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THERMODYNAMIC PROPERTIES OF ALKALI AND THALLIUM NITRITES: THE IONIC PLASTICALLY CRYSTALLINE STATE *

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ABSTRACT

The entropies of melting of $LiNO_2$, $NaNO_2$, KNO_2, $RbNO_2$, $CsNO_2$ and $TlNO_2$ have been determined by DSC. For KNO_2, $RbNO_2$, $CsNO_2$ and $TlNO_2$, they are much smaller than those of the corresponding alkali chlorides. The small entropy values are compensated for by the large entropies of the transitions that occur at lower temperatures. For $LiNO_2$, no phase transition takes place below the melting temperature. $NaNO_2$ undergoes a solid–solid phase transition associated with a small entropy change. The sum of the entropies of melting and transitions (if there are any) is approximately constant (40 J K^{-1} mol^{-1}) for all of the nitrites studied. Plastic flow of the high-temperature phase of $TlNO_2$ under stress was measured and found to be comparable in magnitude with that of typical organic plastic crystals. Literature values of $\Delta_m S$ and $\Delta_{trs} S$ of 19 A^+B^--type ionic crystals were surveyed. It was found that values of $\Delta_m S$ are smaller than those of the corresponding alkali chlorides. The extension of the classification of the plastically crystalline state in the original molecular crystals to the ionic crystal is proposed. In contrast to the accepted view that the weak intermolecular forces in molecular crystals favor formation of plastic phases, an argument is put forward that the strong Coulombic attraction stabilizes the plastically crystalline phase of the ionic crystals by holding together the orientationally disordered molecular ions.

INTRODUCTION

There is a group of substances known as plastic crystals [1]. The term "plastic" derives from the experimental observation that these crystals are very soft and deform easily under an external stress. Their molecules are generally globular in shape and form crystals of high symmetry (mostly f.c.c. or b.c.c.). They are characterized by disordered molecular orientation [2]. Timmermans [1] found that high deformability is accompanied by a low entropy of melting, $\Delta_m S = 21$ J K^{-1} $mol^{-1} = 2.5\ R$, this being a suitable

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entropy value for demarcation between plastic and non-plastic behaviors. Rapid self-diffusion is always found in plastic crystals [3]. Most of the plastic crystals known are organic and inorganic molecular crystals [3,4]. However, we found large entropy changes at the phase transitions of alkali and thallium nitrites [5–9]. It was, therefore, interesting to investigate the melting behavior of these crystals in an attempt to extend the classification of plastic crystals to ionic substances.

We report here the determination of the enthalpy of melting of $LiNO_2$, $NaNO_2$, KNO_2, $RbNO_2$, $CsNO_2$ and $TlNO_2$ by differential scanning calorimetry, and discuss the results in relation to the original classification of molecular plastic crystals. We also report the mechanical properties of the high-temperature phase of $TlNO_2$.

EXPERIMENTAL

The nitrite crystals ANO_2, where A = Li, Na, K, Rb, Cs and Tl, were examined by DSC (Perkin Elmer Model II) from 310 K to above their melting temperatures at a heating rate of 5 K min^{-1}. The only anomalies found in the temperature intervals were those caused by melting of the nitrites and a small peak due to the order–disorder transition in $NaNO_2$. $LiNO_2$ whose low temperature behavior had not been reported previously was examined by DTA between 80 and 350 K.

$RbNO_2$, $CsNO_2$ and $TlNO_2$ were prepared as described in the previous papers [6–9]. $LiNO_2$ and KNO_2 were prepared in the same way as in refs. 6–9, using the appropriate alkali sulfates. $NaNO_2$ (suprapur, Wako Pure Chemicals Co. Ltd.) was recrystallized twice from aqueous solution. All the crystals were purified by zone melting. Atomic absorption spectra showed that foreign alkali ions present in each of the nitrites were less than 0.02 mass%. NO_3^- impurity determined by the method described previously [8] was less than 0.1 mass% in all of the samples. Reproducible melting peaks showed that molten nitrites did not corrode the aluminum sample pans used in the DSC measurement.

The creep measurements were made using a thermomechanical analyzer (TMA) system of Dupont Co. Ltd., model 943. Polycrystalline samples of $TlNO_2$ were pressed to form a cylinder of diameter 2 mm and length 8 mm. The creep rate was measured for six different stresses at six temperatures between 363 and 432 K.

RESULTS AND DISCUSSION

Table 1 summarizes transition entropies $\Delta_{trs}S$ and melting entropies $\Delta_{m}S$ of the alkali and thallium nitrites. The residual antropy S_r inferred from the crystal structure of the low-temperature phase, and the orientational entropy S_h of the NO_2^- ion in the high-temperature phase are also shown in the same table. The $LiNO_2$ crystal does not exhibit a phase transition between 80 K and the melting temperature. The transition entropy of $NaNO_2$ [10] is approximately equal to $R \ln 2$ and is much smaller than those of the other nitrites. The crystal structure of $LiNO_2$ is not known. Sodium nitrite is orthorhombic, whereas the others are cubic in the high-temperature phase. The large transition entropies of KNO_2 [11], $RbNO_2$ [5,9], $CsNO_2$ [6,8] and $TlNO_2$ [7,8] on the one hand, and the lack of a transition in $LiNO_2$ and a transition with a small transition entropy in $NaNO_2$ on the other, correlate well with the crystal symmetries. Table 1 shows that the melting entropy $\Delta_m S$ is very large (36 J K^{-1} mol^{-1}) for $LiNO_2$. The large melting entropy of the Na salt compensates for its small entropy of transition. The small melting entropies of the cubic nitrites are compensated for by the large entropies of the transitions. In fact the sum of the orientational entropy S_h of the high-temperature phase and the melting entropy $\Delta_m S$ is approximately equal (~ 40 J K^{-1} mol^{-1}) for all the nitrites as shown in the last column of Table 1. This suggests the possibility of extending Timmermans' criterion of plastic crystals to ionic substances. It is proposed here that the A^+B^- ionic crystal is classified as an ionic plastic crystal if its entropy of melting is less than that of the corresponding alkali chloride. The melting entropies of NaCl, KCl, RbCl, CsCl, TlCl and AgCl are 28.0 J K^{-1} $mol^{-1} = 3.37\ R$ [12], 26.15 J K^{-1} $mol^{-1} = 3.15\ R$ [13], 23.8 J K^{-1} $mol^{-1} = 2.80\ R$ [14], 20.75 J K^{-1} $mol^{-1} = 2.50\ R$ [15], 24.2 J K^{-1} $mol^{-1} = 2.91\ R$ [16] and 17.2 J K^{-1} $mol^{-1} = 2.07\ R$ [17], respectively. According to this classification, KNO_2, $RbNO_2$, $CsNO_2$ and $TlNO_2$ belong to the ionic plastic crystals. It should be noted that by taking the corresponding alkali halide value of the melting entropy as the reference, we have adopted the basic view of plastic crystals that orientational degrees of freedom of the molecular ions are so highly developed that they are effectively spherical. Such a situation occurs in ordinary (i.e. non-ionic) molecular plastic crystals. The original entropy criterion of plastic crystals (i.e. $\Delta_m S \leqslant 2.5\ R$) is appropriate for the classification of molecular crystals into plastic and non-plastic crystals. For ionic crystals, the total number of ions is obviously larger than the number of the chemical units by a factor of 2 or more (depending on the stoichiometry). Entropy of melting should reflect this difference. In fact, the molar entropy of melting of NaCl (28.0 J K^{-1} mol^{-1}) is twice as large as that of Ar (14.2 J K^{-1} mol^{-1}) [18]. Obviously, one cannot assert that the melting of one mole of NaCl is equivalent to the melting of two moles of Ar, because liquid argon and molten NaCl are quite different in many respects. However, the comparison of the two entropy values emphasizes the obvious (and sometimes forgotten) point that the difference in the number of the molecular (or ionic) units has to be taken into account properly when one compares the entropies of compounds of different nature. This is another

TABLE 1

Thermodynamic quantities associated with transitions and melting of alkali and thallium nitrites

M(I)	T_{trs}(K)	$\Delta_{trs}S(R)$	$S_r(R)$	$S_h(R)$	T_m(K)	$\Delta_m H$(kJ mol^{-1})	$\Delta_m S(R)$	$(S_h + \Delta_m S)(R)$
Li			0	0	472 ± 1	17.1 ± 1.0	4.35 ± 0.31	4.35 ± 0.31
Na	437.4							
	437.9	0.64 ± 0.07 [10]	0	0.64 ± 0.07	556 ± 1	16.5 ± 1.2	3.56 ± 0.26	4.20 ± 0.33
K	264.1	2.87 [11]	0	3.71	710 ± 1	9.9 ± 0.8	1.68 ± 0.14	5.39 ± 0.14
	314.7	0.84						
Rb	83.8	0.07 ± 0.01 [9]	0	4.39 ± 0.23	695 ± 1	11.0 ± 0.9	1.90 ± 0.15	6.29 ± 0.38
	264.0	4.32 ± 0.22						
Cs	209.2	2.08 ± 0.12 [8]	1.09 [8]	3.17 ± 0.12	673 ± 1	12.0 ± 1.0	2.14 ± 0.18	5.31 ± 0.30
Tl	282.4	2.84 ± 0.13 [8]	0.70 [8]	3.54 ± 0.13	459 ± 1	6.9 ± 0.6	1.81 ± 0.16	5.35 ± 0.29

T_{trs}, phase transition temperature; $\Delta_{trs}S$, phase transition entropy; S_r, estimated residual entropy in the low-temperature phase; S_h, orientational entropy in the high-temperature phase; T_m, melting temperature; $\Delta_m H$, melting enthalpy; $\Delta_m S$, melting entropy.

reason for us to take the alkali halides as the reference substances of the entropy criterion. Large mechanical plasticity and ionic conductivity (10^{-3} Ω^{-1} cm^{-1} at 300 K) of $TlNO_2$ [7] attest to the pertinence of the classification with respect to the kinetic properties as well.

The creep behavior of $TlNO_2$ followed the classical pattern of plastic deformation [19]. After a short transient period in which dislocation and work hardening occurred (primary creep), the creep became stationary (secondary or steady state creep). An example of creep under a stress of 48.4 kN m^{-2} is shown in Fig. 1 (the data taken at 332 K). The stationary strain rate $\dot{\varepsilon} = (1/h_0)(dh/dt)$, where h_0 and h are the heights of the crystal at $t = 0$, and t, respectively, was 8.9×10^{-6} s^{-1} in this example. In order to produce the same flow rate in metals [20] or normal organic crystals [21] at the same relative temperatures (reduced by the melting temperatures), stresses 100 times larger in magnitude are necessary. Similar easy creep has been found in cyclohexane and pivalic acid [21]. The measurement of creep thus showed that $TlNO_2$ crystal is actually plastic in the high-temperature phase. Rapid diffusion of the ions has been deduced from the spin-lattice relaxation time of the Tl nuclei [22]. Self-diffusion is also an established characteristic property of a plastic crystal. Dislocations, vacancies and other types of lattice defects as well as the orientational disorder of the NO_2^- ion would be responsible for the rapid migration of the ions. Hirotsu et al. [23] measured the entropies of melting of $NaNO_2$, KNO_2, $RbNO_2$ and $CsNO_2$. The values reported by them are smaller than those found in this study. However, their conclusion that the alkali nitrites are ionic plastic crystals is in agreement with the conclusion reached here.

The heavier alkali nitrites, although evidently exceptional in that their plastically crystalline phases occur at subambient temperatures, are by no means unusual among the other ionic crystals with regard to other properties. This suggests that plastically crystalline phases of ionic crystals may not be limited to nitrite salts. In Table 2, experimental data on ionic substances

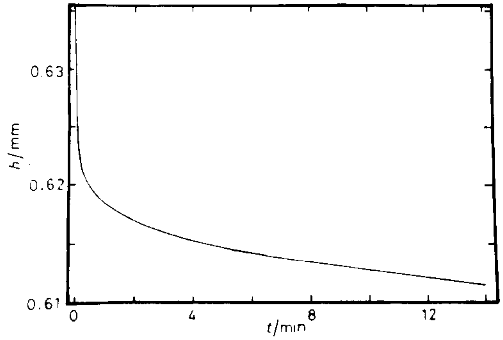

Fig. 1. Decrease in the sample length under a stress of 48.4 kN m^{-2} at 332 K showing the rapid initial creep and the stationary creep at $t \geqslant 6$ min.

which have smaller entropies of melting than the alkali halides are collected. They are hydroxides, nitrites, cyanides, hydrofluorides and other ionic crystals of the A^+B^--type formed mostly by polyatomic anions. They

TABLE 2

Thermodynamic quantities associated with transitions and melting of some monovalent ionic plastic crystals

Compounds	T_{trs}(K)	$\Delta_{trs}S(R)$	T_m(K)	$\Delta_m S(R)$
NaOH	516 ±3	[24]		
	570 ±3	1.34 [25]	595 ± 5	1.28 [25]
KOH	517 ±4	1.31 [26]	678 ± 3	1.66 [27]
RbOH	508 ±3	1.28 [24]	658 ± 3	1.62 [24]
CsOH	410 ±3	0.42 [24]		
	493 ±3	1.48	616 ± 3	1.77 [24]
NaCN	171.9 ±0.2	0.61 [28]		
	287.7 ±0.1	1.41	835 ± 5	2.52 [29]
KCN	82.9 ±0.2	0.66 [30]		
	168.3 ±0.1	1.01	895 ±10	1.97 [31]
CsSCN	470 ±2	2.86 [31]	479 ± 2	1.51 [31]
KHF_2	469.85 ±0.3	2.87 [32]	511.95 ± 0.5	1.56 [32]
$RbHF_2$	444.95 ±0.2	2.81 [33]	482.65 ± 0.3	1.16 [33]
$CsHF_2$	331.45 ±0.1	0.88 [33]	453.25 ± 0.5	0.82 [33]
	450.35 ±0.5	1.11		
$RbNO_3$	473 ±2	1.07 [34]		
	493 ±2	0.79	585 ± 2	0.95 [34]
	563 ±5	0.21		
$CsNO_3$	427 ±3	1.06 [35]	682 ± 2	2.44 [35]
$TlNO_3$	348 ±1	0.35 [36]	479.65 ± 1.0	2.37 [37]
	416.65 ±0.5	0.97		
NH_4NO_3	256.2	0.16 [38]		
	305.33	0.67		
	357.25	0.45		
	399.00	1.34	442.8	1.48 [29]
$NaBF_4$	516 ±2	1.57 [39]	679 ± 2	2.41 [39]
KBF_4	556 ±2	2.99 [39]	843 ± 2	2.57 [39]
$RbBF_4$	519 ±2	2.77 [39]	853.5 ± 2.0	2.76 [39]
$KClO_4$	574 ±1	2.87 [40]	855 ± 3	2.71 [41]
AgI	421.1 ±0.5	4.15 [42]	824 ± 2	1.37 [43]

T_{trs}, transition temperature; $\Delta_{trs}S$, phase transition entropy; T_m, melting temperature; $\Delta_m S$, melting entropy.

undergo phase transitions of large entropy change before melting. The transition entropies are also collected in the table. The small entropies of melting and the large entropies of transitions correlate well with the general characteristics of plastic phases. The structural data are not collected. However, where they are available, most of the high-temperature phases are cubic, as is usual with molecular plastic crystals. Mechanical properties have not been examined in most cases. However, for the hydrofluorides, a wax-like consistency has been reported [32]. The high ionic conductivity of NH_4NO_3 [44] is also indicative of fast ionic mobility and hence of ionic disorder.

Even though a large number of plastic crystals are known in molecular substances, they are still a minority among the host of known molecular crystals. Various qualifications of molecules likely to form plastic phases have been formulated empirically such as molecular shape and charge distribution [3,4]. By contrast, the ionic substances listed in Table 2 are so diverse that they appear to suggest that formation of plastic phases is a rule rather than an exception in the A^+B^--type ionic crystals.

Stability of the molecular plastic crystals depends on the intermolecular forces in a subtle way. The subtlety may be illustrated by a pair of molecular crystals, chlorocyclohexane and bromocyclohexane. The former does form a plastic phase, whereas the latter does not [45]. The minor substitution causes the different phase behavior. The occurrence of the plastically crystalline phase requires that the orientationally disordered phase is more stable than the liquid at the temperature where the latter is more stable than the normal crystal. In ionic crystals, the most important stabilization of the crystal lattice comes from the Coulombic attraction, the Madelung energy. Since the Madelung energy depends on the interionic distance only weakly (as the inverse interionic distance), ionic crystals can accommodate themselves to the local strain in, and the global dilatation of, the lattice that accompanies the orientational disorder. Thus, for an ionic crystal the disordered states are available at a cost of a small fraction of the lattice energy. This favors formation of ionic plastic phases. In molecular crystals, the molecules are held together by short-range forces. Therefore, any disorder would tend to destabilize the crystalline lattice relative to the liquid. This explains the experimental observation that plastic phases are formed mostly by globular molecules that can be disordered with relatively small energy.

The argument presented here to explain qualitatively the diversity of ionic plastic crystals is equivalent to asserting that ionic substances can remain crystalline at temperatures which are sufficiently high so that a decrease in the free energy can be expected to offset the increase in the enthalpy arising from the orientational disorder. A more comprehensive discussion should involve properties of the ionic melts. This has not yet been carried out.

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