Determination of the temperature and enthalpy of the solid–solid phase transition of caesium nitrate by differential scanning calorimetry

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Abstract

The equilibrium temperature of the solid–solid phase transition of high purity caesium nitrate has been measured accurately by stepwise heating and by the extrapolation to zero heating rate method. A mean value of $154.3 \pm 0.1\,^{\circ}C$ was obtained using two different heat flux DSC instruments. A value of $3.44 \pm 0.04\,kJ\,mol^{-1}$ was determined for the enthalpy of transition.
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Keywords: Caesium nitrate; DSC; Transition; Temperature; Enthalpy

1. Introduction

Caesium nitrate is of interest as an oxidiser for pyrotechnic compositions which are required to emit in the infrared region and has recently been studied in compositions containing silicon as the fuel [1]. It shows a solid–solid phase transition from trigonal to CsCl cubic structure in the region of $155\,^{\circ}C$ followed by fusion at about $406\,^{\circ}C$. The literature values [2–7] for the temperature and enthalpy of the solid–solid transition obtained using a variety of experimental techniques are shown in Table 1. The values obtained for the temperature of transition range from 151.5 to $156\,^{\circ}C$, while the quoted enthalpies of transition vary from 3.325 to $5.020\,kJ\,mol^{-1}$. In view of the disparity in these results it was decided to determine accurate values for these quantities using differential scanning calorimetry.

Two approaches may be used for the determination of accurate transition temperatures by DSC. These are based on the accurate temperature calibration of the DSC equipment using materials such as indium or tin, which have fixed temperatures on the International Temperature Scale of 1990 (ITS-90) [8].

In the first method, the extrapolated onset temperature (T_e) of the melting peak for the fixed-point material is measured at a range of heating rates (these are typically from 1 to $10\,^{\circ}C\,min^{-1}$). T_e is then plotted against heating rate and a straight line fitted to the data. The melting temperature is then obtained by extrapolation to zero heating rate and the calibration correction determined by reference to the ITS-90 value for the material. Similar experiments are then performed on the transition under investigation and the measured value is then adjusted by application of the calibration correction. This method was proposed by the Working Group "Calibration of Scanning Calorimeters" of the Gesellschaft für Thermische Analyse ev (GEFTA) Germany [9].

In the second approach, the melting temperature for the fixed-point materials is determined under stepwise heating conditions where the temperature of the sample is raised in small increments (typically 0.1 or $0.05\,^{\circ}C$) so that fusion takes place under near-equilibrium conditions [10]. The melting temperature is obtained from the final step in the melting process and the calibration corrections determined from the ITS-90 values. Accurate temperatures may then be determined for the material under investigation by making stepwise DSC measurements using the calibrated equipment.

Both the stepwise heating and zero heating rate methods have recently been applied to the LGC Ltd. organic melting-point standards [11]. These materials have certified values

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Table 1
Literature values for the temperature and enthalpy of the solid–solid transition of caesium nitrate

First Author	Year	Method	Temperature (°C)	Enthalpy (kJ mol^{-1})	Ref.
Bridgeman	1916	Volume discontinuity	153.7	–	[2]
Mustajoki	1957	Adiabatic calorimetry	151.5	3.74 ± 0.25	[3]
Bakes	1963	Electrochemical measurement	152	–	[4]
Marchidan	1973	Differential calorimeter	156	5.020	[5]
Maeso	1993	DSC	153.4	3.8	[6]
Jriri	1995	DSC	154	3.325	[7]

for the temperature at which the last crystal of the solid melts under stepwise equilibrium heating conditions. The certified values are therefore directly applicable to the stepwise heating DSC method. Comparison of the experimental values for the melting points obtained by both methods has shown that the extrapolation to zero heating rate method gave accurate values for the equilibrium melting-point temperatures.

The transition temperature of caesium nitrate is close to that of the fusion of indium. Thus indium can be used as a single-point calibrant. This approach reduces the error that may arise where the calibration value for the material of interest is determined by interpolation between two-point or multiple-point calibrations.

In the present work, accurate temperature measurements have been performed with two different heat flux DSC instruments using both the extrapolation to zero heating rate and stepwise heating methods. In addition, the value for enthalpy of the caesium nitrate solid–solid transition has been determined in two separate sets of experiments by direct comparison with the enthalpy of fusion of indium.

2. Experimental

The indium sample used for the temperature and enthalpy calibration (Goodfellow Metals) was in the form of a powder and had a purity of 99.999%. The caesium nitrate (Alfa Aesar) had a purity of 99.99% and was crushed and sieved through a 250 μm sieve and dried at 105 °C before use.

The measurements were carried out using a Mettler Toledo DSC 822^{e} and a TA Instruments DSC 2920. The samples were encapsulated in aluminium pans which had been cleaned with ethanol before use. The extrapolation to zero heating rate temperature measurements were performed over the range 0.5–10 °C min^{-1} and duplicate or triplicate stepwise measurements were carried out using temperature increments of both 0.05 and 0.1 °C. A sample mass of 5 mg was used in both methods.

The enthalpy measurements were made in triplicate at a heating rate of 3 °C min^{-1} using a sample mass of 10 mg. A value of 3.296 ± 0.009 kJ mol^{-1} was selected for the enthalpy of fusion of indium based on the determination performed by Grønvold using adiabatic calorimetry [12]. Both the temperature and enthalpy measurements were carried out in an argon atmosphere and a new sample was used for each experiment.
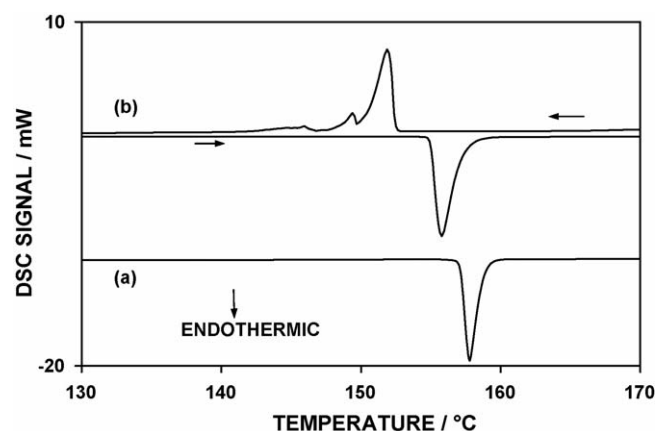

Fig. 1. DSC curves for (a) indium and (b) caesium nitrate (sample mass, 5 mg; heating/cooling rate, 10 °C min^{-1}; atmosphere, argon).

3. Results and discussion

DSC heating and cooling curves for the solid–solid transition of caesium nitrate are given in Fig. 1, which also includes a curve for the fusion of indium obtained under the same conditions. The caesium nitrate transition obtained on heating can be seen to give a well-defined DSC peak. In an experiment where a sample was repeatedly heated and cooled (10 cycles) the T_e values showed good reproducibility with deviations of less than ± 0.1 °C. The sample exhibited a small amount of supercooling (2.3 °C) and small exothermic peaks were observed on the trailing edge of the cooling peak which varied from one experiment to the next.

A typical stepwise heating DSC plot for caesium nitrate is shown in Fig. 2. The equilibrium temperatures determined for caesium nitrate by the stepwise heating method are summarised in Table 2. The uncertainties include a contribution for the error in the calibration correction and the inherent precision of the measurement which we have taken to be half the step height. Good reproducibility was obtained with each of the DSC instruments and excellent agreement between the measured values

Table 2
Measurement of the equilibrium temperature of the solid–solid transition of caesium nitrate using the stepwise heating DSC method

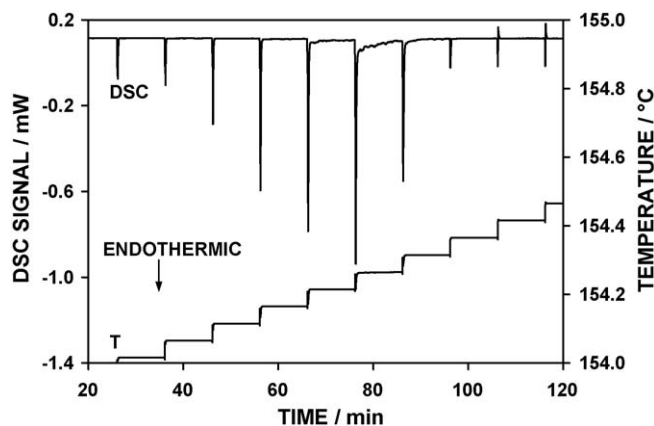| Instrument	Step size (°C)	T_{eq} (°C)
TA DSC 2920	0.1	154.26 ± 0.08
	0.05	154.34 ± 0.06
Mettler DSC 822^{e}	0.1	154.30 ± 0.07
	0.05	154.29 ± 0.05

Fig. 2. DSC curve for the stepwise melting of caesium nitrate (sample mass, 5 mg; step size, 0.05 °C; atmosphere, argon).
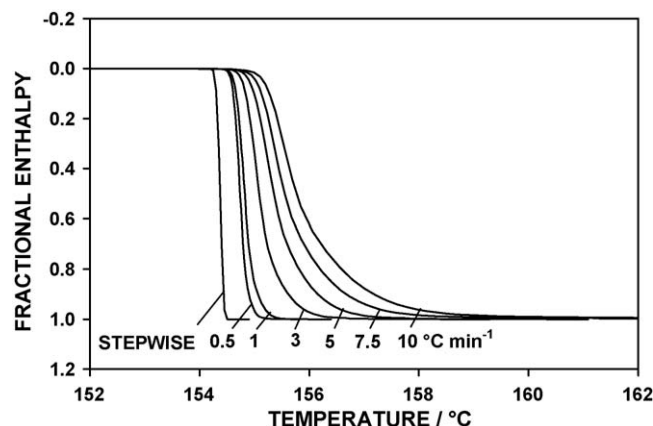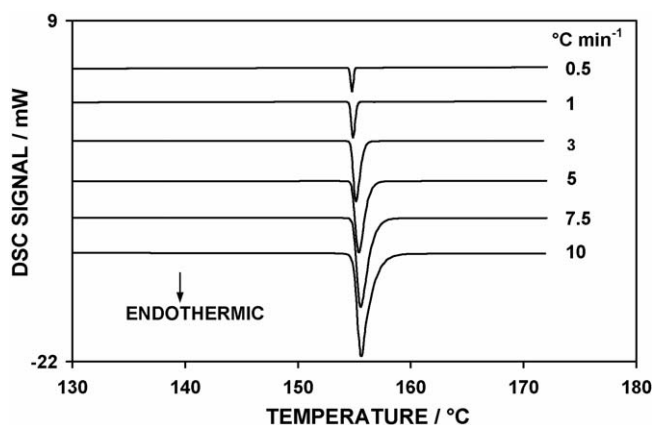

Fig. 3. DSC curves for caesium nitrate at different heating rates (sample mass, 5 mg; atmosphere, argon).

was achieved, giving a mean value of 154.3 ± 0.1 °C, based on the measurements using temperature increments of 0.05 °C.

DSC curves for caesium nitrate obtained at different heating rates are shown in Fig. 3 and well-defined peaks were given in all cases. Plots of T_e against heating rate for indium and caesium nitrate are given in Fig. 4. The values of the equilibrium temper-
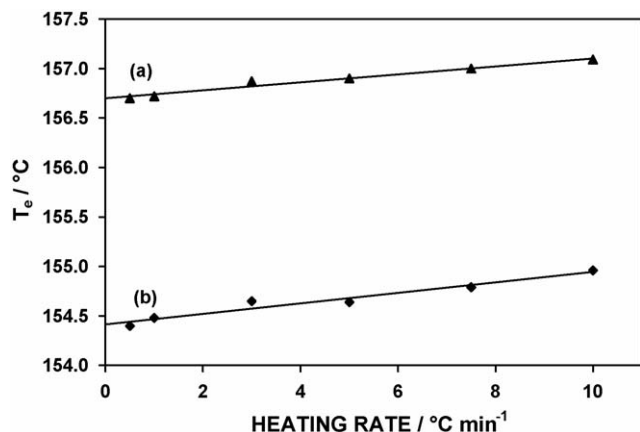

Fig. 4. Plots of T_e against heating rate from DSC measurements on (a) indium and (b) caesium nitrate (sample mass, 5 mg; atmosphere, argon).

Fig. 5. Plot of fractional enthalpy against temperature for caesium nitrate obtained under stepwise and dynamic heating conditions.

atures at zero heating rate were calculated as 154.32 ± 0.04 °C (TA DSC 2920) and 154.45 ± 0.04 °C (Mettler DSC 822^e). The stated errors include both the errors in the calculated values and in the calibration corrections.

The values obtained from the two DSC instruments using the extrapolation to zero heating rate method are in close agreement and give a mean value of 154.4 ± 0.1 °C. This is in agreement with the temperature measured by the stepwise isothermal DSC method and an overall mean value of 154.3 ± 0.1 °C was obtained by combining the results from both techniques. The value of 154 °C obtained by Jriri et al. [7] is closest to our value and the temperatures given by Bridgeman [2] and Maeso and Largo [6] are within 1 °C.

Plotting the fractional enthalpy against temperature enables a direct comparison of the caesium nitrate results from the stepwise and linear heating methods to be made. Fig. 5 illustrates the very narrow temperature range over which the caesium nitrate transition takes place under stepwise heating conditions.

The measured enthalpies of transition were 3.432 ± 0.020 kJ mol^{-1} (TA DSC 2920) and 3.453 ± 0.027 kJ mol^{-1} (Mettler DSC 822^e) and confirm the reproducible nature of the caesium nitrate transition. The values from the two DSC instruments are in good agreement and a mean value of 3.44 ± 0.04 kJ mol^{-1} was given. The indicated uncertainty includes the error in the calibration measurements. The value of 3.325 kJ mol^{-1} obtained by Jriri et al. using DSC [7] is closest to our result.

4. Conclusions

The solid–solid transition of high purity caesium nitrate shows reproducible behaviour on heating. The use of both stepwise heating and extrapolation to zero heating rate methods, with two different DSC instruments, has enabled an accurate value for the equilibrium temperature of the transition to be determined and a mean value of 154.3 ± 0.1 °C was obtained. A mean value for enthalpy of transition of 3.44 ± 0.04 kJ mol^{-1} was obtained, based on measurements using the two DSC instruments.

Acknowledgements

References

[1] B. Berger, S.D. Brown, E.L. Charsley, J.J. Rooney, R.P. Claridge, T.T. Griffiths, Proceedings of the 29th International Pyrotechnics Seminar, IPSUSA, 2002, p. 743.
[2] P.W. Bridgeman, Proc. An. Acad. 51 (1916) 581.
[3] A. Mustajoki, An. Acad. Sci. Fennicae 6 (1957) 1.
[4] M. Bakes, J. Guion, J. Dupuis, C. R. Acad. Sci. 256 (1963) 2376.
[5] D.I. Marchidan, L. Vasu, Rev. Roumaine de Chimie 18 (1973) 1295.
[6] M.J. Maeso, J. Largo, Thermochim. Acta 222 (1993) 195.
[7] T. Jriri, J. Rogez, C. Bergman, J.J. Mathieu, Thermochim. Acta 266 (1995) 147.
[8] H. Preston-Thomas, Metrologia 27 (1990) 3–10.
[9] G.W.H. Höhne, H.K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, Thermochim. Acta 160 (1990) 1.
[10] M.J. Richardson, in: K.D. Maglic, A. Cezairliyan, V.E. Peletsky (Eds.), Compendium of Thermophysical Property Measurement Methods, Plenum Press, New York, 1992, p. 519.
[11] E. L. Charsley, P. G. Laye, V. Palakollu, J. J. Rooney , B. Joseph, Thermochim. Acta, in press.
[12] F. Grønvold, J. Therm. Anal. 13 (1978) 419.