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A new simultaneous apparatus for X-ray diffractometry and differential scanning calorimetry (XRD-DSC)

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Abstract

An instrument was developed for performing simultaneous X-ray diffractometric and differential scanning calorimetric (XRD-DSC) measurement using a power compensation DSC (pc-DSC). The feasibility of the technique is demonstrated by examining the thermal dehydration measurement of zinc formate dihydrate ($\text{Zn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$). The DSC curve shows apparent double endothermic peaks during the dehydration process, while X-ray diffraction analysis indicated that the resulting anhydrous product, $\text{Zn}(\text{HCO}_2)_2$, was crystalline. The simultaneous measurement reveals that the DSC curve arises from a combination of the endothermic dehydration peak and the exothermic crystallization peak which resulted from the progression of the anhydrous products. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most thermal analysis techniques provide physical information, therefore ancillary data is required for chemical interpretation of the observed thermal events. Recently, simultaneous measuring methods have rapidly developed and their achievements have attracted much attention. For example, simultaneous measurements with evolved gas analysis (EGA), namely gas chromatography–mass spectrometry (GC-MS), thermogravimetry–mass spectrometry (TG-MS) [1–7] and thermogravimetry–Fourier trans-

form infrared spectroscopy (TG-FTIR) [8–11], have been developed only in the past decade.

Differential scanning calorimetry (DSC), however, gives physical information and is widely accepted as a useful thermo-analytical tool for the study of phase transitions. A DSC curve may show several endothermic and exothermic peaks, and baseline shifts, since the chemical and physical reactions generally proceed through various steps. Unfortunately, this method does not reveal the identity of the transforming phases. Identification of each peak is often quite impossible without the aid of techniques that yield information regarding structures and reactions.

Phase transitions between the various solid states have been the focus of much attention for several decades, and a variety of methods have been used to

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study their thermodynamic, structural, and kinetic properties. Among them, calorimetry and X-ray diffraction have proven to be two of the most useful techniques.

In this respect, X-ray diffraction (XRD) is probably the most reliable technique for phase identification and structure characterization. Both the methods, namely DSC and XRD, are considered complementary to each other, and the development of the simultaneous measuring instrument of DSC and XRD has been anticipated. Parallel measurements of different specimens using DSC and XRD, and a combination of both data are one of the popular ways of studying thermal reactions of solids. Problems arise, however, because many chemical reactions of solids, for instance the dehydration of hydrates, depend markedly on the sample preparation and on the experimental conditions such as the nature of the atmosphere, shape of the crucible, the heating rate, etc. The differences in measuring conditions complicate the combination and comparison of the obtained data. Such problems can be overcome by simultaneously performing DSC and XRD measurements on the same sample.

Masuda et al. studied crystallinities of dehydrated product phases and described the effect of water vapor pressure on the kinetics of the thermal dehydration of some formate hydrates by means of a combination of TG-DTA and XRD [12,13]. These results reveal that more sophisticated simultaneous measuring systems under identical measuring conditions are preferred for the determination of reaction mechanisms based on structural and thermal data.

We have assembled a simultaneous XRD-DSC measuring apparatus using a power compensation DSC (pc-DSC) which was specially designed for the above-mentioned purposes. Then, we have applied it to the complicated dehydration behavior of zinc formate dihydrate measured by this XRD-DSC, as an example. It is the purpose of this paper to report on this simultaneous apparatus and demonstrate its performance.

1.1. Instrumentation of the simultaneous XRD-DSC measuring apparatus

Generally, a pc-DSC and a heat-flux DSC (hf-DSC) are widely used for DSC measurements. Both these

DSCs provide almost the same information, but their measuring principles are fundamentally different.

In previous similar studies of XRD-DSC, various types of hf-DSC have been used. For example, a commercially available unit developed for optical microscopy [14,15], and an original cell unit modified for this purpose [16,17] have been reported. Such a cell unit has a small aperture through which the X-ray beam can pass unhindered, and a sample material mounted in a standard aluminum DSC crucible with a cover. In this case, the DSC had been modified to allow transmission of the X-ray beam which passes through the specimen and, therefore, the scattering geometry requires mounting the DSC cell vertically. In addition, modification of the XRD-DSC stage is necessary in order to minimize beam attenuation. The sample holder of the DSC cell has apertures of a few-millimeter diameter for the transmission of an X-ray beam. The collimated X-ray beam passes through a smaller aperture in order to eliminate parasitic scattering. A large irradiated area in the sample cell is required to get strong X-ray diffraction patterns. However, this is especially troublesome when using an hf-DSC. Keeping of an open window for the X-ray beam makes it difficult to assure the small heat exchange between the sample and surroundings, and to assure the adequate measuring sensitivity of the DSC.

On the other hand, a pc-DSC has several advantages over hf-DSC for the simultaneous XRD-DSC measurement. Pc-DSCs may be roughly classified into two types by the electrical heater arrangement for heating the sample. In one type, the electrical microheaters separately heat the sample and the reference holders and they control the energy required not only to heat the sample and the reference, but to make the temperature difference zero between the sample and the reference. In the other type, an additional electrical heater located around the sample and reference holders acts as a source of controlled energy to heat both, the sample and the reference. The former type of pc-DSC makes it possible to maintain the path of the X-ray beam, because the additional heater does not interfere with the X-ray beam.

We tried to combine a pc-DSC of the former type with an XRD apparatus to realize simultaneous measurements. Fig. 1 shows a close-up of a pc-DSC whose geometry is designed to perform XRD measurement. The sample was mounted horizontally to the

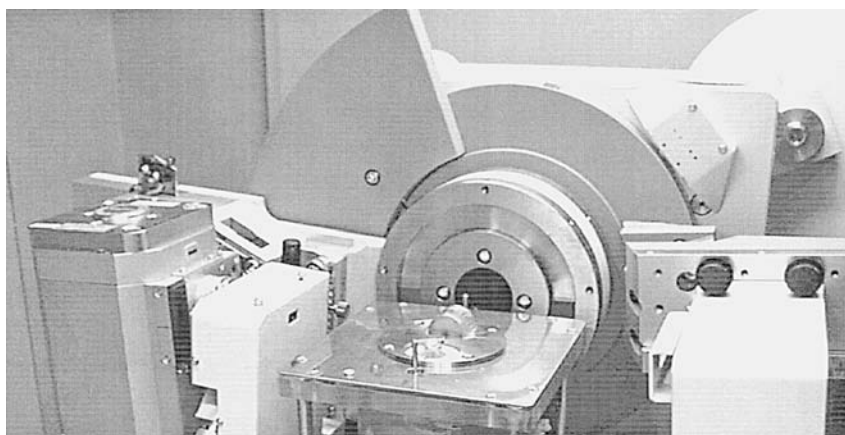


Fig. 1. Photograph showing simultaneous XRD-DSC apparatus.

incident X-ray beam on an optical bench. Fig. 2 shows a schematic diagram of the DSC geometry compartment. In order to realize the smallest heat loss to surroundings and to maintain the highest measuring precision, twin heat-shield covers, with X-ray transmission windows of thin aluminum film, are placed around the DSC holders, and both, the incidence and reflection X-ray beam paths are maintained.

2. Experimental

2.1. Material

Commercially available zinc formate dihydrate ($\text{Zn}(\text{OCH}_2)_2 \cdot 2\text{H}_2\text{O}$) was recrystallized and kindly sup-

plied by Masuda, and it was pulverized with a mortar and pestle, and sieved to a fraction below 150 mesh size. The sample of ca. 30 mg in an open aluminum pan was used for the XRD-DSC measurements in static air.

2.2. Procedure

For the $\text{CuK}\alpha$ radiation, a graphite monochromator was used for the XRD measurements. A line shape X-ray source used was a RIGAKU/RINT-Ultima⁺ system, and it was operated at 50 kV and 30 mA. The X-ray diffraction measurements were carried out in the $5 < 2\theta < 35^\circ$ range at $20^\circ \text{ min}^{-1}$, taken at intervals of 0.02° .

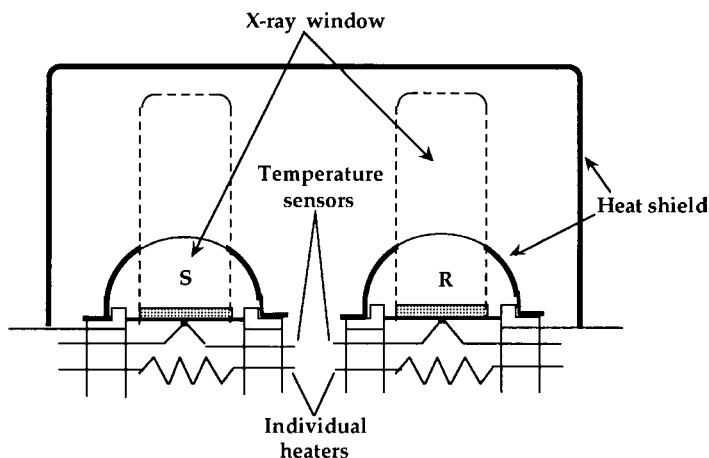


Fig. 2. Schematic power-compensation DSC part.

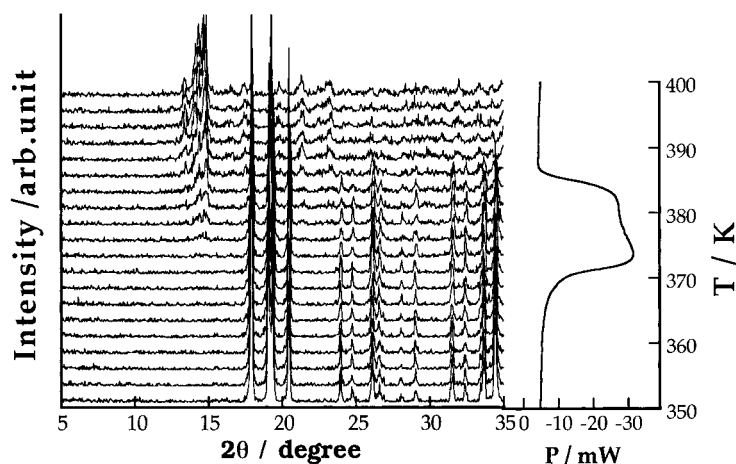


Fig. 3. Relationship between the DSC curve and XRD patterns in the dehydration of $\text{Zn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ by simultaneous XRD-DSC.

3. Results and discussion

Fig. 3 shows the relationship between the DSC curve and X-ray diffraction patterns during the dehydration of zinc formate dihydrate recorded by means of the simultaneous XRD-DSC for a heating rate of 1 K min^{-1} . The DSC curve indicates the dehydration of the sample begins at around 360 K and ends at around 390 K. This curve also shows apparent, double endothermic peaks in the dehydration process. On the other hand, it can be clearly observed that the change in XRD patterns gradually starts from 373 K of the first endothermic peak, and is completed after the second endothermic peak at 383 K. Fig. 4 shows XRD patterns obtained at 354 K with the DSC curve. It is noteworthy that the resulting anhydrous product shows crystalline patterns.

This type of behavior has been observed previously and it was proved that the crystallinity of the dehydrated product was affected by the experimental temperature and the water-vapor pressure in XRD, as has been described recently by Masuda et al. [12,13]. However, the shape of the present DSC curve does not correspond with that of the DTA of a previous TG-DTA, in which the smoothness of curve observed suggested that the dehydration proceeds without an intermediate [12].

As regards the results of the present experiment, the apparent double DSC peaks do not provide enough evidence to decide upon the detailed dehydration behavior. It seems likely, however, that the shape of

DSC peak suggests overlapping of peaks brought about by several concurrent multiple reactions. From the analytical point of view, the DSC curves can be interpreted in two ways. The apparent double endothermic peaks may be attributed to a concurrent phase change brought about by an overlapping of the exotherm and the endotherm. The other hypothesis is that the dehydration may proceed through the formation of an intermediate, such as a monohydrate. As discussed below, the XRD data simultaneously obtained with DSC can give us very important information in regard to the choice of the foregoing alternative hypotheses.

We shall now look more carefully into the relationship between the XRD and DSC data in Fig. 3. The DSC curve and the integrated XRD intensity in the range of the diffraction angles characterizing the structural changes are compared in Fig. 5 as a function of temperature. The integrated intensity curve of XRD patterns of crystalline dihydrate between 17° and 21° shows a broad sigmoidal decay according to the progress of the dehydration, while the increment of the integrated peak intensity in the diffraction angles between 12° and 16° reveals a concurrent growth of the crystalline anhydrous product. These trends could well explain the shift of DSC curve in the exothermic direction between 373 and 383 K. That is, the DSC double peaks are attributable to a combination of the endothermic dehydration peak and the exothermic crystallization peak of the anhydrous product.

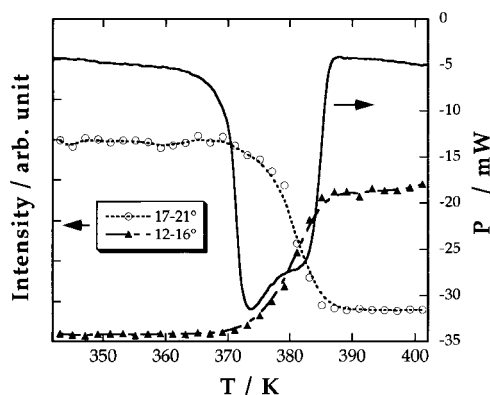
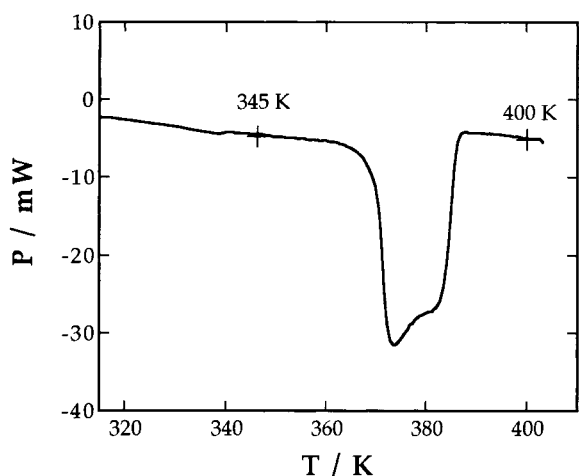


Fig. 5. Comparison of the DSC curve and the integrated XRD curves obtained from the selected diffraction angle range in the dehydration of $\text{Zn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$.

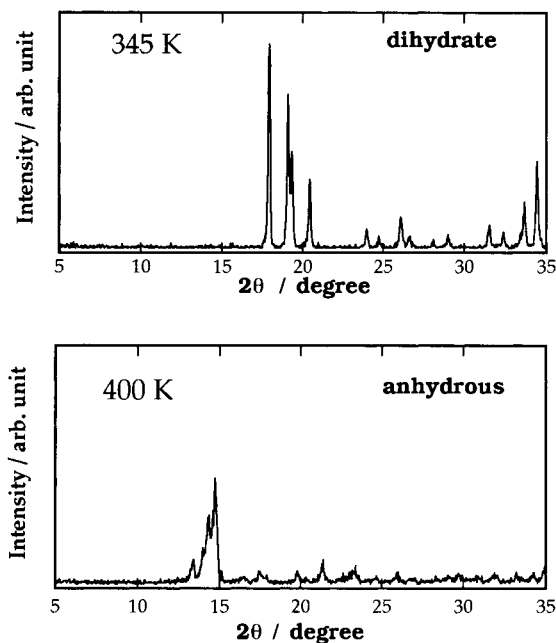


Fig. 4. DSC curve and XRD patterns obtained at 345 and 400 K in the dehydration of $\text{Zn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$.

4. Conclusions

We have described a new type of method by which XRD and pc-DSC measurements can be carried out simultaneously. XRD-DSC is an especially powerful method for collecting structural and thermal data on systems, where separate measurements under identi-

cal conditions are problematic. The XRD-DSC has been applied to the dehydration process followed by concurrent with recrystallization of the anhydrous product. The XRD-DSC data are especially useful to verify the interpretation of thermal transitions (or overlapping transitions) with thermal reactions. The structural changes observed by the XRD-DSC give the strongest proof that explains the actual dehydration process. These results clearly demonstrate the potential capability of this new experimental method, particularly for the examination of the complex thermal behaviors inherent in many important chemical systems.

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References

- [1] E.K. Gibson Jr., S.M. Jonson, *Thermochim. Acta* 4 (1972) 49.
- [2] J. Chiu, A.J. Battie, *Thermochim. Acta* 50 (1981) 49.
- [3] A.R. McGhie, *Thermochim. Acta* 234 (1994) 21.

- [4] E. Dubler, M. Baumgartner, *Solid State Ionics* 43 (1990) 193.
- [5] D. Price, G.J. Milnes, P.J. Tayler, J.H. Scrivens, T.G. Blease, *Polym. Degrad. Stabil.* 25 (1989) 307.
- [6] T. Ariei, T. Senda, N. Fujii, *Thermochim. Acta* 267 (1995) 209.
- [7] T. Ariei, K. Terayama, N. Fujii, *J. Therm. Anal.* 47 (1996) 1649.
- [8] M. Mittleman, *Thermochim. Acta* 166 (1990) 301.
- [9] P.R. Solomon, M.A. Serio, R.M. Carangelo, R. Bassilakis, *Energy & Fuels* 4 (1990) 319.
- [10] R. Kinoshita, Y. Teramoto, T. Nakano, H. Yoshida, *J. Therm. Anal.* 38 (1992) 1891.
- [11] R. Kinoshita, Y. Teramoto, H. Yoshida, *J. Therm. Anal.* 40 (1993) 605.
- [12] Y. Masuda, *Netsu Sokutei* 22 (1995) 203.
- [13] Y. Masuda, K. Nagata, *Thermochim. Acta* 155 (1989) 255.
- [14] T.P. Russell, J.T. Koberstein, *J. Polym. Sci.: Polym. Phys. Ed.* 23 (1985) 1109.
- [15] H. Chung, M. Caffrey, *Biophys. J.* 63 (1992) 438.
- [16] H. Yoshida, R. Kinoshita, Y. Teramoto, *Thermochim. Acta* 264 (1995) 173.
- [17] H. Yoshida, *Thermochim. Acta* 267 (1995) 239.