Difference Thermal Analysis of Crystalline Solids by the Use of Energy-Dispersive X-ray Diffraction

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Abstract
A method is described to study the structural behavior of solids subjected to various temperature programs. The instrumentation consists of a high- or low-temperature device, a temperature programmer, a system for energy-dispersive X-ray diffraction and a data processing and storing unit and allows the fully automatic acquisition of series of spectra. A strong data reduction is performed by summing up difference diagrams. Plotting the resulting values versus temperature yields curves comparable to those obtained by differential scanning calorimetry (DSC) or thermal gravimetry (TG). A kinetic evaluation as used in the case of DSC or TG curves is possible. The method was applied to study the thermal behavior of a mixture of ammonium nitrate with zinc oxide. The curves indicate the strong anisotropic thermal expansion of the ammonium nitrate phase IV below 323 K, its transition to phase II at 325–329 K and the solid-state reaction with zinc oxide within the temperature interval of 353–383 K.

Introduction
The thermal behavior of solids is frequently studied by methods of thermal analysis, like DSC and TG. These methods contain only indirect information on the structural changes involved. Direct information is offered by X-ray diffraction. As conventional angle scanning is rather slow, photographic techniques can be used to record automatically the X-ray diffraction patterns within the desired temperature interval (Bett & Glazer, 1972; Glazer, 1972; Clarke & Morley, 1976). A numerical evaluation, however, requires additional efforts for the digitalization of the data (see e.g. Ihringer, 1982).

Digital data and relatively short recording times are provided by the energy-dispersive X-ray diffraction (EDXRD) introduced by Giessen & Gordon (1968) and Buras, Chwaszczewska, Szarras & Szmid (1968). A further advantage of the method is the fixed angle geometry of the goniometer. The resolution of the EDXRD, however, is low, especially when compared with photographic continuous recording which is carried out at very high Bragg angles. Standard deviations of lattice parameters calculated from EDXRD are higher by one order of magnitude (see e.g. Laine, Lähteenmäki & Kantola, 1972). Therefore, the application is limited to extreme temperature or pressure conditions or to phase transitions or solid-state reactions between known initial and final structures.

The method described in this paper extends the use of EDXRD to the field of thermal analysis including a substantial data reduction by the concept of difference spectra. The resulting curves characterize the structural changes in the same way as DSC and TG inform about thermal effects.

Experimental set up
The measuring system includes a combination of commercially available components for the acquisition of series of X-ray spectra during temperature programs. It consists of an X-ray goniometer, a high- or low-temperature attachment, controlled by a programmable temperature controller, a solid-state detector with an analogue–digital converter (ADC) and multichannel analyzer (MCA) and, finally, a data processing and storing unit. The block diagram of the combination is depicted in Fig. 1.

In our experimental set up a low-temperature attachment TTK, usable within the temperature range 93 to 573 K, or, likewise, a high-temperature chamber HTK, temperature range 293 to 1473 K, of Paar, Graz, Austria, was mounted on a Siemens X-ray
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diffractometer D 500, run with a tungsten X-ray tube providing continuous radiation. The temperature of the sample is controlled by a MicRicon controller of Research Inc.

EDXRD spectra are measured at a fixed angle of the goniometer by a Si(Li) detector combined with an ADC and the MCA NS 880 of Tracor Northern. The data were stored on a floppy-disc unit. Part of the system has been described elsewhere (Engel & Charbit, 1978; Engel, 1979).

By linking the MicRicon controller and the NS 880 the fully automatic acquisition of the spectra under a given temperature program is possible. Three acquisition modes can be selected:

1. Heating or cooling in consecutive steps followed by the measurement of a spectrum.
2. Linear heating, rates comparable to those available in DSC and TG experiments, the spectra being recorded in equal time intervals.
3. Isothermal measurements in desired time intervals.

**Difference spectra**

Starting from stored series of $M$ EDXRA spectra a strong data reduction is obtained computing variables $Y(T_j)$ and $DY(T_j)$ by summing up the absolute values of the channel contents of difference diagrams. $Y(T_j)$ results from the difference diagram formed from each spectrum with the first one.

$$Y(T_j) = \sum_{j=1}^{N} |X_j(T_j) - X_j(T_1)|; \quad i = 2, ..., M. \quad (1)$$

$DY(T_j)$ is obtained from the difference diagram of neighboring spectra:

$$DY(T_j) = \sum_{j=1}^{N} |X_j(T_j) - X_j(T_{j-1})|; \quad i = 2, ..., M. \quad (2)$$

$X_j$ is the content of the $j$th channel of the $i$th spectrum and $N$ is the number of channels into which the spectrum is resolved. $T_j$ represents the independent variable with which the $i$th spectrum is recorded.

Plotting $Y(T)$ and $DY(T)$ versus $T$ results in a representation of any change of the spectra comparable to TG and DSC, respectively.

The variables consist additively of contributions caused by the peak shift $\Delta j$ and the increase and decrease of peak intensities $\Delta I$ and the statistical scatter of the content of every single data channel $S_e$:

$$Y(T) \text{ or } DY(T) = f(\Delta j) + g(\Delta I) + S_e. \quad (3)$$

Further influences assumed to be of less importance here are neglected.

$S_e$ can be estimated by use of the standard deviation of the counts with which a channel is filled and subtracted from $Y(T)$ or $DY(T)$, respectively:

$$S_e = \sum_{j=1}^{N} [X_j(T_j)]^{1/2}. \quad (4)$$

The quantitative character of $DY(T)$ and $Y(T)$ is evident if the evaluation (1) and (2) is restricted to regions of the spectrum which contain only a single peak. The following special cases are encountered.

1. $\Delta j = 0$

   The variation of the peak intensity is found absolutely by

   $$Y(T_j) = I_p(T_j) - I_p(T_1) \quad (5)$$

   $$DY(T_j) = I_p(T_j) - I_p(T_{j-1}). \quad (6)$$

2. $\Delta I = 0$

   In this case $Y(T)$ and $DY(T)$ are functions of the peak shift. If the shift is small compared with the half width of the peak it can be estimated by

   $$Y(T_j) = 2I_n[j_p(T_j) - j_p(T_1)] \quad (7)$$

   $$DY(T_j) = 2I_n[j_p(T_j) - j_p(T_{j-1})]. \quad (8)$$

   where $I_p$ is the intensity of the evaluated peak, $I_n$ the net count rate of the peak maximum channel and $j_p$ the number of its position.

   For the representation of the curves it is convenient to normalize $Y(T)$ and $DY(T)$:

   $$Y^*(T_j) = 1 - (Y(T_j) - Y_{max})/(Y_{max} - Y_{min}) \quad (9)$$

   $$DY^*(T_j) = DY(T_j)/(T_j - T_{j-1}). \quad (10)$$

**Application of the method**

The method was used to investigate mixtures of $\text{NH}_4\text{NO}_3$ (AN) and $\text{ZnO}$ in a molar ratio of 2:1 and 4:1 on heating.

**Experimental details**

The measurements were made with a tungsten X-ray tube run at 35 kV and 20 mA, a fixed goniometer angle of $2\theta = 10^\circ$, aperture slits of 3 and 1 mm and detector slits of 1 and 0.15 mm and an acquisition time of 200 s. The samples were heated from 303 to 403 K in steps of 2 K and time intervals of 8 min from 303 to 403 K. The energy range of 12–32 keV was selected and resolved in 1000 channels. The following measuring loop was used:

1. clock starts
2. data acquisition, 200 s
3. data storage on floppy disc
4. MicRicon controller shifts to next temperature step (+2 K)
5. Wait until clock reaches the end of the time interval (8 min).

Further experiments were carried out with linear heating. The heating rate was varied between 0.5 and 2 K min$^{-1}$ and the exposure time between 20 and 120 s.
For comparison DSC curves were recorded on a Dupont 990 thermal analyzer. The heating rate was 1 K min$^{-1}$ and the sample weight 5 mg.

**Results**

Selected EDXRA spectra measured with the sample of a molar ratio 2:1 at various temperatures are depicted in Fig. 2. The corresponding curves $Y(T)$ and $DY(T)$ are plotted in Fig. 3. For comparison the DSC curve is shown in Fig. 4.

**Discussion**

Heating the samples within the temperature interval three effects and their influence on the curves $Y(T)$, $DY(T)$ and DSC can be demonstrated:

1. **Anisotropic expansion of AN below 323 K.** Dry AN in its phase IV shows a strong anisotropic expansion in the direction of lattice parameter $b$ (Choi & Mapes, 1972; Choi & Prask, 1980), which shifts the partially overlapped 020 peak at 26 keV in the lowest two diagrams of Fig. 2. This results in a continuous decrease of $Y(T)$ and a base-line deflection of $DY(T)$. The DSC curve is not affected.

For a quantitative evaluation the calculation of $Y(T)$ and $DY(T)$ was restricted to the region of the 020 peak, between 24 and 27 keV. Neglecting the intensity decrease of X-ray peaks with rising temperature the shift was estimated to be 0.100 keV using (7) and (8). This deviates from the shift found by the more cumbersome peak profile fit only by 0.005, profiles used according to those proposed by Mantler & Parrish (1976). This is remarkably good because the peak under investigation is overlapped by a stronger ZnO peak.

2. **Phase transition IV/II of AN from 325 to 329 K.**

In the phase-transition interval of AN 325–329 K (see, for example, Heide, 1966) the 020 peak disappears (compare the second and third spectra in Fig. 2). Other phase IV peaks, e.g. the 111 peak, disappear and corresponding phase II peaks appear immediately neighboring and form strongly overlapping peaks in the EDXR diagrams. This causes a step in the $Y(T)$ curve and a sharp peak in the $DY(T)$ curve. The latter is comparable to that of the DSC curve.

In the case of the 111 reflection if constant intensity of the double peak during the transition is assumed, the relative intensities of the single peaks and the position of 111$_{II}$ can be estimated using (5)–(8). Restricting the evaluation to the range of 21.5–24 keV the position was found to be shifted by 0.190 keV within 303–343 K. Fig. 5 illustrates this by comparing the result of a peak profile fit with the evaluation according to (7).

The subsequent expansion of the sample after the phase transition is less intense. This results in a smaller...
decrease of $Y(T)$ within the temperature interval of 333 to 353 K (see Fig. 2).

3. Solid-state reaction of $AN + ZnO$. Within the temperature range of 353–383 K the change of the EDXRD spectra (see Fig. 2) represents the solid-phase reaction of AN with ZnO. This causes a decreasing sigmaoid curve profile of $Y(T)$ and a broad asymmetric peak of $DY(T)$.

The DSC curve in Fig. 4 shows a weakly endothermic reaction within 353–383 K. The sharp peak at 393 K indicates a small residue of AN which undergoes the highly endothermic phase transition II/I.

A comparison of the curve $Y(T)$ obtained from the sample with a molar ratio of 4:1 for AN and ZnO with the sample of molar ratio 2:1 shows that the ratio of the step height of the first sample at 325 K to that at 353–383 K is twice the ratio of the second, which is in agreement with the peak intensities of the curve $DY(T)$. This confirms the assumption of a 2:1 reaction product, which is diammine zinc dinitrate (Eisenreich & Engel, 1982).

The evaluation was also performed with isolated peaks of AN, ZnO or product peaks within the temperature interval of 348–403 K. In all cases, after normalization to 1, curves were obtained identical to that curve including the whole spectra. Intensity curves of the ZnO, AN and product peaks obtained from a peak profile fit of the diagrams within the temperature range had equal curve shapes. A comparison of selected curves is shown in Fig. 6. This suggests that the curves $Y(T)$ are directly related to the concentration of the species involved and $DY(T)$ is proportional to the conversion rate neglecting peak shifts. The attempt to apply the kinetic analysis (see, for example, Koch, 1977) commonly used for DSC or TG for curves obtained after linear heating will be reported elsewhere (Eisenreich & Engel, 1982).

The quantitative interpretation of the variables $Y(T)$ and $DY(T)$ requires the assumption that peak-shift or, alternatively, peak-intensity variation and other effects can be neglected. This cannot always be expected in heating experiments. However, it can be assumed in isothermal experiments. Isothermal investigations were performed and rate constants evaluated which will also be published separately (Eisenreich & Engel, 1982).

The evaluation of experiments with shorter exposure times (20 s) yielded equally smooth curves for $Y(T)$ and $DY(T)$. The original spectra were very noisy and the determination of intensity and position of especially smaller peaks was hardly possible. The information of $Y(T)$ and $DY(T)$ on qualitative as well as quantitative changes of the spectra, however, was substantially the same as obtained from the spectra recorded with longer exposure times.

Because of the low detector resolution the observation of phase transitions by EDXRD is rather limited if cases are studied which involve only small splitting up of peaks. The proposed data evaluation by summing up difference spectra should be able to improve the detection limit considerably. It includes the changes of all peaks, whereas details must not be specified. In contrast, a fit program evaluates the peaks independently and requires at least a peak broadening to indicate a peak splitting. In particular, the curve $Y(T)$ is smooth and, in addition, changes of the spectra cause a step which can be even smaller than the noise of the curve but, nevertheless, can be observed.

Conclusions

The test of the applicability of the EDXRD as a tool of thermal analysis resulted in the following conclusions.
The described measuring system allows the acquisition and storage of series of spectra in three modes of stepwise, linear and isothermal heating. In the linear heating mode rates of 0.5–2 K min⁻¹ can be selected with exposure times of 20–200 s, which correspond to the lower rates of thermal analysis.

The evaluation, based on the concept of difference diagrams, performs a very efficient way of data reduction. It requires shorter exposure times, smaller computing facilities and shorter computing times if compared with an evaluation by peak-fitting procedures.

The resulting curves of the calculated variables Y and DY reflect structural changes in the same way as TG and DSC curves record gravimetric and calorimetric effects. They can be equally used for a kinetic analysis.

Applying the evaluation to selected regions of the spectra, concentration of phases or components in phase transitions and solid-state reactions can be followed. Thermal expansion of different phases can be measured.

In addition, the original spectra can be used for a further phase identification of the sample.

The data evaluation is not restricted to spectra of EDXRD under varied temperature or time. It can be applied to any type of digitized series of spectra recorded under any conditions.

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References