TIME- RESOLVED X-RAY POWDER DIFFRACTOMETRY AS A COMPLEMENTARY THERMAL ANALYSIS METHOD

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The use of a conventional X-ray diffractometry together with curved position sensitive detector (PSD) allows for a complete diffraction pattern to be recorded as a function of time and temperature, so that transformations in the solid state can be traced sequentially. In this way, this technique can be regarded as complementary to the conventional thermal analysis methods, as thermogravimetry and differential scanning calorimetry. Three applications are described: the thermal decomposition of a cadmium hydroxide nitrate, the phase transformation of the dicesium cadmium tetraiodide and the investigation of microsturctural properties as a function of temperature.

Introduction

Time- and temperature-resolved X-ray diffractometry (TRXD) is one of the tools available to investigate solid-state reactions. Whereas conventional thermal analysis such as Differential scanning calorimetry (DSC) and thermogravimetry (TG) allow determination of the energy evolved and the weight change of a sample during its transformation, TRXD appears as the most convenient for the identification of the reaction products and the characterization of the structural or microsturctural (strains and crystalline sizes) modifications occurring in materials. For a few years TRXD has been greatly improved by the advent of position sensitive detectors (PSD), combined to efficient data storage. Examples based on the use of synchroton radiation and neutron sources have been described [1–4].

The present paper reports some results, obtained with a conventional X-ray powder diffractometer through applications of TRXD: the interpretation of the decomposition process of hydroxysalts, the kinetic study of a phase transformation and the analysis of the microstructural properties of solids in reaction.

Experimental considerations

The TG analysis was carried out by using a Rigaku Thermoflex TG–DSC. About 10 mg of the powdered sample was spread out on a large platinum sample holder in order to avoid mass effect and to reproduce, as much as possible, the conditions used in the TRXD study.

For the time-resolved diffractometry the data collection was performed by means of an INEL (CPS 120) curved position sensitive detector, which allows for a simultaneous data recording of a powder pattern over a range of $120°$. The semi-focusing geometry used, combined to strictly monochromatic radiation ($\lambda = 1.5405981$ Å), has been described elsewhere [5]. The sample is stationary and located at the centre of the goniometer. A fixed angle θ_i, in the range 5 to $10°$, between the incident beam and the surface of the sample was selected. A spatial angular resolution is about $0.03°(2\theta)$. To ensure satisfactory counting statistics of the X-ray diffractometry lines an interval time of 1150 s between two successive powder diffraction patterns is selected, in which a counting time of 1000 s is included. The data were stored in a PDP 11–73 computer. For *in situ* high temperature experiments, the sample was located in a high-temperature X-ray diffractometer attachment (Rigaku). In order to each scan corresponds to a narrow temperature range a low heating rate of $5 \text{ K} \cdot \text{h}^{-1}$ is used. To avoid mass effect during the transformations the powdered samples were spread out in a thin layer on a nickel grid used as a sample holder.

Decomposition scheme of hydroxysalts

To illustrate the use of TRXD in the field of the thermal decomposition of solids, the thermal decomposition of the cadmium hydroxide nitrate $Cd_3(OH)_5NO_3$ was analysed [6]. The experiments were performed in a nitrogen stream or in vacuum with residual pressure of 1.3 Pa.

Thermal decomposition in nitrogen

A three-dimensional representation of the evolution of the powder patterns with temperature (3D plot) is shown in Fig. 1 when the decomposition of this hydroxysalt is performed in a nitrogen stream with a heating rate of $5 \text{ K} \cdot \text{h}^{-1}$. This 3D plot points out that the decomposition proceeds in three steps.
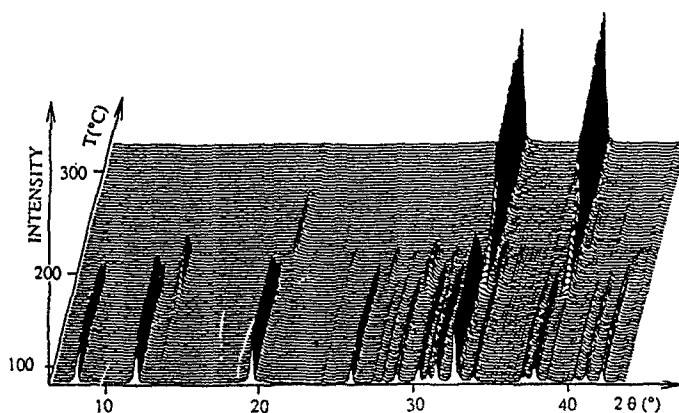
Fig. 1 The TRXD plot of $Cd_3(OH)_5NO_3$ in flowing nitrogen gas

In the first step, the precursor decomposes into a mixture of CdO and a hitherto non identified compound. The second step is characterized by the simultaneous formation of CdO and $Cd(NO_3)_2$ from the intermediate compound. The final product of the decomposition, CdO, is obtained in the last step. Figure 2 shows, as a function of temperature, the changes of the integrated intensity of a diffraction line selected for each compound and the evolution of the sample weight obtained from TG measurement.
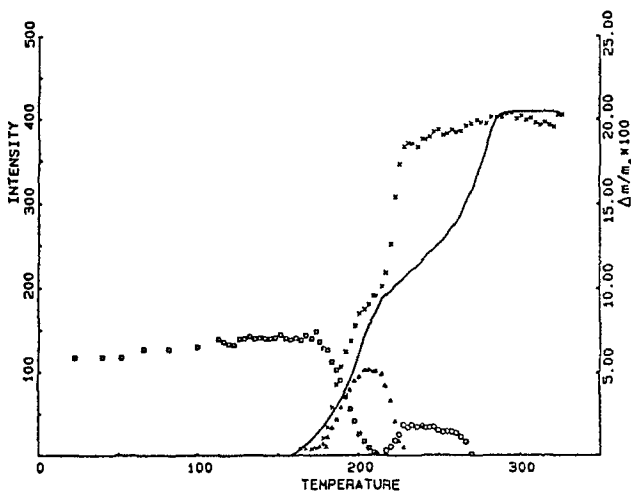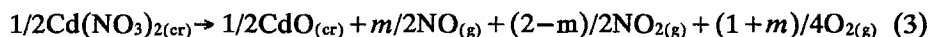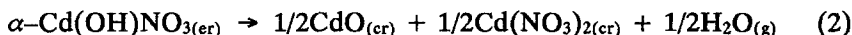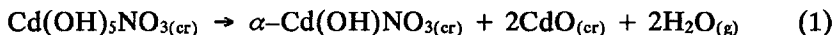

Fig. 2 Integrated intensities of hkl diffraction lines vs. temperature from the TRXD in nitrogen. (□) 001 $Cd_3(OH)_5NO_3$, (x) 220 CdO, (△) first line of α–Cd(OH)NO$_3$, (o) 111 cubic $Cd(NO_3)_2$. The full line represents the TG curve

It can be seen that the two methods provide very similar onset and final temperatures. On the other hand the X-ray diffraction analysis shows quite well the successive stages of the transformation. It is obvious that the TG curve cannot provide any information about the formula of the intermediate compound. At the very most, it exhibits an inflection point for a value of $\Delta m/m_0$ close to 8% when the amount of the intermediate compound is maximum. Another inflection point is also observed when $Cd(NO_3)_2$ begins to decompose. Complementary experiments have revealed that the intermediate compound is a new anhydrous hydroxide nitrate $Cd(OH)NO_3$, which undergoes two modifications α and β. The high temperature phase β appears during the decomposition process only is a 'ramp-hold' method is used. The simultaneous formation of α–$Cd(OH)NO_3$ and CdO in the first step corresponds to the removal of two water molecules and a weight loss of 7.3%, which is approximately the coordinate of the first inflection point on the TG curve.

From these results the following chemical reactions describe the successive steps pf the decomposition:

$$Cd(OH)_5NO_{3(cr)} \rightarrow \alpha\text{–}Cd(OH)NO_{3(cr)} + 2CdO_{(cr)} + 2H_2O_{(g)} \qquad (1)$$

$$\alpha\text{–}Cd(OH)NO_{3(cr)} \rightarrow 1/2CdO_{(cr)} + 1/2Cd(NO_3)_{2(cr)} + 1/2H_2O_{(g)} \qquad (2)$$

$$1/2Cd(NO_3)_{2(cr)} \rightarrow 1/2CdO_{(cr)} + m/2NO_{(g)} + (2-m)/2NO_{2(g)} + (1+m)/4O_{2(g)} \qquad (3)$$

It is clear from the TG curve that these reactions are superimposed, in spite of the low heating rate used for the experiments.

Thermal decomposition under vacuum

The 3D plot (Fig. 3) and the changes of the integrated intensities for selected diffraction lines as a function of temperature (Fig. 4) show that the decomposition proceeds in a single step, the α–$Cd(OH)NO_3$ phase decomposing from its formation.

On the other hand, cadmium nitrate is not observed during the thermal decomposition. An objection can be raised concerning the ability of TRXD to reveal cadmium nitrate with very small crystalline sizes. However, this interpretation is not correct since no subsequent increases of the CdO line intensities is observed at higher temperature. At last, there is a large discrepancy between he final temperature exhibited by TRXD and TG analysis. This indicates that the rate of gaseous removal from the solids is much lower than the rate of the structural transformation. As otherwise confirmed by a mass

spectrometry study would seem that, more particularly NO, NO_2 and O_2 remain adsorbed on the finely divided cadmium oxide and that their desorption is difficult in this temperature range.
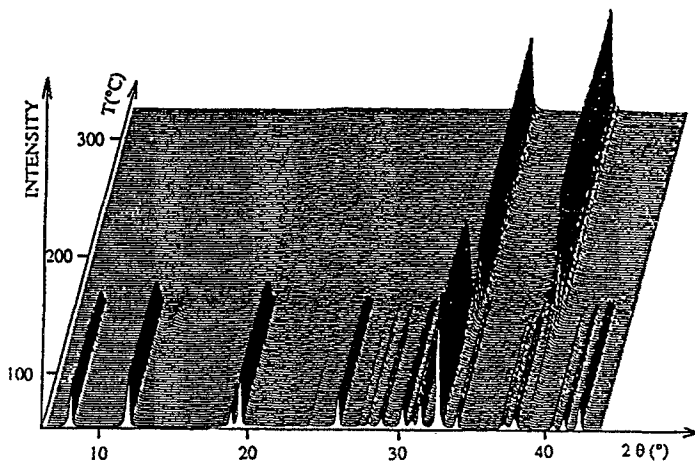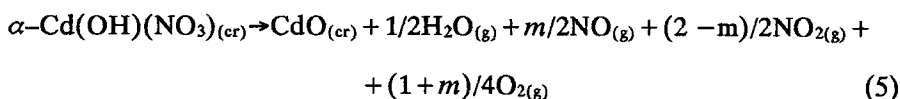

Fig. 3 The TRXD plot of $Cd_3(OH)_5NO_3$ in vacuum. *Spurious diffraction line of 001 reflection of β–CD(OH)$_2$

Consequently, the thermal decomposition of $Cd_3(OH)_5NO_3$ in vacuum takes place in a single step where the two following reactions occur simultaneously:

$$Cd_3(OH)_5(NO_3)_{(cr)} \rightarrow \alpha\text{–}Cd(OH)(NO_3)_{(cr)} + 2CdO_{(cr)} + 2H_2O_{(g)} \quad (4)$$

$$\alpha\text{–}Cd(OH)(NO_3)_{(cr)} \rightarrow CdO_{(cr)} + 1/2H_2O_{(g)} + m/2NO_{(g)} + (2-m)/2NO_{2(g)} +$$
$$+ (1+m)/4O_{2(g)} \quad (5)$$

These experiments demonstrate that TRXD appears as a quite useful tool for understanding the thermal decomposition of solids, particularly in the case of simultaneous formation of several compounds where TG mea-surements provide very poor information.

Kinetic study of a phase transformation

Very slow kinetic of phase transformations cannot be accurately investigated by classical thermal analysis method such as DSC. On the other hand, TRXD allows for tracing *in situ* structural modifications, from the measure-
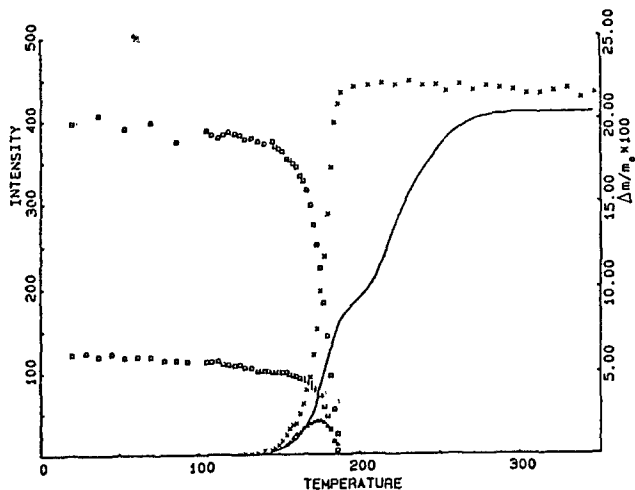
Fig. 4 Integrated intensities of hkl diffraction lines vs. temperature from the TRXD in vacuum. (□) 001,004 Cd$_3$(OH)$_5$NO$_3$, (x) 200 CdO, (Δ) first line if the α–Cd(OH)NO$_3$. The full line represents the corresponding TG curve

ment of the integrated intensity of the diffraction lines as a function of parameters as time or temperature. This is illustrated by the kinetic study of the phase transformation of Cs$_2$CdI$_4$ [5, 7]. This compound undergoes a phase transformation at 120°. The low temperature phase (α) is monoclinic, whereas the high temperature phase (β) has an orthorhombic symmetry. This transformation presents a large hysteresis, so that the β phase can be stabilized at room temperature. Its transformation into the stable α phase takes place very slowly.

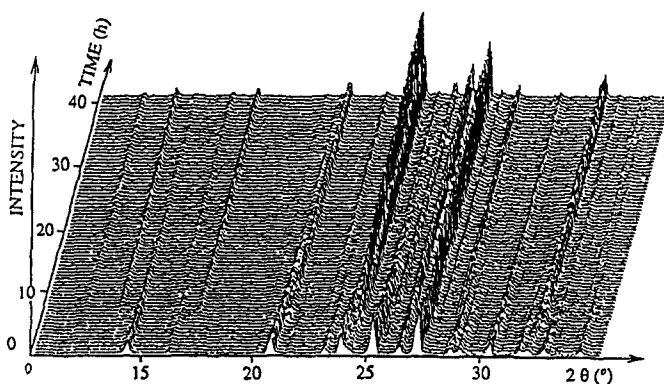Fig. 5 The TRXD plot of the transformation of β–Cs$_2$CdI$_4$ into α–Cs$_2$CdI$_4$ at room temperature

It should be pointed out that the quantitative interpretation, in kinetic terms, of experimental data from TRXD can be influenced by the existence of a preferred orientation of the crystallites in the sample. To avoid this effect a random orientation of the crystallites has to be insured by crushing the crystals and selecting particles with sizes less than 40 μm.

The 3D plot (Fig. 5) shows that the transformation is slow and not complete after 40 hours. From the measurement of the integrated intensity of some selected diffraction lines belonging to the two phases, the volume fraction X of the stable phase α has been obtained as a function of temperature (Fig. 6).
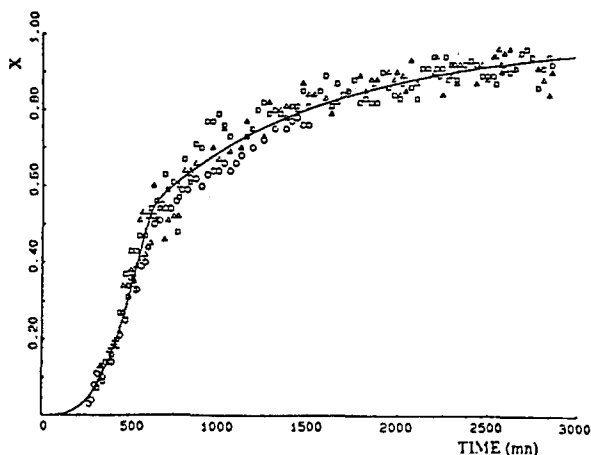

Fig. 6 Time dependence of the volume fraction of the α–phase at room temperature; derived from (Δ)102,111 (β), ($\square$) 011 (α), (o) 200, 103, 121 (α)

The X values derived independently from the two phases agree within about 5% which can be regarded as satisfactory. The first part of the curve indicates that the transformation may be governed by a nucleation and growth process. For X>0.5, the transformation rate decreases drastically so that its completion is not achieved after 40 hours. This feature seems to be due to strains introduced in the solid by grinding the sample, since it is not observed when the grain sizes are larger than 40 μm.

The effect of a preferred orientation of the crystallites within the sample is shown in Fig. 7.

The X values obtained seem to depend on the diffraction line selected and, clearly, a correct averaged value of X cannot be deduced. These results show how a great care must be paid to the sampling.
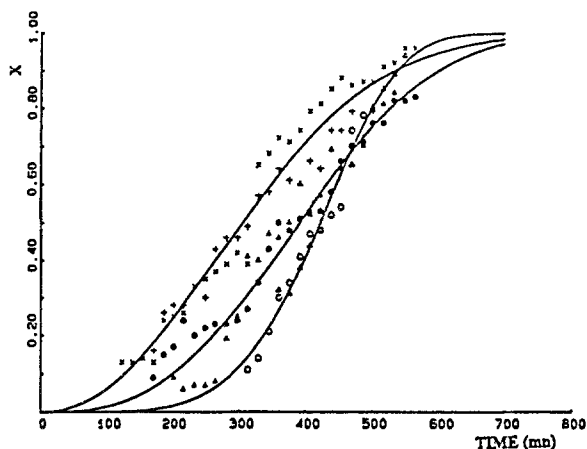
Fig. 7 Time dependence of the volume fraction X deduced from several diffraction lines.
Sample with a preferred orientation effect; (x) 004, 002 (β), (+) 210, 113 (α), (Δ) 301,
104, 122 (β), (o) 102, 111 (β), (o) 020 (α), (Δ) 103, 222 (α)

Microstructural properties of divided solids

Another interesting application of TRXD concerns the ability to evidence
the changes of microstructural properties of solids in reaction, as the size of
the coherently diffracting domains, and microstrains. These parameters can
be obtained from the analysis of the diffraction-line profiles by using simple
Williamson-Hall and single line Voigt methods [8, 9] or a more sophisticated
one such as the Fourier analysis.

As an example, the evolution of the mean crystallite sizes of α-
$Cd(OH)NO_3$, $Cd(NO_3)_2$ and CdO, which appear during the course of the
thermal decomposition of $Cd_3(OH)_5NO_3$ are presented. For this purpose the
approximate single-line Voigt analysis has been used to obtain an evaluation
of size and microstrain parameters. In this 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. Fig-
ure 8 shows the changes of the crystallite sizes perpendicularly to selected
diffractring planes as a function of temperature.

It can be seen that the crystallites of α–$Cd(OH)NO_3$ and CdO grow quick-
ly, while $Cd(NO_3)_2$ is appearing, during the decomposition performed in a
nitrogen stream. On the contrary, in vacuum, the crystallite sizes of CdO are
nearly constant until the end of the decomposition, the annealing of the
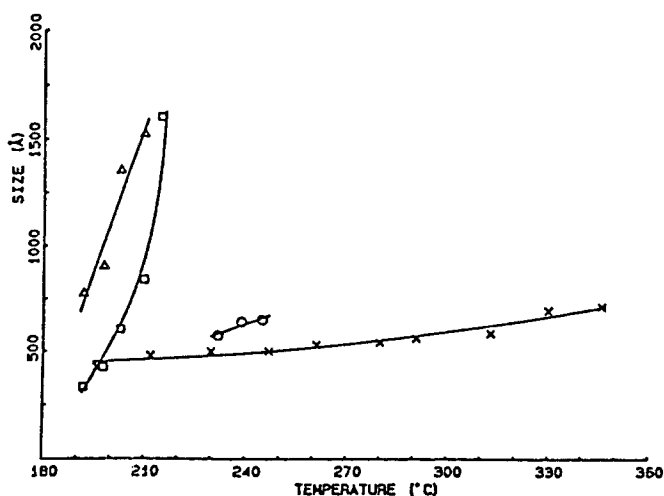material occurring at higher temperature.

Fig. 8 Temperature dependence of crystallite sizes, (Δ) α-Cd(OH)NO$_3$, (□) CdO,
(o) Cd(NO$_3$)$_2$ formed in nitrogen. (x) CdO generated in vacuum

Conclusion

TRXD appears as a useful tool for understanding chemical reaction schemes, for studying phase transformations and giving information about the microstructural properties of finely divided materials. In this way it appears quite complementary to the other regular thermal analysis methods such as TG, DSC and mass spectrometric analysis (MS).

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Zusammenfassung — Der Einsatz konventioneller Röntgen-Diffraktometrie zusammen mit einem gebogenen positionsempfindlichen Detektor (PSD) ermöglicht die Registrierung eines vollständigen Diffraktogramms als Funktion der Zeit oder Temperatur, so dass Festkörper-

umwandlungen fortlaufend verfolgt werden können. Demzufolge kann diese Technik als komplementär zu den konventionellen thermoanalytischen Methoden wie TGA und DSC angesehen werden. Drei Anwendungen werden beschrieben:Die thermische Zersetzung eines Cadmiumhydroxidnitrats, die Phasenumwandlung des Dicäsiumcadmiumtetraiodids und die Messung mikrostruktureller Eigenschaften als Funktion der Temperatur.