JOURNAL OF MATERIALS SCIENCE 17 (1982) 2056–2060

Influence of the grinding of $PbCO_3$ on the texture and structure of the final products of its thermal decomposition

J. M. CRIADO, F. GONZALEZ, M. GONZALEZ, C. REAL
Departmento de Quimica Inorgánica, Facultad de Quimica de la Universidad de Sevilla y Departmento de Investigaciones Fisicas y Quimicas, Centro Coordinado del C.S.I.C., Sevilla, Spain

It is shown that the massicot/litharge ratio of the lead monoxide yielded from the thermal decomposition of ground samples of $PbCO_3$ decreases from 1 to 0 by increasing the grinding time of the above salt. The conclusion has been drawn that the PbO keeps a sort of "memory" of the lattice imperfections of the $PbCO_3$ specimen used as precursor. Both the crystalline size and the root-mean square strain data reported in the present paper support this conclusion.

1. Introduction

Lead monoxide, PbO, exists in two well-recognized polymorphic forms, a low-temperature tetragonal modification, red lead oxide (litharge), and a high-temperature orthorhombic phase, yellow lead oxide (massicot), with a transition temperature, under atmospheric conditions, of about 580° C [1]. Moreover, it is well known [2] that massicot is the final product of the thermal decomposition of $PbCO_3$ at about 600° C, and it is also known that this form does not revert to litharge upon cooling the sample to room temperature. This means that the massicot → litharge transformation rate is very small at temperatures lower than 580° C, at which this reaction is thermodynamically favoured. However, it has been shown [2, 3] that the polymorphic transformation of massicot to litharge is achieved by isothermal ball-milling at room temperature with yields of about 70%. A large number of polymorphic transitions induced by mechanical distortion rather than by supplying thermal energy to the samples have been reported in the literature [4–7]. For instance, it has been claimed [8] that comminution of $CaCO_3$ leads to successive calcite–aragonite and aragonite–calcite phase transformations, induced by the displacement of the dislocations produced in the material during the mechanical treatment.

The scope of the present paper is to investigate whether the distortion of the $PbCO_3$ lattice produced by mechanical grinding has any influence on the texture and structure of the PbO resulting from its thermal decomposition. In other words, we have tried to ascertain if the lead monoxide keeps a sort of a "memory" of the lattice imperfections of the $PbCO_3$ sample used as percursor.

2. Experimental procedure

A planetary ball-mill, Colerecord 20 A, with a speed of 450 rpm was used. The mill was equipped with a Corindon jar (capacity, $300\,cm^3$) containing 10 balls of the same material, 18 mm in diameter. $PbCO_3$ Merck AR, was employed and samples of about 10 mg were ground for periods of 0 to 7 h.

Powder diagrams of the samples were obtained with a Philips PW 1060 instrument equipped with a Geiger counter, using CuKα radiation and a Ni filter. Scanning rates of the goniometer ranging from 0.125 to $2^\circ\,min^{-1}$ can be arbitrarily selected.

3. Results

Both commercial and previously-ground samples of $PbCO_3$ were heated at 600° C under atmospheric conditions for a period of 2 h. The loss of weight after this treatment corresponded to that of the quantitative conversion of $PbCO_3$ to lead monoxide.

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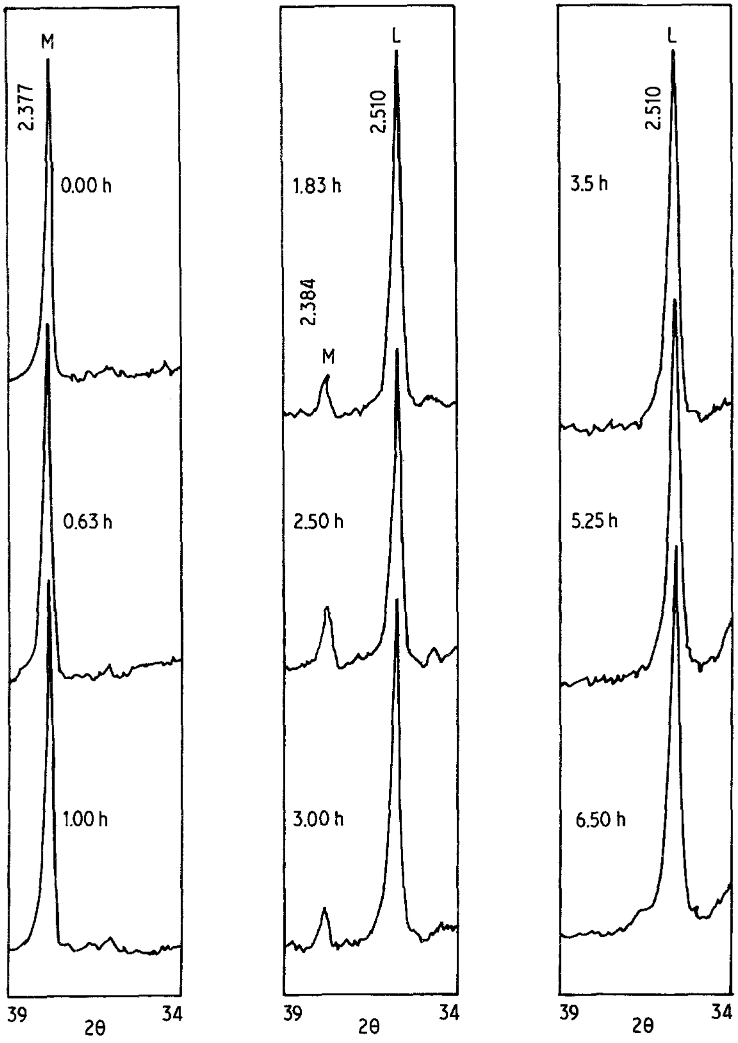

Figure 1 X-ray diffraction patterns of the (020) and (002) reflections of massicot (M) and litharge (L), respectively, in the PbO yielded from $PbCO_3$ sample ground from 0 to 6.5 h. Scanning rate of the goniometer: 1° min^{-1}.

In order to determine the percentage of massicot and litharge, the X-ray diffraction patterns of the samples, shown in Fig. 1, were obtained at room temperature using a goniometer scanning rate of 1° min^{-1}. The lines chosen for comparison [3] were $2\theta = 37.86^\circ$ with $d = 0.2377$ nm for the (020) plane, for massicot, and $2\theta = 35.76^\circ$, with $d = 0.2510$ nm for the (002) plane, for litharge.

The direct comparison method [9] was used. According to this method the ratio between the intensities of the diffraction lines of the two phases, I_M/I_L, is given by

$$\frac{I_M}{I_L} \approx \frac{V_M^{-2}|F|_M^2 P_M\,(1+\cos^2 2\theta/\sin^2\theta\,\cos\theta)_M\,\rho_L X_M}{V_L^{-2}|F|_L^2 P_L\,(1+\cos^2 2\theta/\sin^2\theta\,\cos\theta)_L\,\rho_M X_L}, \qquad (1)$$

where V is the volume of the unit cell, $|F|$ is the structure factor of the reflection considered, P is the multiplicity factor, ρ is the density, X is the weight-fraction of the compound under study and the subscripts M and L refer to the massicot and litharge phases, respectively.

The values calculated in the present paper for the above parameters from the crystallographic structural data given by Wyckoff [10] are shown in Table I. From these data we obtain $I_M/I_L = 1.18\,X_M/X_L$ and, since $X_M + X_L = 1$,

TABLE I Parameters for the calculation of the weight-fraction of massicot and litharge according to Equation 1

Phase	2θ (CuK_α	hkl	V (nm^3)	$\lvert F \rvert^2$	P	ρ ($\mathrm{g\,cm}^{-3}$)
Massicot	37.86	020	0.15261	71609.8	2	9.642
Litharge	35.76	002	0.07922	14066.0	2	9.355

$$X_\mathrm{L} = \frac{1}{1 + 0.85\, I_\mathrm{M}/I_\mathrm{L}}. \tag{2}$$

The values of X_L calculated from the data given in Fig. 1 by means of Equation 2 are plotted in Fig. 2 as a function of the grinding time.

It was concluded in a previous work [11] that the lattice imperfections of $PbCO_3$ increased by increasing the grinding time. Therefore, in order to study the crystallinity degree of the $PbCO_3$, resulting from the thermal decomposition of the former, the profiles of the (020) reflection of massicot and the (002) reflection of litharge of some selected samples were recorded at a scanning rate of the goniometer of 0.125° min^{-1}, as shown in Fig. 3.

Both the crystalline size and the microstrain degree have been derived from the analysis of the profile of a single diffraction line by means of the variance method [12] :

$$W_{2\theta} = \frac{\lambda\, \Delta\, 2\theta}{\pi^2\, D \cos\langle 2\theta\rangle} - \frac{\lambda^2}{4\pi^2\, D^2 \cos^2\langle\theta\rangle} + 4\langle e^2\rangle\, tg^2\langle\theta\rangle, \tag{3}$$

where λ is the wavelength of the X-ray beam, $\langle\theta\rangle$ and $\langle 2\theta\rangle$ are the values of θ and 2θ at the centroid position, D is the crystallite size, $\langle e^2\rangle^{1/2}$ is the root-mean square strain, $\Delta 2\theta$ represents the range of the 2θ value from the X-ray line profile to the centroid and $W_{2\theta}$ is the variance. $W_{2\theta}$ is given by the following expression:

$$W_{2\theta} = \frac{\int_{-2\theta}^{2\theta} (2\theta - \langle 2\theta\rangle)^2 I_{2\theta}\, \mathrm{d}(2\theta)}{\int_{-2\theta}^{2\theta} I(2\theta)\, \mathrm{d}(2\theta)}, \tag{4}$$

where $I(2\theta)$ is the intensity of the line profile at a given position 2θ.

The plot of $W_{2\theta}$ against $\Delta 2\theta$ would give a straight line the slope of which gives the crystallite size and the intercept of which gives the root-mean square strain, once D is known.

The $W_{2\theta}$ values have been calculated as a function of the range $\Delta 2\theta$ by means of a Univac 1108 computer by using a program described by Edwards and Tapman [13] and modified by the

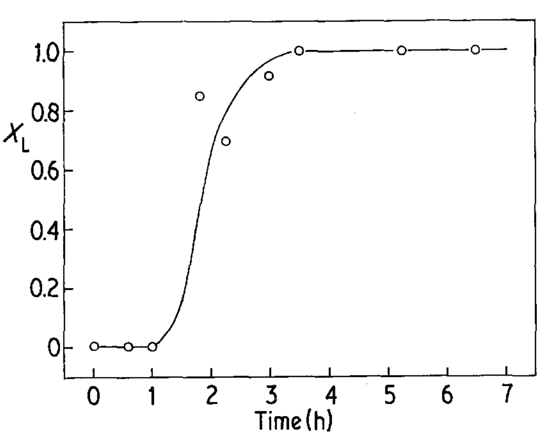

Figure 2 Weight-fraction of litharge in the PbO resulting from the thermal decomposition of ground samples of $PbCO_3$ as a function of the grinding time.

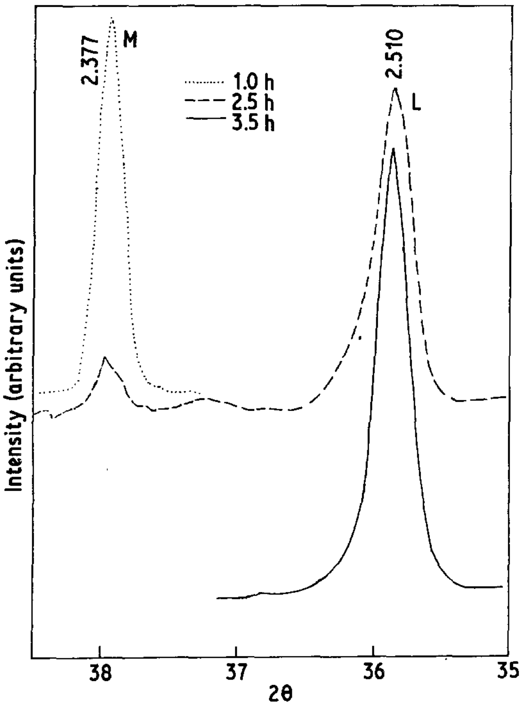

Figure 3 X-ray diffraction patterns of the (020) and (002) reflections of massicot and litharge, respectively, in the PbO yielding from some ground samples of $PbCO_3$. Scanning rate of the goniometer: 0.125° min^{-1}.

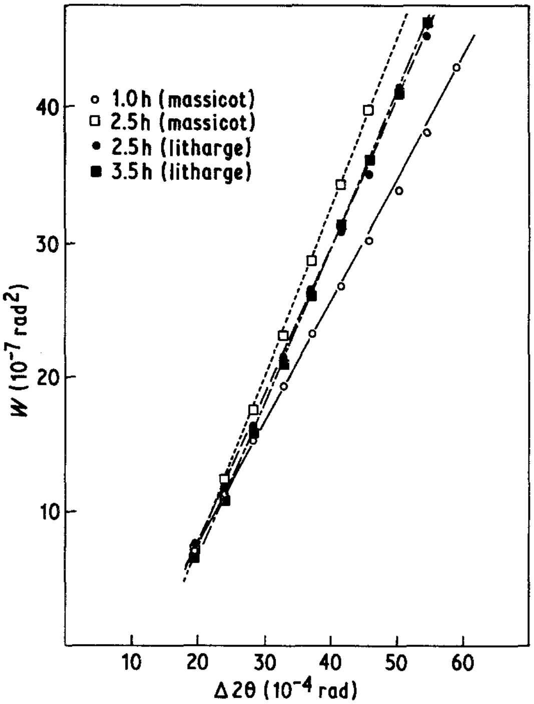

Figure 4 Plots of the variance calculated from data in Fig. 3 as a function of the range, $\Delta 2\theta$.

same authors [14]. This program automatically adjusts the background and corrects for the effect of the so-called "satellite-group" lines on the low-angle side of the $K\alpha_1$ line. The input data were the intensities of the line profile corresponding to values of 2θ taken every 0.05 degrees from the X-ray patterns included in Fig. 3, all over the range of both the diffraction line and the background level. The plots of the values of $W_{2\theta}$ as a function of $\Delta 2\theta$ are shown in Fig. 4.

The values of D and $\langle e^2 \rangle^{1/2}$ calculated from the slope and intercepts of these plots, respectively, by means of the least-square method, are included in Table II.

4. Discussion

Data in Fig. 2 show that mechanical grinding of $PbCO_3$ leads to an increase of the percentage of litharge yielded in the samples heated at 600° C and subsequently cooled down to room temperature. Thus, massicot is the only phase obtained from the as-received $PbCO_3$, while litharge is the only phase yielded from $PbCO_3$ samples ground for more than 3 h.

With regard to the crystallinity degree of the samples, the data in Table II show that the crystalline size decreases while the root-mean square of PbO increases upon increasing time of the $PbCO_3$ used as precursor.

If one assumes [8] that the lattice imperfections act like nucleation sites in phase transformation reactions it would be expected from the above considerations that the higher the comminution time of $PbCO_3$, the higher is the massicot → litharge transformation rate during the cooling of the samples at temperatures lower than the phase transition temperature (580° C). This behaviour explains that the phase compositions of the samples obtained from the thermal decomposition of comminuted $PbCO_3$ moves from 100% of massicot in the gently ground samples, because of the kinetic stabilization of this phase, to 0% of massicot in the strongly comminuted samples, due to thermodynamical stabilization of litharge. This last behaviour is a consequence of the higher concentration of lattice imperfections in these samples, that leads to a higher massicot → litharge transformation rate.

The results reported in the present paper support the conclusion that a solid yielded from the thermal decomposition of another one keeps a sort of memory of the lattice imperfections stored by the compound used as percursor. A similar conclusion was reached in a previous paper with regard to several nickel formiate samples obtained from a solid–gas reaction [15].

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TABLE II Particle size and root-mean square strain of massicot and/or litharge yielded from the thermal decomposition of ground $PbCO_3$ samples

Grinding time of $PbCO_3$ (h)	PbO phases	Particle size (nm)	Root-mean square strain, $\langle e^2 \rangle^{1/2}$ ($\times 10^{-3}$)	Regresion coefficient
1.0	Massicot	20.5	1.10	−0.99882
2.5	Massicot	14.3	1.80	−0.99591
	Litharge	17.5	1.50	−0.99965
3.5	Litharge	15.8	1.61	−0.99990

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Received 5 November
and accepted 10 December 1981