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Short communication

# The beam-heating effect in simultaneous differential scanning calorimetry/synchrotron powder X-ray diffraction

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**Abstract**

An instrument for simultaneous differential scanning calorimetry/synchrotron powder X-ray diffraction was used to detect and quantify the beam-heating effect, i.e. the deposition of measurable energy into a sample by a synchrotron X-ray beam. For beam energy of 17 keV, incident beam flux of $4.27 \times 10^{11}$ photon/s, and beam size of 1000 μm × 300 μm, the measured power input into the sample is on the order of 1 mW. The ability to deliver the energy in the form of an almost ideal square-wave made it possible to accurately analyze the response of the differential scanning calorimeter to such an input. The beam-heating effect needs to be considered in performing and evaluating differential scanning calorimetry measurements involving synchrotron X-ray sources.


*Keywords:* Differential scanning calorimetry; Synchrotron; Beam energy; Beam-heating

## 1. Introduction

Synchrotron light sources made it possible to devise simultaneous techniques that involve X-rays. Combinations of thermal analysis methods with X-ray methods have become common. Among them, simultaneous differential scanning calorimetry and powder X-ray diffraction (DSC/XRD) is one of the most useful. In DSC/XRD, a sample is subject to a DSC thermal program, while an X-ray beam is diffracted by it and detected, thus producing an XRD pattern. It became clear that the very intense synchrotron X-ray beam might be depositing energy into the sample at a rate sufficient for detection by the DSC. While synchrotron X-ray beam sample damage is a well-known phenomenon, quantification of the associated thermal effects by DSC has not been performed to date.

## 2. Experimental

A hermetic enclosure for simultaneous DSC/XRD has been described previously [1]. The results of experiments performed with it have been published elsewhere [2]. The experimental setup used in this work is identical to an improved hermetic enclosure for simultaneous DSC/XRD that has recently been described [3]. The only major difference is that the alternative temperature measurement and control system has been replaced with a Perkin-Elmer Pyris 1 DSC unit. This improved the DSC sensitivity dramatically, making it possible to detect and quantify the beam-heating effect. The temperature and enthalpy

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scales of the DSC have been calibrated with In and Zn standards by standard procedures.

The two samples used in these experiments were slightly compacted mechanical mixtures of zeolite 4A with ∼30 wt.% LiCl weighing 11.1 and 10.7 mg, respectively. They were contained in graphite pans weighing 25.4 and 25.2 mg, respectively. The reference side of the DSC held an empty graphite pan. The enclosure was purged with Ar gas (99.999%) at ∼20 $cm^3$/min. The water chiller temperature was set at 10 °C.

The experiments were performed on a Huber 8-circle diffractometer at the Materials Research Collaborative Access Team (MR-CAT) beam line at the Advanced Photon Source (APS), Argonne National Laboratory (ANL). A cryogenic double-crystal Si(1 1 1) monochromator was used to select the primary beam energy of 17 keV, while a Rh-coated mirror reduced the harmonic content of the beam. The X-ray beam size was 1000 μm horizontal by 300 ± 50 μm vertical. Considering that the sample surface exposed to the X-ray beam is a disk 5 mm in diameter, and that the enclosure was tilted at an angle $\theta = 4.5^\circ$ to the centered horizontal X-ray beam, it follows that the area of the X-ray beam projected onto the sample surface was entirely contained therein. After alignment, the photon shutter was closed and the DSC was allowed to equilibrate for about 1 h at 50 °C. The DSC program consisted of a 3 min isotherm at 50 °C. Initiation of the program was accompanied by an automatic reset of the DSC signal to 0 mW. After sufficient time had passed to allow for positive initial isotherm determination, the photon shutter was opened remotely. The photon shutter movement across the X-ray beam (in both directions) is estimated to take less than 100 ms. After full development of the DSC response, the photon shutter was closed again and a return of the DSC signal to the final isotherm was recorded.

## 3. Theory and calculations

A power-compensated DSC was first described by Watson et al. [4]. Theoretical treatment of an ideal power-compensated DSC with proportional control was given by O'Neill [5]. The theoretical response of an ideal power-compensated DSC with proportional and proportional-integral-differential control to a square-wave heat input was derived by Tanaka [6]. For proportional control (Perkin-Elmer Pyris 1 DSC employs proportional control), setting $p(t) = 0$ at $t < 0$, $v(t) = 0$ at $t < 0$, and $v(t) = v_0$ at $t \geq 0$, the relevant equation is:

$$p(t) = \frac{v_0 K_p}{K_p + h}(1 - e^{-t/\tau}) \quad (1)$$

where $p(t)$ is the DSC signal as a function of time $t$, $v_0$ the amplitude of the square-wave, $K_p$ the proportional control constant (gain), $h$ the heat transfer coefficient between the sample holder and the surroundings, and $\tau$ the time constant. The time constant is given by $\tau = C/(K_p + h)$, where $C$ is the heat capacity of the sample holder (including the sample and pan). Eq. (1) does not take into account dead time, i.e. the time elapsed between the application of the square-wave heat input and the departure of the DSC signal from the isothermal baseline. In other words, the DSC is assumed to react instantaneously. Also, the exact time at which the square-wave is applied is rather difficult to ascertain, since opening and closing the photon shutter involves manually pushing a button, followed by a delay of ∼1 s. Hence, a slightly modified equation that incorporates a time delay, $t_0$, was used for least-squares fitting of the data:

$$p(t) = A(1 - e^{-(t-t_0)/\tau}) + B \quad (2)$$

where $A = (v_0 K_p)/(K_p + h)$ and $B$ is the value of $p(t)$ at $t = t_0$. Coefficients A, $t_0$, and $\tau$ were calculated, while coefficient $B$ was set at the value of the DSC signal immediately prior to the departure from the isothermal baseline. Both the initial and final responses, following photon shutter opening and closing, respectively, were fitted.

The incident beam flux, measured by a nitrogen-filled ion chamber, was $4.27 \times 10^{11}$ photon/s, or 1.16 mW. This calculation assumes that only absorbed X-rays (photo-electric cross-section) are measured by the ionization chamber and not coherently or incoherently scattered X-rays. The air between the ion chamber and the sample absorbed about 5% of the incident beam. The argon inside the DSC head absorbed about 6.5% of the incident radiation, while the Be window absorbed less than 1%. The final correction we applied was to assume that the energy from only half of the coherently scattered X-rays from the sample was deposited to the sample head,

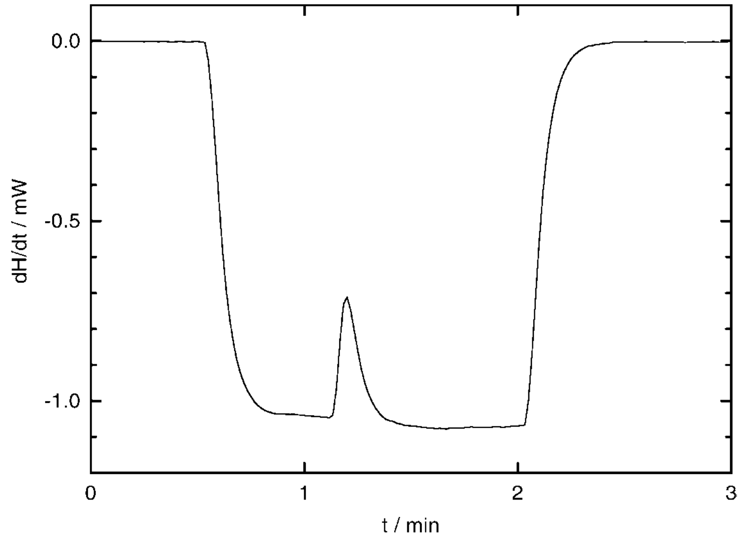


Fig. 1. The DSC response to a square-wave heat input. Shutter opened at ∼0.5 min, closed at ∼2.0 min.

for 98% energy deposition efficiency. After applying these factors, the calculated power is 1.01 mW. Given the assumptions included in the calculation, the error could be as large as 10%.

## 4. Results and discussion

DSC signals obtained are shown in Figs. 1 and 2. The least-squares lines given by Eq. (2) were indiscernible from the DSC signal in all four cases and, hence, are not shown. The least-squares coefficients are given in Table 1. In Fig. 1, as a result of good equilibration, the isothermal baseline is linear with no discernible slope. The photon shutter was opened at ∼0.5 min, intermittently closed at ∼1.1 min and opened at ∼1.2 min, and closed at ∼2.0 min. The time constants, $\tau$, associated with the initial and final response are 4.3 and 3.7 s, respectively. The magnitudes are 1.063 and 1.067 mW, respectively. In Fig. 2, the equilibration was not complete, so that the isothermal baseline exhibits a slight negative slope. The photon shutter was opened at ∼1.0 min, and closed at ∼2.1 min. The time constants, $\tau$, associated with the initial and final response are 3.9 and 3.4 s, respectively. The magnitudes are 1.033 and 0.997 mW, respectively.

The response of the DSC follows the theoretical response of an ideal power-compensated DSC with proportional control to a square-wave heat input, Eq. (1), exceedingly closely. The average time constant is 3.8 s. This is in agreement with a reported time constant of 2 s for an empty sample holder of the essentially identical Perkin-Elmer DSC 7 [7]. Considering that opening of the photon shutter results in heat input into the surface of the 0.5 mm thick sample, while closing it results in cooling of the whole sample, the time constant in the former case should be slightly larger than that in the latter case. This is, in fact, observed (see

Table 1
Least-squares coefficients from Eq. (2)

| | $A$ (mW) | $t_0$ (min) | $\tau$ (s) | $B$ (mW) |
|---|---|---|---|---|
| Experiment 1, initial | −1.063 ± 0.002 | 0.559 ± 0.002 | 4.3 ± 0.1 | 0.00 |
| Experiment 1, final | 1.067 ± 0.001 | 2.061 ± 0.001 | 3.7 ± 0.1 | −1.07 |
| Experiment 2, initial | −1.033 ± 0.002 | 1.029 ± 0.002 | 3.9 ± 0.1 | −0.07 |
| Experiment 2, final | 0.997 ± 0.001 | 2.127 ± 0.001 | 3.4 ± 0.1 | −1.12 |

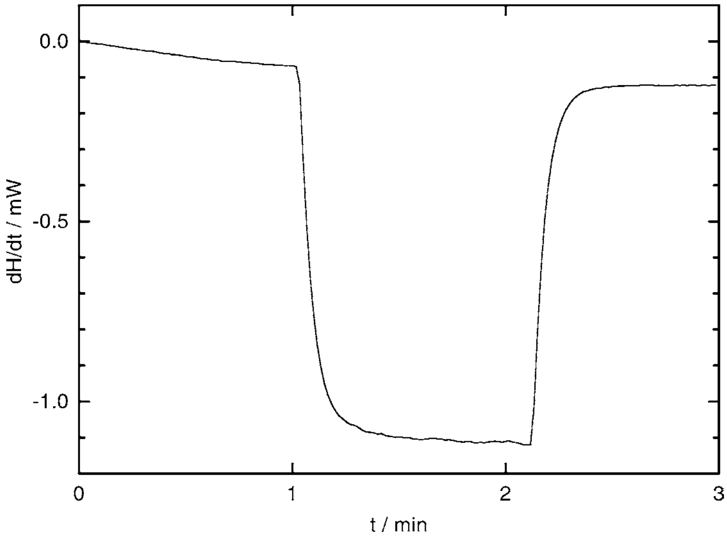


Fig. 2. The DSC response to a square-wave heat input. Shutter opened at ∼1.0 min, closed at ∼2.1 min.

Table 1), with a difference of 0.5 and 0.6 s in the first and second experiments, respectively. From the values of $A$ and $\tau$, $v_0$, $K_p$ and $h$ can be calculated. This was done by assuming $K_p \gg h$, which ensures uniform convergence of the DSC signal to $v_0$ with time [6]. In this case, $A = v_0$ and $\tau = C/K_p$. Hence, considering the heat capacity of a 2 g Pt sample holder [7] is 0.26 J/K (neglecting the heat capacity of the sample and pan), the average value of the proportional control constant (gain), $K_p$, is 0.07 W/K, and the average measured rate of energy deposition into the sample by the synchrotron X-ray beam is 1.04 mW. This value is in excellent agreement with the calculated beam energy deposition rate (power input) of 1.01 mW.

Hence, the magnitude of the beam-heating effect (in this experimental arrangement) is measurable, and the effect needs to be considered in performing and evaluating differential scanning calorimetry measurements involving synchrotron X-ray sources.

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## References

[1] D. Lexa, Rev. Sci. Instrum. 70 (1999) 2242–2245.
[2] D. Lexa, L. Leibowitz, J. Kropf, J. Nucl. Mater. 279 (2000) 57–64.
[3] D. Lexa, Thermochim. Acta, in press.
[4] E.S. Watson, M.J. O'Neill, J. Justin, N. Brenner, Anal. Chem. 36 (1964) 1233–1238.
[5] M.J. O'Neill, Anal. Chem. 36 (1964) 1238–1245.
[6] S. Tanaka, Thermochim. Acta 210 (1992) 67–76.
[7] G. Hõhne, W. Hemminger, H.J. Flammersheim, Differential Scanning Calorimetry, Springer, New York, 1996, p. 15.