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MEASUREMENTS OF SPECIFIC HEAT OF META-NITROBENZOIC ACID·DIETHANOLAMINE CRYSTALS – BY DIFFERENTIAL SCANNING CALORIMETRY

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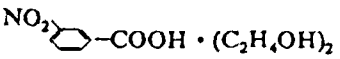
Abstract

The specific heat capacity of M·NBA·DEA crystals were measured by differential scanning calorimetry. Both the direct and ratio methods of DSC were used in the determinations. The relative average deviations are 0.08% to 0.18%. The relative average deviations of ratio method are 0.23–0.69%.

Keywords: DSC, M·NBA·DEA crystal, specific heat capacity

Introduction

The metal-nitrobenzoic acid·diethanolamine crystal is a kind of nonlinear optical crystal of the organic product developed recently. Its constitutional formula is



It is abbreviated to M·NBA·DEA. This product is easy to grow into a monocrystal of large size. Its optical characters are rather perfect and its melting point is 387 K. The M·NBA·DEA crystal is quite thermal stable in the range of 310–370 K.

The specific heat capacity is one of the important parameters of matter. All kinds of the precision calorimeters are used for measurements of specific heat capacity. The classical methods have high precision in determination. However, it takes a lot of trouble and time. O'Neill [1] claims a precision of 0.3% or better in the specific heat capacity determinations by DSC. It measures rapidly and a small sample is sufficient.

We have determined the specific heat capacity of the M·NBA·DEA crystals form 310 to 370 K by the direct method and ratio method. These data were not reported in literature.

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The principle of measurement

When a sample is subjected to a linear temperature increase, the rate of heat flow into the sample is proportional to its instantaneous specific heat capacity [2]. We may write it as follows:

$$\frac{dH}{dt} = m \cdot c_p \cdot \frac{dT}{dt} \tag{1}$$

where m is the mass of the sample in grams, c_p is the specific heat capacity in $J \cdot g^{-1} \cdot K^{-1}$ and dT/dt is the programmed rate of temperature increase. This equation be used directly to obtain values of c_p, known as the direct method.

The procedure was repeated with a known mass of sapphire, the specific heat capacity of which is well established [3] and a new trace was recorded. Thus, only two ordinate deflections at the same temperature (y and y') are required to yield a ratio of the c_p values of sample and sapphire. We may write it as follows:

$$c_p = \frac{y}{y'} \cdot \frac{m'}{m} \cdot c_p' \tag{2}$$

where m and m' are the mass of the sample and sapphire respectively. c_p' is the specific heat capacity of the sapphire. y and y' are the ordinate deflections of the sample and sapphire at the same temperature. This method is known as the ratio method.

Experimental

Apparatus

The differential scanning calorimeter DSC-4 type TADS 3600 data station and the specific heat software kit [4] made by Perkin-Elmer Corp. USA Microbalance, TG332A. Sensitivity: 0.01 mg, made by Shanghai Balance Factory, China.

Preparation of samples

The sapphire came with DSC apparatus, φ3.5×1 mm, with a mass of 27.95 mg. The M·NBA·DEA samples were cut from the whole crystal and then fashioned into round pieces. The masses of three samples are 29.62 mg(1#), 19.18 mg(2#) and 38.32 mg(3#) respectively.

Apparatus (DSC) calibration

DSC-4 differential scanning calorimeter is calibrated with the standard indium. The melting point of indium is 429.76 K. The heat of fusion is

3.27 $kJ \cdot mol^{-1}$. The actual measured values were 429.72 K and 3.27 $kJ \cdot mol^{-1}$ respectively.

Measurements of specific heat capacity

First set the base line. Aluminium pans are used to hold the sample and as reference holder. When the temperature reaches equilibrium, the experiment is started according to a program of the specific heat software and present conditions. Then, the sapphire was placed in the aluminium pan. A DSC curve of the sapphire was made. The specific heat capacity of the sapphire are calculated with the base line and DSC curve of the sapphire. The results are shown in Table 1.

Table 1 Comparison of the measured values of sapphire with the values in literature [3]

Temperature / K	Measured values / $J \cdot g^{-1} \cdot K^{-1}$	Values in literuature / $J \cdot g^{-1} \cdot K^{-1}$	Relative deviations / %
310	0.7981	0.7995	–0.18
320	0.8202	0.8190	+0.15
330	0.8349	0.8375	–0.31
340	0.8560	0.8550	+0.12
350	0.8702	0.8717	–0.17
360	0.8887	0.8878	+0.10
370	0.9050	0.9029	+0.23

According to the method mentioned above, the specific heat capacity of the M·NBA·DEA crystal was determined. The results are shown in Table 2.

Table 2 The specific heat capacities of M·NBA·DEA crystals

Temperature / K	$c_{p(1\#)}$ /	$c_{p(2\#)}$ /	$c_{p(3\#)}$ /	Average values /	Relative average deviations /%
	$J \cdot g^{-1} \cdot K^{-1}$				
310	1.2586	1.2552	1.2569	1.2569	0.09
320	1.2987	1.2943	1.3004	1.2978	0.18
330	1.3355	1.3347	1.3393	1.3365	0.14
340	1.3703	1.3703	1.3749	1.3718	0.15
350	1.4129	1.4146	1.4175	1.4150	0.12
360	1.4544	1.4527	1.4581	1.4551	0.14
370	1.4991	1.5012	1.5021	1.5008	0.08

Measurements of specific heat capacity by ratio method

The procedure is to make the base line, DSC curves of the M·NBA·DEA and the sapphire in sequence. Then y and y' were measured. Equation (2) was used to obtain values of c_p of M·NBA·DEA. The results are listed in Table 3. The procedure has been described in detail elsewhere [1, 5, 6].

Table 3 The specific heat capacities of M·NBA·DEA crystals (ratio method)

Temperature / K	$c_{p(1\#)}$ /	$c_{p(2\#)}$ /	$c_{p(3\#)}$ /	Average values /	Relative average deviations / %
	$J \cdot g^{-1} \cdot K^{-1}$				
310	1.2442	1.2610	1.2590	1.2547	0.56
320	1.2945	1.2837	1.3012	1.2931	0.49
330	1.3418	1.3364	1.3464	1.3415	0.28
340	1.3820	1.3703	1.3790	1.3771	0.33
350	1.4159	1.4226	1.4020	1.4135	0.54
360	1.4774	1.4569	1.4523	1.4622	0.69
370	1.5104	1.5004	1.5062	1.5057	0.23

The above experiments were carried out under the same conditions, i.e., under ordinary pressure; the nitrogen flow is 20 $ml \cdot min^{-1}$; the rate of temperature increment 10 $deg \cdot min^{-1}$; a pair of aluminium pans, identical in mass.

Result and discussion

In order to verify the accuracy of specific heat capacity of DSC. First the specific heat capacity of sapphire is determined. These results were compared with the values in literature.

It could be seen from data in Table 1 that the relative deviations of the measured values from values in literature is less than 0.31%. It shows that the accuracy of determined specific heat capacity is quite high.

The specific heat capacities of M·NBA·DEA determined by direct method are listed in Table 2.

The results show that M·NBA·DEA crystal does not decompose or change in phase in the range of 310 to 370 K. The crystal has a fair thermal stability.

The specific heat capacity of M·NBA·DEA increases linearly with increase in temperature. The relative average deviations are within 0.08–0.18% for three samples. It has been seen that the determination of specific heat capacity is superior in precision by DSC direct method.

In order to compare direct method with ratio method, the specific heat capacities of M·NBA·DEA measured by ratio method are listed in Table 3. The

relative average deviations are in the range of 0.23–0.69%. The deviations seem to be larger than those of the direct method obviously.

The reasons are that the precision of the DSC apparatus has been improved greatly, the sensitivity of determining the heat flow reached a few $\mu w \cdot s^{-1}$ and the precision of the rate of temperature increment can be controlled in ±0.1 K. In addition, the measured results could be processed and printed directly with a microcomputer. In the ratio method, the base line, DSC curves of the sample and the standard material are not plotted accurately on the same sheet, causing errors in y and y', so, derivations by the direct method are smaller than those by the ratio method.

Conclusions

The meta-nitrobenzoic acid·diethanolamine (M·NBA·DEA) crystal does not decompose or change in phase in the range of 310 to 370 K.

The specific heat capacity of the M·NBA·DEA crystal is 1.2659–1.5008 $g^{-1} \cdot K^{-1}$ over the temperature range of 310–370 K.

The relative average deviations of the direct method and the ratio one are 0.08 to 0.18% and 0.23 to 0.69% respectively. The deviations of the direct method are less than those of the ratio method.

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Zusammenfassung — Mittels DSC wurde die spezifische Wärmekapazität von MNBADEA-Kristallen gemessen. Dabei wurde sowohl die direkte als auch die Verhältnismethode verwendet. Die mittlere durchschnittliche Abweichung beträgt 0.08-0.18%, bei der Verhältnismethode 0.23-0.69%.