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The effects of isotopes on the λ-transition and structural phase transition in ammonium chloride

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Abstract

A thermal analysis employing differential scanning calorimetry (DSC) was undertaken to study the effects of isotopes^{14}N–^{15}N, H–D, and Cl–^{35}Cl on the λ-transition and structural CsCl⇔NaCl type phase transition of ammonium chloride using $^{14}NH_4Cl$, $^{15}NH_4Cl$, $^{14}ND_4Cl$, $^{15}ND_4Cl$, $^{14}NH_4{}^{35}Cl$, $^{15}NH_4{}^{35}Cl$, and $^{14}ND_4{}^{35}Cl$. The endothermic and exothermic peak temperatures of the λ-transition were 7°C higher when D was substituted for H in $^{14}NH_4Cl$, $^{15}NH_4Cl$, and $^{14}NH_4{}^{35}Cl$. In the structural phase transition, the lighter isotope-substituted ammonium chloride exhibited a higher transition temperature, except that there was a change in the endothermic peak temperature when ^{14}N–^{15}N was substituted in $^{14}NH_4Cl$, $^{14}ND_4Cl$, and $^{14}NH_4{}^{35}Cl$ and in the exothermic peak temperature when Cl–^{35}Cl was substituted in $^{14}NH_4Cl$ and $^{14}ND_4Cl$. The isotope effect also tended to expand the hysteresis as a result of the difference between the endothermic and exothermic peak temperatures except for the H–D and Cl–^{35}Cl exchanged samples in $^{15}NH_4Cl$. No clear relationship was found between the isotope effect of the λ- and structural CsCl⇔NaCl type phase transitions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ammonium chloride; Cl–^{35}Cl; DSC; H–D; Isotope effect; λ-transition; ^{14}N$-$^{15}N; Structural phase transition

1. Introduction

It has been reported that the structural phase transition temperature of dielectric crystals such as $LiTaO_3$, $PbZrO_3$, KH_2PO_4, $NH_4H_2PO_4$, K_2SeO_4, Rb_2ZnCl_4, $NaNO_3$, and KNO_3 changes when the stable isotope of their constituent element (^{6}Li,^{7}Li,^{90}Zr,^{94}Zr,^{41}K,^{18}O,^{15}N,^{85}Rb,^{87}Rb,^{64}Zn, and ^{68}Zn) is enriched. Specifically, all these crystals exhibit higher transition temperatures when the lighter isotopes are substituted [1]. By contrast, the effects of H–D isotope on the λ-transition for KH_2PO_4 (KDP) type crystals and ammonium chloride (NH_4Cl) are well known [2,3]. NH_4Cl exhibits a λ-transition due to intramolecular re-orientation at -30.5°C as well as a structural CsCl⇔NaCl type phase transition due to lattice elongation at 184.3°C [3]. In a previous report [4], we studied the isotope effect of ^{14}N$-$^{15}N and H–D on the structural phase transition temperature in NH_4Cl and found that NH_4Cl enriched with a lighter isotope (H and ^{14}N) exhibits a higher or the same transition temperature for the CsCl → NaCl type transition and a lower or the same temperature for the reverse transition in comparison with D and ^{15}N-enriched NH_4Cl. It was also found that the isotope effect tends to enlarge the

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difference between the peak temperatures of the forward and reverse transitions, compared with $^{14}NH_4Cl$.

However, there has been no systematic study of the isotope effects of each constituent element, hydrogen, nitrogen and chlorine, on the two phase transitions of NH_4Cl. In this paper, we investigate the effects of the isotopes $^{14}N-^{15}N$, H–D and Cl–^{35}Cl on the λ-transition and structural CsCl⇔NaCl type phase transition of NH_4Cl using differential scanning calorimetry (DSC) and compare the transition with those for $^{14}NH_4Cl$ with a natural abundance of nitrogen, hydrogen and chlorine.

2. Experimental procedure

2.1. Samples

$^{14}NH_4Cl$ with a natural abundance of nitrogen, hydrogen and chlorine was supplied by Kanto Chemicals. ^{15}N- and D-enriched ammonium chlorides consisting of $^{15}NH_4Cl$ with 99.8 atomic% ^{15}N,$^{15}ND_4Cl$ with 99 atomic% ^{15}N and 99.2 atomic% D, and $^{14}ND_4Cl$ with 99.4 atomic% D were supplied by ISOTEC (lot Nos. SY4037, VX4134, and VX4133, respectively). To study the isotope effect of chlorine, we used ^{35}Cl-enriched ammonium chloride as a sample since ^{37}Cl-enriched ammonium chloride is very expensive and difficult to obtain because it is a minor isotope. ^{35}Cl-enriched ammonium chloride of $^{14}NH_4{}^{35}Cl$ with 99 atomic% ^{35}Cl, $^{15}NH_4{}^{35}Cl$with 99 atomic% ^{15}N and 99 atomic% ^{35}Cl, and $^{14}ND_4{}^{35}Cl$ with 98 atomic% D and 99 atomic% ^{35}Cl were supplied by ICON (lot Nos. IKsp6431, IKsp6432, and IKsp6433, respectively). All the ammonium chloride samples were ground using an agate mortar and sieved to under 177 μm. X-ray diffraction analysis confirmed that all the samples had a CsCl structure at room temperature.

2.2. Thermal analysis

We undertook a DSC thermal analysis (Mac Science model 3120). The temperature was corrected by measuring the melting point ($T_m = 156.6°C$) of indium metal and the onset temperature was in good agreement (within 0.5°C) with the reported T_m value. A sample about 13 mg was put in a sealed-type sample pan and subjected to a repeated heating/cooling cycle between −50°C and room temperature (RT), followed by a repeated heating/cooling cycle between RT and about 200°C. The heating and cooling rates were 1°C min^{-1} and each cycle was repeated three times. We used α-Al_2O_3 as a reference sample in all the experiments.

3. Results and discussion

Fig. 1 shows the DSC curves obtained in the second run of the three heating/cooling cycles of seven

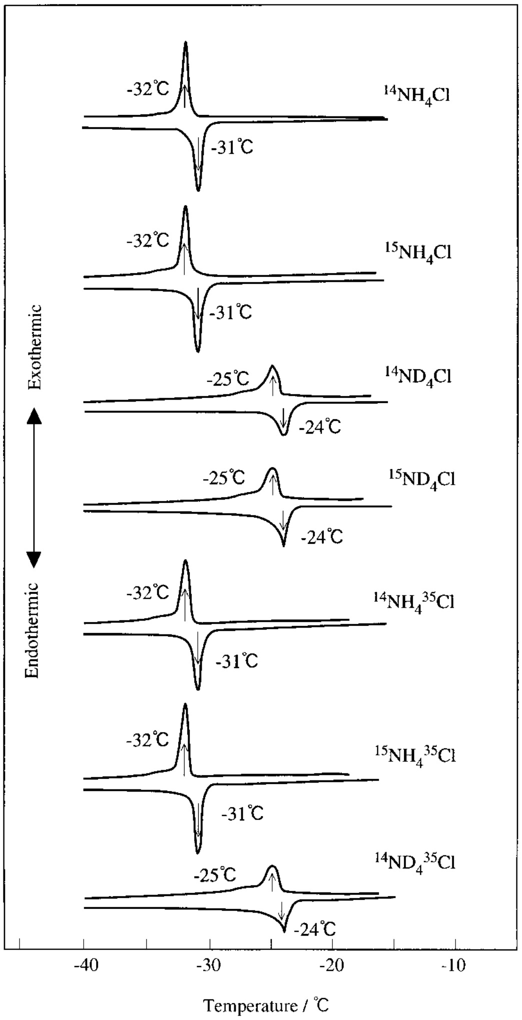

Fig. 1. DSC curves obtained in the second run of three heating/cooling cycles for seven NH_4Cl powders between −50°C and RT.

ammonium chlorides between −50°C and RT. Endothermic and exothermic peaks due to the λ-transition were observed in all the samples. The respective endothermic and exothermic peak temperatures for $^{14}NH_4Cl$, $^{15}NH_4Cl$, $^{14}NH_4{}^{35}Cl$ and $^{15}NH_4{}^{35}Cl$ were −31°C and −32°C, while the endothermic and exothermic peaks of $^{14}ND_4Cl$, $^{15}ND_4Cl$, and $^{14}ND_4{}^{35}Cl$ exhibited higher temperatures of −24°C and −25°C, respectively. It was found that the endothermic and exothermic temperatures in the λ-transition become 7°C higher with broader peaks when D was substituted for H in $^{14}NH_4Cl$, $^{15}NH_4Cl$ and $^{14}NH_4{}^{35}Cl$. It is also found that the λ-transition for all the ammonium chlorides had a narrow hysteresis (1°C), that is the difference between the endothermic and exothermic peak temperatures. It is clear that the H–D substitution has an isotope effect on the λ-transition of NH_4Cl, as reported in [3].

Fig. 2(a) and (b) show the DSC curves obtained in the second run of the three heating/cooling cycles between RT and 200°C using the seven ammonium chlorides. All the samples exhibited an endothermic peak due to the structural CsCl → NaCl type phase transition on heating. The peak temperature was 187°C for $^{14}NH_4Cl$, 192°C for $^{15}NH_4Cl$, 179°C for $^{14}ND_4Cl$, 181°C for $^{15}ND_4Cl$, 189°C for $^{14}NH_4{}^{35}Cl$, 190°C for $^{15}NH_4{}^{35}Cl$, and 188°C for $^{14}ND_4{}^{35}Cl$. These temperatures are higher or nearly equal to that

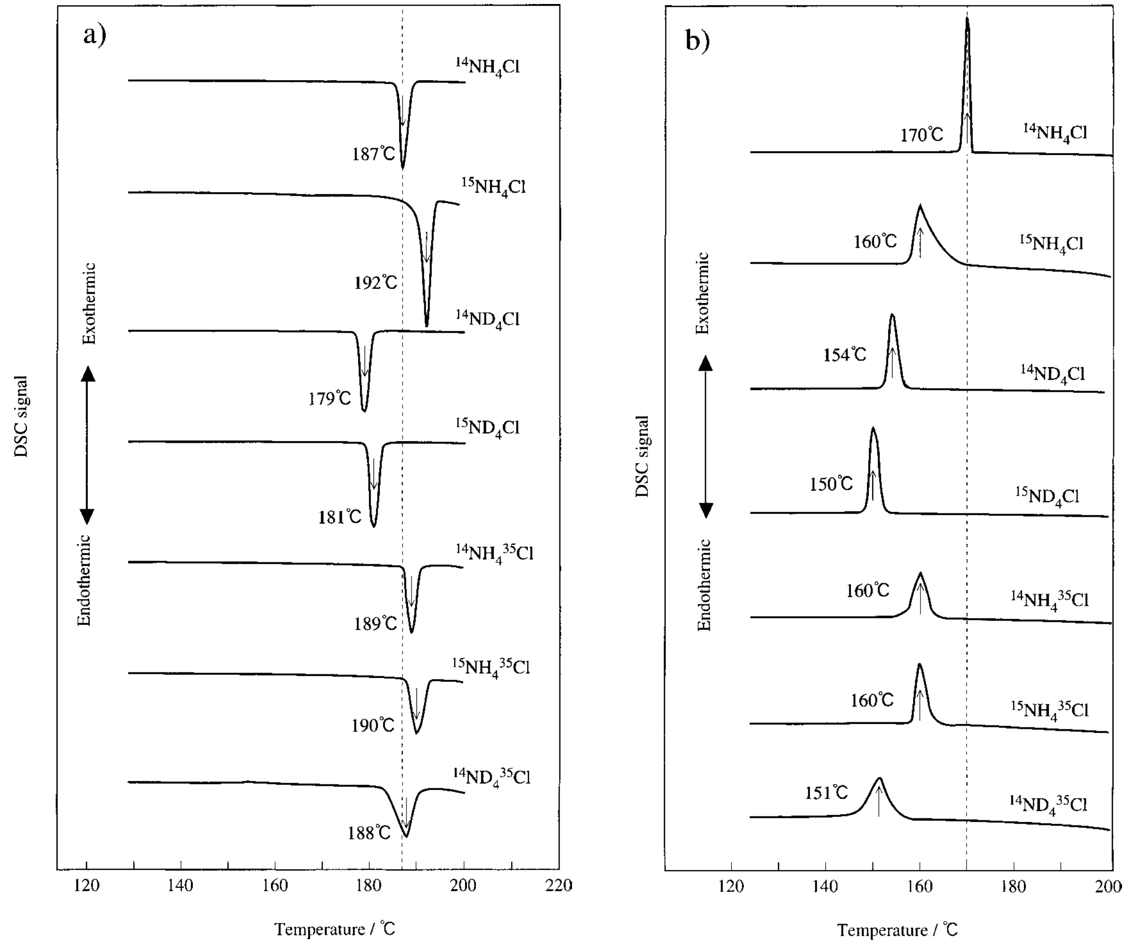

Fig. 2. DSC curves obtained in the second run of three heating/cooling cycles for seven NH_4Cl powders between RT and 200°C: (a) heating process, (b) cooling process. The dotted lines correspond to the endothermic and exothermic peak temperatures for $^{14}NH_4Cl$.

Table 1
Structural phase transition temperature during heating and cooling of $^{14}NH_4Cl$, $^{15}NH_4Cl$, $^{14}ND_4Cl$, $^{15}ND_4Cl$, $^{14}NH_4{}^{35}Cl$, $^{15}NH_4{}^{35}Cl$, and $^{14}ND_4{}^{35}Cl$

Sample	T_{endo}[a] (°C)	T_{exo}[a] (°C)	ΔT[b] (°C)
$^{14}NH_4Cl$	187.0 ± 0.0	169.5 ± 0.5	17.5
$^{15}NH_4Cl$	192.3 ± 0.5	159.8 ± 0.8	32.5
$^{14}ND_4Cl$	178.7 ± 0.5	155.0 ± 0.6	23.7
$^{15}ND_4Cl$	181.0 ± 0.0	150.2 ± 0.4	30.8
$^{14}NH_4{}^{35}Cl$	189.2 ± 0.4	159.8 ± 0.4	29.4
$^{15}NH_4{}^{35}Cl$	190.8 ± 0.4	160.0 ± 0.9	30.8
$^{14}ND_4{}^{35}Cl$	187.2 ± 0.8	152.2 ± 1.5	35.0

[a] T_{endo} and T_{exo} indicate the endothermic and exothermic peak temperatures of ammonium chloride during heating and cooling, respectively.

[b] $\Delta T = T_{endo} - T_{exo}$.

Table 2
Isotope shift of T_{endo}, T_{exo} and ΔT by substitution of $^{14}N-^{15}N$ (a), H–D (b) and Cl–^{35}Cl (c)

Sample	Shift (°C)		
	T_{endo}	T_{exo}	ΔT
(a) $^{14}N-^{15}N$ substitution ($^{14}N \rightarrow {}^{15}N$)			
$^{14}NH_4Cl/^{15}NH_4Cl$	+5.3	−9.7	+15.0
$^{14}ND_4Cl/^{15}ND_4Cl$	+2.3	−4.8	+7.1
$^{14}NH_4{}^{35}Cl/^{15}NH_4{}^{35}Cl$	+1.6	+0.2	+1.4
(b) H–D substitution (H → D)			
$^{14}NH_4Cl/^{14}ND_4Cl$	−8.3	−14.5	+6.2
$^{15}NH_4Cl/^{15}ND_4Cl$	−11.3	−9.6	−1.7
$^{14}NH_4{}^{35}Cl/^{14}ND_4{}^{35}Cl$	−2.0	−7.6	+5.6
(c) Cl–^{35}Cl substitution (Cl → ^{35}Cl)			
$^{14}NH_4Cl/^{14}NH_4{}^{35}Cl$	+2.2	−9.7	+11.9
$^{15}NH_4Cl/^{15}NH_4{}^{35}Cl$	−1.5	+0.2	−1.7
$^{14}ND_4Cl/^{14}ND_4{}^{35}Cl$	+8.5	−2.8	+11.3

of $^{14}NH_4Cl$ except for those of $^{14}ND_4Cl$ and $^{15}ND_4Cl$. As shown in Fig. 2(b) obtained from the DSC curves during the cooling process, all the samples exhibited an exothermic peak temperature due to the reverse transition. They appeared at 170°C for $^{14}NH_4Cl$, 160°C for $^{15}NH_4Cl$, 154°C for $^{14}ND_4Cl$, 150°C for $^{15}ND_4Cl$, 160°C for $^{14}NH_4{}^{35}Cl$, 160°C for $^{15}NH_4{}^{35}Cl$, and 151°C for $^{14}ND_4{}^{35}Cl$, which is 10–20°C lower than that of $^{14}NH_4Cl$. A hysteresis caused by the difference between the endothermic and exothermic peak temperatures is observed in all the curves. The endothermic and exothermic peak shapes for the six labeled samples ($^{15}NH_4Cl$, $^{14}ND_4Cl$, $^{15}ND_4Cl$, $^{14}NH_4{}^{35}Cl$, $^{15}NH_4{}^{35}Cl$, and $^{14}ND_4{}^{35}Cl$) became broader than those of $^{14}NH_4Cl$.

Table 1 summarizes the structural phase transition temperatures (T_{endo}, T_{exo}) for the seven ammonium chloride samples. They are the average values for three heating/cooling cycles and have a good reproducibility. It is noted that the endothermic and exothermic peak temperatures are almost the same as or a few degrees lower than those reported in our previous paper in which we used a different DSC apparatus [4]. Table 1 also shows ΔT ($=T_{endo} - T_{exo}$), indicative of the width of the hysteresis. On the basis of these results, Table 2 summarizes the isotope effect of $^{14}N-^{15}N$, H–D and Cl–^{35}Cl substitution on the structural phase transition temperature. The isotope shift of T_{endo}, T_{exo} and ΔT as the result of $^{14}N-^{15}N$ substitution is shown in Table 2(a). The T_{endo} and ΔT of the ^{15}N-enriched samples ($^{15}NH_4Cl$, $^{15}ND_4Cl$, and $^{15}NH_4{}^{35}Cl$) are 1.6–5.3°C higher and 1.4–15°C broader than those of the corresponding ^{14}N-enriched samples, while the T_{exo} is almost the same or 4.8–9.7°C lower. The T_{endo} and T_{exo} of the D-enriched samples ($^{14}ND_4Cl$, $^{15}ND_4Cl$ and $^{14}ND_4{}^{35}Cl$) are 2–11.3°C and 7.6–14.5°C lower, respectively, than those of the corresponding H-enriched samples (Table 2(b)). ΔT is 5.6–6.2°C broader, in contrast to $^{15}NH_4Cl$ where the value is −1.7°C. The isotope shift caused by Cl–^{35}Cl substitution is also shown in Table 2(c). T_{endo}, T_{exo} and ΔT of the ^{35}Cl-enriched samples ($^{14}NH_4{}^{35}Cl$ and $^{14}ND_4{}^{35}Cl$) are 2.2–8.5°C higher, 2.8–9.7°C lower and about 11–12°C broader than those of $^{14}NH_4Cl$ and $^{14}ND_4Cl$. In contrast, the isotope shift for $^{15}NH_4Cl$ caused by Cl–^{35}Cl substitution exhibits the reverse tendency or little change compared with $^{14}NH_4Cl$ and $^{14}ND_4Cl$. It is found that such isotope effects as shifts of T_{endo} and T_{exo} and increases in ΔT by Cl–^{35}Cl substitution were large in comparison with those obtained by the substitution of $^{14}N-^{15}N$ and H–D although the atomic concentration of ^{35}Cl in NH_4Cl is varied from 75.77 to 99 atomic%, while the atomic concentration of D and ^{15}N is increased from 0.0148% and 0.365%, respectively, to more than 98%.

We conclude that the isotope H–D substitution has a rising effect on the λ-transition temperature of NH_4Cl and the H–D, $^{14}N-^{15}N$, and Cl–^{35}Cl substitutions also have a changing effect on the structural CsCl⇔NaCl type phase transition temperature. The λ-transition temperature during heating and cooling was increased by 7°C when H was substituted with D. In the structural phase transition, the lighter isotope in ammonium chlorides exhibited a higher transition temperature during heating and cooling except for the endothermic peak temperature in the substitution of ^{14}N$-$^{15}N ($^{14}NH_4Cl$, $^{14}ND_4Cl$, $^{14}NH_4{}^{35}Cl$) and the exothermic peak temperature in the substitution of Cl–^{35}Cl ($^{14}NH_4Cl$, $^{14}ND_4Cl$). The isotope effect also tended to expand the hysteresis (ΔT) expect for the H–D and Cl–^{35}Cl substitution in $^{15}NH_4Cl$. In terms of the isotope effects, there seems to be no clear relation between the λ- and structural phase transition.

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