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Changing structural properties of mixed crystals $[N(CH_3)_4]_2Zn_{1-x}Co_xCl_4$ ($x = 0, 0.5, 0.7, 0.9$, and 1) by magic angle spinning nuclear magnetic resonance

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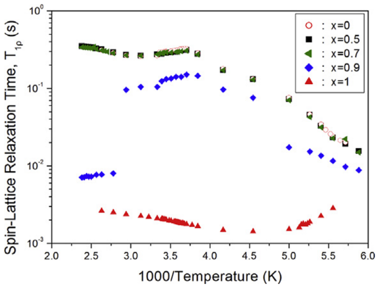
HIGHLIGHTS

- Chemical shift and spin-lattice relaxation time in rotating frame.
- Two crystallographically different ions a-$N(CH_3)_4$ and b-$N(CH_3)_4$.
- Structural properties of mixed crystals.

GRAPHICAL ABSTRACT



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ABSTRACT

Temperature dependences of the chemical shift and spin-lattice relaxation time in the rotating frame $T_{1\rho}$ were measured for ^1H and ^{13}C nuclei in mixed crystals of the form $[N(CH_3)_4]_2Zn_{1-x}Co_xCl_4$ ($x = 0, 0.5, 0.7, 0.9$, and 1). The mixed crystals varied in color according to the amount of Co^{2+} ions, whereas the phase transition temperatures remained nearly unchanged. $[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2CoCl_4$ crystals contain two nonequivalent types of a-$N(CH_3)_4$ and b-$N(CH_3)_4$. The two crystallographically different ions a-$N(CH_3)_4$ and b-$N(CH_3)_4$ were distinguished using ^{13}C CP/MAS NMR spectroscopy. The NMR spectrum and $T_{1\rho}$ for ^1H and ^{13}C in case of $x = 0.5$ and $x = 0.7$ were similar to those for $[N(CH_3)_4]_2ZnCl_4$, whereas those for $x = 0.9$ were absolutely different. Additionally, $[N(CH_3)_4]_2Zn_{0.1}Co_{0.9}Cl_4$ exhibited the structural properties of both $[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2CoCl_4$.

1. Introduction

Single crystals of the forms $[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2CoCl_4$ belong to the group of A_2BX_4-type crystals, many of which have an incommensurate (INC) phase in their phase transition sequence [1–4]. Crystals of this type have attracted considerable interest owing to their several phase transitions. Tetramethylammonium tetrachlorozincate, $[N(CH_3)_4]_2ZnCl_4$, undergoes five phase transitions, which occur at 161 K ($=T_{C5}$), 181 K ($=T_{C4}$), 276.3 K ($=T_{C3}$), 279 K ($=T_{C2}$), and 296 K ($=T_{C1}$), respectively [5–11]. Previous studies have concluded that $[N(CH_3)_4]_2ZnCl_4$ crystals exist in six phases: I, II, III, IV, V, and VI, in order of decreasing temperature. The crystal structure of phase I is orthorhombic. The transition from the normal (I) to the incommensurate (II) phase occurs at $T_{C1} = 296$ K. The corresponding symmetry changes are as follows: the ferroelectric phase III is orthorhombic

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with space group $P2_1cn$; the ferroelastic phase IV is monoclinic with space group $P2_1/n$; the ferroelastic phase V is monoclinic with space group $P2_1/c$; and finally, phase VI is orthorhombic with space group $P2_12_12_1$ [9]. Tetramethylammonium tetrachlorocobaltate, $[N(CH_3)_4]_2CoCl_4$, undergoes six phase transitions, which occur at 122 K ($=T_{C6}$), 192 K ($=T_{C5}$), 276 K ($=T_{C4}$), 277.6 K ($=T_{C3}$), 280.1 K ($=T_{C2}$), and 293 K ($=T_{C1}$), respectively [12–14]. Previous studies have shown that $[N(CH_3)_4]_2CoCl_4$ crystals exist in seven phases: I, II, III, IV, V, VI, and VII, in order of decreasing temperature [12]. Phase I, which occurs at the highest temperature among all of the phases, has *Pmcn* symmetry and an orthorhombic structure. The phase existing between 293 and 280.1 K is incommensurate [15–18], and that between 280.1 and 277.6 K is an orthorhombic commensurate ferroelectric phase [19]. Phase IV, which exists between 277.6 and 276 K, is an orthorhombic ferroelectric phase, phase V is a monoclinic ferroelastic phase, and phase VI is a monoclinic paraelectric phase [20]. It should be noted that $[N(CH_3)_4]_2CoCl_4$ undergoes successive phase transitions that are similar to those of $[N(CH_3)_4]_2ZnCl_4$ [21–23].

$[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2CoCl_4$ have been studied using various experimental techniques and by several research groups [24–40]. Blinc et al. [41] investigated ^{13}C spin-lattice relaxation time using nuclear magnetic resonance (NMR) measurements and revealed reorientation motion of both the CH_3 groups and the $N(CH_3)_4$ ions in $[N(CH_3)_4]_2ZnCl_4$. Additionally, Niemela and Heinila [42] reported on ^1H spin-lattice relaxation time in polycrystalline $[N(CH_3)_4]_2ZnCl_4$. They discussed the reorientation motion of CH_3 groups at low temperatures and the tumbling motion of $N(CH_3)_4$ ions at high temperatures. In our previous studies, ^1H spin-lattice relaxation times in the laboratory frame, T_1, and in the rotating frame, $T_{1\rho}$, were discussed near the phase transition temperatures in $[N(CH_3)_4]_2ZnCl_4$ crystals [23,43,44]. From these results, the molecular motion resulting from the T_1 values for ^1H were reported, and the existence of chemically equivalent $N(CH_3)_4$ ions in phase I and the existence of the ferroelastic characteristic of the $N(CH_3)_4$ ions in phases IV and V were discussed. The ^1H NMR and ^{13}C NMR of the phase transition in $[N(CH_3)_4]_2ZnCl_4$ were studied by Blinc et al. [41] and Dolinsek et al. [45]. Additionally, ^1H spin-lattice relaxation times in the laboratory frame, T_1, and in the rotating frame, $T_{1\rho}$, near the phase transition temperatures of $[N(CH_3)_4]_2CoCl_4$ have been investigated [46,47]; ^1H $T_{1\rho}$ in the ferroelastic phase undergoes the molecular motion, and the existence of two chemically nonequivalent a-$N(CH_3)_4$ and b-$N(CH_3)_4$ ions in the ferroelectric phase and the existence of the ferroelastic twin structure of the $N(CH_3)_4$ ions in the ferroelastic phase were reported through ^{13}C MAS NMR. Recently, the various crystallographic structures of the mixed crystals $[N(CH_3)_4]_2Zn_{1-x}Cu_xCl_4$ ($x = 0$, 0.1, 0.3, 0.5, and 1) have been discussed by considering the different chemical shifts observed in ^1H MAS and ^{13}C CP/MAS NMR spectra [48].

In the present study, $[N(CH_3)_4]_2Zn_{1-x}Co_xCl_4$ ($x = 0$, 0.5, 0.7, 0.9, and 1) single crystals were grown from aqueous solutions using the slow evaporation method. We measured the temperature dependence of the cross-polarization/magic-angle spinning (CP/MAS) NMR spectrum for ^1H and ^{13}C nuclei of $[N(CH_3)_4]_2Zn_{1-x}Co_xCl_4$ in these solid solutions. In addition, spin-lattice relaxation times in the rotating frame, $T_{1\rho}$, for ^1H and ^{13}C nuclei in $[N(CH_3)_4]_2Zn_{1-x}Co_xCl_4$ according to the amount of impurity Co^{2+} ions were determined. This is the first investigation of the local structures of $[N(CH_3)_4]_2Zn_{1-x}Co_xCl_4$, and we use our results to analyze the environments of the $N(CH_3)_4$ ions. The results also enable us to compare the structural properties of $[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2CoCl_4$: we examined the effect of substituting Zn ions with Co ions in $[N(CH_3)_4]_2ZnCl_4$, with a focus on the effects of Co impurities on structural geometry and relaxation mechanisms.

2. Crystal structure

$[N(CH_3)_4]_2ZnCl_4$ in its highest-temperature phase, phase I, has an orthorhombic structure with space group *Pmcn*. Its orthorhombic lattice constants are a = 8.946 Å, b = 15.515 Å, and c = 12.268 Å [10,49]. In phase I, one unit cell contains four formula units comprising two nonequivalent types of tetramethylammonium ions, hereafter abbreviated as "a-$N(CH_3)_4$" and "b-$N(CH_3)_4$", and one type of the $ZnCl_4^{2-}$ ion [10]. A projection of the structure in the normal phase I viewed from the c-direction is shown in Fig. 1. In phase I, the two stable configurations of the $ZnCl_4$ ion and the a-$N(CH_3)_4$ ion are related to each other by a rotation about an axis passing through the center of mass, which lies almost parallel to the c-direction. In b-$N(CH_3)_4$, this axis lies almost parallel to the b-direction. The $ZnCl_4$ ion and the a-$N(CH_3)_4$ ion are positioned in a strongly correlated manner, whereas the b-$N(CH_3)_4$ ion shows less correlation with other types of ions.

The highest-temperature phase of $[N(CH_3)_4]_2CoCl_4$, phase I, has an orthorhombic structure with space group *Pmcn* and the lattice constants a = 9.001 Å, b = 15.539 Å, and c = 12.276 Å. Phase I comprises nonequivalent tetramethylammonium ions and one type of $CoCl_4^{2-}$ ion [10]. In the case of ferroelectric–ferroelastic phase transition, the loss of symmetry during transition from the *Pnma* parent phase to the $P2_1/n$ ferroelastic phase, together with the multiplication of the unit cell by a factor of 3 in the a-direction, allows for prediction of the ferroelastic twin domains described by Sapriel [50]. The degree of deformation of the b-$N(CH_3)_4$ ion is larger than that of the a-$N(CH_3)_4$ ion, and it increases in the ferroelectric phase.

3. Experimental method

Single crystals of the form $[N(CH_3)_4]_2Zn_{1-x}Co_xCl_4$ ($x = 0$, 0.5, 0.7, 0.9, and 1) were grown at room temperature through the slow evaporation of an aqueous solution containing $ZnCl_2$, $CoCl_2$, and $N(CH_3)_4Cl$ in stoichiometric proportions. $[N(CH_3)_4]_2Zn_{1-x}Co_xCl_4$ single crystals varied in color according to the amount of Co^{2+} ions, as shown in Fig. 2.

Solid-state NMR experiments were performed using a Bruker DSX 400 FT NMR spectrometer at the Korea Basic Science Institute Seoul Western Center. ^1H MAS NMR and ^{13}C CP/MAS NMR experiments were performed at Larmor frequencies of 400.12 MHz and 100.61 MHz, respectively. Samples in powder form were placed into the 4-mm CP/MAS probe. The MAS rate was set to 10 kHz and 7 kHz for ^1H MAS and ^{13}C CP/MAS, respectively, to minimize spinning

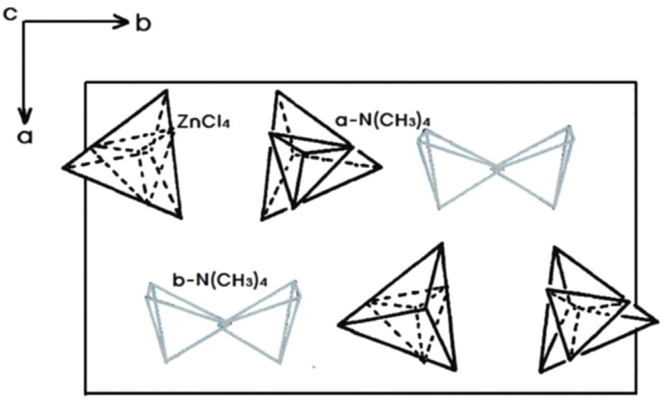

Fig. 1. Crystal structure of $[N(CH_3)_4]_2ZnCl_4$ in phase I. Two inequivalent kinds of tetramethylammonium ions, a-$N(CH_3)_4$ and b-$N(CH_3)_4$, and one kind of $ZnCl_4^{2-}$ ion. The hydrogen atoms of the CH_3 ion are not shown.