Crystal Structure of the High-temperature Solid Phases of Choline Tetrafluoroborate and Iodide

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The crystal structure of the highest- and second highest-temperature solid phases of choline tetrafluoroborate and iodide was determined by X-ray powder diffraction. The structure in the highest-temperature phase of both salts is NaCl-type cubic ($a = 10.16(2)$ Å, $Z = 4$ for tetrafluoroborate; $a = 10.08(2)$ Å, $Z = 4$ for iodide). The second highest-temperature phase of tetrafluoroborate and iodide is CsCl-type cubic ($a = 6.198(6)$ Å and $Z = 1$) and tetragonal ($a = 8.706(2)$ Å, $c = 6.144(6)$ Å, and $Z = 2$), respectively. DSC was carried out for the iodide, where the presence of three solid-solid phase transitions was confirmed. Enthalpy and entropy changes of these transitions were evaluated.

Key words: Crystal structure; Powder X-ray diffraction; Phase transition.

In [1] we have shown that choline tetrafluoroborate, $[(CH_3)_3NCH_2CH_2OH]BF_4$, in the temperature range from the melting point at 485 K to 160 K has three solid phases named I, II, and III. In Phase I and II, stable between 485 and 402 K and between 402 and 268 K, respectively, isotropic rotation and translational self-diffusion of both cation and anion were observed by ^{1}H and ^{19}F NMR measurements. From the dynamical behaviour of the ions and the small entropy of fusion ($6.4 \text{ J K}^{-1} \text{ mol}^{-1}$) we concluded that this salt forms ionic plastic crystals in Phases I and II, the structures of which are expected to be of a high symmetry. A similar dynamical behaviour of the cation was observed in choline iodide, $[(CH_3)_3NCH_2CH_2OH]I$, by ^{1}H NMR [2–5]. Differential scanning calorimetry (DSC) [6] seemed to indicate that this salt undergoes two solid-solid phase transitions at 436 and 367 K with enthalpy changes of 6.23 and 12.8 kJ mol^{-1}, respectively. The isotropic rotation and self-diffusion of the cation in the highest-temperature phase [2, 3] and the second highest-temperature phase [3–5] (named Phase I and II, respectively, in this text [7]) were detected by ^{1}H NMR. Furthermore, both salts show an unusual phenomenon, i.e. "quenching" of the cationic self-diffusion at the transition point from Phase II to Phase I [1, 3].

In the present study, X-ray powder diffractions in Phases I and II of the two salts were taken. In addition, DSC was carried out for the iodide to confirm the presence of a third highest-temperature phase existing between 366–360 K, as reported by Burnett et al. [5].

$[(CH_3)_3NCH_2CH_2OH]BF_4$ was prepared as described in [1]. $[(CH_3)_3NCH_2CH_2OH]I$ was purchased from Sigma Chemical Co. and recrystallized from ethanol. X-ray powder patterns were taken using a Philips X'pert PW3040/00 diffractometer. DSC was carried out using a Perkin-Elmer DSC7 in the range from 450 to 330 K.

The X-ray powder diffraction angles (2θ) in Phases I and II of tetrafluoroborate taken at ca. 420 and 300 K, respectively, are shown in Table 1. The structure of Phase I could be interpreted by an NaCl-type cubic lattice with $a = 10.16(2)$ Å, $Z = 4$, $V = 1049(7)$ Å^3 and $D_x = 1.209(8) \text{ Mg m}^{-3}$, and that of Phase II by a CsCl-type cubic lattice with

Table 1. Observed and calculated 2θ values of X-ray powder patterns in the highest- and second highest-temperature phases (Phase I and II) of $[(CH_3)_3NCH_2CH_2OH]BF_4$ taken at ca. 420 and 300 K, λ (Cu K_α) = 1.5418 Å, (Phase I: NaCl-type cubic, $a = 10.16(2)$ Å, $Z = 4$, $V = 1049(7)$ Å^3, and $D_x = 1.209(8) \text{ Mg m}^{-3}$; Phase II: CsCl-type cubic, $a = 6.198(6)$ Å, $Z = 1$, $V = 238.1(7)$ Å^3, $D_x = 1.332(4) \text{ Mg m}^{-3}$)

Observed		Calculated	
2θ (deg) ($\pm$ 0.02)	I (%)	2θ (deg)	*hkl*
Phase I			
15.12	2	15.10	111
17.47	100	17.46	200
24.78	20	24.79	220
29.12	1	29.15	311
30.48	5	30.48	222
35.33	2	35.34	400
Phase II			
14.30	1	14.29	100
20.24	100	20.26	110
24.87	2	24.88	111
28.80	2	28.81	200
32.33	5	32.30	210

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Table 2. Observed and calculated 2θ values of X-ray powder patterns in the highest- and second highest-temperature phases (Phase I and II) of $[(CH_3)_3NCH_2CH_2OH]I$ taken at ca. 460 and 400 K, λ (Cu K_α) = 1.5418 Å, (Phase I: NaCl-type cubic, $a = 10.08(2)$ Å, $Z = 4$, $V = 1024(7)$ Å^3, and $D_x = 1.50(1)$ Mg m^{-3}; Phase II: tetragonal, $a = 8.706(2)$, $c = 6.144(6)$ Å, $Z = 2$, $V = 465.7(7)$ Å^3, $D_x = 1.648(3)$ Mg m^{-3})

Observed		Calculated	
2θ (deg) ($\pm$ 0.03)	I (%)	2θ (deg)	hkl
Phase I			
15.25	20	15.22	111
17.62	100	17.60	200
24.99	60	24.99	220
29.38	70	29.39	311
30.73	30	30.73	222
35.57	2	35.63	400
38.93	10	38.95	331
39.97	5	40.00	420
Phase II			
14.39	10	14.39	110
		14.42	001
17.69	7	17.67	101
20.42	100	20.40	200
		20.42	111
25.05	10	25.07	201
27.08	10	27.11	211
29.00	5	29.01	220
30.84	5	30.81	300
		30.87	102
32.49	10	32.52	310
35.72	7	35.74	311
42.81	1	42.83	410

$a = 6.198(6)$ Å, $Z = 1$, $V = 238.1(7)$ Å^3 and $D_x = 1.332(4)$ Mg m^{-3}. The "quenching" of the cationic self-diffusion in tetrafluoroborate, therefore, can be understood in terms of the change of lattice structure. The self-diffusion processes, in which the constituent ions in the CsCl-type structure migrate more easily than those in the NaCl-type, were discussed in [8, 9].

Table 2 shows the X-ray data in Phases I and II of the iodide obtained at ca. 460 and 400 K, respectively. The data of Phase I were assigned to an NaCl-type cubic lattice with $a = 10.08(2)$ Å, $Z = 4$, $V = 1024(7)$ Å^3 and $D_x = 1.50(1)$ Mg m^{-3} isomorphous with Phase I of the tetrafluoroborate, while that of Phase II was assigned to a tetragonal lattice with $a = 8.706(2)$, $c = 6.144(6)$ Å, $Z = 2$, $V = 465.7(7)$ Å^3 and $D_x = 1.648(3)$ Mg m^{-3}. The low symmetry of the structure in Phase II of the iodide is consistent with the fact that the activation energy of cationic self-diffusion in Phase II of the iodide is much larger than that of the tetrafluoroborate (105–110 kJ mol^{-1} for the iodide [3, 5] and 62 kJ mol^{-1} for the tetrafluoroborate [1]).

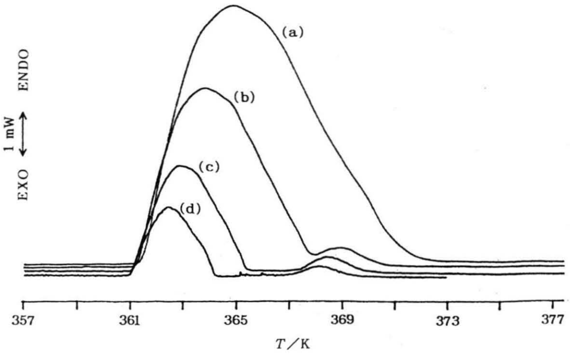

Fig. 1. DSC curves recorded for $[(CH_3)_3NCH_2CH_2OH]I$ around 365 K with heating rates of 10 K min^{-1} (a), 5 K min^{-1} (b), 2 K min^{-1} (c), and 1 K min^{-1} (d).

DSC measured on $[(CH_3)_3NCH_2CH_2OH]I$ with a heating rate of 2 K min^{-1} showed three thermal anomalies attributable to solid-solid transitions at 362, 368, and 435 K, indicating clearly the existence of the fourth solid phase found by Burnett et al. [5]. Corresponding enthalpy (entropy) changes were evaluated to be 11.9 ± 0.1 (32.9 ± 0.3), 0.87 ± 0.04 (2.4 ± 0.1), and 6.19 ± 0.03 kJ mol^{-1} (1.42 ± 0.07 J K^{-1} mol^{-1}) in the same order. When the sample heating rate was raised, the anomaly peak at 362 K overlapped with the peak at 368 K, as shown in Figure 1. This may be the reason why the previous DSC showed only two solid-solid phase transitions.

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