdot 7CaO$ composition exhibits three endothermic effects at 1003 K, 1063 K and 1123 K and three shoulders at 973 K, 1015 K and 1078 K, accompanied by a corresponding weight loss in the 833–1093 K range. The recorded

Table 2
DTA–TGA and X-ray diffraction results for the binary compositions

Sample	Starting composition	Temperature range/K	Thermal effects (endo)	Weight loss/%		Phase composition[a]
				Exp.	Calc.	
A	$4Bi_2O_3 \cdot 6PbO$	673–823	773, 798, 823			
		823–853				$4Bi_2O_3 \cdot 6PbO$
		853–1123	866, 923, 1013			Melting
B	$2CaO \cdot PbO$	673–873		17.2	20.88	B, $CaCO_3$, M
		873–993	978			B, $CaCO_3$, M
		993–1123	1008			B
C	$5Bi_2O_3 \cdot 7CaO$	673–873		10.31	10.16	$CaCO_3$, M, Bi_2O_3
		873–973	973			$CaCO_3$, D
		973–1033	1003, 1015			C′, D + $CaCO_3$
		1033–1093	1063, 1078			C, D + $CaCO_3$
		1093–1123	1123			C + $CaCO_3$

[a] B = $2CaO \cdot PbO_2$, C′ = $3Bi_2O_3 \cdot 4CaO$, D = $3Bi_2O_3 \cdot CaO$ M = Massicote.

effects may be assigned to the polymorphic transformation of Bi_2O_3 (1003 K) and to the reaction between Bi_2O_3 and $CaCO_3$ (1063 K and 1123 K). The presence of a great number of thermal effects on the DTA curve suggests that this reaction occurs stepwise. The compound formation effects overlap the stronger $CaCO_3$ decarbonation effect, leading to a global endothermic result. The TG curve indicates the complete decarbonation of $CaCO_3$ up to 1093 K, the experimental weight loss being in agreement with the calculated value (Table 2).

The X-ray diffraction results of mixtures with $5Bi_2O_3 \cdot 7CaO$ starting composition presented in Fig. 2c and Table 2 show that at 853 K and 873 K, only the reactants are identified. The reaction products are observed starting at 973 K. The first identified compound is $3Bi_2O_3 \cdot CaO$ solid solution (Sillen phase) [8], in which the Bi_2O_3/CaO ratio is higher than in the initial composition.

At higher temperatures, $3Bi_2O_3 \cdot CaO$ reacts with excess $CaCO_3$, leading to formation of $3Bi_2O_3 \cdot 4CaO$. At 1073 K both phases coexit; at 1123 K, compound $3Bi_2O_3 \cdot 4CaO$ is, in fact, the only phase observed.

The X-ray diffraction results confirm the complex DTA curve due to the stepwise formation of the compound. $3Bi_2O_3 \cdot 4CaO$.

Comparison of the DTA–TGA curves and the X-ray diffraction results for the three studied compositions clearly shows that the reaction which occurs at the lowest temperature is that between PbO and Bi_2O_3 followed by reaction between PbO–CaO and Bi_2O_3–CaO.

3.2. Ternary mixtures

DTA curves of the studied ternary mixtures in the Bi_2O_3–CaO–PbO system are presented in Figs. 3 and 4 in the same temperature range as for the binary mixtures. The

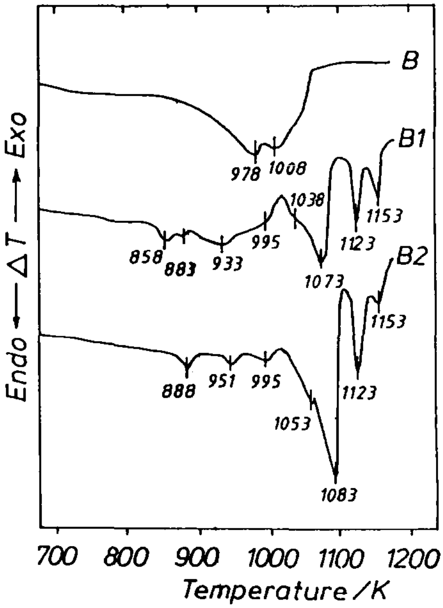

Fig. 3. DTA curves of the ternary mixtures starting with the composition $2CaO \cdot PbO_2$: B1 = B with $x = 0.5Bi$, B2 = B with $x = 0.8Bi$.

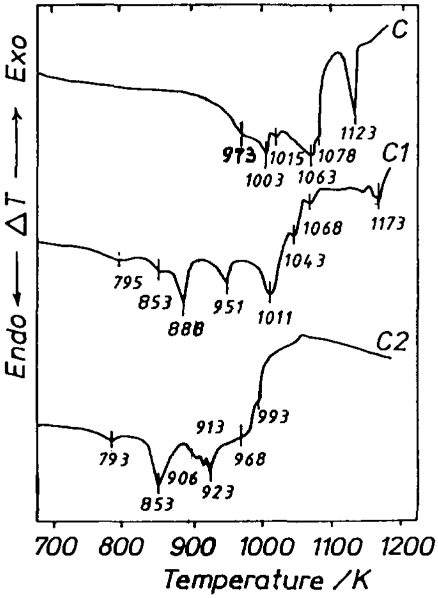

Fig. 4. DTA curves of the ternary mixtures starting with the composition $5Bi_2O_3 \cdot 7CaO$: C1 = C with $y = 0.2Pb$, C2 = C with $y = 0.5Pb$.

results are summarized in Table 3 together with the corresponding X-ray diffraction analysis. The phase composition presented in Table 3 was obtained under the same conditions as for the binary mixtures (Table 2.)

Fig. 3 presents the DTA curves for mixtures corresponding to the formation of $2CaO \cdot PbO_2$ where part of the Pb is substituted by Bi. When Bi_2O_3 coexists with PbO and $CaCO_3$ one can notice several low-temperature endothermic effects (below 973 K). These effects, which do not appear in the DTA curves of the binary PbO–CaO composition, are related to the reaction between Bi_2O_3 and PbO, and also the melting of the compound obtained. Besides $4Bi_2O_3 \cdot 6PbO$, literature data [9, 11] mention several other binary Bi_2O_3–PbO compounds (e.g. $4Bi_2O_3 \cdot 5PbO$ and $3Bi_2O_3 \cdot 2PbO$) which form and melt around 873 K. This is the reason why the exact formula of the binary compound Bi_2O_3–PbO formed in ternary mixtures is difficult to assign.

Thermal effects at 978 K and 1008 K corresponding to formation of $2CaO \cdot PbO_2$ in the binary system are less pronounced and shifted to lower temperatures (933 K and 995 K). The effects at 1063 K and 1123 K corresponding to the reaction between Bi_2O_3–CaO in the binary system are as more evident as the Bi content is higher.

DTA data reveal that, under non-isothermal conditions even in the presence of $CaCO_3$, the first reaction which occurs is that between PbO and Bi_2O_3. The formed compound then melts, so that further reactions take place in the presence of a liquid phase.

Table 3
DTA–TGA and X-ray results for the ternary compositions

Sample	Composition	Temperature range/K	Thermal effects (endo)	Weight loss/%		Phase composition[a]
				Exp.	Calc.	
B1	B, with $x = 0.5$ Bi	673–823		18.70	20.55	G, H, B, $CaCO_3$, M
		823–873	858			$CaCO_3$, M, B
		873–973	883, 933			B, C′
		973–1073	995, 1038, 1073			B, C′
		1073–1123	1103			
B2	B, with $x = 0.8$ Bi	673–873		19.71	20.40	$CaCO_3$, M, α-Bi_2O_3, B, E, F
		873–973	888, 951			$CaCO_3$, B, C′
		973–1093	995, 1053, 1083			B, C′
		1093–1123				B, C′
C1	C, with $y = 0.2$ Pb	673–873	795, 853	9.55	10.22	$CaCO_3$, B, E
		873–973	888, 951			B, C′, E
		973–1073	1011, 1043, 1068			B, C′, E
		1073–1123				B, C′, E
C2	C, with $y = 0.5$ Pb	673–823	793	9.01	10.33	G, H, $CaCO_3$, M, B traces
		823–873	853			$CaCO_3$, B, E
		873–973	906, 913, 923, 968			B, E
		973–1123	993			B, E

[a] B = $2CaO \cdot PbO_2$, C′ = $3Bi_2O_3 \cdot 4CaO$, E = α'_1-$4Bi_2O_3 \cdot 3CaO$, F = α''_1-$4Bi_2O_3 \cdot 3CaO$ M = Massicote G = $3Bi_2O_3 \cdot 2PbO$ H = $6Bi_2O_3 \cdot PbO$

X-ray diffraction analysis (Table 3) shows that addition of 0.5 mole Bi_2O_3 results in greater crystallinity of the $2CaO\cdot PbO_2$ formed at 873 K. At 973 K besides $2CaO\cdot PbO_2$, $3Bi_2O_3\cdot 4CaO$ also appears. At 1073 K and 1123 K the same phase composition is apparent; the intensity of the corresponding diffraction pattern increases due to completion of the reactions. At 1153 K the composition melts.

Increasing of the Bi quantity to 0.8 moles at 873 K results in formation of Bi_2O_3-based solid solutions (α'_1 and α''_1) [8] together with $2CaO\cdot PbO_2$. Starting at 973 K, $2CaO\cdot PbO_2$ and $3Bi_2O_3\cdot 4CaO$ are identified. This phase composition is also present at 1073 K and 1123 K. The endothermic effect at 1153 K may be assigned to the melting of the composition.

Fig. 4 shows the DTA curves of the mixtures with starting composition $5Bi_2O_3\cdot 7CaO$, where part of Bi is substituted by Pb.

DTA curves again show the low temperature effects (in the 793–953 K range) assigned to the formation and melting of the compound in the Bi_2O_3–PbO system. The further effects are less evident and shifted to lower temperatures, as compared with the Pb-free mixture. This could be explained by the presence of the liquid phase in the system.

The phase composition presented in Table 3 shows that the addition of 0.2 moles PbO again leads to the formation of $2CaO\cdot PbO_2$ together with some solid soltion where the Bi_2O_3/CaO ratio is higher than in the initial composition. At 973 K, $3Bi_2O_3\cdot 4CaO$ is also formed. Between 1073 K and 1123 K the mixture of $2CaO\cdot PbO_2$ and $3Bi_2O_3\cdot 4CaO$ coexists and the non-equilibrium phases formed between Bi_2O_3 and CaO diminish. At 1173 K the composition melts.

In the mixture with addition of 0.5 moles PbO, $2CaO\cdot PbO_2$ is formed and non-equilibrium Bi_2O_3–CaO compounds are noticed starting at 873 K. Up to 1123 K, the same phase composition is observed.

In order to clarify the formation of the Bi_2O_3–PbO compounds in the ternary mixtures, the compositions B_1 and C_2 with same degree of substitution ($x, y = 0.5$) were treated under non-isothermal conditions, at low temperature, up to 823 K (below the potential melting temperatures).

The X-ray diffraction analyses of the B_1 and C_2 compositions are presented in Fig. 5 and confirm the formation of $3Bi_2O_3\cdot 2PbO$ and $6Bi_2O_3\cdot PbO$ compounds with patterns in good agreement with literature data [12, 13]. Small amounts of $2CaO\cdot PbO_2$, unreacted $CaCO_3$ and PbO are also identified.

The X-ray diffraction patterns for the two studied compositions (B_1 and C_2) are very similar (in sample B_1 the presence of $2CaO\cdot PbO_2$ is more evident than in sample C_2). In both cases, although the initial Bi/Pb ratio was 1, compounds with higher ratio (3 : 1 and 12 : 1) were obtained, confirming the tendency of Bi_2O_3 at low temperatures, to form, non-stoichiometric compounds with high Bi_2O_3 content. Above 873 K these compounds are no longer observed, due to their melting.

In all the ternary mixtures, studied $CaCO_3$ completely decomposes up to 1073 K. The experimental weight losses presented in Table 3 are lower than the calculated values. The explanation could be the oxidation of PbO to PbO_2 during $2CaO\cdot PbO_2$ formation, as this compound was identified in all the ternary mixtures studied whatever the starting composition.

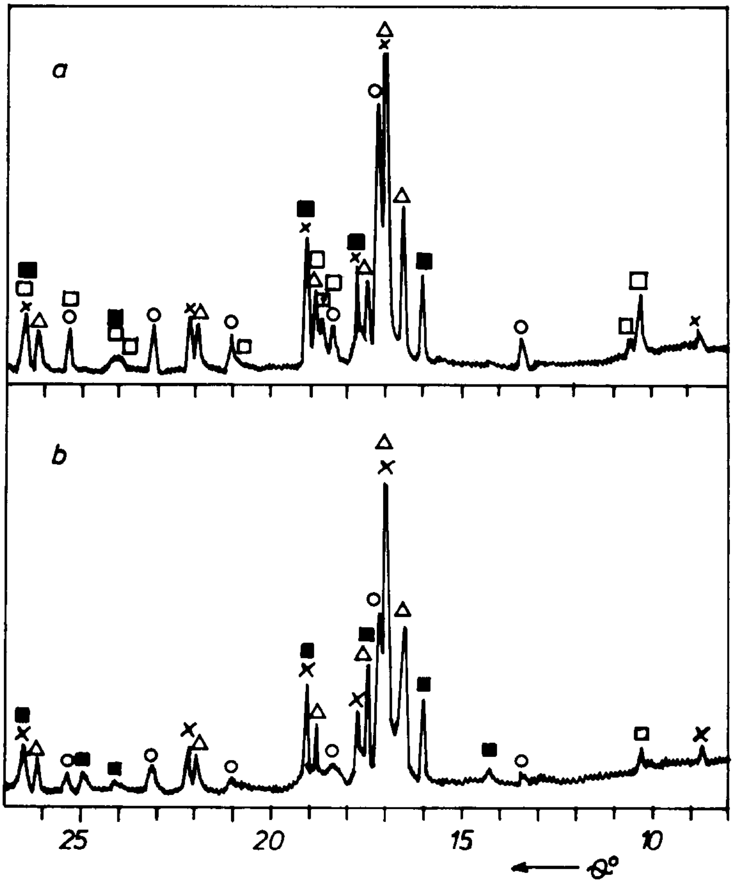

Fig. 5. X-ray diffraction patterns of samples B1 (a) and C2 (b) thermally treated to 823 K: ○ - $CaCO_3$, x - PbO massicote, □ - $2CaO \cdot PbO_2$ Δ - $3Bi_2O_3 \cdot 2PbO$, ■ - $6Bi_2O_3 \cdot PbO$.

The X-ray diffraction results have established that in all studied compositions even under non-isothermal conditions, well-crystallized compounds have been obtained, underlying the high reactivity of the oxides in the studied systems.

No ternary compounds were identified in the ternary mixtures studied.

4. Discussion

The Bi_2O_3–CaO–PbO system has been studied previously in the Bi-rich region. The equilibrium domains of existence of three solid solutions with rhombohedral (β_1 and β_2) and cubic (δ) structure have been determined. These materials have interesting electrical properties, being considered new oxide electrolytes [14–16].

The equilibrium domains of the solid solutions mentioned and the compositions studied in this work are presented in Fig. 6. The ternary compositions we have studied are situated in the CaO-rich region.

Taking into account DTA–TGA and X-ray diffraction results of the binary compositions studied, we established that the compound which is formed at the lowest temperature is $4Bi_2O_3 \cdot 6PbO$, followed by $2CaO \cdot PbO_2$ and $3Bi_2O_3 \cdot 4CaO$. The $4Bi_2O_3 \cdot 6PbO$ compound melts at 923 K.

According our results the following formation mechanism for the binary compounds could be proposed:

$$\text{A. } 4Bi_2O_3 + 6PbO \xrightarrow{853\,K} 4Bi_2O_3 \cdot 6PbO \xrightarrow{923\,K} \text{melting}$$

$$\text{B. } PbO + 2CaCO_3 + 1/2O_2(\text{air}) \xrightarrow{853-1073\,K} 2CaO \cdot PbO_2 + 2CO_2$$

$$\text{C. } 5Bi_2O_3 + 7CaCO_3 \xrightarrow{973-1073\,K} 3Bi_2O_3 \cdot CaO + CO_2 + \text{unreacted}\,(2Bi_2O_3 + 6CaCO_3)$$

$$3Bi_2O_3 \cdot CaO + \text{unreacted}\,(2Bi_2O_3 + 6CaCO_3) \xrightarrow{1073-1123\,K} 3Bi_2O_3 \cdot 4CaO + \text{excess}\ CaCO_3$$

The compounds resulting from the above mentioned, non-isothermal reactions, are highly crystalline due to the high reactivity of the oxides in the corresponding systems.

The high reactivity observed in binary mixtures characterizes the ternary compositions also. In the ternary system the first compounds formed are also those between Bi_2O_3 and PbO, with the compositions $3Bi_2O_3 \cdot 2PbO$ and $6Bi_2O_3 \cdot PbO$ identified at

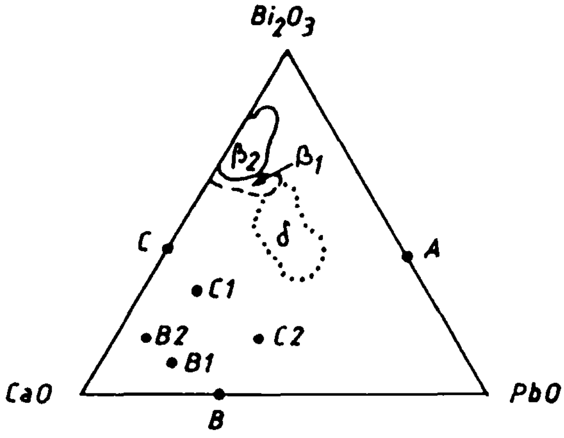

Fig. 6. The equilibrium domains of the Bi_2O_3-rich solid-solution [14–16] and the compositions studied in this work.

823 K. At higher temperatures (873 K) they are not longer observed due to their melting. In the ternary studied compositions, the formation and the melting of binary Bi_2O_3–PbO compounds seem to be shifted to lower temperatures.

The formation of $2CaO \cdot PbO_2$ occurs simultaneously with the melting of the Bi_2O_3–PbO compounds.

In all the ternary mixtures investigated, the formation of $2CaO \cdot PbO_2$ is the prevailing reaction, regardless of the initial composition and of the Bi_2O_3/PbO ratio. The reaction rate is enhanced by the presence of the liquid phase which results from the melting of Bi_2O_3–PbO compounds.

The formation process occurs stepwise. Firstly, solid solution with Bi_2O_3/CaO molar ratio higher than in the initial mixture is obtained. The structure of the Bi_2O_3-based solid solutions depends on the starting composition of the studied mixtures. On increasing the temperature they react with excess $CaCO_3$ leading to the formation of $3Bi_2O_3 \cdot 4CaO$.

No ternary compounds have been identified in the ternary compositions.

5. Conclusions

DTA–TGA and X-ray diffraction investigations have been performed on the system Bi_2O_3–PbO–CaO. In all the investigated mixtures only binary compounds have been identified.

When PbO and Bi_2O_3 coexist with CaO, the first reaction which occurs is that between Bi_2O_3 and PbO. On increasing the temperature this compound melts leading, in the presence of CaO, to the preferential formation of $2CaO \cdot PbO_2$. The last compound formed in the ternary composition is $3Bi_2O_3 \cdot 4CaO$.

The preferential formation and the stability of $2CaO \cdot PbO_2$, over the whole temperature range studied, confirms that this compound represents one of the first steps in the production of high-T_c phases in Bi-based systems containing PbO.

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