

Note

SOME OBSERVATIONS ON THE THERMAL BEHAVIOUR OF LEAD MONOXIDE, PbO

J. MORALES and A. SANCHEZ

Departamento de Química Inorgánica y Departamento de Investigaciones Físicas y Químicas, Centro Coordinado del C.S.I.C., Facultad de Ciencias, Universidad de Sevilla (Spain)

(Received 27 February 1979)

Recently, Russell and Spink [1], in a systematic study of lead zirconate titanate (PZT) ceramics using DTA, have reported different thermal reactions of lead monoxide PbO in the vicinity of 250–400°C. According to these authors, the processes responsible for these reactions are not completely clear. This statement is principally based upon the elimination of the oxidation of PbO, since the same thermograms are obtained both in N₂ and air. Moreover, the X-ray pattern before and after heating through the thermal changes are the same.

On the other hand, Mackenzie [2], quoting different authors, claims that lead(II) monoxide shows an endothermic orthorhombic (yellow PbO, massicot) → tetragonal (red PbO, litharge) transition peak at 480–490°C. However, simple thermodynamic calculations indicate that if such a phase transition occurs, an exothermic effect must be observed as a result of the greater stability of the tetragonal form at low temperature ($\Delta H_f^0 \text{ tet} = -52.34 \text{ kcal mole}^{-1}$, $\Delta H_f^0 \text{ orth} = -51.94 \text{ kcal mole}^{-1}$ [3]).

The above considerations justify the need for additional work to clarify the nature of the thermal activity of lead(II) monoxide. The present note deals with the influence of the history of the sample on the thermal behaviour of PbO, and the study of the intermediates formed during the thermal treatment of this oxide.

EXPERIMENTAL

Three different samples of commercial lead monoxide were used for this study: D'Hemio, r.a. (sample I), Merck-Darmstad (sample II) and Fluka AG, Chemische Fabrik CH-9470 Buchs s.g. (sample III). The X-ray diffraction patterns show that the main polymorph component of these samples is orthorhombic PbO (massicot). From these data it was concluded that the sample of greater purity was that supplied by Fluka. Tetragonal PbO (litharge, sample IV) was prepared following a slightly modified method of Moore and Pauling [4] and X-ray diffraction patterns confirm this polymorph to be of high purity.

Thermal studies were carried out using a Stanton-Redcroft model 673-4 DTA system and a Stanton-Redcroft TG-770 thermobalance, working with static air atmosphere and flowing gas (O_2 , N_2 , CO_2) at about 80 ml min^{-1} . Sample weights of 100–500 mg and a heating rate of $10^\circ\text{C min}^{-1}$ were used throughout every run.

X-Ray diffraction patterns were obtained with a Philips P.W. 1060 X-ray diffractometer, using $CuK\alpha$ radiation, Ni filter, and a scanning rate of 1° min^{-1} .

IR measurements were made using a Perkin-Elmer 577 and KBr discs containing the solid under investigation.

RESULTS AND DISCUSSION

The differential thermal analysis curves of samples I and II obtained with a static air atmosphere, as illustrated in Fig. 1, agree in part with the curve published by Russell and Spink [1], although temperatures as high as the melting point of PbO have not been recorded. However, sample I shows additional complexity as two fluctuations, one exothermic and one endothermic at 460 and 560°C , respectively, have been produced. Sample II, shows two endothermic peaks at 260 and 341°C which are of smaller intensity than those for sample I. Orthorhombic PbO from Fluka, sample III, provides no evidence of thermal reactions since changes of the base line of the DTA curve were not observed. On the other hand, tetragonal PbO (litharge, sample IV) shows two endothermic reactions of small magnitude with peak maxima at 335 and 602°C . Therefore, the data obtained for the various samples of PbO seem to indicate that the measurable thermal activity depends on the history of the sample rather than on the structural nature of the oxide.

Additional information concerning the nature of the changes undergone by the PbO is provided by thermogravimetric analysis curves included in Fig. 1. These TG curves confirm that most of the peaks recorded on DTA curves are related to weight changes of the solid. The differences in temperatures observed between DTA peaks and the corresponding DTG peaks must be connected to a different position of the thermocouple with regard to the samples, since the same experimental conditions have been used for obtaining DTA and DTG curves. It seems that only the endothermic reaction at 600°C shown by sample IV (litharge) could be associated with a phase transition of PbO since no weight changes are observed in this temperature range. Another observation of interest is that the weight of sample III remains unchanged, as expected from the DTA curve. These results clearly demonstrate that the thermal behaviour of PbO reported by Russell and Spink [1], and also confirmed in some of the samples studied in this note, is caused by thermal decomposition of impurities of the oxide coming probably from the method of preparation.

The IR spectrum of sample I showed a strong, broad band at 1385 cm^{-1} and two small bands at 835 and 671 cm^{-1} . These bands correspond to the stronger bands of the carbonate ion, and they are usually assigned to the

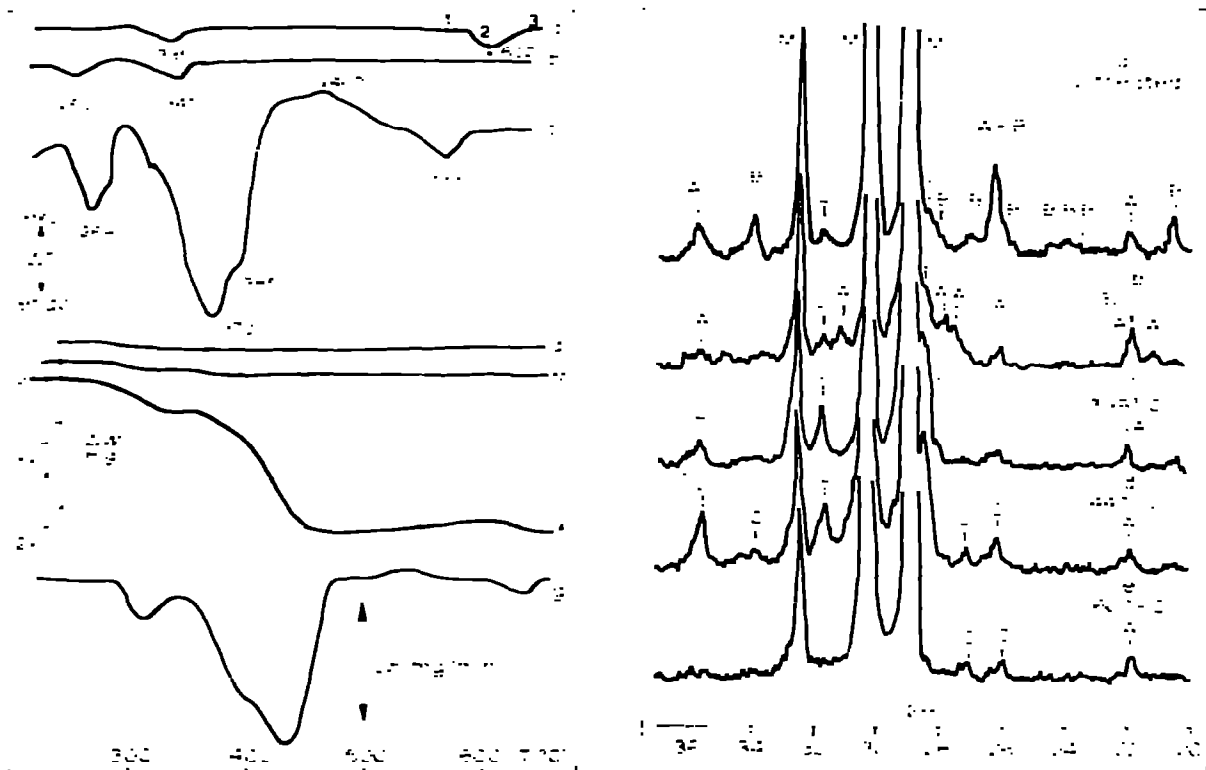


Fig. 1. DTA, TG and DTG curves of different samples of PbO. Curves a and d, sample IV; curves b and e, sample II; curves c, f and g, sample I.

Fig. 2. X-Ray diffraction patterns of PbO, sample I, heat-treated at different temperatures. M, massicot; L, litharge; A, $\text{PbCO}_3 \cdot \text{PbO}$; B, $4 \text{PbCO}_3 \cdot 3 \text{PbO}$; C, Pb_3O_4 .

stretching and bending modes of the carbonate group [5].

According to data given in the ASTM index [6,7], X-ray diffraction patterns for sample I (see Fig. 2, profile a) confirm the existence of two lead oxycarbonates: $4 \text{PbCO}_3 \cdot 3 \text{PbO}$ and $\text{PbCO}_3 \cdot \text{PbO}$. Thus, combining X-ray evidence with the fact that the thermal decomposition of lead oxycarbonates in air occurs in the range 200–450°C [8], we provide a clear explanation of the endothermic peaks at 250 and 250–400°C of PbO, reported by Russell and Spink, and the additional and surprising experimental data described in their paper.

In order to understand better the reactions responsible for the thermal activity shown by the different samples of PbO, a full X-ray diffraction analysis of all the intermediates was performed. The samples for X-ray analysis were taken from DTA runs, removing the residue at selected temperatures on the DTA diagram. In this way DTA results can be directly related to X-ray results, although the residues can be contaminated due to some oxidation or recarbonation of lead oxide during the cooling process. Typical X-ray diffraction results showing the different phase components of the solid are shown in Fig. 2. According to X-ray diffraction data, and in conjunction with the weight-loss results, the first endothermic peak at 269°C can be

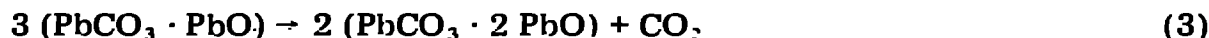
attributed to the following process



while the peaks at 370 and 385°C can be related to the overall process



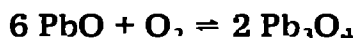
Ball and Casson [9] have identified $\text{PbCO}_3 \cdot 2 \text{PbO}$ as an intermediate of the decomposition of $\text{PbCO}_3 \cdot \text{PbO}$ in N_2 and CO_2 atmospheres. If this intermediate, not detected in the present study, is accounted for in reaction (2) this reaction might thus occur in two stages



which could explain the existence of the two peaks at 370 and 385°C, respectively.

From X-ray diffraction lines, the end product of the decomposition of lead oxycarbonate, $\text{PbCO}_3 \cdot \text{PbO}$, was identified as litharge of small crystallite size and probably with a high microstrain content, since well-defined broadening of the X-ray diffraction lines was observed (see Fig. 2, profile d).

The resultant oxide of high reactivity is probably responsible for the two minor fluctuations, one exothermic and another endothermic at 460 and 560°C, respectively, which are associated with an increase and a decrease in the weight of sample (see Fig. 1, curves c, f, g). Thus, these peaks are considered to be due to the oxidation and subsequent reduction of tetragonal lead monoxide, according to the following reversible reaction



The end products of the reaction (see Fig. 2, profile e) are yellow PbO , massicot, contaminated by Pb_3O_4 , and lead oxycarbonate $\text{PbCO}_3 \cdot \text{PbO}$ coming from the oxidation and recarbonation produced during the cooling process of PbO . This fact explains the reduced thermal activity observed when one repeats the DTA experiment on a once-cycled sample I of PbO .

As already mentioned, litharge, sample IV, shows an endothermic peak at 335°C related to a weight loss (see Fig. 1, curves a and d, respectively). In order to explain this behaviour, attempts were also made to identify the impurities of sample IV. Only a broad band of small intensity at 3360 cm^{-1} was observed, suggesting the presence of OH^- in the crystal structure of PbO . This fact is not surprising since the sample was prepared mixing a suspension of lead(II) nitrate with ammonia. Thus, such a peak at 335°C may be considered as a dehydroxylation process of litharge. Regarding the endothermic effect observed at 602°C (Fig. 1, curve a), X-ray diffraction study gives evidence of the phase transformation, litharge \rightarrow massicot, as can be observed in Fig. 3. In this figure, diffraction patterns of samples of litharge heated at three different temperatures throughout the peak (Fig. 1, curve a, points 1, 2, 3) are included.

No evidence of the phase transformation, massicot \rightarrow litharge, has been obtained throughout this study. However, when heating sample I, a change

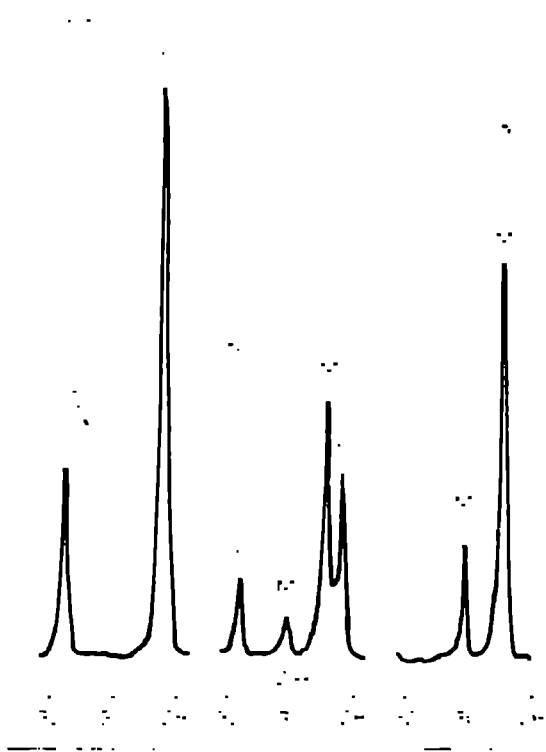


Fig. 3. X-Ray diffraction patterns of PbO, sample IV, heat-treated at different temperatures.

in colour, from yellow to red, is observed in the range 300–400°C. The red colour remains unchanged up to 630°C. However, the initial yellow colour reappears in the cooling process, showing the crystals in their original orthorhombic structure. Structural alterations responsible for the observed changes in colour could be explained using high temperature X-ray technique. Studies on this subject are now in progress in this Department.

The present work clearly shows that most of the thermal activity of lead(II) monoxide reported in the literature comes from impurities of the sample and not from structural changes of the oxide. One must be cautious when DTA is used as an analytical technique to characterize the nature of this material.

ACKNOWLEDGEMENT

Thanks are due to Dr. F. Cabrera for reading the manuscript.

REFERENCES

- 1 V.A. Russell and C.H. Spink, *Thermochim. Acta*, 19 (1977) 45.
- 2 R.C. Mackenzie, *Differential Thermal Analysis*, Academic Press, London and New York, 1970, p. 245.

- 3 K.H. Stern, *J. Phys. Chem. Ref. Data*, 1 (1972) 747.
- 4 W.J. Moore and L. Pauling, *J. Am. Chem. Soc.*, 63 (1941) 1392.
- 5 F.A. Miller and C.S. Williams, *Anal. Chem.*, 24 (1952) 1253.
- 6 ASTM Index, Card No. 17-732.
- 7 ASTM Index, Card No. 17-729.
- 8 S.St.J. Warne and P. Bayliss, *Am. Mineral.*, 47 (1962) 1011.
- 9 M.C. Ball and M.J. Casson, *J. Inorg. Nucl. Chem.*, 37 (1975) 2253.