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Structural characteristics of $[N(CH_3)_4]_2CdCl_4$ determined by ^1H MAS NMR, ^{13}C CP/ MAS NMR, and ^{14}N NMR

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Abstract The structural geometry of $[N(CH_3)_4]_2CdCl_4$ in a hexagonal phase is studied by ^1H MAS NMR, ^{13}C CP/MAS NMR, and ^{14}N NMR. The changes in the chemical shifts for ^{13}C and ^{14}N in the hexagonal phase are explained by the structural geometry. In addition, the temperature dependencies of the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ for ^1H MAS NMR and ^{13}C CP/MAS NMR are measured.

Keywords $[N(CH_3)_4]_2CdCl_4$, Magic angle spinning, Static NMR, Nuclear magnetic resonance

Introduction

The sequence of phase transitions in $[N(CH_3)_4]_2BX_4$ (where *B*=Co, Cu, Zn, Cd; X=Cl, Br) compounds has made them the subject of numerous investigations in recent years[1-3]. These materials have attracted attention in the field of fundamental physics primarily because of a complicated sequence of structural phase transitions. These crystals are isomorphous, with space group *Pmcn*, and there are four formula units per unit cell with dimensions of approximately a=9 Å, b=15 Å, and c=12 Å[4]. In particular, the appearance of successive lattice transformations from a prototype structure to an incommensurate structure, and then to a commensurate structure is a ferroelastic phenomenon in the investigation of phase transitions. Compounds such as $[N(CH_3)_4]_2ZnCl_4$ [5-8] and $[N(CH_3)_4]_2CoCl_4$ [9-11] have shown ferroelectric phases around room temperature for very narrow temperature ranges, while no ferroelectric phase was detected in other crystals such as $[N(CH_3)_4]_2CuCl_4$. However, $[N(CH_3)_4]_2CdCl_4$ does not show any phase transition around room temperature, and the crystals undergo two phase transitions at low temperatures of 105 K and 120 K[1,12]. At room temperature, $[N(CH_3)_4]_2CdCl_4$ contains two formula weights per unit cell and belongs to the hexagonal system $P6_3/m$ with unit cell dimensions specified by a=9.138 Å, c=6.723 Å, and γ=120° [13]. At 120 K, this structure is transformed to a monoclinic structure belonging to space group $P2_1/m$ [14]. Although the $[N(CH_3)_4]_2BCl_4$ crystals are of the A_2BX_4-type, their phase transition temperatures and crystal structures are different from each other. Different structural phase transitions for the compounds containing different metal ions indicate that these transitions cannot be only due to the ordering of the organic groups, but that the metal chloride tetrahedral structure may also be responsible for the structure of these phases. In a previous study,

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the optical birefringence and phase transitions in $[N(CH_3)_4]_2CdCl_4$ were reported[15]. However, the detailed structural property of the hexagonal phase of $[N(CH_3)_4]_2CdCl_4$ has not been studied yet.

In this paper, we measured the temperature dependencies of the chemical shifts and the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ for ^1H MAS NMR and ^{13}C CP/MAS NMR, respectively, in order to understand the structural geometry in $[N(CH_3)_4]_2CdCl_4$. Furthermore, ^{14}N NMR spectra of $[N(CH_3)_4]_2CdCl_4$ single crystals are obtained as a function of temperature by a static NMR method. Based on these results, we discuss the roles of the $N(CH_3)_4$ ions in the hexagonal phase.

Experimental procedure

$[N(CH_3)_4]_2CdCl_4$ single crystals were grown from an aqueous solution by slow evaporation at 293 K. The starting materials were $N(CH_3)_4Cl$ and $CdCl_2$. The obtained $[N(CH_3)_4]_2CdCl_4$ single crystals were colorless and transparent with a pseudohexagonal shape and grew easily within a few weeks.

^1H MAS NMR and ^{13}C CP/MAS NMR experiments on $[N(CH_3)_4]_2CdCl_4$ were performed using a Bruker DSX 400 FT NMR spectrometer at the Korea Basic Science Institute Seoul Western Center. The ^1H MAS NMR and ^{13}C CP/MAS NMR experiments were performed at a Larmor frequency of $\omega_o/2\pi$=400.12 MHz and 100.61 MHz, respectively. The samples were placed as powders in a CP/MAS probe with a size of 4 mm. The magic angle spinning rate was set at 10 kHz and 7 kHz for the ^1H MAS NMR and ^{13}C CP/MAS NMR measurements, respectively, in order to minimize the spinning sideband overlap. The chemical shifts and spin-lattice relaxation times for ^1H and ^{13}C in the rotating frame $T_{1\rho}$ were measured by applying ^1H and ^{13}C spin-locking pulses, respectively. The $\pi/2$ pulse-times for ^1H and ^{13}C were 5 μs and 10 μs, respectively, according to a spin-locking field strength of 50 kHz and 25 kHz. The temperature-dependent NMR measurements were performed in a temperature range of 180–400 K.

The ^{14}N NMR spectra of $[N(CH_3)_4]_2CdCl_4$ single crystals were measured by a static NMR method using a Unity INOVA 600 NMR spectrometer at the Korea Basic Science Institute Seoul Western Center. The static magnetic field was 14.1 T and the Larmor frequency was set to $\omega_o/2\pi$=43.342 MHz. The ^{14}N NMR experiments were performed using a solid state echo sequence, 4 μs–τ (20 μs)–4 μs–τ (20 μs). The temperature-dependent NMR measurements were performed in a temperature range of 180–400 K. The samples were maintained at a constant temperature by controlling the helium gas flow and the heater current, which yielded an accuracy of ±0.5 K.

Results and Discussion

The lattice constants of $[N(CH_3)_4]_2CdCl_4$ single crystals at room temperature were determined with an X-ray diffraction system (Bruker AXS GMBH) at the Korea Basic Science Institute. A hexagonal structure with cell parameters given by a=9.1239 Å, c=6.7253 Å, and γ=120° was obtained for $[N(CH_3)_4]_2CdCl_4$. These values are consistent with previously reported values given by a=9.138 Å, c=6.723 Å, and γ=120° [13, 14].

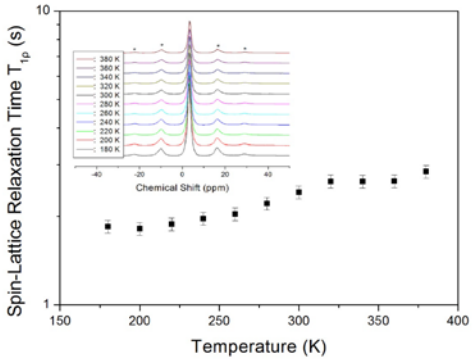

Figure 1. Spin-lattice relaxation times $T_{1\rho}$ in the rotating frame for ^1H in $[N(CH_3)_4]_2CdCl_4$ as a function of temperature (inset: ^1H MAS NMR spectra as a function of the temperature).

A structural analysis for the protons in $[N(CH_3)_4]_2CdCl_4$ was performed using the MAS NMR method. The temperature-dependent ^1H MAS NMR spectra of $[N(CH_3)_4]_2CdCl_4$ are shown in the inset of Fig. 1. The NMR spectra exhibit a peak at a chemical shift of δ=3.38 ppm. The spinning sidebands are marked with asterisks. The signal at

δ=3.38 ppm is assigned to methyl protons. The ^{1}H chemical shift does not change with increasing temperature as shown in the inset of Fig. 1. For the protons in $[N(CH_3)_4]_2CdCl_4$, the spin-lattice relaxation times in the rotating frame $T_{1\rho}$ were also measured as a function of the temperature. The nuclear magnetization recovery traces obtained for the protons were described by the following single-exponential function[16-19]: $S(t)=S_0 \exp(-t/T_{1\rho})$, where S(t) is the magnetization at time t and S_0 is the total nuclear magnetization of ^{1}H at thermal equilibrium. The recovery traces showed a slightly non-exponential decay due to the correction for the relative positions of the three protons in each CH_3 group, but the effects are too small to be detected in our experiments, and are therefore neglected. The ^{1}H spin-lattice relaxation time in the rotating frame $T_{1\rho}$ is shown as a function of the temperature in Fig. 1. The values of the spin-lattice relaxation times in the rotating frame $T_{1\rho}$ slowly increase for higher temperatures.

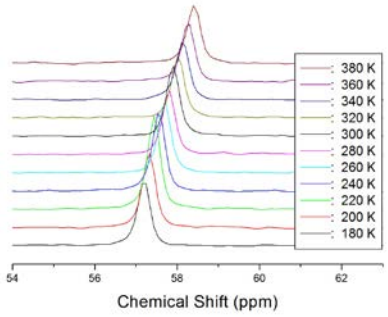

Figure 2(a). Chemical shifts of ^{13}C CP/MAS NMR spectra as a function of the temperature

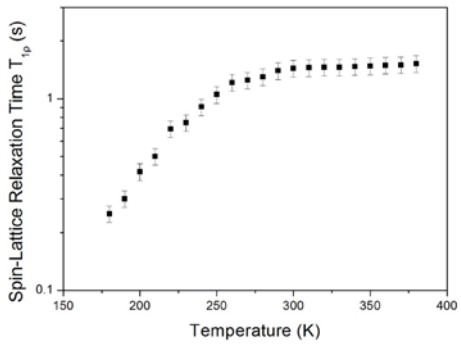

Figure 2(b). The spin-lattice relaxation times $T_{1\rho}$ in the rotating frame for ^{13}C in $[N(CH_3)_4]_2CdCl_4$ as a function of the temperature.

A structural analysis of the carbons in $[N(CH_3)_4]_2CdCl_4$ was conducted using ^{13}C NMR spectroscopy. Fig. 2(a) shows the solid-state ^{13}C CP/MAS NMR spectra as a function of temperature. At room temperature, a ^{13}C CP/MAS NMR line shifted by δ=57.89 ppm with respect to tetramethylsilane (TMS), as observed for the powdered $[N(CH_3)_4]_2CdCl_4$ sample. The signal observed at δ=57.89 ppm represents the methyl carbon in $N(CH_3)_4$. In this case, only continuous quantitative changes in the chemical shift were measured, where the ^{13}C chemical shift slowly and monotonously increased with increasing temperatures. The chemical shifts for ^{13}C in $[N(CH_3)_4]_2CuCl_4$ [20] and $[N(CH_3)_4]_2CoCl_4$ [11] decreased with increasing temperature, whereas those for ^{13}C in $[N(CH_3)_4]_2CdCl_4$ and $[N(CH_3)_4]_2ZnCl_4$ [8] increased for higher temperatures.

The spin-lattice relaxation times in the rotating frame $T_{1\rho}$ were measured for each carbon atom in $[N(CH_3)_4]_2CdCl_4$ at several temperatures, with variable spin-locks on the carbon channel following cross-polarization. The ^{13}C magnetization was generated by cross-polarization after the spin-locking of the protons. The proton field was then turned off for a variable time t, while the ^{13}C RF field remained turned on. Finally, the ^{13}C free induction decay (FID) was observed under high-power proton decoupling and was subsequently subjected to Fourier transformation. The values of $T_{1\rho}$ could be selectively obtained by the Fourier transformation of the FID after the end of spin-locking when the experiment was repeated for different times t. All of the traces obtained for the carbons were described by a single-exponential function. The spin-lattice relaxation time in the rotating frame increased with increasing temperature, and became nearly constant above 300 K.

In addition, the NMR spectrum of ^{14}N (I=1) was obtained using a static NMR method in the laboratory frame at a frequency of $\omega_o/2\pi$=43.342 MHz. The ^{14}N NMR study revealed a relatively small quadrupole coupling constant and two resonance lines of the NMR spectra owing to the spin quantum number I=1. The ^{14}N NMR spectra of $[N(CH_3)_4]_2CdCl_4$ single crystals are shown in Fig. 3(a) and (b) as a function of temperature. The splitting between the resonance

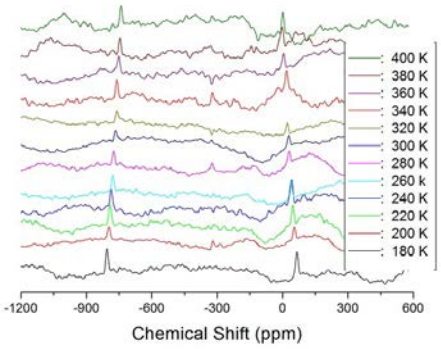

Figure 3(a). ^{14}N NMR spectra as a function of the temperature

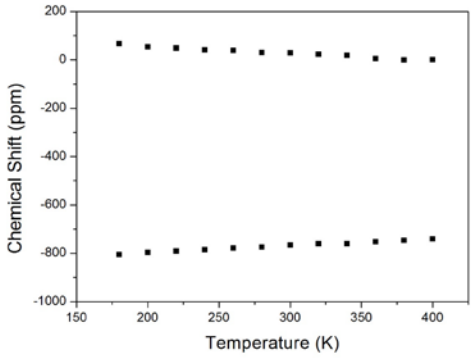

Figure 3(b). The chemical shifts of ^{14}N NMR spectra as a function of temperature.

lines decreased gradually with increasing temperature, indicating that the quadrupole coupling constant of the ^{14}N nuclei decreased as a function of the temperature. The temperature-dependent changes of the ^{14}N chemical shift are generally due to a change in structural geometry. Variations of the electric field gradient (EFG) tensor at the N sites reflect changes in the configuration of the atoms neighboring the ^{14}N nuclei.

Conclusion

Information on the structural geometry of $[N(CH_3)_4]_2CdCl_4$ in a hexagonal phase was obtained by observing the temperature-dependent chemical shifts of the ^{1}H, ^{13}C, and ^{14}N ions in the $[N(CH_3)_4]_2$ groups. The chemical shift for ^{1}H above 180 K did almost not change, while small changes of chemical shift are observed for ^{13}C and ^{14}N. Especially, the ^{13}C NMR spectra reflected changes in the crystal symmetry near 300 K, which are related to the ordering of $N(CH_3)_4$ groups; the mechanism for the structural geometry is mainly related to the ^{13}C ions in $N(CH_3)_4$ ions. These results can be explained by a structural change, meaning that the structural geometry depends on the temperature.

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References

1. M. Kahrizi and M. O. Steinitz, *Solid State Commun*. **70**, 599 (1989)
2. J. Berger, J. P. Benoit, C. W. Garland, and P. W. Wallace, *J. Phys.* **47**, 483 (1986)
3. H. Z. Cummins, *Phys. Rep*. **185**, 211 (1990)
4. W. Rehwald and A. Vonlanthen, *Z. Phys. B: Condens. Matter* **61**, 25 (1985)
5. P. S. Gregoire, K. Tchakpele, and T. Assih, *Ferroelectrics* **126**, 319 (1992)
6. K. Hasebe, H. Mashiyama, N. Koshiji, and S. Tanisaki, *J. Phys. Soc. Jpn*. **56**, 3543 (1987)
7. A. R. Lim, K. W. Hyung, K. S. Hong, and S.-Y. Jeong, *Phys. Stat. Solidi* (b) **219**, 389 (2000)
8. A. R. Lim and K.-Y. Lim, *Solid State Science* **31**, 70 (2014)
9. M. Ribet, S. Leon, F. Lefaucheux, and M. C. Robert, *J. Appl. Cryst*. **23**, 277 (1990)

10. J. R. Wiesner, R. C. Srivastava, C. H. L. Kennard, M. Divira, and E. C. Lingafelter, *Acta Crystallogr*. **23**, 565 (1967)
11. A. R. Lim, *Chem. Phys*. **436-437**, 46 (2014)
12. A. R. Lim and W. K. Jung, *J. Phys. Chem. Solids* **66**, 1795 (2005)
13. M. Pasciak, M. Wolcyrz, and A. Pietraszko, *Phys. Rev*. B **78**, 24114 (2008)
14. I. Peral, G. Madariaga, A. Perez-Etxebarria, and T. Breczewski, *Acta Cryst*. B **56**, 215 (2000)
15. O. G. Vlokh, *Ukrainskii Fizicheskii Zhurnal* **35**, 54 (1990)
16. J. L. Konig, "Spectroscopy of Polymers", Chap. 10, Elsevier, New York, 1999.
17. B. Cowan, "Nuclear Magnetic Resonance and Relaxation", Chap. 5, Cambridge Univ. UK, 1997.
18. Y. K. Paik and C. L. Chang, *J. Kor. Mag. Reson*. **17**, 19 (2013)
19. J. H. Choi and A.R. Lim, *J. Kor. Mag. Reson*. **18**, 41 (2014)
20. A. R. Lim, *J. Mol. Structure* **1056-1057**, 233 (2014)