JOURNAL OF MATERIALS SCIENCE 20 (1985) 2119–2127

Calorimetric and X-ray diffraction studies of mechanically activated α-PbF$_2$ in relation to its conversion into β-PbF$_2$

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Calorimetric measurements and X-ray diffraction line-broadening analysis on α-PbF$_2$ reveal that significant amounts of energy and microstrains can be introduced in the solid as a result of grinding. The stored energy is closely related to microstrains. Thermal annealing in the temperature range from 25 to 280° C relieves some of the strains and energy stored and leads to a sample characterized by residual microstrains and an energy stored whose amount depends on the initial mechanical treatment. The remaining stored energy at 295° C is the actual parameter acting on the $\alpha \rightarrow \beta$ transformation and is entirely liberated during this conversion. The initial temperature and heat of this transformation are very sensitive to the microstructure and they are 328° C and 1630 J mol^{-1} for a strain-free material.

1. Introduction

It is known that energy stored by mechanical treatment affects the physico-chemical properties of inorganic materials (see, for example, [1–3]). Mechanical activation studies of a solid therefore imply the characterization of the stored energy or strains related to microstructural distortions as well as the analysis of the resulting changes of the reactivity properties. In order to discuss the effects mechanical treatment can produce on a phase transformation, it is necessary to differentiate between the stored energy used to promote the transformation and the energy dissipated during the foregoing annealing process. In practice, such features can be investigated by calorimetric and X-ray diffraction (XRD) measurements.

The orthorhombic phase of lead fluoride (α-PbF$_2$) becomes transformed into a cubic fluorite structure (β-PbF$_2$) at moderate temperature. The transition temperature seems to be somewhat dependent on the experimental conditions; it varies from 309 to 340° C [4–9]. In connection with this fact, divergent thermodynamical properties of the transformation are reported [10, 11]. In the present paper, the influence of microstructural parameters (modulated by grinding) on the orthorhombic-to-cubic conversion is described. Particular attention is paid to the use of two independent approaches, i.e. calorimetric measurements and XRD line-broadening analysis which lead to complementary results. As a consequence, thermodynamical properties of the transformation are proposed for a strain-free material.

2. Experimental details and method

2.1. Material

Lead fluoride "suprapur" MERCK was used in the present study. Modifications of the microstructural parameters (microstrains and size of diffracting domains) were performed by grinding. The grinding apparatus was a Fritsch ("Pulverisette 2") grinder equipped with an agate mortar.

2.2. X-ray diffraction analysis

In order to characterize the microstructure of the mechanically deformed material, an analysis of the broadening of some XRD lines was performed. This analysis allows deviations from the perfect crystal structure to be measured. Due to the orthorhombic symmetry of the α phase, higher

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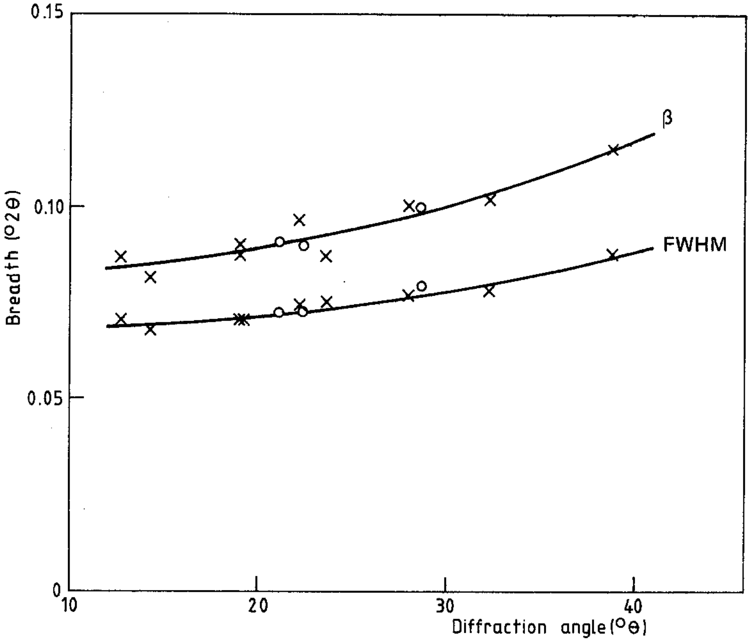

Figure 1 Angular dependence of FWHM and integral breadth β for standard materials with diffraction angle θ. × Si, Au, $Pb(NO_3)_2$; ○ α-PbF_2.

orders of a reflection cannot be measured reliably [12]. Therefore, a single peak method has been used to obtain microstrains and size parameters. Another reason for this procedure is that the number of samples analysed did not justify the time required for a precise treatment. At the expense of some loss in accuracy, the peak-breadth analysis recently published by de Keijser *et al.* [13] seems to be acceptable because its application is both simple and rapid. In this single-line Voigt procedure it is assumed that the Cauchy component of the structurally broadened profile f is solely due to crystallite size and that the Gaussian contribution arises from strains. The estimation of the volume-weighted crystallite size D, as well as a "microstrain" $\tilde{e}$ averaged over all the coherence lengths perpendicular to the diffracting planes are given as follows:

$$D = \frac{\lambda}{\beta_c^f \cos\theta}$$

and

$$\tilde{e} = \frac{\beta_g^f}{4\tan\theta}$$

β_c^f and β_g^f being the integral breadth of the Cauchy and Gaussian components respectively; θ stands for the Bragg angle and λ for the wavelength. Errors concerning the derived quantities and examples have been discussed by the authors [13, 14].

A Siemens type F diffractometer (Cu*K*α radiation) equipped with standard Soller slits and a graphite monochromator in the diffracted beam was used. Two reflections (1 2 1 and 1 0 3) of the diffraction pattern of α-PbF_2 were carefully scanned in steps of 0.01°(2θ) over a wide angular range and fixed-time counting was employed. The background was estimated by calculating a least squares straight line through intensities at the extremities of the measure range; α_2 elimination was carried out by the Rachinger method [15].

In order to correct the experimental line profiles, the instrumental contribution has to be removed; particular attention was therefore paid to the standard sample. Indeed, α-PbF_2 appears to be very sensitive to thermal treatment used during the annealing process, and especially to the cooling rate: slow cooling resulted in a sample which was not completely free from microstrains. This observation is in analogy to the annealing of β-PbF_2. In the latter it has recently been observed that cooling produces defects in crystals [16]. Finally, quick cooling of α-PbF_2 from 300° C to room temperature led to a sample similar to the commercially available product, and was taken as the standard. It was then compared to the other standards. Fig. 1 shows the angular variation of FWHM (full width of the line profile at half maximum intensity) and the integral breadth β for four materials. In spite of differences occurring in the transparencies of the considered solids, no significant deviation is observed for α-PbF_2.

2.3. Calorimetric and surface area measurements

A Calvet microcalorimeter, operating at 25°C, was used for enthalpy solution measurements. The design of this apparatus has been described elsewhere [17]. The procedure used as well as the calibration of this calorimeter have been published previously [18]. The samples of PbF_2 were dissolved in 2 M nitric acid solution. As preliminary experiments have shown, efficient stirring of the solution was required to dissolve the material quickly. The mass of the samples was of about 35 mg and the molality of the final solution of $0.025\,mol\,kg^{-1}$.

The stored energy liberated during annealing and the heat of the transformation α-PbF_2 into β-PbF_2 were registered by "Thermanalyse" microcalorimeter. All experiments were carried out under nitrogen. The heating rates ranged from 0.033 to $4\,°C\,min^{-1}$. The calorimeter was electrically calibrated during the experiments.

The specific surface area was calculated from adsorption measurements of Kr at liquid nitrogen temperature, which were carried out by using a volumetric apparatus equipped with MacLeod gauges. Prior to the measurements, the samples were outgassed for 24 h at room temperature under vacuum (1.33 mPa) in order to remove physisorbed gas.

3. Results

3.1. Effects of milling on the microstructure

Lead fluoride was ground, the grinding time varying from 2 min to 26 h. The XRD analysis has shown that there was no conversion into the β phase, but has revealed an increase of the line broadening with milling time. Only the lines 1 0 3 and 1 2 1 are sufficiently resolved for all the samples to allow a correct application of the single peak Voigt analysis. The microstrains $\tilde{e}_m$ and apparent sizes D_m in directions perpendicular to the planes (1 0 3) and (1 2 1) as a function of the milling time are given in Table I. The crystallite sizes quickly reach a limit which is of 32 and 72 nm in directions perpendicular to (1 0 3) and (1 2 1), respectively. Different values are also observed for the corresponding microstrains. It can therefore be deduced that the mechanical deformation of α-PbF_2 is anisotropic. In the present analysis, the crystallographic directions considered are quite different from one another, the angle between the diffracting vectors 1 2 1 and 1 0 3 is of 53.8°. Changes in the crystallite sizes occurring by milling are confirmed by the BET specific surface areas (Table I), which increase from 0.19 to $1.66\,m^2\,g^{-1}$.

3.2. Stored energy in milled α-PbF_2

The energy stored in milled α-PbF_2 can be evaluated in measuring the enthalpy of dissolution. Indeed, the stored energy ΔU_m is the difference between the measured heats of solution ΔH_s of the milled sample and the strain-free starting material. This results from the dissolution reaction of α-PbF_2 in nitric acid which can be represented by the following equation:

$$\alpha\text{-}PbF_{2\,(c)} + [75\,HNO_3 + 1940\,H_2O] \rightarrow$$
$$[Pb(NO_3)_2 + 2\,HF + 73\,HNO_3 + 1940\,H_2O]$$

The experimental values for ΔH_s and ΔU_m are listed in Table I. As can be seen from the standard deviations of the mean value of ten measurements, the accuracy of the present calorimetric analysis is

TABLE I Changes in α-PbF_2 properties with milling time

t_m (h)	$\tilde{e}_{m(1\,0\,3)} \times 10^3$	$D_{m(1\,0\,3)}$ (nm)	$\tilde{e}_{m(1\,2\,1)} \times 10^3$	$D_{m(1\,2\,1)}$ (nm)	S ($m^2\,g^{-1}$)	ΔH_s ($J\,mol^{-1}$)	ΔU_m ($J\,mol^{-1}$)
0	–	–	–	–	0.19	19 370(220)*	0
0.033	0.48	∞†	1.05	∞	0.30	–	–
0.10	0.83	80	1.88	∞	0.42	–	–
0.50	1.63	39	2.30	135	0.95	–	–
1	1.88	34	2.25	68	1.00	18 530(310)	840
3	2.43	32	2.56	68	1.12	18 070(310)	1300
6	2.53	31	2.58	71	1.26	–	–
9	2.63	31	2.55	66	1.35	–	–
18	3.10	33	2.76	74	1.53	17 820(220)	1550
26	3.40	33	3.20	72	1.66	17 320(430)	2050

*Standard deviations are given in brackets.
†∞ denotes $D > 150$ nm.

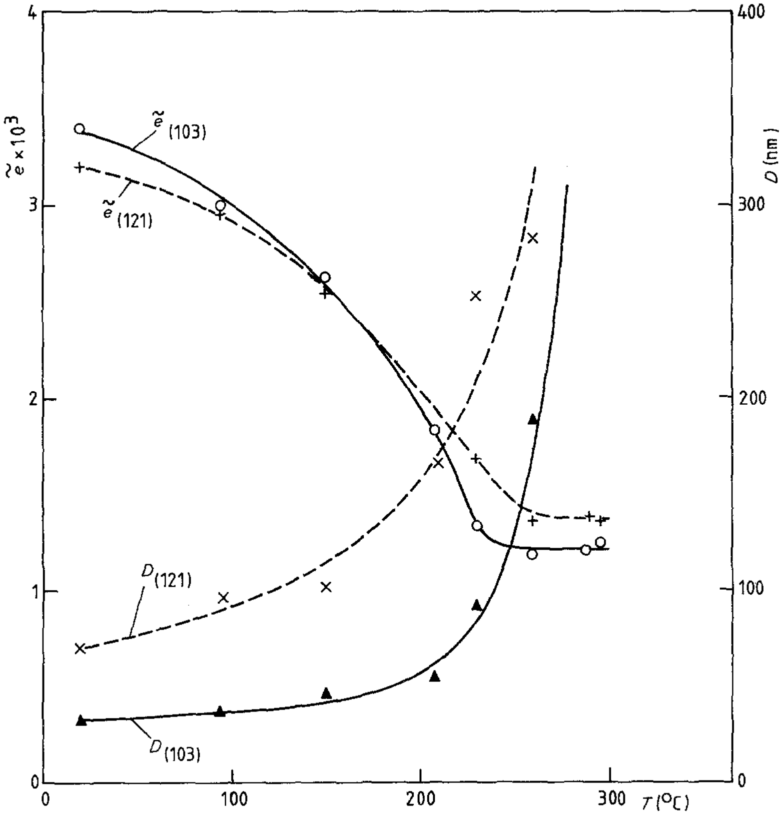

Figure 2 Variations of microstructural properties ($\tilde{e}$ and D) of α-PbF$_2$ milled for 26 h with annealing temperature.

low. Consequently, the terms ΔU_m and ΔH_s were only evaluated for five samples, where significant differences in the amount of microstrains could be observed. Table I shows that ΔU_m grows with the increase of lattice distortions as well as of the specific surface area.

3.3. Microstructural change before the $\alpha \rightarrow \beta$ conversion

The study of the transformation α-PbF$_2 \rightarrow \beta$-PbF$_2$ implies that the samples are heated up to about 300° C. It is well known that strained materials, when subjected to heating, release some stored energy and become more stable with decrease in free energy. Consequently, it is important to analyse the microstructural parameters as well as the amount of energy stored in α-PbF$_2$ just before its transformation. So, one can see if the residual stored energy is used to promote the subsequent reaction.

Heating of the milled lead fluoride powder effected a sharpening of the diffraction lines. The results of the line broadening analysis for sample milled during 26 h are presented in Fig. 2. All the samples were submitted to heating from 20° C up to a temperature T(300° C) with a heating rate of 220° Ch^{-1}, and then quickly cooled in air. As previously mentioned, such a quenching introduces no substantial modification in the microstructure of the standard. The amount of strains relieved increased gradually from 25 to 200° C, and slight modifications in crystallite sizes are observed. A rapid size increase occurs above 200° C, but microstrains remain constant until the transition temperature is reached. It is noticeable that even after 20 h of annealing, the same amount of strains was still retained. Of course, an eventual artefact due to the method has to be discarded. Fig. 3 clearly shows that line broadening is still significant. This figure presents the cosine Fourier transforms of observed line profiles registered under strictly monitored experimental conditions, as a function of the length L (nm), a real distance perpendicular to the reflecting planes.

The amount of microstrains, $\tilde{e}_\mathrm{a}$, in the pretransitional region depends on the initial amount, $\tilde{e}_\mathrm{m}$, in the starting material. In Table II the parameters $\tilde{e}_\mathrm{a}$ and D_a, after anisothermic annealing at 290° C, are given as a function of t_m. The present study nevertheless cannot explain why microstrains are retained between 250° C and the transition

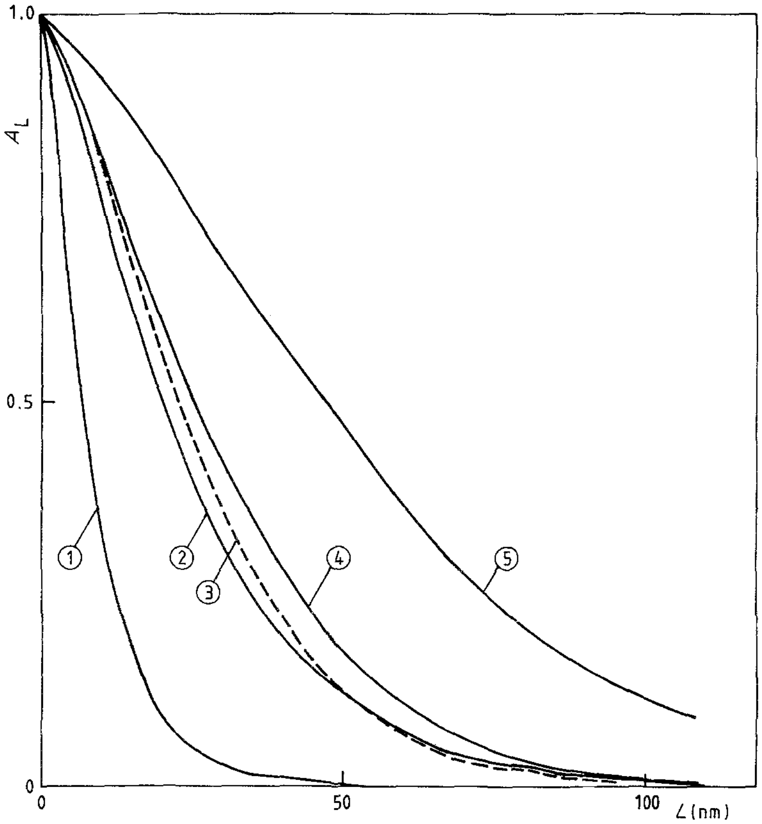

Figure 3 Fourier cosine coefficients A_L against L for 1 0 3 line of α-PbF$_2$. Curve 1: milled for 26 h; curves 2, 3 and 4: milled for 26 h and annealed at 250° C, 290° C during 20 h and 295° C, respectively; curve 5: standard sample.

temperature. A similar curve was observed by Gillies and Lewis [19] for the annealing of tungsten carbide, where residual strains still existed even above 1400° C. However, in the present case pretransitional effects may play some role. In fact, microstrains have sometimes been observed in pretransitional regions [20, 21].

3.4. Liberation of energy on annealing

It was therefore of great interest to establish the relation between the release of the stored energy on linear heating and the decrease of microstrains. Calorimetric thermograms obtained at $60° \mathrm{C\,h^{-1}}$ are shown in Fig. 4 for samples ground for 3, 6 and 26 h. Broad exothermic peaks were observed between about 60 and 280° C, which suggests a gradual energy release. The initial temperature of this phenomenon and the amount of energy liberated depend on the milling time. It is noticeable that there is no energy release from 280° C to the starting temperature of $\alpha \rightarrow \beta$ conversion.

These thermograms allow one to calculate the

TABLE II Changes in residual microstructural properties of α-PbF$_2$ after annealing and in thermodynamical properties of $\alpha \rightarrow \beta$ conversion with milling time

t_m (h)	$\tilde{e}_{a(1\,0\,3)} \times 10^3$	$D_{a(1\,0\,3)}$ (nm)	T_i (° C)	T_f (° C)	$\Delta H_{\alpha\rightarrow\beta}$ (J mol^{-1})
0	0	∞†	337	376	1630(30)*
0.033	0.20	∞	321	366	1530(30)
0.10	0.34	∞	317	365	1490(20)
0.50	0.70	∞	317	354	1385(40)
1	0.78	∞	318	356	1250(20)
3	0.94	∞	317	354	1150(35)
6	0.94	∞	317	358	1155(40)
9	0.96	∞	316	357	1130(25)
18	1.10	∞	305	357	1040(30)
26	1.20	∞	295	357	890(30)

*Standard deviations are given in brackets.
†∞ denotes $D > 150$ nm.

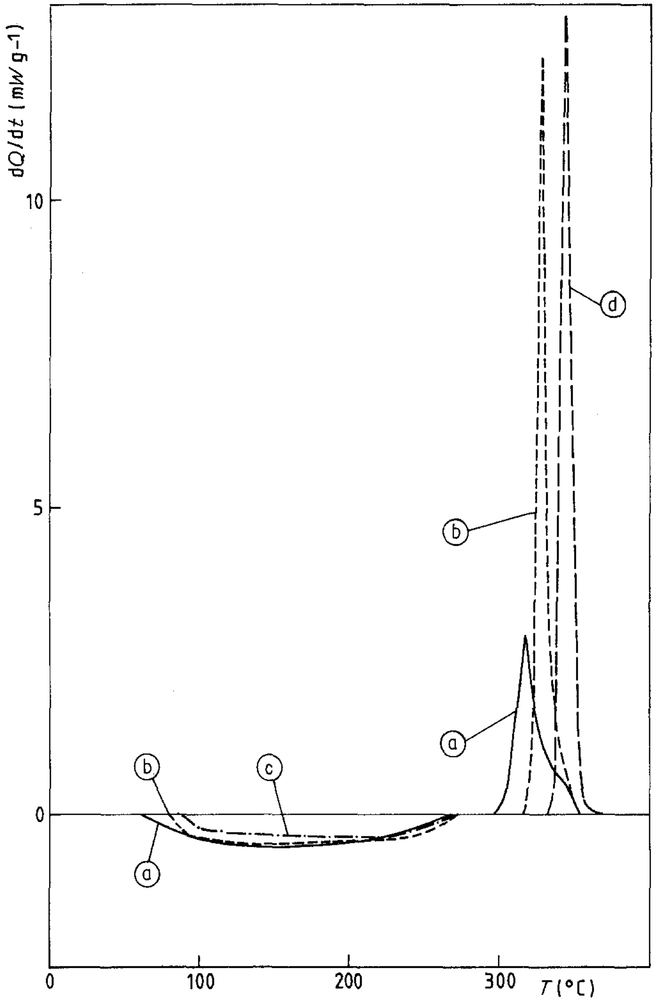

Figure 4 Calorimetric curves (heating rate 60°C h^{-1}): sample milled for 26 h (a), 6 h (b) and 3 h (c), standard sample (d) (the endothermic peaks for b and c are superimposed).

total amount ΔH_a of energy released at a given temperature, and consequently the proportion $-\Delta H_a/\Delta U_m$. On the other hand, the proportion of released microstrains $(\tilde{e}_m - \tilde{e}_a)/\tilde{e}_m$ in crystallographic directions perpendicular to (1 0 3) and (1 2 1) can be deduced from the curves given in Fig. 2. In Fig. 5 the resulting values are plotted as a function of the annealing temperature for a sample ground during 26 h. These curves suggest that there is a narrow relationship between energy and microstrains release. However, these curves are not superimposable, a fact which is not surprising as the calorimetric measurements are representative for the sample as a whole, while X-ray diffraction depends on the crystallographic directions. Furthermore, these curves simultaneously reach almost the same plateau above 260° C, which indicates that the material does not release the total amount of stored energy and microstrains before the $\alpha \rightarrow \beta$ transformation. This phenomenon was observed for all the studied samples, the plateau being always at about 0.6. It is noticeable that in this study the calorimetric measurements confirm the results obtained by simplified X-ray diffraction analysis.

3.5. Influence of residual microstrains on $\alpha \rightarrow \beta$ phase transformation

As a consequence of the observations discussed above, one can expect that, at 280° C, the ground samples retain about 40% of their total initially stored energy. The influence of this residual energy on the phase transformation is clearly visualized in Fig. 4. It does not only affect the initial and final temperature, T_i and T_f, but also the reaction kinetics and the heat of transformation $\Delta H_{\alpha \rightarrow \beta}$. The values of T_i, T_f and $\Delta H_{\alpha \rightarrow \beta}$ are summarized in Table II. They are a function of the residual microstrains $\tilde{e}_a$ present in the solid just before the transition. As can be seen, $\tilde{e}_a$ is a

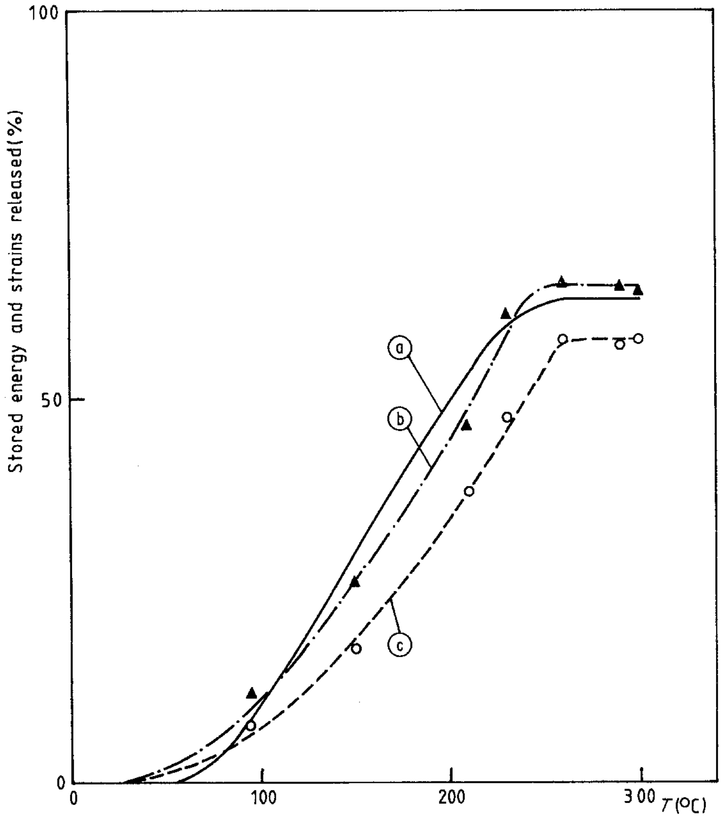

Figure 5 Relationships between $-\Delta H_a/\Delta U_m$ (a), $(\tilde{e}_m-\tilde{e}_a)/\tilde{e}_m(1\,0\,3)$ (b), $(\tilde{e}_m-\tilde{e}_a)/\tilde{e}_m(1\,2\,1)$ (c), and annealing temperature, for a sample milled for 26 h.

primordial parameter in this reaction. However, as Kennedy *et al.* [4] expected, the transition temperature observed in the case of PbF_2 also depends on the heating rate. Some experiments performed on a sample milled for 9 h, showed a decrease in T_i and T_f of about 3 and 10° C, respectively, when the heating rate varied from 220 to 30° C h^{-1}. On the other hand, no change in $\Delta H_{\alpha\to\beta}$ was observed. This fact strongly implies that the properties of the sample in the pretransitional range only depend on the annealing temperature and not on the duration of the annealing process. It further confirms the results obtained by X-ray diffraction analysis.

These observations can explain the divergences between several values of T_i found in the literature [4–9]. Indeed, in the case of a sample milled during only 2 min, one notices a decrease in T_i of 16° C compared to the standard. The latter, when heated slowly (2° C h^{-1}), has a T_i of 328° C. The corresponding values given by Mahajan *et al.* [6] and Janaf [11] are of 312 and 310° C, respectively, would suggest that the samples used by Mahajan *et al.* have retained many microstrains. In any case, the thermodynamic properties of the PbF_2 transition seem to depend on the sample and the treatment it was submitted to. As a conclusion from the data discussed above one can propose a $\Delta H_{\alpha\to\beta}$ of 1630 J mol^{-1} for the case of a strain-free sample. Assuming that the transition is of 328° C, the transition entropy is estimated as 2.71 J mol^{-1}, which is in good agreement with the value of 2.5 mol^{-1} given by Linsey [22].

In connection with these conclusions, it is important to examine if the energy retained in the samples until 295° C is then completely liberated during the transition. The XRD line profiles of cubic β-PbF_2 obtained from the ground starting material and quenched at 400° C revealed no significant line broadening, which might indicate that residual microstrains in α-PbF_2 were released during the phase transformation. Consequently, the observed heat of transition has to be considered as being the sum of the actual heat of transformation and of residual stored energy of the ground sample. For example, in the case of α-PbF_2 milled for 26 h, the experimental $\Delta H_{\alpha\to\beta}$ of 890 J mol^{-1} is in good agreement with 860 J mol^{-1} calculated in this way. Indeed, the initial stored energy and the amount of energy released by annealing are

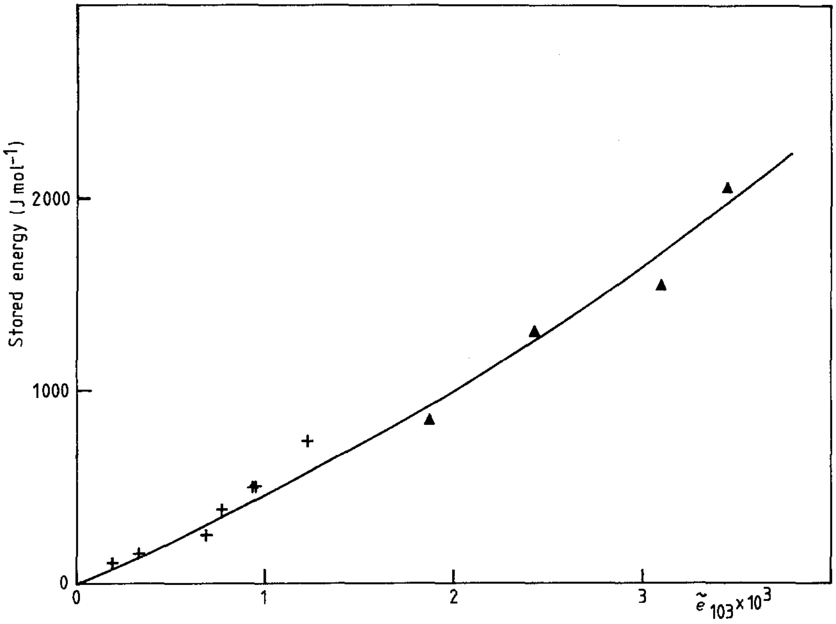

Figure 6 Relationship between stored energy and microstrains perpendicular to (1 0 3). ▲ results from solution calorimetry; + calculated values after annealing at 295° C.

2050 and 1280 J mol^{-1}, respectively, so that the remaining value in the solid is 770 J mol^{-1} just before the transition.

Starting with the $\Delta H_{\alpha \to \beta}$ value listed in Table II, it is now possible to determine for all the samples the remaining energy stored at T_i. As can be seen in Fig. 6, this energy is strongly related to the microstrains perpendicular to the (1 0 3) plane and, as supposed, to microstrains all through the sample.

4. Conclusions

Microstrains and stored energy in α-PbF$_2$ introduced by mechanical deformation, are liberated in two steps. In the temperature range from 60 to 280° C, part of the energy and strains are released during the annealing process, so that, in the pretransitional region, the material retains strains and stored energy in amounts depending on the initial mechanical treatment. In the second step these residual strains and energy are liberated during the conversion of α-PbF$_2$ to β-PbF$_2$, which affects the thermodynamical properties of this transformation. It is noticeable that already very small microstrains are able to modify these properties. The present study shows that the association of calorimetric measurements and X-ray diffraction line broadening analysis constitutes a reliable method in order to interpret changes in the activity of mechanically deformed materials.

Acknowledgement

This research was supported by DGRST.

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Received 5 July
and accepted 31 July 1984