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Continuous, martensitic nature of the transition $\beta \rightarrow \gamma$ Li_3PO_4

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The transformation $\beta \rightarrow \gamma$ Li_3PO_4 shows characteristics of both continuous and martensitic transformations. Below ~ 340° C, no detectable transformation occurs; between 340 and 410° C, the transformation goes only partially to completion; above ~ 410° C the transformation rapidly goes to completion. At any temperature in the range 340 to 410° C, transformation proceeds rapidly in the initial stages to attain a certain degree of transformation. With prolonged isothermal heating or grinding of the samples, further transformation does not occur. The reverse transformation could not be effected under normal, dry conditions.

1. Introduction

Polymorphic phase transformations show a variety of behaviour and may be classified in different ways depending on their kinetic, thermodynamic and structural characteristics. Many transformations do not, however, belong obviously to one or other of the various categories that have been proposed. Thus Ubbelohde [1] has identified a class of transformations in which the transformations take place continuously and over a range of temperatures. This is in contrast to the behaviour expected according to the thermodynamic classification scheme of Ehrenfest [2] in which, for instance, first order transformations occur, under equilibrium conditions, at a fixed temperature only. In order to explain continuous transformations, which apparently violate the phase rule, Ubbelohde introduced extra degrees of freedom, associated with strain energy and other terms, to give a modified form of the phase rule:

$$P + F = C + 2 + \Sigma\pi$$

where P, F and C have their normal meanings, numbers of phases, degrees of freedom and components, respectively, and $\Sigma\pi$ refers to the number of additional degrees of freedom that are introduced. Strain energy may be important in those types of transformation in which the product crystal grows inside the parent crystal. The strain energy arises if there is a difference in density and hence molar volume between the parent and product crystals.

Martensitic transformations are a kind of continuous transformation and have certain characteristic features which include very rapid initial rates of transformation. This is because the structural changes that accompany the transformations are small and the transformations can proceed by a diffusionless mechanism involving bond bending rather than bond breaking. Martensitic transformations also stop short of completion over a range of temperatures and this is again attributed to the strain energy associated with the reactant/product crystal interface. The most widely studied martensitic transformation in non-metallic materials is the tetragonal to monoclinic transformation in ZrO_2. In spite of a great deal of work, this is still a very active field of study [3, 4].

The present work forms part of a study of phase transformations in complex oxides with tetrahedral structures. So far, a detailed kinetic study of the reversible transformation $\beta \rightleftarrows \gamma$ Li_2ZnSiO_4 has been reported [5, 6]. This transformation appeared to be a clear case of a first order, reconstructive [7] transformation in which transformation rates were sufficiently slow that the kinetics

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could be studied over a wide temperature range, in both forward and reverse directions. In order to explain the results, it was suggested that the principle of microscopic reversibility, well-established in gas-phase reactions, could have a controlling influence on transformation rates, especially at temperatures in the vicinity of the equilibrium transformation temperature [6].

2. Polymorphism and crystal structure of Li_3PO_4

Li_3PO_4 is dimorphic [8–11]. The low temperature, β polymorph has an ordered wurtzite structure in which lithium and phosporus are ordered over one set of tetrahedral sites in an approximately hexagonal close-packed oxide array [10]. The high temperature, γ polymorph has a closely related structure with tetrahedrally coordinated cations [8]. Half of the cations, both lithium and phosphorus, are in the same tetrahedral sites as in the β polymorph but the other half are in different positions. The oxide array may be regarded as a rather distorted or buckled hexagonal close packed array or, more correctly, as a slightly distorted form of the recently discovered tetragonal packed array [12].

The transformation $\beta \rightarrow \gamma$ Li_3PO_4 involves half of the cations, both lithium and phosphorus, in a filled to empty tetrahedron jump [13]. Strong P–O bonds must, therefore, break and reform in this process. At the same time, oxide ions undergo small shuffles to accomplish the hcp to tp transformation. The transformation $\beta \rightarrow \gamma$ Li_3PO_4 appears to be topotactic since, from a petrographic examination, crystals of β retained their optical continuity and quality on transformation to γ [11].

The lattice parameters of the orthorhombic unit cells of the two polymorphs are [10]:

$$\beta: a = 0.611\,50, \quad b = 0.523\,94, \quad c = 0.485\,54\,\text{nm}$$

$$\gamma: a = 0.611\,47, \quad b = 1.047\,5, \quad c = 0.492\,28\,\text{nm}$$

Hence the $\beta \rightarrow \gamma$ transformation is accompanied by an increase in volume of $\sim 1.4\%$ which is largely caused by expansion of the c-axis.

The $\beta \rightarrow \gamma$ transformation is reported to be monotropic [11]: it occurs rapidly at e.g. 500° C, but on reducing the temperature, the reverse transformation cannot be induced to occur under dry conditions. In order to prepare the β polymorph, hydrothermal conditions must be used [9]. Alternatively, it may be prepared by slow evaporation of dilute aqueous solutions of sparingly soluble Li_3PO_4 [10].

3. Experimental techniques

A commercial grade of Li_3PO_4 (Hopkin and Williams) was used, in the form of a fine powder. X-ray diffraction showed it to be the β polymorph. Only limited attempts were made to characterize the material in terms of its particle size. From optical microscopy, the individual grains could be barely resolved, placing an upper limit of say, 5×10^3 nm on the grain size. From the absence of significant broadening of the peaks in the X-ray powder pattern, a lower limit to the grain size of $\sim 10^2$ nm could be fixed.

For the transformation experiments, samples were used straight from the bottle and were placed in platinum crucibles in an electric muffle furnace whose temperature was controlled and measured to ± 5° C. The degree of transformation was determined by X-ray powder diffraction using a Siemens D500 diffractometer, Cu$K\alpha$ radiation. The powder patterns of the β and γ polymorphs have many peaks in common but the 0 0 2 peaks of each occur in somewhat different positions due to the different c values of their unit cells. The relative intensities of the 0 0 2 peaks were used as a measure of the β/γ content and hence as a measure of the degree of transformation.

In order to calibrate the method, a series of nine standard samples was prepared from mechanical mixtures of samples of pure β and pure γ in different ratios (10:90, 20:80, etc.). Two methods were used to estimate intensities, based on peak heights and peak areas. The difficulty in using peak areas was that each component 0 0 2 was, in fact, a poorly resolved doublet due to the nature of the $K\alpha_1$, $K\alpha_2$ radiation. Furthermore, the $K\alpha_2$ peak of the γ polymorph overlapped somewhat with the $K\alpha_1$ peak of the β polymorph. Hence complete resolution of the 0 0 2 peaks was not obtained in the diffractometer traces. The peak height method for estimating intensities suffered from the possible drawback that, if any peak broadening occurred, for example due to a particle size effect, then the peak heights would be automatically reduced. A calibration curve was constructed for each of these two methods of estimating peak intensity. For all experiments, both methods were used to estimate the degree of transformation and for the final results, an average of the results obtained from the two methods was taken.

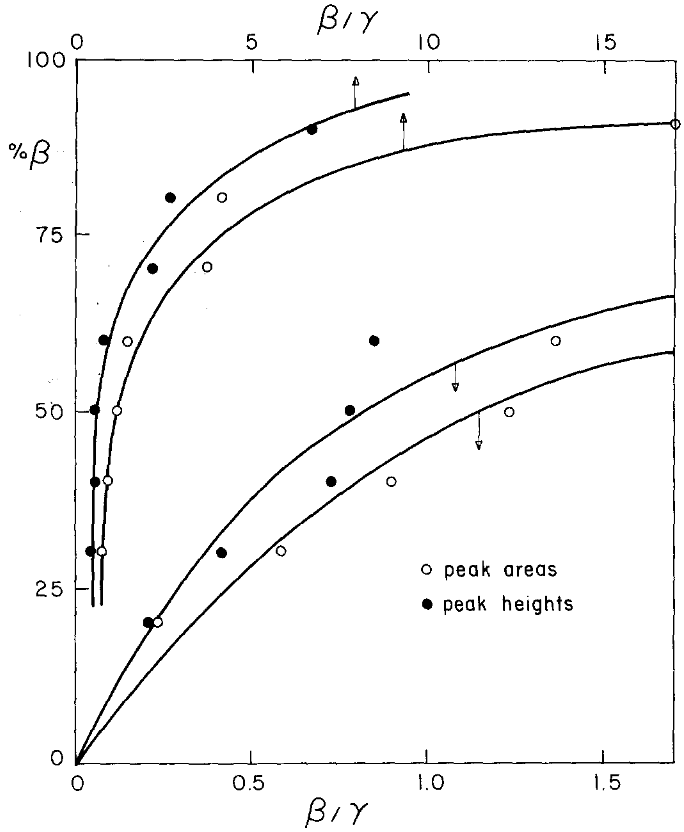

Figure 1 Calibration curves of %β against the ratio of the intensities of the 0 0 2 peaks in the X-ray powder patterns of β/γ mixtures.

4. Results

The calibration curves were plots of the ratio of the β to γ peak intensity against %β content. These are shown in Fig. 1. The data points show some scatter but generally fall on smooth curves. The two calibration curves are quite different. The reasons for this are not fully understood but, in part, may be associated with the different systematic errors inherent in the two methods, as indicated above. Using either of these graphs, it was estimated that the %β content in an unknown could be determined to within ± 5%. On comparing the results obtained by the two methods, it was found that the results for %β content obtained from peak areas were generally 10 to 15% higher than those obtained from peak heights.

The degree of transformation was determined in samples that had been heated isothermally for times ranging from 1 h to 2 days and subsequently quenched to room temperature. Results were obtained at eight temperatures in the range 340 to 410° C. Detailed results of the degree of conversion against heating time are shown for two temperatures in Fig. 2. In both cases it was found that the degree of conversion was essentially constant over the complete range of heating times that were used. Hence the initial degree of conversion, from e.g. 0 to 45% γ at 370° C, must take place extremely rapidly and well within the first hour of heating.

Similar results were obtained at other temperatures in the range 340 to 410° C: a certain degree of conversion was reached very rapidly, in less than 1 h, and then remained constant with further isothermal heating. However, with increasing temperature in the range 340 to 410° C, the degree of transformation increased and was essentially 100% $\gtrsim$ 410° C. No significant amount of transformation could be detected $\lesssim$ 340° C. These results are summarized in Fig. 3. The degree of transformation, taken as the average of the results obtained from the two methods, is plotted against temperature. The results clearly fall on an S-shaped curve over the range 340 to 410° C.

Unsuccessful attempts were made to carry out the transformation in the reverse direction, $\gamma \rightarrow \beta$. In one experiment samples of γ prepared by transformation from β at 575° C, were heated at 270 and 280° C for 1 day but no β was produced. In another experiment, a β/γ mixture prepared by

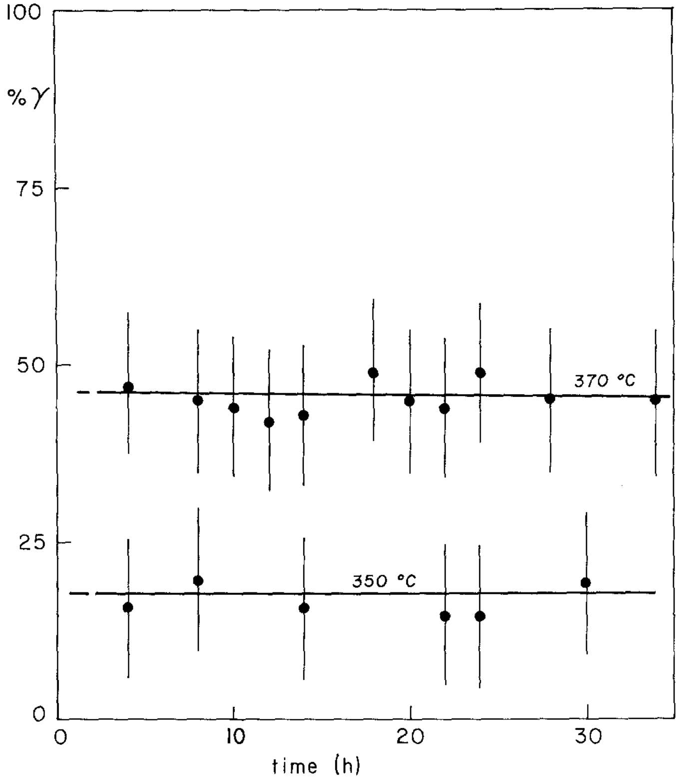

Figure 2 Degree of transformation as a function of time at two temperatures.

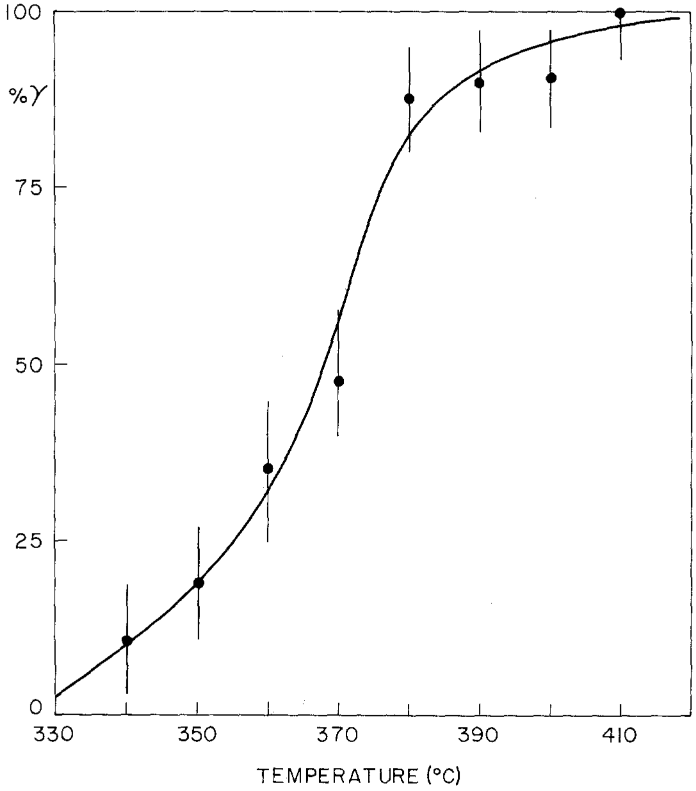

Figure 3 Degree of transformation as a function of temperature.

partial transformation of β at 360° C, was heated at 290° C but no subsequent variation in the %γ content occurred.

An unsuccessful attempt was also made to influence the degree of transformation by grinding samples: one sample of β was partially converted to γ by heating at 370° C, after which it was ground with an agate mortar and pestle and returned to the furnace at 370° C for a further 24h. However, no change in the %γ content occurred as a result of this heat treatment.

5. Discussion and conclusions

The transformation $\beta \rightarrow \gamma$ Li_3PO_4 appears to be a continuous transformation, in the manner defined by Ubbelohde [1]: a temperature range of ~ 70° C covers the various stages from 0 to 100% transformation. It seems likely that hybrid crystals containing both β and γ components form and that strain energy at the β/γ interface is responsible for the observed wide temperature range that covers the stages from 0 to 100% transformation. This is because, at lower temperatures, e.g. 360° C, the difference in free energy between β and γ polymorphs is small and equals the strain energy associated with partial conversion. Above ~ 410° C, the difference in free energy between β and γ polymorphs is larger and is more than sufficient to off-set any strain energy term. Hence the transformation proceeds to completion.

The $\beta \rightarrow \gamma$ transformation also shows characteristics of a martensitic transformation in that at a particular temperature, the transformation begins very rapidly and then ceases at a certain value.

The results of the experiment in which the sample was ground finely and subsequently reheated must be regarded as inconclusive. Thus, perhaps the crystal intergrowths occurred on a very fine scale and grinding in an agate mortar was insufficient to break up the crystals. If this had happened, the strain energy should have been released and transformation continued, perhaps to completion.

It is interesting to compare these results with those for the related transformation, $\beta \rightleftarrows \gamma$ Li_2ZnSiO_4 [5, 6]. In the latter, transformation rates were much more sluggish and took place in measurable times of hours to days over the temperature range 450 to 940° C. In the Li_3PO_4 transformation, the rates were too rapid to be measured easily and were relatively, for much lower temperatures, 340 to 410° C. Since phosphorus atoms (or ions) must move between tetrahedral sites in order to accomplish the $\beta \rightarrow \gamma$ transformation and one P–O bond is broken for each phosphorus that moves, then this cannot be a particularly difficult process. Assuming that silicon atoms can also move as easily between adjacent tetrahedral sites, then the slow step in the $\beta \rightleftarrows \gamma$ Li_2ZnSiO_4 transformation probably involves migration of the much larger zinc atoms.

It is also possible that the hopping of phosphorus atoms between adjacent tetrahedral sites in Li_3PO_4 is greatly assisted by the shuffling of the oxide ions associated with the hcp to tp transformation. It is known that half of the tetrahedral sites in a hcp array become grossly distorted as the array changes to a tp array by a displacive or partial shearing mechanism [12]. Those phosphorus atoms located in such sites would probably find it easy to escape into a more regular tetrahedral site during the hcp to tp transformation of the oxide array.

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