ELSEVIER

Thermochimica Acta 306 (1997) 153–157

thermochimica acta

The effects of isotopes on structural phase transition in ammonium chloride

K. Shikano[a,*], K. Katoh[a], S. Shimada[b], M. Katoh[a]

[a] *NTT Science and Core Technology Laboratory Group, Nippon Telegraph and Telephone Corporation, Tokai, Ibaraki 319-11, Japan*
[b] *Laboratory of Solid State Chemistry, Research Group of Materials Chemistry, Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, North 13, West 8, Sapporo, 060, Japan*

Received 17 March 1997; received in revised form 24 June 1997; accepted 30 June 1997

Abstract

The effects of the isotopes ^{14}N–^{15}N and/or H–D on the structural CsCl$\rightleftarrows$NaCl type phase transition temperature of ammonium chloride using $^{14}NH_4Cl$, $^{15}NH_4Cl$, $^{14}ND_4Cl$, and $^{15}ND_4Cl$ have been studied by thermal analysis, TG–DTA and DSC. The TG–DTA curves revealed that these ammonium chlorides exhibit an endothermic peak in the range 183.8–197.3°C with a good reproducibility in spite of sublimation. The exact transition temperatures of these four ammonium chlorides during heating and cooling were measured by DSC. The endothermic peak temperature became 0.4°C lower by substituting ^{14}N with ^{15}N in $^{14}ND_4Cl$, and 2.3 and 8.7°C lower by substituting H with D in $^{14}NH_4Cl$ and $^{15}NH_4Cl$, respectively, while the temperature became 6°C higher by substituting ^{14}N with ^{15}N in $^{14}NH_4Cl$. The exothermic peak temperature was reduced by 15.7 and 14.4°C by substituting ^{14}N with ^{15}N and H with D in $^{14}NH_4Cl$, respectively.

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

1. Introduction

The effects of H–D isotopes in KDP(KH_2PO_4) type crystals are well known in solid-state physics [1] and the isotope effects of other elements in these crystals have been also studied. Hidaka measured the structural phase transition temperature for nine dielectric crystals enriched with the stable isotopes of seven constituent elements by using differential scanning calorimetry (DSC) and reported that all the crystals exhibited higher transition temperatures when lighter isotopes were substituted [2–4].

*Corresponding author. Tel.: 00 81 29 287 7746; fax: 00 81 29 287 7193; e-mail: shikano@iba.iecl.ntt.co.jp

PII S0040-6031(97)00288-8

The H–D isotope effects of the λ-transition at − 30.5°C are also known for ammonium chloride which exhibits two phase transitions at − 30.5 and 184.3°C [5]. However, there have been no reports on the isotope effects of other heavier elements such as nitrogen and chlorine on the CsCl$\rightleftarrows$NaCl type phase transition at 184.3°C.

This paper describes the effects of the isotopes ^{14}N–^{15}N and H–D on the structural phase transition of ammonium chloride by undertaking measurements with such thermal analysis techniques as thermogravimetric and differential thermal analysis (TG–DTA) and DSC and by a comparison with that for ammonium chloride which has a natural abundance of nitrogen and hydrogen.

2. Experimental procedure

2.1. Samples

Ammonium chloride with a natural abundance of nitrogen and hydrogen ($^{14}NH_4Cl$) was supplied by Wako Pure Chemical Industries. ^{15}N- and/or D-enriched ammonium chlorides of $^{15}NH_4Cl$ with 99.8 at% ^{15}N, $^{15}ND_4Cl$ with 99 at% ^{15}N and 99.2 at% D, and $^{14}ND_4Cl$ with 99.4 at% D were supplied by ISOTEC Inc. (lot Nos. SY4037 and SY4839, lot No. VX4134, and lot No. VX4133). All ammonium chloride samples were ground using an agate mortar and sieved under 177 μm. These samples were confirmed to have the same structure by X-ray diffraction.

2.2. Thermal analysis

Thermal analysis was undertaken with Mac Science models TG–DTA 2000 and DSC 3100. 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.

In the TG–DTA measurement, each of about 20 mg of the test and reference (ex. Al_2O_3) samples was mounted in a sample pan and heated from room temperature (R.T.) to about 300°C at a rate of 1°C min^{-1} under an argon gas flow of 100 ml min^{-1}.

In the DSC measurement, a test sample about 13 mg in weight was mounted in a sealed-type sample pan and heated from R.T. to about 200°C at 1°C min^{-1}. α-Al_2O_3 was used as a reference sample in all the experiments.

3. Results and discussion

Fig. 1 shows simultaneous TG–DTA curves obtained by heating $^{14}NH_4Cl$, $^{15}NH_4Cl$, $^{14}ND_4Cl$ and $^{15}ND_4Cl$ between R.T. and 300°C. These chlorides exhibited a weight loss due to sublimation at temperatures higher than 170°C and an endothermic peak at 189, 197, 184 and 183°C, respectively, due to the structural CsCl⇄NaCl type phase transition at which their weight loss was estimated to be a few percent as a result of sublimation. The peak temperature of $^{15}NH_4Cl$ is about 8°C higher than that of $^{14}NH_4Cl$ and about 14°C higher than that of $^{15}ND_4Cl$ while the peak temperature of $^{14}NH_4Cl$ is about 5°C higher than that of $^{14}ND_4Cl$. However, the difference between the peak temperatures of $^{14}ND_4Cl$ and $^{15}ND_4Cl$ was negligible. The average peak temperatures obtained for four measurements were $189.3 \pm 1.0°C$ ($n = 4$), $197.3 \pm 1.0°C$ ($n = 4$), $183.8 \pm 1.0°C$ ($n = 4$) and $183.8 \pm 0.5°C$ ($n = 4$) for $^{14}NH_4Cl$, $^{15}NH_4Cl$, $^{14}ND_4Cl$ and $^{15}ND_4Cl$, respectively. This shows that the measured peak temperatures have a good reproducibility despite the occurrence of slight sublimation.

It is important to follow thermal change due to the structural CsCl⇄NaCl type phase transition during heating and cooling between R.T. and 200°C at which sublimation was suppressed to less than a few percent in order to understand the isotope effect. Fig. 2 shows the DSC curves obtained in three repeated heating/cooling cycles with these ammonium chlorides between R.T. and about 200°C. As shown in the figure, there was a hysteresis in all the DSC curves because the endothermic peak temperature was higher than the exothermic one. $^{14}NH_4Cl$ exhibits the endothermic and exothermic peaks at about 187 and 175°C with heating and cooling, respectively. The average endothermic and exothermic peak temperatures in the three cycles were 187.0 ± 0.0 and $174.7 \pm 0.6°C$, respectively (Fig. 2a). For $^{15}NH_4Cl$, the average endothermic and exothermic peak temperatures were 193.0 ± 0.0 and $159.0 \pm 1.0°C$, being 6°C higher and 15.7°C lower, respectively, than those of $^{14}NH_4Cl$ (Fig. 2b). The peak shapes in all the runs were a little broader than those of $^{14}NH_4Cl$. With $^{14}ND_4Cl$, the average endothermic and exothermic peak temperatures were 184.7 ± 0.6 and $160.3 \pm 1.1°C$. These are 2.3 and 14.4°C lower than those of $^{14}NH_4Cl$, respectively. The shapes of the exothermic peaks during cooling became broader than that of $^{14}NH_4Cl$. With $^{15}ND_4Cl$, the average endothermic and exothermic peak temperatures were 184.3 ± 1.2 and $159.0 \pm 1.0°C$, the former being 8.7°C lower than that of $^{15}NH_4Cl$ and the latter having the same value. The shape of the exothermic peak was as broad as that of $^{14}ND_4Cl$. These peak temperatures obtained by DSC were 2–3°C lower than those obtained by TG–DTA.

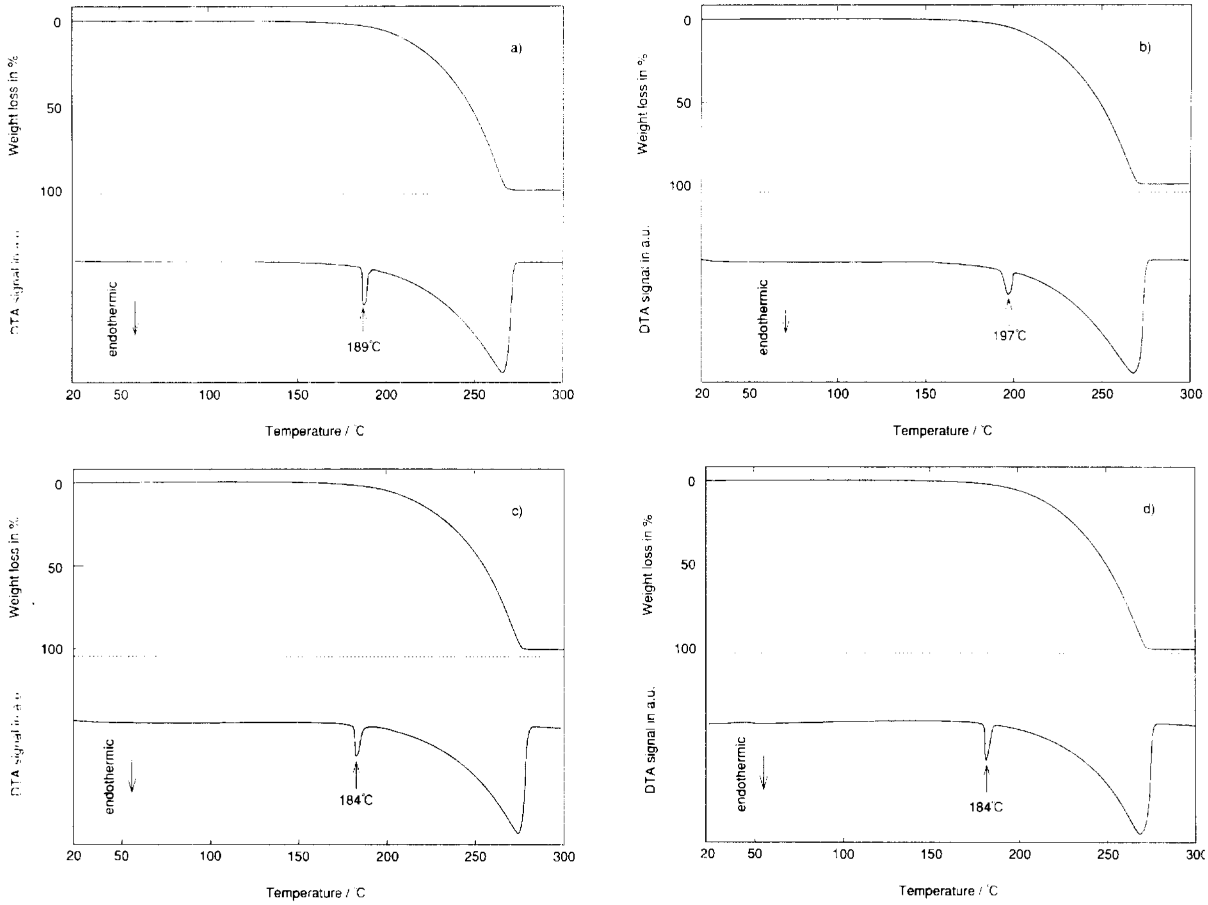

Fig. 1. Simultaneous TG–DTA curves obtained by heating a powder sample between room temperature and 200°C. Curve (a) $^{14}NH_4Cl$, (b) $^{15}NH_4Cl$, (c) $^{14}ND_4Cl$, (d) $^{15}ND_4Cl$.

Table 1 summarizes the structural phase transition temperature (T_{endo}, T_{exo}) of $^{14}NH_4Cl$, $^{15}NH_4Cl$, $^{14}ND_4Cl$ and $^{15}ND_4Cl$ during heating and cooling and the temperature shift caused by substituting the ^{14}N and H with ^{15}N and D, respectively. The endothermic peak temperature became 6°C higher and 2.3°C lower by substituting ^{14}N with ^{15}N and H with D, respectively, in $^{14}NH_4Cl$. The peak temperature also became 0.4°C lower by substituting ^{14}N with ^{15}N in $^{14}ND_4Cl$, and 8.7°C lower by substituting H with D in $^{15}NH_4Cl$. In addition, all the temperature shifts were in the minus direction except for $^{15}NH_4Cl$ compared with $^{14}NH_4Cl$ where the shift was +6°C.

On the other hand, during cooling, the exothermic peak temperature was reduced by 15.7 and 14.4°C by substituting ^{14}N with ^{15}N and H with D in $^{14}NH_4Cl$, respectively. The peak temperature shift, however, was negligible when ^{14}N was substituted with ^{15}N in $^{14}ND_4Cl$ and there was no shift when H was replaced by D in $^{15}NH_4Cl$. All temperatures were shifted in the minus direction except for $^{15}ND_4Cl$ compared with $^{14}ND_4Cl$ where the peak temperature remained unchanged.

It was also found that the exothermic peak temperatures of $^{15}NH_4Cl$, $^{14}ND_4Cl$ and $^{15}ND_4Cl$ were the same within an acceptable margin of error while these endothermic peak temperatures were different. Therefore, it is believed that the width in a structural phase transition was changed by the substitution of ^{14}N–^{15}N and/or H–D. Table 1 also shows ΔT (= $T_{endo} - T_{exo}$). It seems that ΔT indicates the width of the hysteresis. As shown in the table, the hysteresis can be expanded

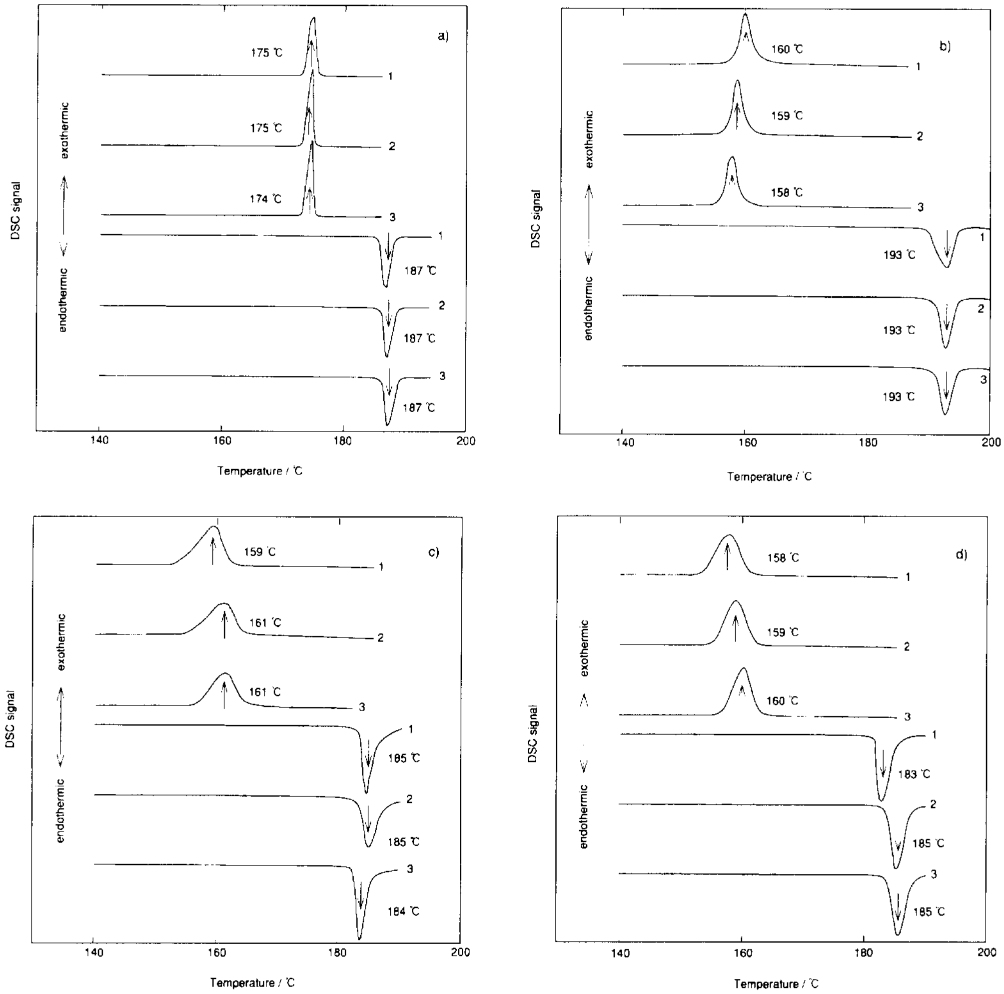

Fig. 2. DSC curves obtained in three repeated heating/cooling cycles of powder samples between room temperature and 200°C. 1, 2 and 3 indicate the run No. and the curves are obtained from (a) $^{14}NH_4Cl$, (b) $^{15}NH_4Cl$, (c) $^{14}ND_4Cl$ and (d) $^{15}ND_4Cl$.

from 12.3 to 34.0°C by substituting ^{14}N with ^{15}N in $^{14}NH_4Cl$ and also expanded from 12.3 to 24.4°C by substituting H with D in $^{14}NH_4Cl$. The hysteresis, however, is narrowed from 34.0 to 25.3°C by substituting H with D in $^{15}NH_4Cl$ and the substitution of ^{14}N–^{15}N in $^{14}ND_4Cl$ causes negligible change in the hysteresis width.

Therefore, it is concluded that the isotopes ^{14}N–^{15}N and/or H–D have an effect on the structural CsCl⇄NaCl type phase transition temperature of ammonium chloride. That is, ammonium chloride exhibits a higher transition temperature during heating and cooling when lighter isotopes are substituted except for the endothermic peak temperature caused by the substitution of ^{14}N–^{15}N in $^{14}NH_4Cl$ and this tendency is in good agreement with the results reported in Ref. [4]. The isotope effect also tends to expand the hysteresis except when H is substituted with D in $^{15}NH_4Cl$.

It is well known that in ammonium chloride, a λ-transition occurs at − 30.5°C caused by an intramolecular re-orientation and that there is a structural CsCl⇄NaCl type phase transition at 184.3°C caused by lattice elongation. The isotope effect of ^{14}N–^{15}N and/or H–D in the higher temperature transition was demonstrated in the present experiment, whereas it

Table 1
Structural phase transition temperature during heating and cooling of $^{14}NH_4Cl$, $^{15}NH_4Cl$, $^{14}ND_4Cl$ and $^{15}ND_4Cl$ and temperature shift caused by isotope effect

Sample	T_{endo} [a] (°C)	Shift (°C) ($^{14}N/^{15}N$)	Shift (°C) (H/D)	T_{exo} [b] (°C)	Shift (°C) ($^{14}N/^{15}N$)	Shift (°C) (H/D)	ΔT [c] (°C)	Shift (°C) ($^{14}N/^{15}N$)	Shift (°C) (H/D)
$^{14}NH_4Cl$	187.0	—	—	174.7	—	—	12.3	—	—
$^{15}NH_4Cl$	193.0	+6.0 [d]	—	159.0	−15.7 [d]	—	34.0	+21.7 [d]	—
$^{14}ND_4Cl$	184.7	—	−2.3 [e]	160.3	—	−14.4 [e]	24.4	—	+12.1 [e]
$^{15}ND_4Cl$	184.3	−0.4 [d]	−8.7 [e]	159.0	−1.3 [d]	0.0 [e]	25.3	+0.9 [d]	−8.7 [e]

[a] Endothermic peak temperature of ammonium chloride during heating.
[b] Exothermic peak temperature of ammonium chloride during cooling.
[c] $T_{endo} - T_{exo}$.
[d] Show temperature shifts caused by substituting ^{14}N with ^{15}N in $^{14}NH_4Cl$ and $^{14}ND_4Cl$.
[e] Show temperature shifts caused by substituting H with D in $^{14}NH_4Cl$ and $^{15}NH_4Cl$.

was reported that the λ-transition temperature becomes 7.1°C higher by substituting H with D in $^{14}NH_4Cl$ [5].

References

[1] R. Blinc, J. Phys. Chem. Solids 13 (1960) 204.
[2] T. Hidaka, K. Oka, Phys. Rev. B35 (1987) 8502.
[3] T. Hidaka, K. Oka, Ferroelectrics 108 (1990) 1777.
[4] T. Hidaka, K. Oka, Phys. Rev. B42 (1990) 8295.
[5] N.L. Ross Kane, in J.W. Mellor (Ed.), Inorganic and Theoretical Chemistry, Vol. 8, Suppl. 1, Nitrogen (Part 1), Longmans, London, 1964, p. 387.