Thermochimica Acta, 137 (1989) 177–187
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOANALYTICAL STUDY OF THE SYSTEM Pb^{2+}–Zn^{2+} COPRECIPITATED AS BINARY CARBONATES

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(Received 22 December, 1987)

ABSTRACT

This study concerns the coprecipitation of the cerussite–hydrozincite system in different molar ratios carried out under the same experimental conditions as the Pb–Ba, Pb–Sr and Pb–Ca systems studied previously. It has been established that mixtures of $PbCO_3$ and $Zn_5(OH)_6(CO_3)_2$ are always obtained.

Isothermal decomposition at 200–240 ° C in a stream of oxygen at normal pressure produces the lead oxide Pb_2O_3, generally prepared by the thermal decomposition of PbO_2.

The Pb_2O_3 obtained in the present work crystallizes as a cubic system with laminar morphology.

INTRODUCTION

The preparation of binary carbonates by the method of coprecipitation, applied previously by the present authors for different systems M_1^{2+}–M_2^{2+}, has permitted us to establish that the precipitation conditions have a definite influence upon the composition and structure of precipitates. So, amorphous or crystalline precipitates [1], solid solutions [2], double carbonates [3] or mixtures of simple carbonates [2,4] may be obtained.

On the other hand, coprecipitation also influences the thermal behaviour of a product prepared in this way. Calcination of such products frequently gives compounds different from those obtained starting from the respective binary mixtures [2,4]. Sometimes solid-phase reactions occur between the products of decomposition with formation of different compounds [4].

In this paper we present the results of a study of the coprecipitation of the system Pb^{2+}–Zn^{2+} in molar ratios 1 : 1, 1 : 2 and 2 : 1. The precipitating

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agent and the experimental conditions are the same as those used previously by the present authors [1,2,4] for systems with $M_1 = Pb$ and $M_2 = Ba$, Ca, Sr or Cd.

EXPERIMENTAL

Materials

$Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2CO_3$ were from Merck, AnalaR quality.

Preparation of the samples

The samples were prepared by precipitation from aqueous solutions of mixtures of $Pb(NO_3)_2$ and $Zn(NO_3)_2 \cdot 4H_2O$ with an aqueous solution of $(NH_4)_2CO_3$. A seven-times excess of carbonate was used.

The Pb : Zn molar ratios in the aqueous solutions of the nitrates were 1 : 2, 1 : 1 and 2 : 1.

The precipitates were obtained by adding the aqueous $(NH_4)_2CO_3$ solution, at boiling point, to the aqueous solutions of the nitrates, also at boiling point, and vice versa. The digestion times of the precipitates in the mother liquors were 0, 0.5, 1 and 3.5 h. The precipitates obtained were filtered through a No. 4 coarse filter, washed with cold distilled water and dried at room temperature.

The compositions of the different precipitates was determinated by quantitative chemical analysis: CO_3^{2-} by elemental microanalysis of C, Perkin-Elmer 240 analyser; Pb^{2+} and Zn^{2+} by complexometric titration.

Mechanical mixtures of $PbCO_3 : Zn_5(OH)_6(CO_3)_2$ were prepared in the same molar ratios as the coprecipitated samples, using carbonate precipitates obtained in the same way as the binary carbonates.

Apparatus

TG

A Chevenard thermobalance (model 93) from Adamel was used with photographic recording, heating rate 300 °C h^{-1}. A Mettler TA3000 thermobalance was also used, heating rate 600 °C h^{-1}.

DTA

A homemade system using a vertical furnace and a temperature regulation system, both from Adamel, was used. A differential chromel–alumel thermopar was used. Heating rate, 300 °C h^{-1}.

X-ray powder diffraction

A Siemens D-500 diffractometer was used with a graphite monochromater, K 805 generator and Cu $K\alpha_1$ radiation.

Scanning electron microscopy

A Philips 500 instrument was used. The samples were metallized with gold by sputtering.

RESULTS AND DISCUSSION

The precipitates obtained under the experimental conditions mentioned above were studied by X-ray powder diffraction. This technique indicated that they were composed of mixtures of cerussite $PbCO_3$ and hydrozincite $Zn_5(OH)_6(CO_3)_2$.

Chemical analysis showed that the precipitation of the Pb^{2+} present in the solution was quantitative for all precipitates. This was not the case with zinc.

If the precipitates were filtered immediately after precipitation, chemical analysis showed that practically all the zinc was left in the mother liquors. It is necessary to boil the precipitate in their respective mother liquors in order to precipitate quantitatively all of the Zn. This is also the case for the isolated precipitation of hydrozincite. The optimum digestion times were 0.5 and 1 h. Quantitative precipitation of all the Pb^{2+} and Zn^{2+} present in the solution were 0.5 and 1 h.

Boiling the precipitates in their mother liquors for 3.5 h caused the partial dissolution of hydrozincite, thus altering the molar ratios of the precipitates. The result is the same if the precipitate was prepared by adding the $(NH_4)_2CO_3$ aqueous solution to the aqueous solution of nitrates or viceversa.

Thermal studies

Thermal studies of the coprecipitated samples and mechanical mixtures, prepared by the methods mentioned in the previous section, were carried out in a static atmosphere.

The TG and DTA curves of coprecipitated samples and of mechanical mixtures of molar ratios Pb : Zn = 1 : 1 and 1 : 2 are identical. In Fig. 1, only the TG and DTA curves of coprecipitated sample of molar ratio Pb : Zn = 1 : 1 are shown. From the TG curve it may be observed that the precipitate does not contain water of crystallization. The TG data correspond to the decomposition of both carbonates to their respective oxides. The decomposition of hydrozincite occurred at the same time as that of cerussite; we can also see an intermediate compound, $PbCO_3 \cdot 2PbO$, which has been isolated from the decomposition products of cerussite [5] as well as in those from the mechanical mixtures prepared from the carbonates of Ca, Sr and Ba [1,2].

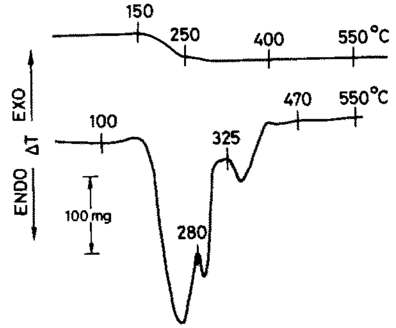


Fig. 1. TG (upper) and DTA (lower) curves of a precipitate with Pb : Zn = 1 : 1. Digestion time 30 min; sample weight 198.7 mg.

The DTA curve agrees with the TG curve, in it is distinguished the decomposition of the hydrozincite from the first stage of the decomposition of the cerussite.

Analysis by X-ray powder diffraction of samples taken at predetermined points of the DTA curve allowed us to establish the reactions that take place during heating. Between 180–280 °C the following reaction occurs:

$$PbCO_3 + \tfrac{1}{5}Zn_5(OH)_6(CO_3)_2 \rightarrow PbCO_3 + PbCO_3 \cdot PbO + PbCO_3 \cdot 2PbO + ZnO \qquad (1)$$

The decomposition of the hydrozincite has finished. The isolated hydrozincite is decomposed over the same temperature interval. According to Mackenzie [6], in 1946 Beck and in 1964 Smykatz-Kloss established that the decomposition of hydrozincite is a single endothermic reaction involving the combined loss of water and carbon dioxide. However, the thermal behaviour of cerussite is different; when cerussite alone is decomposed only dioxycarbonate is obtained.

The thermal behaviour of the coprecipitated sample of cerussite and hydrozincite (eqn. (1)) is similar to that of the mechanical mixture $PbCO_3$ + $CdCO_3$ in the range 200–300 °C [4]; the cerussite is transformed to a mixture of monoxycarbonate and dioxycarbonate.

Between 280–325 °C the following reaction takes place:

$$PbCO_3 + PbCO_3 \cdot PbO + PbCO_3 \cdot 2PbO + ZnO \rightarrow PbCO_3 \cdot PbO + PbCO_3 \cdot 2PbO + ZnO \qquad (2)$$

Finally, between 325–470 °C

$$PbCO_3 \cdot PbO + PbCO_3 \cdot 2PbO + ZnO \rightarrow \alpha\text{-}PbO + ZnO \qquad (3)$$

The TG and DTA curves of the mechanical mixtures (cerussite and hydrozincite), Pb : Zn = 1 : 1 and 1 : 2, are identical to those of the coprecipitated samples, so the mechanical mixtures also showed the stages of the decomposition given in eqns. ((1)–(3)).

Fig. 2, the TG and DTA curves of the coprecipitated sample of molar ratio Pb : Zn = 2 : 1 are shown. The TG curve is similar to that in Fig. 1, but

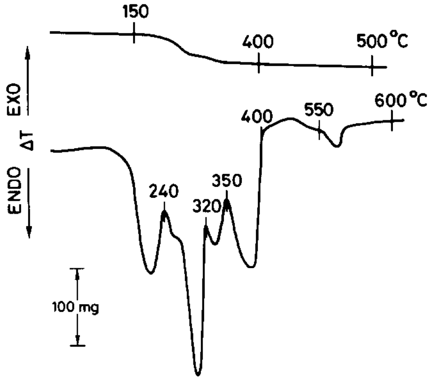


Fig. 2. TG (upper) and DTA (lower) curves of a precipitate with Pb : Zn = 2 : 1. Digestion time 30 min; sample weight 206.5 mg.

the step corresponding to the dioxycarbonate is sharper owing to the greater proportion of cerussite in the precipitate. The DTA curve shows four endothermic peaks, instead of the three peaks of that in Fig. 1.

Analysis by X-ray powder diffraction of samples taken at predetermined points on the DTA curve allows us to establish the reactions that correspond to each endothermic peak.

Between 180 and 240 °C decomposition of hydrozincite takes place

$$PbCO_3 + \tfrac{1}{5}Zn_5(OH)_6(CO_3)_2 \rightarrow PbCO_3 + ZnO \tag{4}$$

Between 240 and 320 °C the transformation of cerussite to oxycarbonates takes place. Reaction (5) is analogous to the reaction (2) for precipitates with molar ratios Pb : Zn = 1 : 1 and 1 : 2

$$PbCO_3 + ZnO \rightarrow PbCO_3 \cdot 2PbO + PbCO_3 \cdot PbO + ZnO \tag{5}$$

Between 320 and 350 °C, the monoxycarbonate is transformed to the dioxycarbonate

$$PbCO_3 \cdot 2PbO + PbCO_3 \cdot PbO + ZnO \rightarrow PbCO_3 \cdot 2PbO + ZnO \tag{6}$$

The transformation of lead monoxycarbonate to the dioxycarbonate was not detected in the samples of molar ratios Pb : Zn = 1 : 1 and 1 : 2.

Between 350 and 400 °C the total decomposition of the sample to a mixture of both oxides occurs

$$PbCO_3 \cdot 2PbO + ZnO \rightarrow \alpha\text{-}PbO + ZnO \tag{7}$$

From 400 to 550 °C an oxidation phenomenon takes place: the transformation of PbO to Pb_3O_4. A small exothermic peak is observed in the DTA curve

$$ZnO + \alpha\text{-}PbO \rightarrow ZnO + Pb_3O_4 + \alpha\text{-}PbO + \beta\text{-}PbO \tag{8}$$

Above 550 °C, for the coprecipitated sample, a small endothermic peak which corresponds to the decomposition of minimum, is observed. Analysis by X-ray powder diffraction of a sample taken at 600 ° C on the DTA curve confirms the reaction between 550 and 600 ° C as

$$ZnO + Pb_3O_4 + \alpha\text{-}PbO + \beta\text{-}PbO \rightarrow ZnO + \beta\text{-}PbO \qquad (9)$$

The thermal behaviour of the mechanical mixture of molar ratio Pb : Zn 2 : 1 was the same as that of the coprecipitated sample, except for the formation of Pb_3O_4 from α-PbO, coming from the decomposition of cerussite. In the DTA curve for the mechanical mixture between 400 and 600 ° C no such phenomenon was observed.

In summary, the present thermal study has shown that the behaviour of the coprecipitated samples and mechanical mixtures is similar.

The Pb–Zn system is similar to the Pb–Ca and Pb–Cd systems [2,4]; in these systems, by coprecipitation, binary mixtures of carbonates are also obtained.

In fact, the oxidation of α-PbO to Pb_3O_4 is only detectable in the coprecipitated Pb–Ca system. The decomposition of cerussite occurs with the intermediate formation of monoxycarbonate and dioxycarbonate, as in the Pb–Cd system (mechanical mixture).

The formation of plumbates, by the reaction of lead oxide with the respective carbonate, takes place in all the systems studied. However, when the dissociation temperatures of the carbonates, coprecipitated with the lead carbonate, are much higher than that of cerussite, two plumbates are obtained successively: first the metaplumbate and then the orthoplumbate are found (Pb–Ba and Pb–Sr systems). In both systems the metaplumbates appear as the only phase, while the orthoplumbates are accompanied by lead oxide (β-PbO).

When the dissociation temperature of the corresponding carbonate is near to that of cerussite, only orthoplumbate is formed (Pb–Ca and Pb–Cd systems). In the latter system, $CdCO_3$ decomposes at the same time as $PbCO_3 \cdot 2\ PbO$. It is possible to favour the formation of Cd_2PbO_4 and to obtain a practically pure compound by isothermal calcination. However, for the Pb–Zn system, hydrozincite is decomposed completely at the temperature at which the decomposition of the cerussite begins, by which stage the plumbates of zinc do not appear.

In spite of this, we carried out isothermal calcination experiments over two temperature ranges: 200–400 ° C and 550–750 ° C.

Isothermal calcination

The isothermal calcination experiments were carried out in a stream of air and in a stream of oxygen (as in the study of the Pb–Cd system). Coprecipitated samples and mechanical mixtures of molar ratio Pb : Zn = 1 : 2, 1 : 1 and 2 : 1 were used for this study.

The temperatures used were 200, 240, 280, 300, 350 and 430 ° C, covering the interval over which the dissociation of the carbonates takes place. We

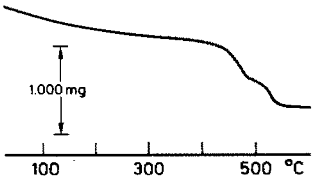


Fig. 3. TG curve of a residue of isothermal calcination in a nitrogen stream (240 ° C 2 h) of a precipitate with Pb : Zn = 1 : 1. Sample weight 30.8 mg.

also carried out three isothermal experiments at 550, 650 and 750 ° C, since at 550 ° C both oxides are already formed. The experiments were left for 0.5, 1, 2, 3, 5 and 24 h.

The residues of isothermal calcination were studied by X-ray powder diffraction. The composition of the residues depended on the gas stream employed. In an air stream, mixtures of α-PbO, ZnO and traces of Pb_3O_4 were found, while at 550 ° C, mixtures of β-PbO and ZnO were obtained. In an oxygen stream, the isotherms at 200 and 240 ° C showed a mixture of ZnO and Pb_2O_3.

From 280 to 430 ° C the residues were a mixture of ZnO and Pb_3O_4. And at 550, 650 and 750 ° C binary mixtures of ZnO and β-PbO were obtained. The isotherms at 200 and 240 ° C required a minimum time of 2 h for the transformations to be completed. If the reaction time is shorter than this, as well as the oxides, lead dioxycarbonate will be formed.

The TG and DTA curves of the residues of isothermal calcination at 200 and 240 ° C in an oxygen stream confirm the presence of Pb_2O_3. In Fig. 3 the TG curve of a residue of isothermal calcination at 240 ° C (2 h) is shown.

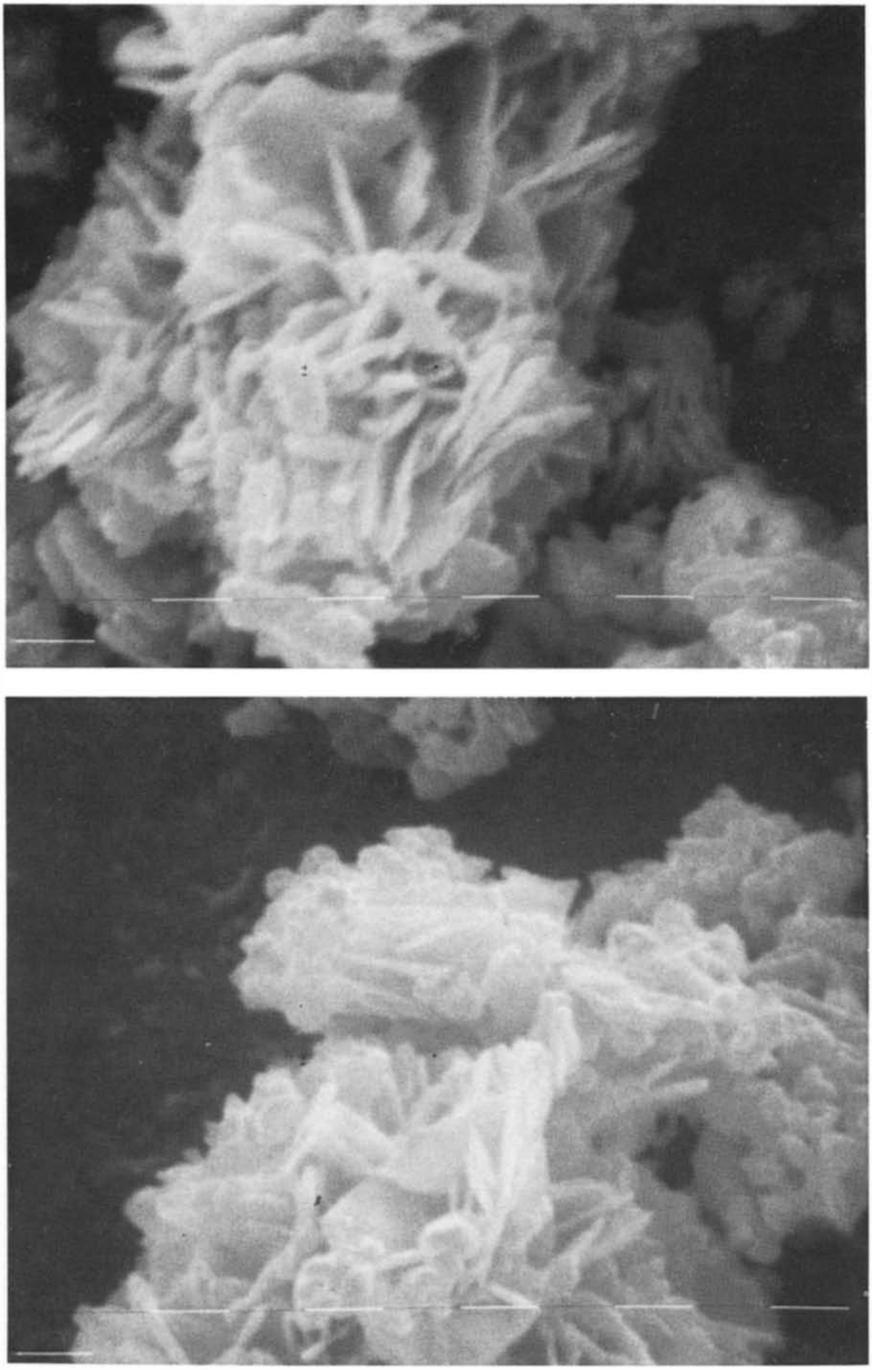
After the loss of a small amount of adsorbed gas, at about 370 ° C the decomposition of the Pb_2O_3 to PbO begins, with the intermediate formation of Pb_3O_4.

The TG data and X-ray powder diffraction results of the residue obtained at 560 ° C confirm the following reaction:

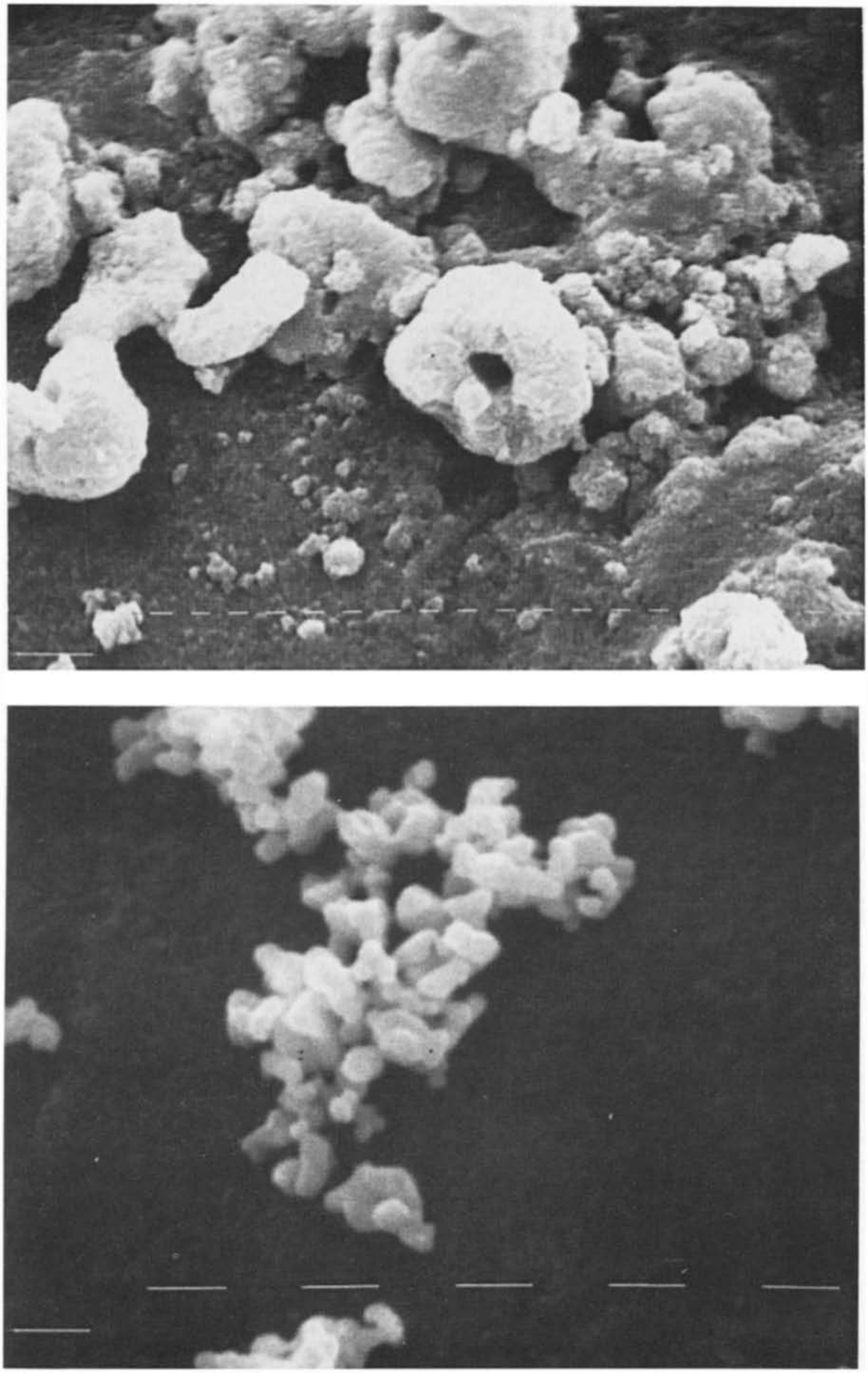
$$\tfrac{1}{2}Pb_2O_3 + ZnO \rightarrow PbO + ZnO + \tfrac{1}{4}O_2$$

We also carried out isothermal calcination, in a stream of oxygen, of the cerussite used with hydrozincite in the preparation of the mechanical mixtures. In these experiments the Pb_2O_3-like intermediate product of the transformation $PbCO_3 \rightarrow \alpha$-PbO was detected, but at temperatures higher than those at which coprecipitated residues are formed and always accompanied by minium.

So, the residue of the isothermal calcination at 260 ° C and 2 h is a mixture of three components: lead dioxycarbonate (major component), Pb_2O_3 and Pb_3O_4 (minor component). At 300 ° C the Pb_2O_3 has disappeared and the residue is dioxycarbonate and minium, and finally, at 350–450 ° C, the residue is exclusively minium.



Scanning electron micrographs (lines represent 1 μm): 1, precipitate Pb : Zn = 1 : 1, calcinated at 240 ° C for 2 h; 2, precipitate Pb : Zn = 1 : 2, calcinated at 240 ° C for 2 h.



Scanning electron micrograph (lines represent 1 μm): 3, hydrozincite, calcinated at 240 ° C for 2 h; 4, cerussite, calcinated at 260 ° C for 2 h.

Therefore, the presence of the hydrozincite, coprecipitated with the cerussite, favours slightly the decomposition of the cerussite and the formation of the intermediate compound Pb_2O_3.

Generally, Pb_2O_3 is prepared by thermal decomposition of PbO_2 [7–11]. Only Spinedi and Gauzzi [7] deduce the formation and quick disappearance of the Pb_2O_3, of the atomic ratio Pb : O calculated from the weight losses that occur in the isothermal calcination of cerussite in an air stream.

Among the authors who have identified Pb_2O_3 by X-ray diffraction, Baroni [10] proposes a cubic cell with $a = 5.50$ Å, while White and Roy [11] suggest a monoclinic cell. The X-ray diffractogram of the Pb_2O_3 obtained in the present study coincides exactly with that given by Baroni.

Scanning electron microscopy allows us to identify Pb_2O_3 in the residues of isothermal calcination (240 ° C, 2 h) of the precipitates of molar ratio Pb : Zn = 1 : 1 and 1 : 2 in a stream of oxygen. Scanning electron micrograph 1 corresponds to the residue of the coprecipitated sample of molar ratio Pb : Zn = 1 : 1. This residue is a mixture of Pb_2O_3 and ZnO. In this micrograph above all, laminar crystals may be observed (see also micrograph 2) corresponding to the residue of the coprecipitated sample of molar ratio Pb : Zn = 1 : 2.

In micrograph 2, near the laminar crystals, other crystals, not easily seen in micrograph 1, may be observed. These are attributed to ZnO since they are similar to the crystals in micrograph 3 which correspond to the residue of isothermal calcination of hydrozincite.

The laminar morphology is typical of Pb_2O_3. These crystals have also been obtained by Clark et al. [9].

Micrograph 4 shows the residue of isothermal calcination at 260 ° C of cerussite. The laminar crystals are not seen, since the major component is $PbCO_3 \cdot 2\ PbO$, according to X-ray powder diffraction.

ACKNOWLEDGEMENT

We thank sincerely Dra. Martín-Patino for obtaining the scanning electron micrographs.

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