

Note

Thermoanalytical study of coprecipitated lead and barium carbonates

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Following a study on coprecipitation of carbonates, which we began years ago with the alkaline-earth carbonates¹⁻⁴, we present a study of the $\text{PbCO}_3\text{-BaCO}_3$ system. Nitta et al.⁵, employing samples of various Pb/Ba ratios, obtained solid solutions whose decomposition proceeds in a manner similar to that of cerussite, with formation of the intermediate $\text{PbO} \cdot \text{PbCO}_3$. They carried out the precipitation at room temperature by adding aqueous solutions of $\text{Pb}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ to Na_2CO_3 solution. They found adsorbed Na^+ on the precipitates (0.08 mg g^{-1}) by atomic absorption measurements. We also used $\text{Pb}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$, however, while they used Na_2CO_3 , we used $(\text{NH}_4)_2\text{CO}_3$ because its easy volatilization ensures the non-existence of foreign ions in the precipitate. Starting from $\text{Pb}(\text{NO}_3)_2/\text{Ba}(\text{NO}_3)_2$ solutions in the relationship 1/1, changes in the precipitation conditions produce a definite change in the composition and structure of the precipitates. The decomposition mechanism proposed by us is essentially different from that given by Nitta et al.⁵.

EXPERIMENTAL

Reactants

The reactants were $\text{Ba}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ supplied by Merck (A.R. quality) and $(\text{NH}_4)_2\text{CO}_3$ supplied by Carlo Erba (A.R. quality).

Preparation of the samples

We prepared 24 samples by precipitation from aqueous solutions of equimolecular mixtures of $\text{Ba}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ with $(\text{NH}_4)_2\text{CO}_3$ aqueous solution. We employed an amount of carbonate seven times larger than the theoretical one.

We studied how the following variable parameters affect precipitation conditions: (a) temperature (at room temperature and boiling point); (b) aggregation velocity of solutions (abruptly and by continuous dripping at an interval of 2 to 4 sec between drops ($\approx 0.03 \text{ ml}$)); (c) the way in which the said addition is carried out

TABLE I

CONDITIONS OF PRECIPITATION AND THE COMPOSITION AND STRUCTURE OF THE PRECIPITATES OBTAINED

Sample No.	Temp.	Aggregation velocity	Addition way	Digesting time (h)	Digesting temp.	Composition $PbCO_3/BaCO_3$	Structure
1	B.p.	Abruptly	N/C	1.5	B.p.	1/0.980	Solid solution
2	B.p.	Abruptly	C/N	1.5	B.p.	1/0.982	
3	B.p.	Abruptly	N/C	7.5	B.p.	1/0.253	
4	B.p.	Abruptly	C/N	7.5	B.p.	1/0.256	
5	B.p.	Abruptly	N/C	12	B.p.	1/0.137	
6	B.p.	Abruptly	C/N	12	B.p.	1/0.139	
7	B.p.	Abruptly	N/C	0		1/0.975	
8	B.p.	Abruptly	C/N	0		1/0.978	
9	Room temp.	Abruptly	N/C	0		1/1.068	Amorphous
10	Room temp.	Abruptly	C/N	0		1/1.071	
11	Room temp.	Abruptly	N/C	24	Room temp.	1/1.071	
12	Room temp.	Abruptly	C/N	24	Room temp.	1/1.072	
13	B.p.	Abruptly	N/C	0.5	B.p.	1/1.00	Cerussite and witherite mixture
14	B.p.	Abruptly	C/N	0.5	B.p.	1/0.994	
15	B.p.	0.03 ml/2 sec	N/C	0		1/0.967	
16	B.p.	0.03 ml/2 sec	C/N	0		1/0.968	
17	B.p.	0.03 ml/4 sec	N/C	0		1/0.990	
18	B.p.	0.03 ml/4 sec	C/N	0		1/0.975	
19	B.p.	0.03 ml/4 sec	N/C	24	Room temp.	1/1.01	
20	B.p.	0.03 ml/4 sec	C/N	24	Room temp.	1/0.975	
21	Room temp.	0.03 ml/4 sec	N/C	0		1/0.99	
22	Room temp.	0.03 ml/4 sec	C/N	0		1/0.97	
23	Room temp.	0.03 ml/4 sec	N/C	24	Room temp.	1/1.00	
24	Room temp.	0.03 ml/4 sec	C/N	24	Room temp.	1/0.98	

(nitrates solution on carbonate solution and vice versa); (d) digesting time of precipitates in the mother liquors (0, 1.5 h, 7.5 h and 24 h); (e) digesting temperature (at room temperature and boiling point). All precipitates were filtered through a No. 4 coarse filter, washed with cold distilled water and dried at room temperature.

In Table 1, we give conditions of precipitation, the composition and the structure of all precipitates obtained.

Composition of the different precipitates has been determined by quantitative chemical analysis. CO_3^{2-} : elemental microanalysis of C, analyzer Perkin-Elmer 240; Pb^{2+} *: complexometric titration with EDTA using as indicator Eriochrome Black T; Ba^{2+} : substitution titration with magnesium complexonate also using Eriochrome Black T.

The study of precipitates has been carried out by thermogravimetry, DTA and X-ray powder diffraction.

Apparatus

TG apparatus. A Chevenard thermobalance (model 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 Staatlich Berlin porcelain crucible (A 4/0), and the temperature measured was 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 ($19 \times 12.5 \times 14$ 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 and the data recorded using a Metrohm 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 Philipps P.W. 1010 generator was used with a diffractometer P.W. 1050 Geiger counter and $\text{Cu K}\alpha_1$ radiation with a Ni filter. The data was recorded graphically (P.W. 1051).

RESULTS AND DISCUSSION

According to the obtained diffractograms, the different samples may be classified into three groups.

(1) *Amorphous precipitates.* These precipitates are obtained by the abrupt addition of the solutions (nitrates solution on carbonate solution and vice-versa) at

* Concerning this titration, literature about complexometry (by example Schwarzenbach⁶, Bermejo Martinez⁷), suggests that the alkaline-earth metals are titrated together with the Pb^{2+} . Now, in the original papers, Flaschka⁸ and Flaschka and Huditz⁹ definitely say that ions titrated together with the Pb^{2+} , are Ca^{2+} and Mg^{2+} . We have verified that the ion Ba^{2+} does not perturb the Pb^{2+} titration, since it does not form complex with the indicator, under the conditions of this titration.

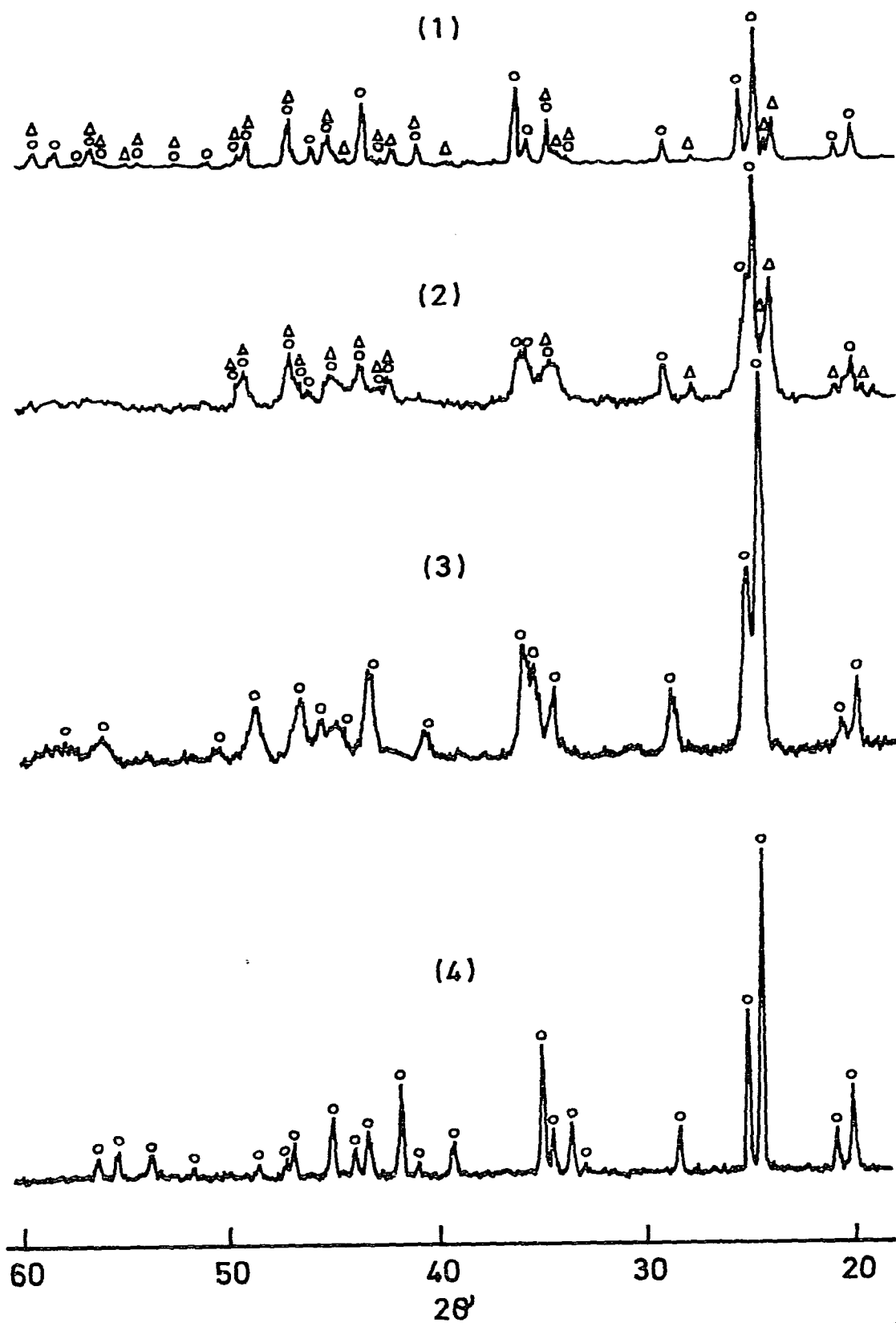


Fig. 1. Δ , BaCO_3 ; \circ , PbCO_3 . (1) Cerussite and witherite mechanical mixture; (2) cerussite and witherite coprecipitated mixture; (3) solid solution; (4) PbCO_3 .

high temperature and without digestion of precipitates in the mother liquors. If the precipitation is carried out at room temperature, with or without digestion of precipitates in the mother liquors, the start of crystallization is observed, but we cannot determine exactly if it is a cerussite and witherite mixture, or a solid solution. The composition of these precipitates is $\text{PbCO}_3/\text{BaCO}_3 = 1/1$ M, according to the quantitative chemical analysis.

(2) *Cerussite and witherite mixtures*, non-perfectly crystallized (Fig. 1). They have been obtained in most of the studied cases: (a) when the precipitate obtained at boiling point by abrupt addition of the solutions is heated in the mother liquors at this temperature for 30 min; (b) they are also obtained when solutions are added slowly or very slowly, with or without digestion of the precipitates in the mother liquors; operating in this manner it was found that no matter what the temperature of solutions, the structure of the precipitates was the same. The cerussite/witherite ratio is equimolecular in all samples.

In Fig. 1, the diffractogram 1 corresponds to an equimolecular mixture obtained by mechanical agitation of PbCO_3 and BaCO_3 , both obtained by us. Diffractogram 2 corresponds to the diagram of sample number 22, one of the 12 giving identical diagrams.

In both diagrams all the characteristic lines of the PbCO_3 and BaCO_3 appear. We can also see the worse crystallization of the coprecipitated mixture respecting the mechanical mixture.

(3) *Solid solution*. Solid solutions are obtained when the precipitates, obtained with heat and by means of mixing solutions abruptly, remain in the mother liquors at the boiling point for 1.5 h or longer. Composition of the solid solution obtained boiling for 1.5 h is $\text{Pb}/\text{Ba} = 1/1$ M. By boiling it for a longer period, BaCO_3 dissolves partially, so the composition for 7.5 h and 12 h is $\text{Pb}/\text{Ba} = 1/0.25$ and $1/0.1$, respectively.

The diffractogram of sample 5 is shown in Fig. 1, diagram 3, (which is identical with the diffractogram shown by sample number 6). The diffractogram of PbCO_3 prepared by us* is shown in diagram 4.

The diagram of the solid solution is similar to the diffractogram of the PbCO_3 with the lattice slightly deformed. Both the chemical analysis and the thermal studies (TG and DTA) show the existence of barium in samples 5 and 6. We also made the diffractogram of a mechanical mixture with a relationship in similar order to the relationship of the formerly mentioned samples, that is $\text{PbCO}_3/\text{BaCO}_3 = 1/0.1$. In this diagram appear all the characteristic lines of both compounds, so we can deduct that in the coprecipitated samples the barium is forming part of the lattice of the PbCO_3 .

* We have prepared the PbCO_3 by mixing hot solutions of $\text{Pb}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{CO}_3$ and keeping the precipitate obtained in the mother liquors at boiling point for a long time. In the literature¹⁰, we had found that solutions must be kept cold in order to avoid formation of basic carbonate, but the diagram of the precipitate obtained by us confirms the formation of PbCO_3 , in spite of the prolonged boiling.

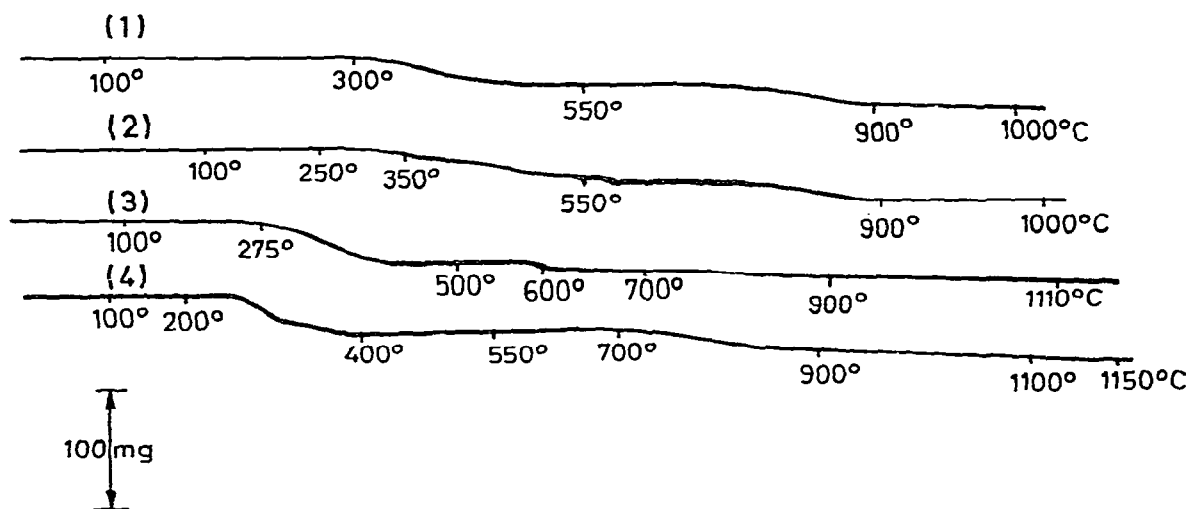


Fig. 2. TG curves. (1) Amorphous precipitate sample weight 290.6 mg; (2) cerussite and witherite coprecipitated mixture, 360.2 mg; (3) solid solution sample weight 413.0 mg; (4) cerussite and witherite mechanical mixture sample weight 347.7 mg.

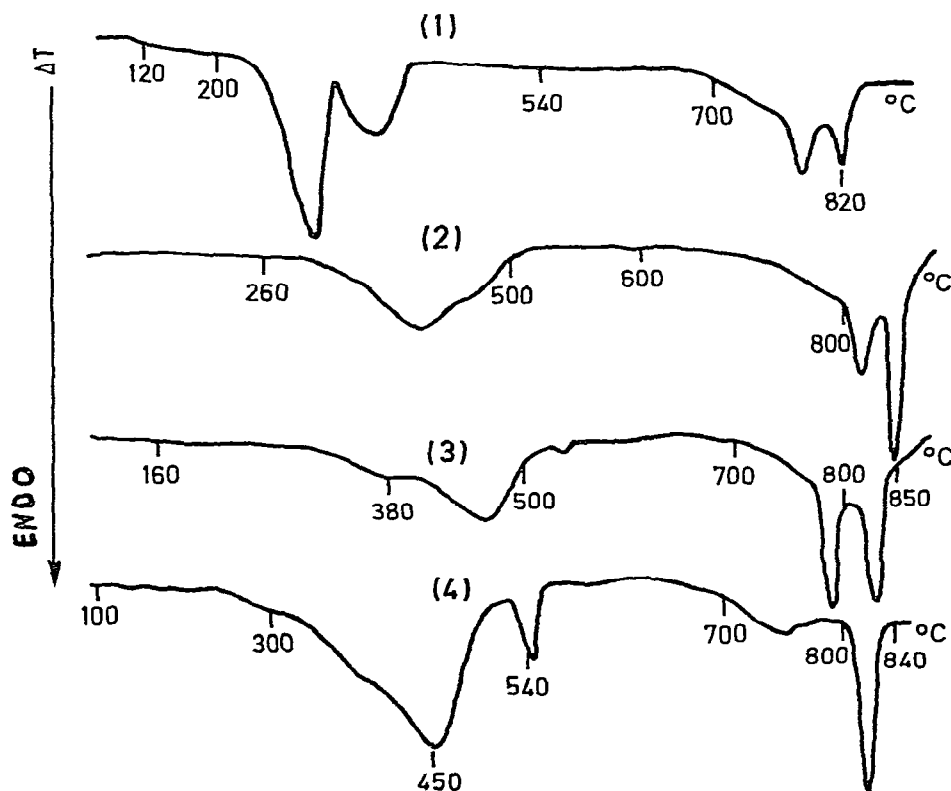
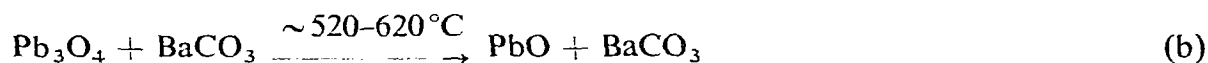
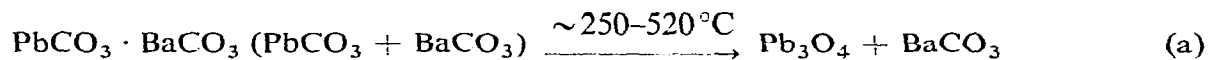


Fig. 3. DTA curves. (1) Cerussite and witherite mechanical mixture; (2) amorphous precipitate; (3) cerussite and witherite coprecipitated mixture; (4) solid solution.

On making the thermal study of the different precipitates and examining samples by X-ray diffraction taken at predetermined points of the TG (Fig. 2) and DTA curves (Fig. 3), it has been found that in the calcination of all of them the same

reactions are produced. These reactions and the approximate temperature intervals for which the reactions take place, are as follows

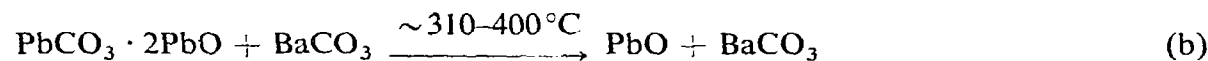
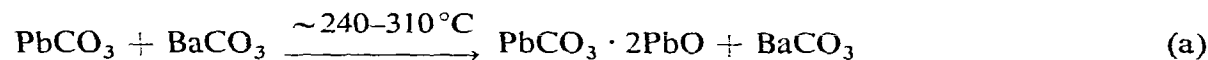


The presence of Pb_3O_4 (sometimes with BaCO_3 alone, and sometimes with red PbO too) is detected by TG in the curves of solid solutions and cerussite and witherite mixtures, but it is not verified in the case of amorphous samples. The transformation $\alpha\text{-PbO} \rightarrow \beta\text{-PbO}$ is detected only by DTA curves of solid solutions and carbonates mixtures.

Reaction (c) corresponding to the formation of BaPbO_3 is registered in DTA curves as two consecutive endothermic peaks.

Reaction (d) due, on one hand, to the high temperatures in which this reaction takes place, and on the other, to the fact that the residue, a Ba_2PbO_4 and PbO mixture, is melted, has been established by TG only.

The thermal behaviour is completely different from that of the mechanical mixture, in which the following reactions are produced; they are the same as that of cerussite decomposition¹¹



Later the formation of BaPbO_3 and Ba_2PbO_4 takes place according to the reactions (c) and (d) aforementioned.

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