THERMOANALYTICAL STUDY OF THE SYSTEMS $PbCO_3$–$SrCO_3$ AND $PbCO_3$–$CaCO_3$

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ABSTRACT

This study concerns the coprecipitation of the $PbCO_3$–$SrCO_3$ and $PbCO_3$–$CaCO_3$ systems in different molar relationships carried out under the same experimental conditions as the $PbCO_3$–$BaCO_3$ system studied previously. The precipitates obtained were studied by chemical analysis, thermogravimetry, differential thermal analysis and X-ray powder diffraction. It has been established that, for the $PbCO_3$–$SrCO_3$ system, solid solutions are obtained under all the different experimental conditions and for the $PbCO_3$–$CaCO_3$ system the precipitates obtained are always mixtures of $PbCO_3$ and $CaCO_3$.

INTRODUCTION

In a previous study on the coprecipitation of lead and barium carbonates [1], it was verified that changes in the precipitation conditions have a definite influence upon the composition and structure of precipitates: amorphous precipitates, cerussite and witherite mixtures or solid solutions are obtained. In the present work the $PbCO_3$–$SrCO_3$ and the $PbCO_3$–$CaCO_3$ systems have been studied under the same experimental conditions as $PbCO_3$–$BaCO_3$, and it has been established that in the case of the $PbCO_3$–$SrCO_3$ system, solid solutions are obtained under all the different experimental conditions. The solid solution $PbCO_3$–$SrCO_3$ has also been studied by Nitta et al. [2]. In the case of the lead–calcium system, the precipitates are mixtures of lead carbonate crystals (cerussite) and calcium carbonate (calcite or calcite and aragonite). Heating of the precipitates in the mother liquors at boiling point for a long time determines the partial or complete dissolution of the calcium carbonate. As far as we know, studies of this system do not exist.

EXPERIMENTAL

Reactants

The reactants were AR quality $Pb(NO_3)_2$, $Sr(NO_3)_2$ and $Ca(NO_3)_2$, Merck, and $(NH_4)_2CO_3$, Carlo Erba.

Preparation of the samples

Aqueous solutions of $Pb(NO_3)_2$ and $Sr(NO_3)_2$, and $Pb(NO_3)_2$ and $Ca(NO_3)_2$, which were precipitated with aqueous $(NH_4)_2CO_3$ solution, were used. An amount of carbonate seven times larger than the theoretical value was used. The Pb/Sr and Pb/Ca molar ratios in the aqueous nitrate solutions were 5/1, 2/1. 1/1, 1/2 and 1/5. The precipitates obtained were filtered through a No. 4 coarse filter, washed with cold distilled water, and dried at room temperature.

Preparation of the samples for the 1/1 M molar ratio for the systems Pb–Sr and Pb–Ca was as follows.

(1) Boiling $(NH_4)_2CO_3$ solution was poured onto the boiling nitrate solutions, and the precipitate obtained was filtered immediately. (Under these conditions, for the $PbCO_3$–$BaCO_3$ system, amorphous precipitates are obtained.)

(2a) The precipitate obtained from (1) was heated in the boiling mother liquors for 30 min.

(2b) The $(NH_4)_2CO_3$ was added slowly to the nitrate solutions both at boiling point; the precipitate so obtained was filtered immediately. (In both cases, for the $PbCO_3$–$BaCO_3$ system, cerussite and witherite mixtures are obtained.)

(3) The precipitate obtained in (1) was heated in the boiling mother liquors for 1.5 h or longer. (Under these conditions, for the $PbCO_3$–$BaCO_3$ system, solid solutions are obtained.)

According to the results obtained for the different precipitates with the relationship 1/1 M, the precipitates obtained from solutions with relationships Pb/Sr and Pb/Ca 5/1, 2/1, 1/2 and 1/5 M have been obtained only under conditions (2a).

Composition of the different precipitates was determined by quantitative chemical analysis. CO_3^{2-}: elemental microanalysis of C, Perkin-Elmer 240 analyzer; Pb^{2+}: complexometric titration with EDTA using Eriochrome Black T as indicator [3]; Sr^{2+}: substitution titration with EDTA with magnesium complexonate using Eriochrome Black T as indicator [3]; Ca^{2+}: complexometric titration with EDTA using calcein as indicator [4].

The precipitates were studied using thermogravimetry, DTA, and X-ray powder diffraction.

Apparatus

TG apparatus

A Chevenard thermobalance, model 93 from Adamel, was used, with a maximum operating temperature of 1250°C. Photographic recording was used. The heating rate was 300°C h^{-1}. The samples were packed into a Staalich Berlin porcelain crucible (A 4/0), and the temperature measured was that of the air surrounding the crucible.

DTA apparatus

This was constructed in the laboratory using a vertical furnace and a temperature regulation system (both Adamel). A sintered alumina holder (19 × 12.5 × 14 mm, shaped in the form of a rectangular parallelepiped divided into two equal cavities, with a wall thickness of 1.5 mm) was used. A differential chromel/alumel thermocouple was used, which was in contact with the sample. The data were recorded using a Methrom Labograph E478. The temperature of the air surrounding the specimen holder was measured. A heating rate of 300°C h^{-1} was employed.

X-Ray powder diffraction

A Philips P.W. 1010 generator was used with a diffractometer P.W. 1050 Geiger counter and CuK_{α_1} radiation with a Ni filter. The data were recorded graphically (P.W. 1051).

RESULTS AND DISCUSSION

PbCO$_3$–SrCO$_3$ system

A study of the precipitates by X-ray diffraction shows that solid solutions are obtained under all precipitation conditions for the PbCO$_3$–SrCO$_3$ system. The Pb/Sr relationship of these precipitates is the same as that of the nitrate solutions from which we obtain the carbonates precipitates, i.e., the precipitation was quantitative in all cases. Lattices of lead and strontium carbonates are very similar, which helps the formation of a single lattice with lead–strontium isomorphic substitutions. Calculation of the unit cell parameters of the precipitates with different Pb/Sr ratios, and their graphic representation indicated a linear variation between the said parameters and molar ratio (Fig. 1).

A study of the thermal behaviour was carried out only with precipitates of 1/1 molar ratio. Figures 2 and 3 show the TG and DTA curves of the coprecipitated sample and the mechanical mixture, the latter employed as a
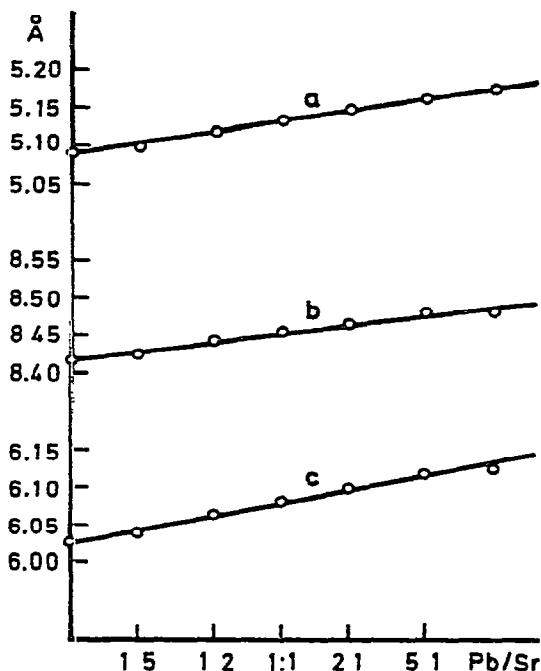
Fig 1 Variation of the unit cell parameters as a function of the Pb/Sr molar ratio.

reference. Figure 2 also shows the TG curve of the coprecipitated sample in a stream of nitrogen (curve 3).

A comparison of the curve of the coprecipitated sample (Fig. 2, curve 1) with that of the mechanical mixture (Fig. 2, curve 2) reveals a great dif-
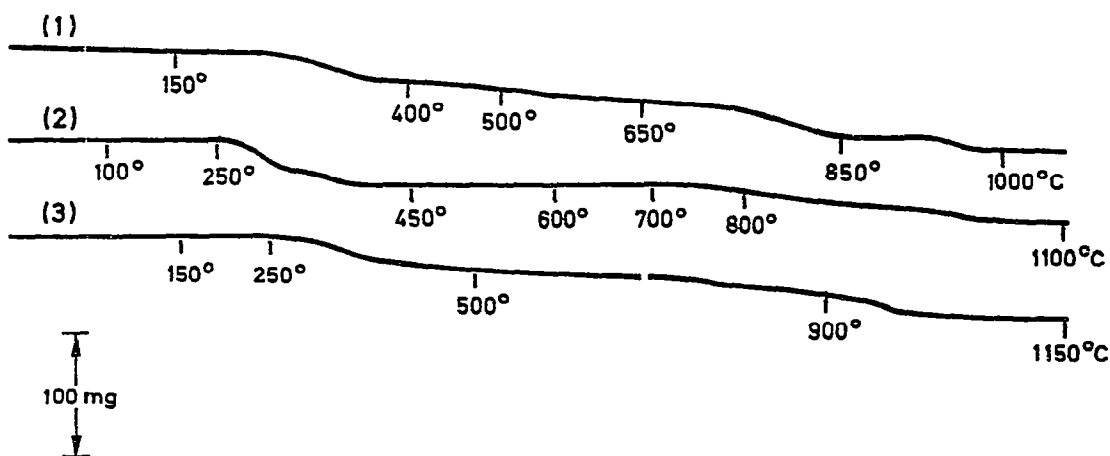

Fig 2. TG curves: (1) coprecipitated sample, sample weight=372.2 mg; (2) mechanical mixture, sample weight=350.3 mg; (3) coprecipitated sample in a stream of N_2, sample weight=328.7 mg.
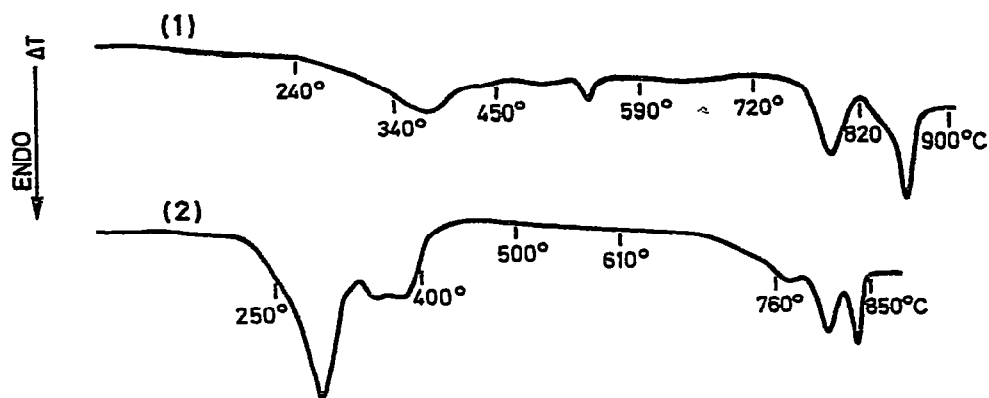
Fig. 3. DTA curves: (1) coprecipitated sample; (2) mechanical mixture.

ference between both curves in the interval 20–650°C. Curve 2 shows the complete transformation of the cerussite into lead oxide carried out between 250 and 450°C, with the intermediate formation of lead dioxycarbonate. On the contrary, in the coprecipitated sample (solid solution) the dioxycarbonate is not formed, also it is necessary to reach 650°C for all the lead to be transformed into PbO. Oxidation of PbO to Pb_3O_4 is not visible in curve 1, but the X-ray diffraction of a sample heated up to 500°C shows the existence of minium. The presence of this compound at 500°C justifies the sudden change which appears around 525°C. On the other hand, this weight loss does not appear in curve 3 (in the stream of nitrogen). Between 650 and 1100°C the curves of the coprecipitated sample and mechanical mixture are similar.

The reactions of formation of metaplumbate and orthoplumbate are stoichiometric: $\epsilon < 2.5$ and 2%, respectively. In general, the DTA curves (Fig. 3, curves 1 and 2) confirm the thermogravimetric results.
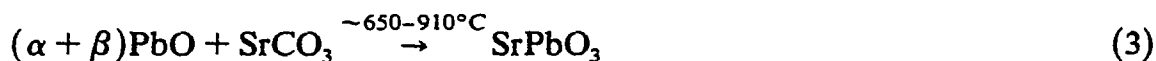
Although the decomposition of the strontium carbonate and the formation of $SrPbO_3$ are simultaneous reactions, the DTA curves present two endothermic peaks between of 720 and 900°C. Analysis by X-ray diffraction of a sample heated at 820°C, the dividing temperature between the two peaks on the DTA curve of the coprecipitated sample, indicates the existence of three compounds: PbO, $SrCO_3$ and $SrPbO_3$, which confirms the simultaneous decomposition of $SrCO_3$ and the formation of $SrPbO_3$.

Examination of samples by X-ray diffraction taken at predetermined points on the TG and DTA curves of the 1/1 M Pb/Sr solid solution, reveals that the following reactions take place in the temperature intervals indicated

$$PbSr(50 \text{ at.}\%)CO_3 \xrightarrow{230-400°C} \alpha\text{-}PbO + SrCO_3 \qquad (1)$$

$$\alpha\text{-PbO} \rightarrow \text{Pb}_3\text{O}_4 \rightarrow \alpha\text{-PbO} \rightarrow \beta\text{-PbO} \tag{2}$$

Reactions (2) are not stoichiometric; they take place in the temperature interval 430–650°C.

$$(\alpha + \beta)\text{PbO} + \text{SrCO}_3 \xrightarrow{\sim650-910°C} \text{SrPbO}_3 \tag{3}$$

$$\text{SrPbO}_3 \xrightarrow{\sim940-1020°C} \text{Sr}_2\text{PbO}_4 + \beta\text{-PbO} \tag{4}$$

Reaction (4) was established only by TG and not by DTA due to the fact that lead oxide resulting from the reaction of the formation of the strontium orthoplumbate melts at those temperatures, attacking the differential thermocouple with which the sample is in contact.

The equimolecular mechanical mixture has a different thermal behaviour in the interval 220–450°C. The successive reactions are

$$\text{PbCO}_3 \xrightarrow{\sim220-325°C} \text{PbCO}_3 \cdot 2\,\text{PbO} \tag{5}$$

$$\text{PbCO}_3 \cdot 2\,\text{PbO} \xrightarrow{\sim325-425°C} \alpha\text{-PbO} \tag{6}$$

As in the case of the mechanical mixture $\text{PbCO}_3 + \text{BaCO}_3$, the lead carbonate in this mechanical mixture behaves in the same way thermally as when it is isolated. The formation of SrPbO_3 and Sr_2PbO_4 takes place according to reactions (3) and (4).

PbCO₃–CaCO₃ system

All the precipitates with the 1/1 M Pb/Ca relation obtained under the different experimental conditions studied are mixtures of lead carbonate and calcium carbonate as is seen from the X-ray powder diffraction diagrams shown in Fig. 4.

Two samples were prepared according to method (1): (a) pouring the ammonium carbonate solution onto the nitrate solution (Fig. 4A), and (b) pouring the nitrate solution onto the carbonate solution (Fig. 4B). In both cases the precipitates are a mixture of cerussite and calcite. But in the second precipitate the cerussite is not so well-crystallized and the calcite presents the line 2θ, 22.85, abnormally intense. This line, corresponding to the *hkl* 102 plane, normally has an $I/I_1 = 12$, and it is one of the characteristic lines of calcite. If the precipitate is prepared according to method (2a), the diagram is a mixture of cerussite, calcite and aragonite (Fig. 4C).

Since the precipitation according to method (1) is quantitative and all the calcium is found in the form of calcite, at least within the limits of detection of X-ray diffraction, it must be admitted that the boiling of precipitates in
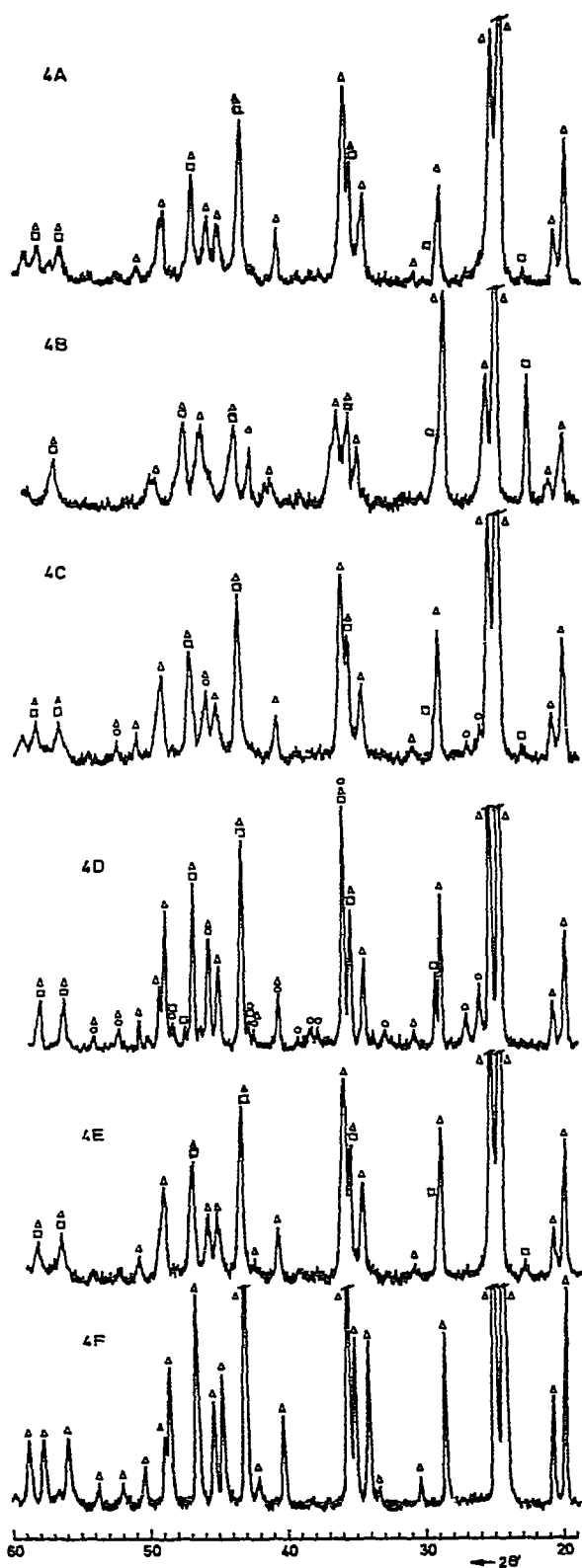
Fig. 4. X-ray diagrams of samples with 1/1 Pb/Ca molar ratio. △, Cerussite; □, calcite; ○, aragonite.

the mother liquors for 30 min determines the partial transformation from calcite to aragonite.

The precipitate prepared according to method (2b) is identical to that from method (2a). As a point of reference, Fig. 4D reproduces the diagram of a 1/1 M mechanical mixture prepared from a cerussite and a calcium carbonate both obtained according to method (2a).

Due to the weak relative intensity of calcium carbonate with respect to lead carbonate, the line 3.86 $I/I_1 = 12$ of the calcite is not visible. However, that line appears in all coprecipitated samples, and it is sometimes even quite intense; the abnormal crystallization of the calcite in those cases is due to the presence of lead in the solution in which it is being formed.

If the digestion of the precipitate in the mother liquors is prolonged more than 1 h, the progressive disolution of calcium carbonate is produced. X-Ray diffraction of samples heated at boiling point for 1 h 10 min, 1 h 30 min and 3 h gives identical diagrams, so only the diagram corresponding to 1 h 30 min of digestion is reproduced here (Fig. 4E), in which only two components appear: cerussite and calcite; this indicates that aragonite is the first to dissolve. If the digestion of the precipitate is prolonged for 7 h, all the calcium carbonate is dissolved, and Fig. 4F corresponds exclusively to the cerussite.

The precipitates of the other molar relationships studied were prepared according to procedure (2a), exclusively as we said at the beginning. Their corresponding diagrams are reproduced in Fig. 5. It is seen that the precipitates with small lead content, Pb/Ca molar ratios 1/5 and 1/2, consist of three components: cerussite, calcite and aragonite. The other two in which the lead is predominant, Pb/Ca 2/1 and 5/1 M, are composed of cerussite and calcite exclusively.

Since the preparation procedure is the same for all of them, we conclude that the excess of lead in the solution is what impedes the evolution calcite → aragonite. As with the system $PbCO_3$–$SrCO_3$, the thermal study was carried out only with 1/1 M Pb/Ca precipitates. In this system there are no notable differences in the thermal behaviour of the coprecipitated samples with relation to the mechanical mixture. In all of them, the decomposition of lead carbonate takes place in two steps, with the formation of lead dioxycarbonate as intermediate, identified by X-ray diffraction in samples heated at 340°C.

Figures 6 and 7 give the TG and DTA curves of the coprecipitated sample and mechanical mixture, both obtained by procedure (2a). The oxidation from α-PbO to minium is only visible in the coprecipitated sample. Figure 7 shows the DTA curve of calcium carbonate obtained by procedure (2a) only.

The transformation of aragonite into calcite around 500°C observed by Mackenzie [5] in natural aragonite is not visible in the curves of Fig. 7,

although aragonite exists in the three samples.

The decomposition reactions of cerussite and the formation of calcium orthoplumbate are quantitative: $\epsilon < 1$ and 2%, respectively.
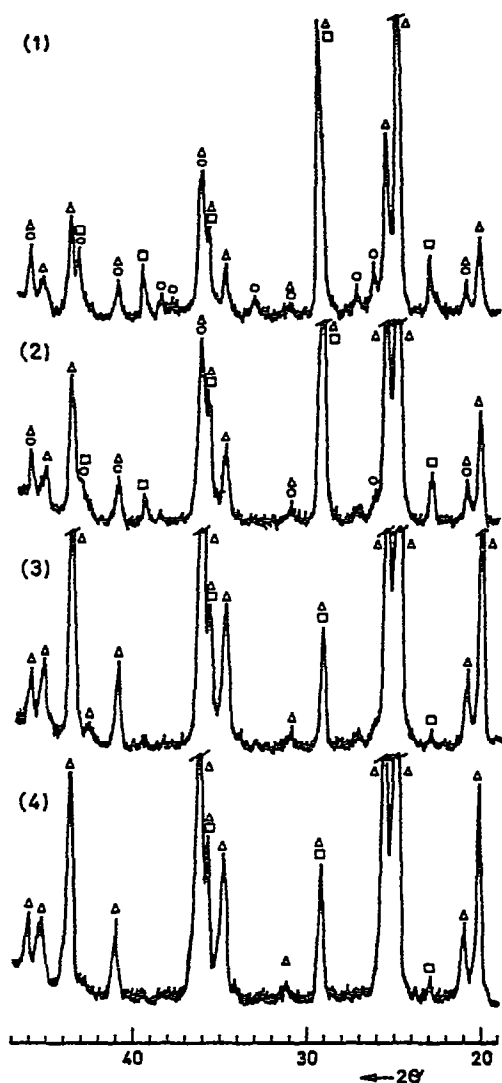

Fig. 5. X-ray diagrams of coprecipitated samples with different Pb/Ca molar ratios : (1) 1/5; (2) 1/2; (3) 2/1; (4) 5/1.

The series of reactions which are produced by heating in the system 1/1 M $PbCO_3/CaCO_3$, and the corresponding approximate temperature ranges are:

$$PbCO_3 + CaCO_3(C + A) \xrightarrow{\sim 240-320°C} PbCO_3 \cdot 2\,PbO + CaCO_3(C + A) \qquad (7)$$
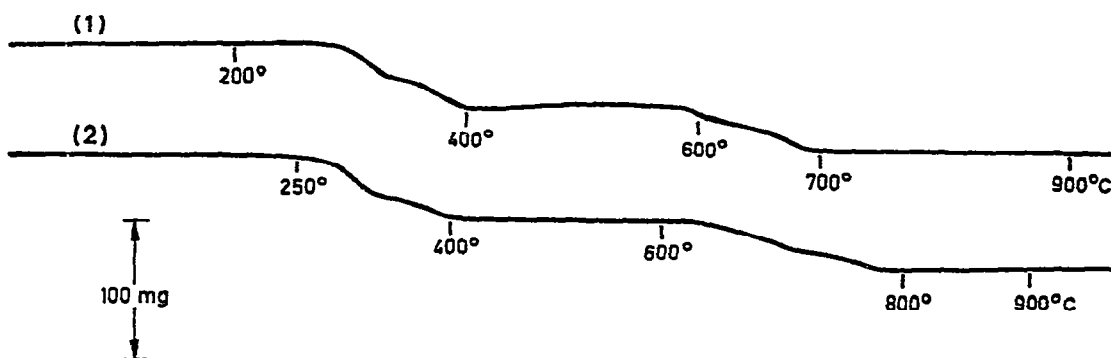
Fig. 6. TG curves: (1) coprecipitated sample, sample weight=363.5 mg; (2) mechanical mixture, sample weight=369.0 mg.

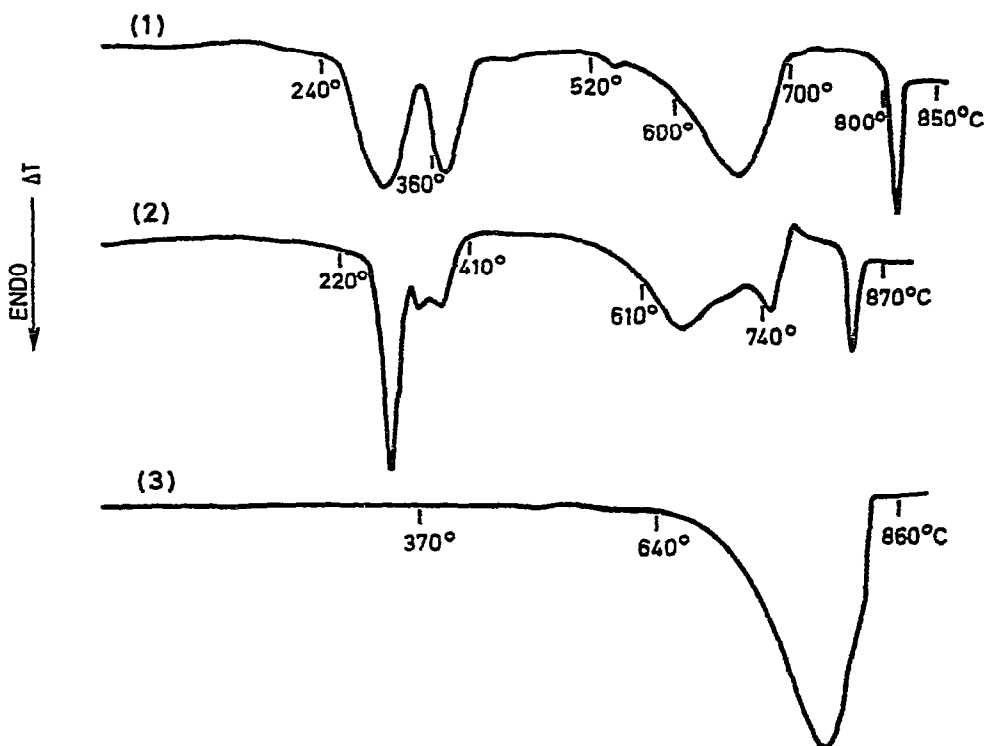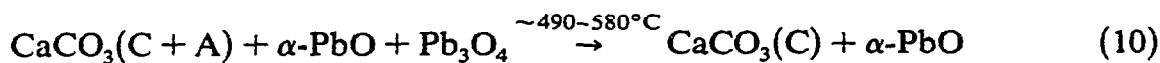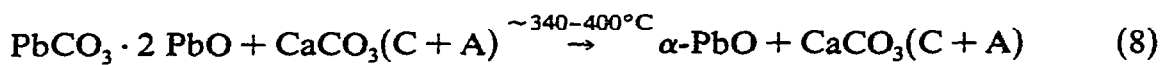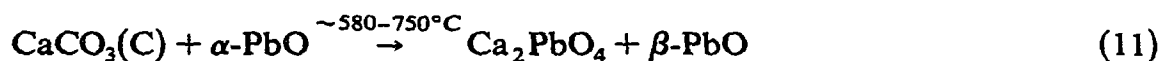$$PbCO_3 \cdot 2\,PbO + CaCO_3(C+A) \xrightarrow{\sim 340-400°C} \alpha\text{-}PbO + CaCO_3(C+A) \qquad (8)$$

$$\alpha\text{-}PbO + CaCO_3(C+A) \xrightarrow{\sim 400-490°C} CaCO_3(C+A) + \alpha\text{-}PbO + Pb_3O_4 \qquad (9)$$

$$CaCO_3(C+A) + \alpha\text{-}PbO + Pb_3O_4 \xrightarrow{\sim 490-580°C} CaCO_3(C) + \alpha\text{-}PbO \qquad (10)$$

Fig. 7. DTA curves: (1) coprecipitated sample; (2) mechanical mixture; (3) CaCO₃.

$$CaCO_3(C) + \alpha\text{-PbO} \xrightarrow{\sim 580-750°C} Ca_2PbO_4 + \beta\text{-PbO} \qquad (11)$$

(C = calcite; A = aragonite). In contrast to the systems $PbCO_3$–$BaCO_3$ and $PbCO_3$–$SrCO_3$, in the system $PbCO_3$–$CaCO_3$ there is no formation of calcium *meta*-plumbate. Also the temperatures of formation of calcium *ortho*-plumbate are much lower—about 700°C.

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