Journal of Thermal Analysis, Vol. 29 (1984) 433–437

DIFFERENTIAL SCANNING CALORIMETRIC STUDIES OF SEVERAL COMPOUNDS SHOWING ORDER-DISORDER TRANSITION

B. P. Ghosh and *K. Nag**

DEPARTMENT OF INORGANIC CHEMISTRY, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA 700 032, INDIA

(Received October 3, 1983; in revised form December 10, 1983)

Differential scanning calorimetric measurements have been carried out for CuI, CuBr, AgI, Ag_2S, $NaNO_2$, $NaNO_3$ and KSCN. First-order phase transformations occur with the compounds CuI, CuBr, AgI and Ag_2S; $NaNO_2$, $NaNO_3$ and KSCN exhibit λ-type transformations. The enthalpy changes due to phase transitions have been determined. Thermal hysteresis exhibited by these compounds have been examined in the light of their change in unit cell volumes.

Order-disorder types of phase transitions in solids have received considerable attention both from theoretical and experimental standpoints [1–4]. There are three principal kinds of order-disorder transitions, viz. positional, orientational, and the one involving electronic or nuclear spin states. Here we shall be concerned with the first two types.

Positional disordering can take place either due to the occupation of atoms or ions at the inappropriate positions of sublattice, or when there are more numbers of available lattice sites than required. Orientational disordering occurs when a polyatomic ion can occupy lattice positions in more than one orientation. An order-disorder transition often occurs in the manner of λ-transition. It may also take place as a first-order transition involving a change in volume, or begin as a λ-transition but terminate as a first-order transition.

The present study deals with differential scanning calorimetric (DSC) measurements of CuI, CuBr, AgI and Ag_2S which are known to undergo positional order-disorder transitions [1], and of $NaNO_2$, $NaNO_3$ and KSCN that exhibit orientational order-disorder transitions [1]. Crystallographic and various other changes in properties that are associated with the phase transitions in CuI [5–7], CuBr [5–7], AgI [5, 8], Ag_2S [8–10], $NaNO_2$ [11, 12], $NaNO_3$ [2, 11, 13] and KSCN [14–17] are catalogued in literature.

Experimental

Materials

CuBr [18], CuI [19], AgI [20] and Ag_2S [20] were prepared according to the reported methods. $NaNO_2$, $NaNO_3$ and KSCN were all Merck (Darmstadt) "guaranteed reagent" quality and used as received.

Differential scanning calorimetric measurements were performed on a Perkin–Elmer DSC-2 equipment. The samples were heated and cooled at programmed rates (mostly 1.25 deg/min) under a constant flow rate of purified dry nitrogen. The specimen (*ca.* 5 mg) in finely divided form was contained in an aluminium pan and lid assembly by crimping. A matched gold pan served as the reference. The DSC equipment was calibrated [21] to obtain a temperature accuracy of ±0.2 degree. Special care was taken to maintain flatness of the baseline. The enthalpy changes (ΔH) were determined by comparing the areas of heating/cooling curves of the materials with those obtained for high purity indium, zinc and tin of accurately known heats of fusion [21] under identical experimental conditions. All measurements were carried out in triplicate and the enthalpy changes reported are the average values. The accuracy of ΔH determinations were limited by the precision of integrating the DSC curves by a planimeter; maximum error involved in ΔH determination was estimated to be 10%.

Results and discussion

The phase transition behaviour of the compounds under consideration in the forward (heating) and reverse (cooling) directions are exemplified by Fig. 1–2. Figure 1 shows first-order phase transition of Ag_2S and is representative of the compounds undergoing positional disordering (CuI, CuBr, AgI). The λ-type transition shown in Fig. 2 for $NaNO_3$ is typical of orientational disordering ($NaNO_2$, KSCN). The crystallographic changes that are associated with these phase transitions are summarized below

CuI: γ (fcc; $Td^2(F\bar{4}3m)$) $\rightleftharpoons$ β (hexagonal; $D^1_{3h}(P\bar{6}m2)$) $\rightleftharpoons$ α (bcc; $O^5(I4_132)$)

CuBr: γ (fcc; $Td^2(F\bar{4}3m)$) $\rightleftharpoons$ β (hexagonal; $C^4_{6v}(P6mc)$) $\rightleftharpoons$ α (bcc; $O^9_h(Im3m)$)

AgI: β (hexagonal; $C^4_{6v}(P6_3mc)$) $\rightleftharpoons$ α (bcc; $O^9_h(Im3m)$)

Ag_2S: β (monoclinic; $C^5_{2h}(P2_1/c)$) $\rightleftharpoons$ α (α–AgI)

$NaNO_2$: γ (orthorhombic; $C^{20}_{2v}(Imm2)$) $\rightleftharpoons$ β (?) $\rightleftharpoons$ α (orthorhombic; $D^{25}_{2h}(Immm)$)

$NaNO_3$: β (rhombohedral; $D^6_{3D}(R\bar{3}c)$) $\rightleftharpoons$ α (disordered rhombohedral)

KSCN: β (orthorhombic; $D^{11}_{2h}(Pbcm)$) $\rightleftharpoons$ α (tetragonal; $D^{18}_{4h}(I4/mcm)$)

From the nature of DSC curves for all of the compounds it has turned out that the span of temperature at which a phase transformation takes place is greater during

cooling than heating. This indicates that the rates for disordering and ordering processes are unequal. It can be shown [1, 3] on the basis of first-order kinetics that for an order-disorder phenomenon

$$\ln \frac{Q_f - Q_0}{Q_f - Q_t} = \frac{\tau}{t}$$

where Q_0, Q_t and Q_f refer to the quantities measured initially, at a time 't' and when the full value is attained, respectively, and τ is the relaxation time. Evaluation of the relaxation time from heating (disordering) and cooling (ordering) curves revealed that in general τ is less for disordering. However, the above relation is based on an over-simplified approach and subject to criticism [3, 4], therefore, the magnitude of τ has little significance beyond drawing a qualitative conclusion.

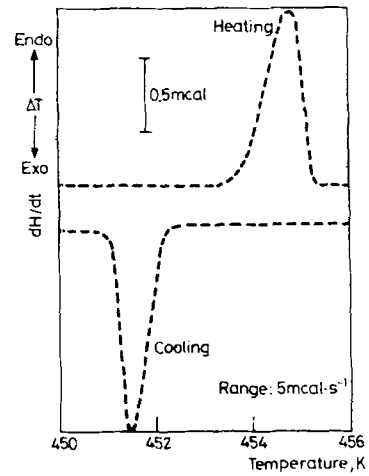

Fig. 1 DSC curves for Ag_2S. Heating and cooling rate: 1.25 deg min^{-1}

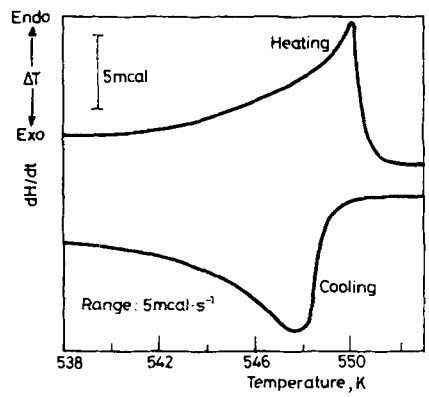

Fig. 2 DSC curves for $NaNO_3$. Heating and cooling rate: 1.25 deg min^{-1}

Table 1 summarizes the peak temperatures (Tm) for phase transitions, corresponding enthalpy changes (ΔH) and the width of thermal hysteresis (ΔT) as defined by the difference in Tm observed during heating and cooling. It may be noted that there exists some difference in ΔH values obtained from the heating and cooling curves. The uncertainty (less than 10%) is a sequel to error involved in integrating these curves. The width of thermal hysteresis given in Table 1 were determined at a slow rate of heating or cooling (1.25 degree) in order to avoid superheating or supercooling effects. Additional experiments carried out at higher heating/cooling rates showed shift in peak temperatures with concomitant increase in the width of hysteresis. For example, the ΔT value increased from 2.5 to 7° by varying the heating/cooling rate from 1.25 to 10 deg/min. Width of thermal hysteresis has been reported [1] to vary with the change in volume of crystal lattices (ΔV) on phase transformation. Such correlation is based on the assumption that a greater change in ΔV will be accompanied by increased kinetic barrier for nucleation which in effect will shift the transition temperature differently during heating and cooling. However, Table 1 shows that in the compounds under consideration no systematic variation in ΔT with ΔV could be noted.

Table 1 Transition temperatures (Tm), enthalpy changes (ΔH) and width of thermal hysteresis (ΔT) for the compounds during heating and cooling cycles

Compound	Heating mode			Cooling mode			ΔT, °C	ΔV, Å^3
	Phase change	Tm, K	ΔH, kJ mol^{-1}	Phase change	Tm, K	ΔH, kJ mol^{-1}		
CuI	$\gamma \rightarrow \beta$	648.5	5.1	$\beta \rightarrow \gamma$	639.2	4.75	9.3	2.3
	$\beta \rightarrow \alpha$	671.2	0.75	$\alpha \rightarrow \beta$	669.2	0.8	2	2.7
CuBr	$\gamma \rightarrow \beta$	660	4.9	$\beta \rightarrow \gamma$	655.4	4.6	4.6	2.8
	$\beta \rightarrow \alpha$	742.8	1.15	$\alpha \rightarrow \beta$	739.8	1.1	3	−0.2
AgI	$\beta \rightarrow \alpha$	423.2	6.36	$\alpha \rightarrow \beta$	414.1	6.3	9.1	5.9
Ag_2S	$\beta \rightarrow \alpha$	464.1	3.55	$\alpha \rightarrow \beta$	451.5	3.4	2.6	7
$NaNO_2$	$\gamma \rightarrow \alpha$	439.1	1.2	$\alpha \rightarrow \gamma$	435.4	1.25	3.7	4.4
$NaNO_3$	$\beta \rightarrow \alpha$	550	1.7	$\alpha \rightarrow \beta$	547.6	1.85	2.4	−0.5
KSCN	$\beta \rightarrow \alpha$	416.3	1.55	$\alpha \rightarrow \beta$	414.8	1.6	1.5	–

References

1 C. N. R. Rao and K. J. Rao, Phase Transitions in Solids, McGraw-Hill Inc., 1978.

2 N. G. Parsonage and L. A. K. Stavely, Disorder in Crystals, Oxford University Press, 1977.

3 M. A. Krivogalz and A. Smirnov, The Theory of Order-Disorder in Alloys, Macdonald, London, 1964.

4 H. Warlimont, ed., Order-Disorder Transformation in Alloys, Springer-Verlag, Berlin, 1974.

5 C. N. R. Rao and M. Natarajan, Crystal Structure Transformations in Binary Halides, NSRDS-NBS Monograph 41, Washington, D. C., 1972.

6 W. Buhrer and W. Halg, Electrochim. Acta, 22 (1977) 701.

7 J. Notting, Angew. Chem., 82 (1970) 498.

8 K. Funke, Progr. Solid State Chem., 11 (1976) 345.

9 A. J. Fruch, Jr., Z. Krist., 110 (1958) 136.

10 C. M. Perrott and N. H. Fletcher, J. Chem. Phys., 50 (1969) 2344.
11 C. N. R. Rao, B. Prakash and M. Natarajan, Crystal Structure Transformations in Inorganic Nitrites, Nitrates and Carbonates, NSRDS-NBS Monograph 53, Washington, D. C., 1975.
12 W. Buchheit, G. Herth and J. Petterson, Solid State Commun., 40 (1981) 411.
13 D. M. Newns and L. A. K. Stavely, Chem. Rev., 66 (1966) 267.
14 M. Sakiyama, H. Suga and S. Seki, Bull. Chem. Soc. Jpn., 36 (1963) 1025.
15 Y. Yamada and T. Watanabe, Bull. Chem. Soc. Jpn., 36 (1963) 1025.
16 R. Savoic and J. Mezolet, Can. J. Chem., 45 (1967) 1677.
17 Z. Iqbal, L. H. Sharma and K. D. Moller, J. Chem. Phys., 57 (1972) 4728.
18 R. N. Keller and H. D. Wycoff, Inorg. Synth., 2 (1946) 1.
19 K. Nag and S. Geller, J. Electrochem. Soc., 128 (1981) 2670.
20 G. Brauer, Handbook of Preparative Inorganic Chemistry, Vol. 2, p. 1035, Academic Press, New York, 1965.
21 J. L. McNaughton and C. T. Mortimer, IRS; Physical Chemistry Series 2, Vol. 10, Butterworths, London, 1975.

Zusammenfassung – Es wurden DSC-Untersuchungen von CuI, CuBr, AgI, Ag_2S, $NaNO_2$, $NaNO_3$ und KSCN ausgeführt. Phasenübergänge erster Ordnung verlaufen bei den Verbindungen CuI, CuBr, AgI und Ag_2S, während $NaNO_2$, $NaNO_3$ und KSCN Übergänge des λ-Typs zeigen. Die Phasenübergängen zuzuschreibenden Enthalpieveränderungen wurden bestimmt. Die bei diesen Verbindungen auftretende thermische Hysterese wurde im Zusammenhang mit den Veränderungen des Elementarzellenvolumens untersucht.

Резюме – Проведено ДСК-исследование соединений CuI, CuBr, AgI, Ag_2S, $NaNO_2$, $NaNO_3$ и KSCN. Установлено, что CuI, CuBr, AgI и Ag_2S подвергаются фазовым переходам типа порядок-беспорядок, а $NaNO_2$, $NaNO_3$ и KSCN-переходам λ-типа. Определены изменения энтальпий при фазовых переходах. Термический гистерезис, проявляемый изученными соединениями, изучен в аспекте изменения объема их элементарной ячейки.