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Time-resolved study by X-ray powder diffraction with position-sensitive detector: rate of the β-Cs_2CdI_4 transformation and the effect of preferred orientation

J. PLEVERT, J. P. AUFFREDIC, M. LOUËR, D. LOUËR*
Laboratoire de Cristallochimie (U.A. 254 au C.N.R.S.), Université de Rennes I,
Avenue du Général Leclerc, 35042 Rennes Cédex, France

A time-resolved X-ray powder diffraction of the transformation, at room temperature, of the metastable β-Cs_2CdI_4 phase into α-Cs_2CdI_4 is described. It is based on data collected by means of a conventional X-ray diffraction system combined to a curved position-sensitive detector. The transformation is governed by a nucleation and a three-dimensional growth process, and its rate depends on the particle size and crystal imperfections. When particle sizes are less than 40 μm, the rate of the transformation strongly decreases in the later stage of growth, due to the stresses produced by structural modifications. Particular attention is paid to the fact that the quantitative interpretation of experimental data in kinetic terms, can be influenced by the existence of a preferred orientation effect of the crystallites in the sample.

1. Introduction

A position sensitive detector (PSD), combined to efficient data storage, has greatly increased the possibility of time- and temperature-resolved diffractometry for tracing structural changes occurring in materials. Extensive investigations by means of neutron powder diffraction [1] have shown how the examination of solid-state transformations can profit from time-resolved studies based on diffraction. Applications have also been reported with X-ray synchrotron radiation [2]. In spite of the lower intensity obtained with high-power X-ray tubes currently available, the use of PSD in X-ray laboratories is also a relevant tool for characterizing the structural [3, 4] or microstructural (strains and crystallite sizes) modifications occurring in materials. The temperature-resolved diffractometry is then a complementary technique to the thermogravimetric analysis (TG) or differential scanning calorimetry (DSC) measurements. An important feature of diffractometry is based on the fact that the observable Bragg intensities are related to the diffracting volume of the matter. Therefore, the increase in data acquisition by means of a PSD can be used for obtaining kinetic data from solid-state reactions, provided that the counting statistics are good enough. In the work presented here, this property is used for the kinetic interpretation of the time-resolved diffraction data obtained during the transformation of the metastable β-Cs_2CdI_4 phase into α-Cs_2CdI_4.

Evidence of polymorphism in the dicesium cadmium tetraiodide Cs_2CdI_4 has been recently reported [5], as well as the crystal structure of two phases [6]. The monoclinic phase α-Cs_2CdI_4 ($P2_1/m$; $a = 0.7838$ nm, $b = 0.8403$ nm, $c = 1.1048$ nm, $\beta = 110.57°$), stable in normal conditions, has a Sr_2GeS_4-type structure. A phase transition occurs at about 120° C. The high temperature phase β-Cs_2CdI_4 is orthorhombic (Pnma, $a = 1.0859$ nm, $b = 0.8506$ nm, $c = 1.4869$ nm) and its structure is related to the K_2SeO_4-type structure. It has been shown that, by cooling rapidly, the high temperature phase can be obtained at room temperature. With time or by mechanical treatment this metastable phase transforms into the α phase. A kinetical approach of this transformation at room temperature is described in this paper. It is based on data collected from a conventional X-ray diffraction system involving a stationary flat powder sample and PSD. In addition, emphasis is placed on the dramatic effect of a preferred orientation of the crystallites in the sample on the kinetic interpretation of the reaction.

2. Experimental procedure

Crystals of α-Cs_2CdI_4 were obtained at room temperature from an aqueous solution of CsI and CdI_2 in stoichiometric proportions. After grinding, the samples were heated at 160° C for 1 h, and then cooled at room temperature to obtain the β-Cs_2CdI_4 phase.

Data acquisition was performed by means of a INEL cylindrical position sensitive detector (CPS 120), which allows for a simultaneous recording of a powder pattern over a range of 120°. The detector has been used in a semi-focusing arrangement by reflection. Strictly monochromatic $CuK\alpha_1$ radiation

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*Author to whom all correspondence should be addressed.

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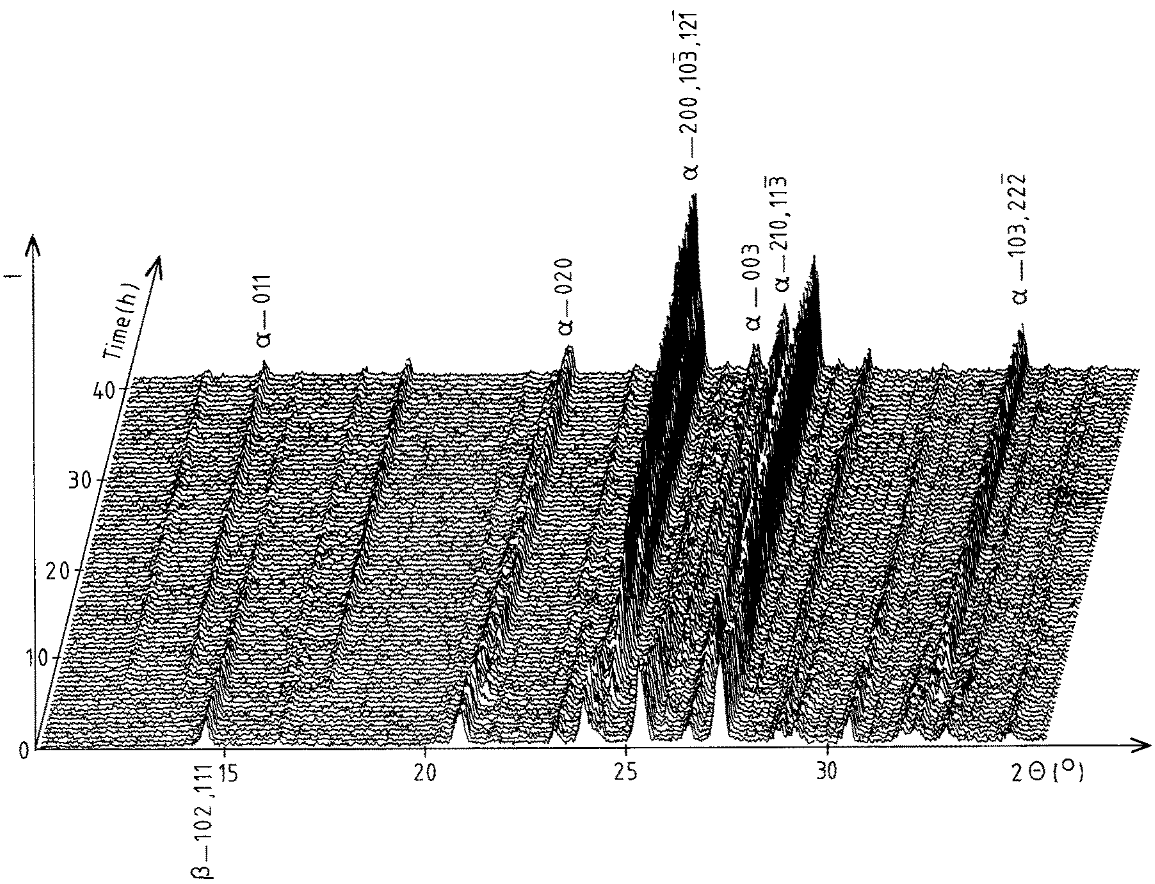

Figure 1 Time-resolved study of the transformation of β-Cs_2CdI_4 into α-Cs_2CdI_4 at room temperature. Sample with negligible preferred orientation effect; θ_i = 10°.

(λ = 0.154 059 81 nm) was selected by means of an incident-beam curved-crystal quartz monochromator with asymmetric focusing (short focal distance = 130 mm, long focal distance = 510 mm). In using a long focal distance the deviation from parallelism of the diffracted beam decreases. The stationary powder sample is located at the centre of the goniometer (R = 250 mm) and intercepts the convergent X-ray beam which is focused on the goniometer circle. The curved PSD coincides with the goniometer circle. A fixed angle θ_i of 10° between the incident beam and the surface of the sample was selected. This means that parafocusing is only obtained for a diffracted beam located at 20°(2θ). This arrangement combined with an incident beam limited by a slit of 0.2 mm wide, to restrict the diffracting area of the sample, ensures satisfactory diffraction lines over a useful angular range. This optical principle presents similarities with the geometry used in semi-focusing cameras described 34 years ago [7, 8]. The data acquisition was performed by the PSD with a spatial resolution of about 0.03°(2θ). The time interval between successive powder patterns was 960 sec including a measuring time of 800 sec. The data were stored in a PDP 11-73 computer. The integrated intensities of some lines for both phases have been evaluated by means of a least squares profile fitting program "FIT", available in the Siemens DIFFRAC-11 software package. Due to the low counting statistics of some lines and to the defocusing effect, Gaussian functions appeared to be satisfactory for the line profile fitting of the raw data. The 3-D plot of the collected raw data was performed by means of a computer program written locally for a HP-7475A plotter.

3. Results

Several experiments to study the phase transition β-$Cs_2CdI_4 \rightarrow \alpha$-$Cs_2CdI_4$ were carried out at room temperature, with controlled granulometry. Surprisingly, it appeared that the quantitative interpretation of the experimental data, in kinetic terms, was affected by the existence of a preferred orientation effect of the crystallites in the sample. Consequently, it seems of interest to present the results of two selected experiments: one with negligible preferred orientation effect and the other with a partial preferred orientation of the crystallites. These two situations are described as follows.

3.1. Samples with random orientation of crystallites

Special care was taken in the sample preparation to obtain a completely random-orientation of crystallites of both the α and β phases of Cs_2CdI_4. Crystals of α-Cs_2CdI_4 were grinded and particles with sizes less than 40 μm were selected. To minimize the orientation effects when powdered samples were pressed, a side-loading method was used. In this case the crystallites of the β phase obtained from the α phase, after thermal treatment, also had a random orientation. Indeed, the observed intensities of the diffraction lines for the two phases were in good agreement with the intensities calculated from the program LAZY-PULVERIX [9]. The evolution with time of the transformation of the

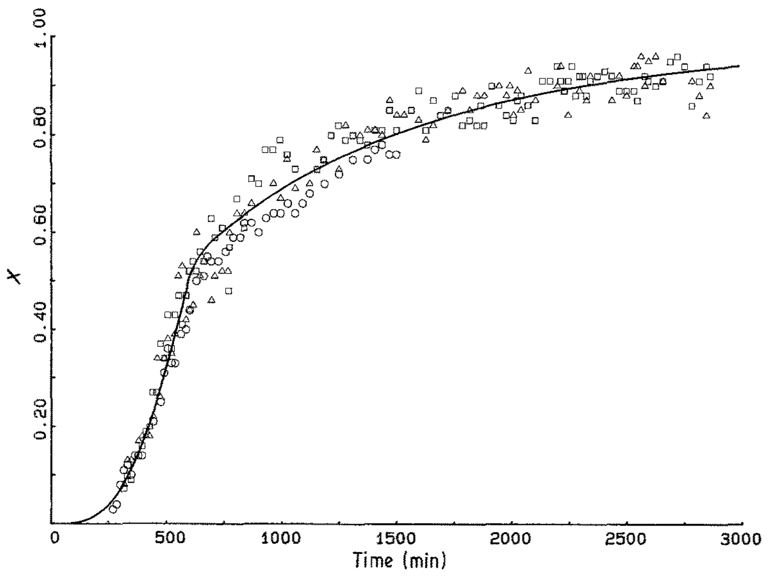

Figure 2 Time dependence of the volume fraction of the α-phase at room temperature. Sample with negligible preferred orientation effect; (△) 1 0 2, 1 1 1(β), (□) 0 1 1(α), (○) 2 0 0, 1 0 $\bar{3}$, 1 2 $\bar{1}$(α).

β-phase is illustrated in Fig. 1, as a 3-D plot of the measured diffraction pattern. First, it can be seen that the transformation $\beta \rightarrow \alpha$ started after about 3 h and was still not complete after 35 h. Secondly, the relative intensities of the diffraction lines of the α phase obtained are quite similar to those observed when crystallites are randomly distributed throughout the sample. The volume fraction of the stable α phase is given by the equation

$$X(t) = \frac{I(t)}{I(\infty)} = \frac{I'(0) - I'(t)}{I'(0)} \qquad (1)$$

where $I(t)$ and $I'(t)$ are the integrated intensities of the diffraction lines of the α and β phases, respectively, at the time, t. The two powder patterns are complex and are superposed during the transformation; consequently, the number of possible diffraction lines to be analysed was limited. The following lines or clusters of lines (due to individual components which strongly overlap) were selected: the cluster (1 0 2, 1 1 1) [14.43 and 14.50°(2θ)] for the β phase, the single line (0 1 1) [13.58°(2θ)] and the cluster (2 0 0, 1 0 $\bar{3}$, 1 2 $\bar{1}$) [24.31, 24.32 and 24.43°(2θ)] for the α phase. As the reaction was not complete, the values of $I(\infty)$ were calculated from Equation 1 with $X = 0.90$ and $t = 2500$ min.

The variation of $X(t)$ with time is given in Fig. 2. The values derived independently from $I(t)$ and $I'(t)$ agree within about 5%, which can be regarded as satisfactory, bearing in mind the poor diffracting power of the sample. It can be seen that, in a first stage, the transition rate increases to $t \approx 600$ min and that, in a second stage, it decreases drastically, so that the value of $X(t)$ is only 0.90 when $t = 2500$ min.

The first part of the curve shown in Fig. 2 is similar to the curves typically found for the transformation of solids, for which the induction period is large (see, for example, [10–12]). Such a situation is indicative of a process which can be governed by nucleation and growth phenomena. This kind of transformation can be described by the generalized equation [13–18]:

$$X(t) = 1 - \exp(-Kt^n), \qquad (2)$$

where $X(t)$ represents the volume fraction of a solid isothermally transformed at time t. K and n are constants which are independent of both t and X. The n value depends on the nucleation rate and the D-dimensional space of nuclei growth [19]. Equation 2 can be rewritten as

$$\ln(1 - X(t)) = -Kt^n \qquad (3)$$

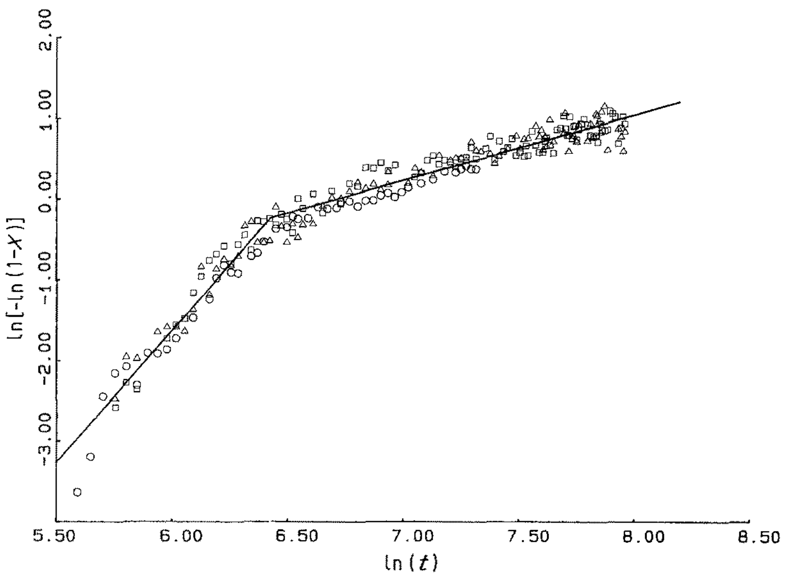

Figure 3 Plot of ln [−ln (1 − X)] as a function of ln$t$. Sample with negligible preferred orientation effect; (△) 1 0 2, 1 1 1(β), (□) 0 1 1(α), (○) 2 0 0, 1 0 $\bar{3}$, 1 2 $\bar{1}$(α).

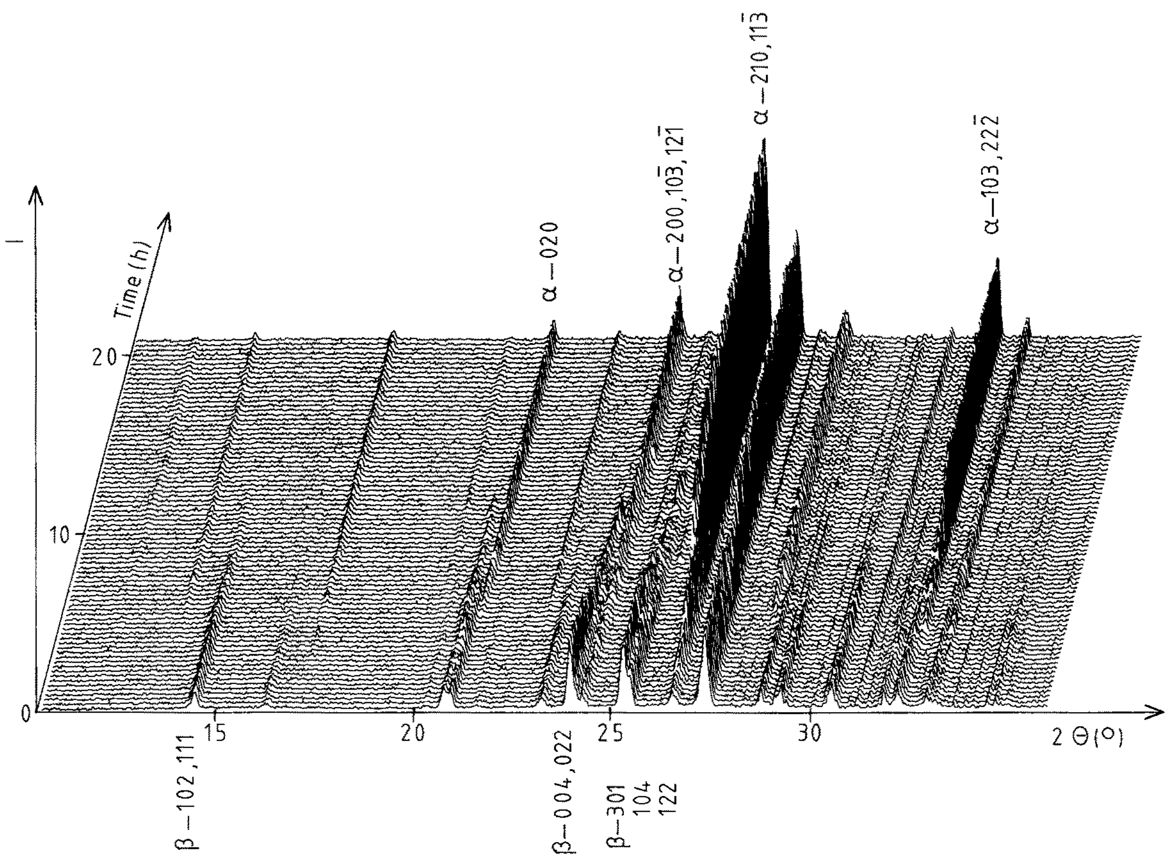

Figure 4 X-ray diffraction 3-D plot for the transformation β-Cs_2CdI_4 → α-Cs_2CdI_4. Sample with preferred orientation effect; $\theta_i = 10°$.

or

$$\ln\{-\ln[1 - X(t)]\} = \ln(K) + n\ln(t) \quad (4)$$

A good fit of the experimental results to this linear equation would suggest the hypothesis that the transformation is governed by a nucleation and growth process. As shown in Fig. 3, the results do not fit one straight line, but two lines which intercept for $X \approx 0.5$. For X less than 0.5, the value of the kinetic law exponent n was found to be 3.28, with a standard deviation of 0.08. For X greater than 0.5, $n = 0.80$, with a standard deviation of 0.02. These results compare well with those obtained by Hamaya *et al.* [12] in a study of the first order transition of RbI.

It is well known that the interpretation of the experimental n value has to be supported by additional information about the process, for example from direct macroscopic observations of the transforming particles as a function of time. In this study, macroscopic investigation did not bring any supplementary information, because of the slowness of the reaction and the imperfection of the grains. However, such an analysis was made with platelet crystals of the α phase during its conversion into the β phase [20]. It was shown that this transformation proceeds in all directions while cleavage lines progress through the crystals up to the apparition of cracks. Finally, single crystals split into a mosaic of smaller crystals. Similar features were recently described in transformations of lithium iodate [21]. Thus, it is possible to suggest that the reverse transformation $\beta \to \alpha$ presents similar properties. According to this hypothesis, the value of $n = 3.28$ obtained in the first stage of the reaction would mean that the nuclei growth rate or the nucleation rate decrease with time. As emphasized by Hamaya *et al.* [12] the time dependence of the domain wall velocity can be induced by *the slow relaxation of the internal stresses produced in the vicinity of domain walls* by the structural modifications between the two phases. This effect would be due to a value of strains energy ε which can be compared to the free energy of the transition. Thus, the smaller value for n in the second stage of the reaction could be related to the increase of the stress relaxation time, probably enhanced by crystal imperfections.

3.2. Samples with a preferred-orientation effect

Typical overviews of the transformation of β-Cs_2CdI_4 are given in Figs 4 and 5 for samples in which the particle size was selected between 40 and 50 μm. These 3-D plots correspond to incident angles $\theta_i = 10°$ and $\theta_i = 6°$, respectively. It can be noted that, even if the induction period is different for these two experiments, the transformation is complete after a few hours. This feature shows that the transformation rate is highly dependent on the particle size and crystal imperfections due to grinding. On the other hand, the relative intensities of the diffraction lines for the two phases, and particularly for the α phase, not only change from one experiment to the other, but are quite different from those previously observed (Fig. 1). For example, in the case of Fig. 4, the intensity of the clusters (2 1 0, 1 1 $\bar{3}$) and (1 0 3, 2 2 $\bar{2}$) of the α phase is largely enhanced while the 0 0 3 line does not appear. In the second situation (Fig. 5), the intensity of the 0 2 0 line (α phase) is amplified. Consequently, these observations clearly show that a preferred orientation of crystallites

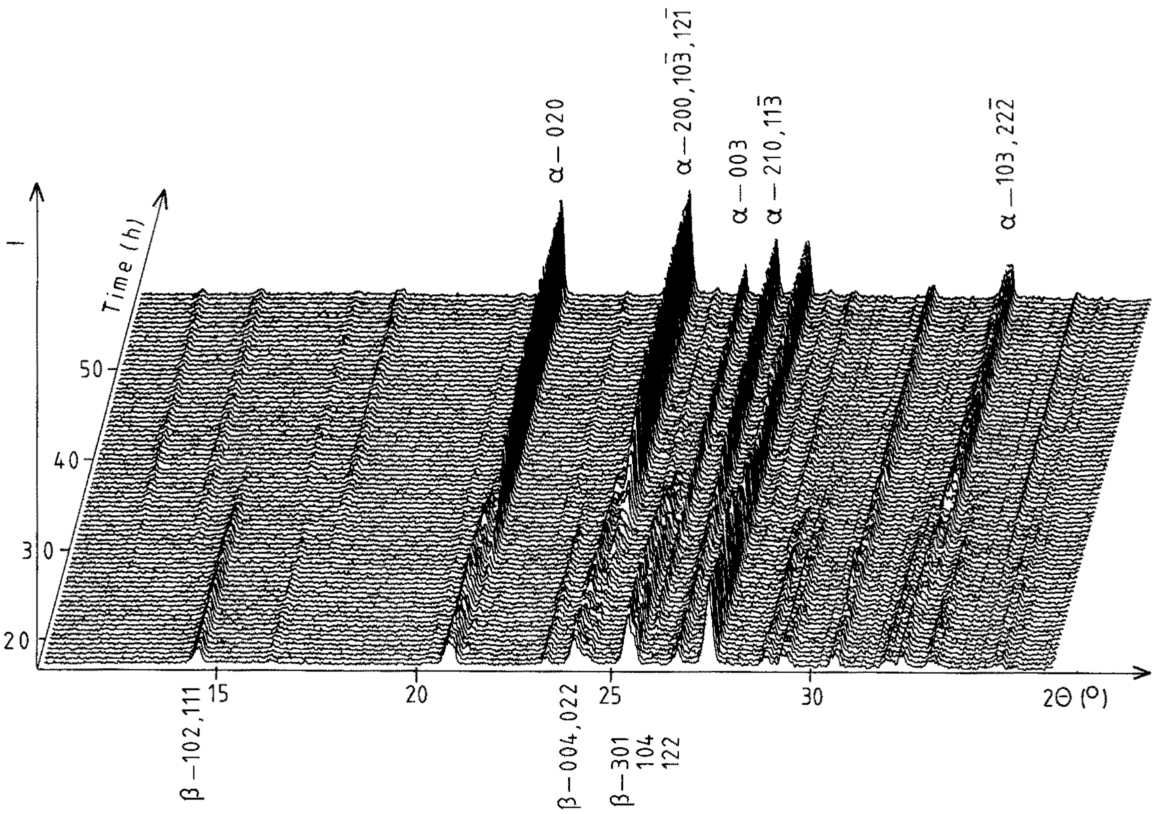

Figure 5 X-ray diffraction 3-D plot for the transformation β-Cs$_2$CdI$_4$ → α-Cs$_2$CdI$_4$. Sample with preferred orientation effect; $\theta_i = 6°$.

existed in the β phase and has induced a similar effect in the α phase. In practice, it has been shown that these modifications are strongly dependent on the selected incident angle θ_i used in the geometry of the instrument. Clearly, this situation is not true when the crystallites are randomly distributed. These observations therefore suggest a simple test for the detection of a preferred orientation effect in a flat powder sample.

The results concerning the kinetic interpretation of the transformation shown in Fig. 4 are now presented. More clusters of lines could be selected due to the increase of some interesting lines (1 0 2, 1 1 1), (0 0 4, 0 2 2) and (3 0 1, 1 0 4, 1 2 2) for the β phase and the line 0 2 0, the clusters (2 1 0, 1 1 $\bar{3}$) and (1 0 3, 2 2 $\bar{2}$) for the α phase. The experimental values $X(t)$ deduced from these lines present a large scatter, as shown in Fig. 6 and appear to lie roughly on three curves. These discrepancies were also evident in the logarithmic plot $\ln[-\ln(1 - X)]$ against $\ln t$, from which the n calculated values were 2.16, 2.83 and 5.00, respectively. Clearly, these n values have no physical significance. Consequently, in this case, the true value of X at a time t cannot be obtained from the variation of the X-ray diffraction line intensities. These rather surprising results can only be explained by the preferred orientation effect of the crystallites. Indeed, the intensity $I(h\,k\,l)$ of a reflection $h\,k\,l$ is given by the equation

$$I(h\,k\,l) = mLF^2(h\,k\,l)Vp(h\,k\,l), \qquad (5)$$

where m is the multiplicity factor, L the combined Lorentz-polarization factor, $F(h\,k\,l)$ the structure factor for a reflection $h\,k\,l$, V the volume of the diffracting

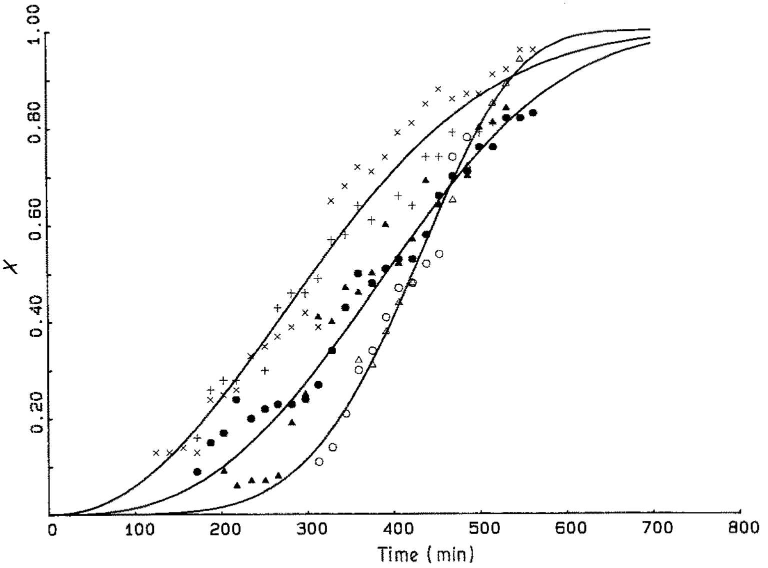

Figure 6 Time dependence of the volume fraction X deduced from several diffraction lines. Sample exhibiting a preferred orientation effect; (x) 0 0 4, 0 2 2(β), (+) 2 1 0, 1 1 $\bar{3}$(α), (▲) 3 0 1, 1 0 4, 1 2 2(β), (●) 1 0 2, 1 1 1(β), (○) 0 2 0(α), (△) 1 0 3, 2 2 $\bar{2}$(α).

matter and p the preferred orientation factor for the reflection $h\,k\,l$.

When the transformation occurs in the material diffracting, the diffracting volume V and as a consequence the intensity $I(h\,k\,l)$ vary as a function of time. The p factor is only dependent on the angle ϕ between the preferred orientation direction and the scattering vector. In principle, it should have a constant value when the solid state transformation occurs, since the sample is stationary. However, in the present study, the inconsistancies previously reported can only be explained from Equation 5 if the $p(h\,k\,l)$ factor varies during the transformation. From these considerations the following picture of the transformation process can be suggested for the explanation of the discordance between the X values obtained from the selected diffraction lines of α and β phases. As mentioned above, internal stresses which appear during the transition induce in their vicinity a slight modification of the orientation of the crystallographic planes $h\,k\,l$. In the diffraction geometry using a stationary flat sample and PSD, a slight modification of the incident angle θ_i ($\approx 0.10°$) can modify the intensities $I(h\,k\,l)$ in the case of the preferred orientation effect; therefore, it is clear that the $p(h\,k\,l)$ factor is strongly influenced by changes in orientation of $h\,k\,l$ planes. The dependence of the factor p with time and crystallographic direction explains the erroneous kinetic interpretation of the reaction when a preferred orientation of the crystallites is present in the sample. This result is important, indeed if the power of the PSD for the acquisition of diffraction data is a considerable improvement, it is fundamental to know that incorrect kinetic interpretation of a reaction can result if no attention is paid to the random orientation of the crystallites in a stationary sample. In practice, the use of the intensity of only one diffraction line should be avoided for the examination of the kinetic of a reaction, without checking before that crystallites are randomly distributed in the sample.

5. Conclusion

The present study has shown that the position-sensitive detector is a useful tool, in conventional X-ray laboratories, for tracing structural modifications occurring in materials. The relation between the intensities of the reflections with the volume of diffracting matter is also advantageous for the examination of the kinetic of solid-state reactions.

The precise analysis of the transformation, at room temperature, of the metastable β-Cs_2CdI_4 phase into the α-C_2CdI_4 phase has revealed that the reaction is governed by a nucleation and a three-dimensional growth of nuclei. It has been shown that the dependence of line intensities with the volume of the diffracting matter was also affected by the presence of a preferred orientation of the crystallites in the sample. This observation has been obtained from a specific diffraction geometry and a transformation characterized by topotactic properties. As an extension to this work it would be interesting to study, with the technique we described in this work, other phase transformations in order to confirm the restricting effects mentioned in the present study.

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