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Effect on Local Structure and Phase Transition of Perovskite-Type $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) Crystals with the Various Doping of Cu^{2+} Ions

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This study focused on how the local structures in pure $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ crystal are affected by the partial replacement of Zn^{2+} ions with Cu^{2+} ions. The structures and phase transition temperatures T_c of perovskite-type $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) mixed crystals were almost unchanged by the partial doping of Cu^{2+} ions. The environments for the local structures of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ mixed systems were studied according to differences in the chemical shifts of the ^1H magic angle spinning (MAS) NMR, ^{13}C cross-polarization (CP)/MAS NMR, and ^{14}N NMR spectra. The ^1H and ^{13}C NMR results showed that the local environments of ^1H and ^{13}C nuclei near T_c are not affected by substituting Zn^{2+} ions with Cu^{2+} ions, whereas the ^{14}N NMR results showed that the local environment is affected near T_c . Consequently, the main indicators of the phase transition in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ are related to the ferroelastic characteristics with different orientations.

Metal-organic hybrids, which consist of organic and inorganic components, have recently attracted much attention because these materials have many possibilities for the tailoring of their functionalities and physical properties including optical, electrical and magnetic properties. Hybrid organic-inorganic compounds based on perovskite structures are an interesting class of materials^{1,2}. $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ and $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ are members of the $[\text{N}(\text{CH}_3)_4]_2\text{MX}_4$ (M = transition metal ion; Co, Cu, Zn, Cd, and X = halide; Br, Cl) family. These structures undergo successive structural phase transitions, including an incommensurate–commensurate phase transition^{3–11}. In the case of $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$, the paraelastic orthorhombic phase at the phase transition temperature $T_c = 287.6$ K undergoes a second-order transition to the ferroelastic monoclinic phase^{3,5,6}. The paraelastic and ferroelastic phases are denoted as I and II in order of decreasing temperature. In phase I, $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ has an orthorhombic structure with the space group $Pm\bar{c}n$ in the paraelastic phase. Its orthorhombic lattice constants are $a = 12.681$ Å, $b = 9.239$ Å, $c = 16.025$ Å, and $Z = 4$ ¹². In phase II, $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ has a monoclinic structure with the space group $P12_1/c1$, and the lattice constants are $a = 12.534$ Å, $b = 9.142$ Å, $c = 15.772$ Å, $\gamma = 89.69^\circ$, and $Z = 4$ ¹³. On the other hand, $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ undergoes three phase transitions at 272 K ($=T_{C1}$), 242 K ($=T_{C2}$), and 237 K ($=T_{C3}$) as it gradually cools¹⁴. The four phases are denoted as I, II, III, and IV in order of decreasing temperature. At room temperature, the crystal is in the orthorhombic phase I. As the temperature decreases, the crystal transforms to the intermediate phase II at about 272 K and then to the ferroelectric orthorhombic phase III at about 242 K. The ferroelectric phase III transforms to the lowest-temperature ferroelastic monoclinic phase IV at about 237 K^{15,16}. With decreasing temperature, the crystal structure of each phase becomes orthorhombic with space group $Pnma$, incommensurate, orthorhombic with space group $Pbc2_1$, and finally monoclinic with space group $P12_1/c1$ ^{17–19}. At room temperature, $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ has an orthorhombic structure with the lattice constants $a = 12.600$ Å, $b = 9.326$ Å, $c = 15.825$ Å, and $Z = 4$ ²⁰. For two crystals, the unit cell at room temperature contains four formula units consisting of two crystallographically independent $\text{N}(\text{CH}_3)_4^+$ ions and an MBr_4^{2-} ($M = \text{Zn}, \text{Cu}$) ion. The MBr_4 tetrahedron is almost undistorted, while the $\text{N}(\text{CH}_3)_4$ tetrahedra

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Figure 1. Structure of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ on the bc plane. $\text{Cu}/\text{ZnBr}_4^{2-}$ anions are represented by gray tetrahedrons. $\text{N}(\text{CH}_3)_4^+$ cations are represented by empty tetrahedrons. (a) $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$, (b) $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Br}_4$, and (c) $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$.

have large distortions. Figure 1 shows the crystal structures of $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$, $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Br}_4$, and $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ at room temperature. The two compounds of $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ and $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ have the ferroelastic property at low temperatures.

Until now, various experimental techniques have been used to report the crystal structure, phase transitions, and ferroelectricity of $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ and $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ ^{3–5,14–18}. Perret *et al.*¹⁹ used ^{79}Br nuclear quadrupole resonance (NQR) to measure the second-order phase transition between the orthorhombic and monoclinic structures in $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$. Recently, static nuclear magnetic resonance (NMR) and magic angle spinning

Figure 2. Colors of mixed crystals $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1).

(MAS) NMR spectrometry have been used to measure the chemical shifts and spin-lattice relaxation times of ^1H and ^{13}C nuclei in $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ as a function of temperature²⁰. Two chemically inequivalent sites, $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$, have been distinguished by using ^{13}C cross-polarization (CP)/MAS NMR. Based on these results, the behaviors of these two chemically inequivalent $\text{N}(\text{CH}_3)_4$ groups were discussed.

In this work, perovskite-type $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) mixed crystals were grown from aqueous solutions by the slow evaporation method. The ^1H MAS NMR spectrum and ^{13}C CP/MAS NMR spectrum of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ were measured as a function of temperature. The spin-lattice relaxation times in the rotating frame $T_{1\rho}$ were determined for ^1H and ^{13}C nuclei in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ for varying amounts of paramagnetic Cu^{2+} ions. In addition, the ^{14}N NMR spectrum for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ was observed in order to understand the role of the phase transitions. The results allowed the structural properties of pure $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ and $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ to be compared, and the effect of substituting Zn^{2+} ions in $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ with Cu^{2+} ions was examined. And, the ferroelastic phase transition of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ at low temperatures was considered. This study represents the first investigation of the local structures of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$, and the results were used to analyze the role of $\text{N}(\text{CH}_3)_4$ ions.

Experimental Method

$[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) single crystals were grown at room temperature by slow evaporation of an aqueous solution containing ZnBr_2 , CuBr_2 , and $\text{N}(\text{CH}_3)_4\text{Br}$ in stoichiometric proportions. The $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ single crystals varied in color according to the amount of Cu^{2+} ions, as shown in Fig. 2.

At room temperature, the structures of the $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7, 1$) crystals were determined with an X-ray diffraction system (PANalytical, X'pert pro MPD) with a $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation source at the Korea Basic Science Institute, Western Seoul Center. Measurements were taken with θ - 2θ geometry from 10° to 60° at 45 kV and with a tube power of 40 mA . Table 1 presents the lattice constants of the four crystals at room temperature. All of the $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ crystals containing Cu^{2+} ions had the same orthorhombic structure as pure $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ and $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$.

In order to determine the phase transition temperatures, differential scanning calorimetry (DSC) was carried out on the crystals with a Dupont 2010 DSC instrument. The measurements were performed at a heating rate of $10^\circ\text{C}/\text{min}$ in the temperature range of 190 – 550 K . Figure 3 shows the endothermic peaks for $x = 0, 0.5, 0.7$, and 1 . For $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5$, and 0.7), the DSC measurements showed only one endothermic peak at 287 K , and the phase transition temperature hardly changed when the amount of impurity Cu^{2+} ions was varied. The three endothermic peaks at 237 K (T_{C3}), 245 K (T_{C2}), and 272 K (T_{C1}) for $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ are related to phase transitions, and these temperatures are consistent with those previously reported¹. When the amount of

	<i>a</i>	<i>b</i>	<i>c</i>
$[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ ($x=0$)	12.691	9.244	16.012
$[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Br}_4$ ($x=0.5$)	12.676	9.249	16.039
$[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{0.3}\text{Cu}_{0.7}\text{Br}_4$ ($x=0.7$)	12.675	9.245	16.035
$[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ ($x=1$)	12.647	9.341	15.906

Table 1. Lattice constants of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0, 0.5, 0.7$, and 1) at room temperature.

Figure 3. Differential scanning calorimetry (DSC) thermogram of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0, 0.5, 0.7$, and 1) single crystals.

paramagnetic Cu^{2+} ions was varied, the phase transition temperatures for $x=0.5$ and 0.7 were nearly unchanged and were similar to those for pure $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$, although the colors of the samples were different. Thus, the impurity Cu^{2+} ions had an insignificant effect on the phase transition temperature.

The ^1H MAS NMR and ^{13}C CP/MAS NMR spectra of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0, 0.5, 0.7$, and 1) in the rotating frame were measured by using a Bruker DSX 400 FT NMR spectrometer at the Korea Basic Science Institute, Western Seoul Center. ^1H MAS NMR and ^{13}C CP/MAS NMR experiments were performed at the Larmor frequencies of 400.12 and 100.61 MHz, respectively. The samples were placed in a 4 mm CP/MAS probe as powders. The MAS rate was set to 5 kHz for ^1H MAS and ^{13}C CP/MAS to minimize the spinning sideband overlap. The chemical shifts of the spectrum for ^1H and ^{13}C nuclei were expressed with respect to tetramethylsilane (TMS). The spin–lattice relaxation times in the rotating frame $T_{1\rho}$ for ^1H and ^{13}C were measured by using $\pi/2$ - t -acquisition. The $T_{1\rho}$ values were measured by varying the length of the spin-locking pulses. The $\pi/2$ pulse widths used for $T_{1\rho}$ were 3.85 μs for ^1H and ^{13}C ; this corresponded to the frequency of the spin-locking field of 64.94 kHz.

The ^{14}N NMR spectra of the $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0, 0.5, 0.7$, and 1) single crystals in the laboratory frame were measured by using the Bruker DSX 400 FT NMR spectrometer and Unity INOVA 600 NMR spectrometer at the Korea Basic Science Institute, Western Seoul Center. The static magnetic fields were 9.4 and 14.1 T, and the Larmor frequency was set to $\omega_0/2\pi = 28.90$ and 43.34 MHz. The ^{14}N NMR experiments were performed by using a solid-state echo sequence: 4 μs - t -4 μs - t . The samples were maintained at a constant temperature with an accuracy of ± 0.5 K by controlling the nitrogen gas flow and heater current. The temperature-dependent NMR measurements were carried out in the temperature range of 180–420 K.

Experimental Results and Analysis

^1H MAS NMR in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0, 0.5, 0.7$, and 1). The ^1H chemical shifts in order to the structural analysis of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0, 0.5, 0.7$, and 1) were carried out with the MAS NMR method. The ^1H chemical shifts in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ were measured over the temperature range of 180–420 K, as shown in Fig. 4(a and b). At room temperature, the NMR spectrum of $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ consisted of one peak at a chemical shift of $\delta = 3.32$ ppm, which was assigned to the methyl proton. The chemical shifts of the ^1H NMR signal showed a slight and continuous decrease near T_c . At $x=0.5$ and 0.7 , the chemical shifts at room temperature were 3.58 and 3.54 ppm higher, respectively, than the ^1H chemical shift in pure $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$. The ^1H chemical shifts increased continuously as the temperature increased and differed from those of pure $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$.

Figure 4. (a) Chemical shifts of the ^1H MAS NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5$, and 0.7). (b) Chemical shifts of the ^1H MAS NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 1$).

Figure 5. Temperature dependences of the ^1H spin-lattice relaxation time in the rotating frame $T_{1\rho}$ for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1).

On the other hand, the chemical shifts at 300 K for $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ with $x = 1$ consisted of two peaks at chemical shifts of $\delta = 3.60$ ppm and $\delta = 6.65$ ppm. Two chemical shifts were assigned to the methyl protons, and they may be due to two inequivalent sites of the $\text{N}(\text{CH}_3)_4$ molecule: $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$. The chemical shift below T_{C2} has only one resonance line. In contrast, two resonance lines were present above T_{C2} , as shown in Fig. 4(b). The chemical shifts near T_{C1} and T_{C3} were the only continuous changes, whereas there was an abrupt change near T_{C2} . The change in the chemical shift indicates that a structural phase transition occurred at this temperature. The chemical shift for $x = 1$ was completely different from those for $x = 0, 0.5$, and 0.7 . This difference was due to variations in the electronic structure of the Zn^{2+} and Cu^{2+} ions.

The recovery traces of the magnetization for the ^1H nuclei in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) were obtained at several temperatures. The saturation recovery pulse sequence was utilized to obtain the $T_{1\rho}$ values over the whole temperature range. The nuclear magnetization recovery curves obtained for protons can be described by the following single exponential function: $M(t) = M_0 \exp(-t/T_{1\rho})$, where $M(t)$ is the magnetization at the time t , and M_0 is the total nuclear magnetization of ^1H at thermal equilibrium²¹. The recovery traces of the ^1H nuclei were measured at several delay times. Based on the slope of the plot of $\log M(t)/M_0$ versus the delay time t , the spin-lattice relaxation times in the rotating frame $T_{1\rho}$ for the proton in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) were obtained as a function of the temperature, as shown in Fig. 5. When the paramagnetic Cu^{2+} ions were included, $T_{1\rho}$ for $x = 0.5$ and 0.7 differed from ^1H $T_{1\rho}$ for pure $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$, whereas the trends of ^1H $T_{1\rho}$ were similar with that of ^1H $T_{1\rho}$ for pure $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$. ^1H $T_{1\rho}$ was generally continuous near T_C . On the other hand, ^1H $T_{1\rho}$ of $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ with $x = 1$ increased with the temperature. The $T_{1\rho}$ values for $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ were nearly identical within the experimental error range. The proton $T_{1\rho}$ data did not show any

Figure 6. Chemical shifts of the ^{13}C CP/MAS NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5$, and 0.7). Inset: Chemical shifts of the ^{13}C CP/MAS NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 1$).

evidence of an anomalous change near the phase transition temperatures of $T_{\text{C}1}$, $T_{\text{C}2}$, and $T_{\text{C}3}$. However, the ^1H $T_{1\rho}$ curves of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Br}_4$ with $x = 0.5$ and $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{0.3}\text{Cu}_{0.7}\text{Br}_4$ with $x = 0.7$ were markedly different from those observed for pure $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ with $x = 0$ and $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ with $x = 1$. The ^1H $T_{1\rho}$ values for $x = 0.5$ and $x = 0.7$ were larger than those for $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ and $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$.

^{13}C CP/MAS NMR in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1). Structural analysis of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) was carried out with a ^{13}C CP/MAS NMR method. The chemical shifts for ^{13}C in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Cl}_4$ were measured over the temperature range of 180–420 K, as shown in Fig. 6. In the case of $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$, the ^{13}C CP/MAS NMR spectrum at room temperature showed two signals at chemical shifts of $\delta = 57.97$ and 57.72 ppm with respect to the reference TMS signal. These signals can be attributed to the methyl carbons in the two chemically inequivalent ions $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$. At all temperatures, the ^{13}C CP/MAS NMR spectrum of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) consisted of two resonance lines, one for $\text{N}(1)(\text{CH}_3)_4$ and the other for $\text{N}(2)(\text{CH}_3)_4$. This is shown in Fig. 6. This is because the ^{13}C environments at these two chemically inequivalent sites were slightly different. The two different ^{13}C resonances of $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ had almost the same chemical shift differences. This difference did not change as the temperature increased because the ^{13}C environments at the two chemically inequivalent $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ changed almost equally with the temperature. The chemical shifts of the $\text{N}(1)(\text{CH}_3)_4$ ions were larger than those of the $\text{N}(2)(\text{CH}_3)_4$ ions, which is consistent with the results of previous X-ray and ^{14}N NMR analyses on $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$, which belongs to this family^{22,23}. Hasebe *et al.*²³ X-ray diffraction study indicated that the deformation of the $\text{N}(2)(\text{CH}_3)_4$ ion in $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ is larger than that of the $\text{N}(1)(\text{CH}_3)_4$ ion. Based on these results, $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ were defined according to the change in the relaxation time as a function of temperature, which was previously reported²⁴. For $x = 0.5$ and 0.7 , the ^{13}C CP/MAS NMR spectrum of CH_3 in the two inequivalent kinds of $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ were measured within this temperature range, and their chemical shifts were similar with that in $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ with $x = 0$. At 286 K, i.e., the transition temperature, the ^{13}C chemical shifts for $x = 0, 0.5$, and 0.7 slowly and monotonically increased with increasing temperature. For $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ with $x = 1$, the ^{13}C CP/MAS NMR spectrum at room temperature had two signals at $\delta = 76.74$ and 165.21 ppm. The signals at $\delta = 76.74$ ppm and $\delta = 165.21$ ppm represent the methyl carbons in the inequivalent $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$, respectively. The chemical shifts near $T_{\text{C}2}$ changed abruptly, whereas those near $T_{\text{C}3}$ and $T_{\text{C}1}$ showed a continuous change. Near $T_{\text{C}2}$, the change in chemical shift for $\text{N}(2)(\text{CH}_3)_4$ was larger than that for $\text{N}(1)(\text{CH}_3)_4$. These results are consistent with the deformation of the $\text{N}(2)(\text{CH}_3)_4$ ion being greater than that of the $\text{N}(1)(\text{CH}_3)_4$ ion, as shown by Hasebe *et al.*²³ X-ray diffraction study. The ^{13}C chemical shifts for $x = 0, 0.5$, and 0.7 increased with the temperature, whereas those for $x = 1$ decreased with increasing temperature. Based on these results, $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ can be defined by the change in the relaxation time as a function of the temperature. This is discussed in more detail below.

The nuclear magnetization recovery curves for carbons in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) were fitted to a single exponential function. The recovery traces of the ^{13}C nuclei were measured at various delay times. Based on these results, the spin-lattice relaxation times in the rotating frame $T_{1\rho}$ in the $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ were obtained for each carbon as a function of temperature. Figure 7 shows the $T_{1\rho}$ values for ^{13}C in the cases of $x = 0, 0.5, 0.7$, and 1 . The ^{13}C $T_{1\rho}$ values of $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5$, and 0.7) were very similar, and those for $\text{N}(2)(\text{CH}_3)_4$ were longer than those of $\text{N}(1)(\text{CH}_3)_4$. The slopes of the $T_{1\rho}$ values near 287 K ($=T_{\text{C}}$) were nearly continuous. In the case of $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ with $x = 1$, the ^{13}C $T_{1\rho}$ values for $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ showed a similar trend, especially at higher temperatures. However, the change in

Figure 7. Temperature dependences of the ^{13}C spin-lattice relaxation time in the rotating frame $T_{1\rho}$ for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1).

Figure 8. (a) *In-situ* ^{14}N NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0$). (b) Resonance frequency of the ^{14}N NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0$).

the ^{13}C $T_{1\rho}$ value for $\text{N}(2)(\text{CH}_3)_4$ near T_{C2} was discontinuous. This result is consistent with the larger change of the ^{13}C chemical shift for $\text{N}(2)(\text{CH}_3)_4$. The ^{13}C $T_{1\rho}$ values for $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ were very small, and these $T_{1\rho}$ values of materials containing paramagnetic Cu^{2+} ions were shorter than those of materials without paramagnetic ions. The $T_{1\rho}$ values for CH_3 were not affected when Zn^{2+} ions were substituted with Cu^{2+} ions in $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$.

^{14}N NMR in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1). The NMR spectra of ^{14}N ($I = 1$) in the $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) single crystal were obtained with static NMR in the laboratory frame at Larmor frequencies of $\omega_0/2\pi = 28.90$ and 43.34 MHz. Figures 8–11 show the *in situ* ^{14}N NMR spectra and resonance frequencies of the ^{14}N NMR spectra in the $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) single crystal as functions of the temperature. Four resonance lines for two groups at the ^{14}N site in the two chemical inequivalent $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ were expected because of the quadrupole interaction of the ^{14}N nucleus in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ single crystals. In the case of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ with $x = 0, 0.5$, and 0.7 , the ^{14}N NMR spectra above T_C exhibited four groups of two signals for both $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$, as shown in Figs 8–10. Therefore, the eight resonance lines above T_C were due to two chemically inequivalent $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ ions and two magnetically inequivalent $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$. This phase I–II transition resulted in an abrupt splitting of the ^{14}N NMR line into several groups of lines corresponding to $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$. The chemical shifts of the ^{14}N signals below T_C varied almost continuously, and those of the ^{14}N signals above this temperature also changed continuously. At low temperatures below T_C , the ^{14}N NMR signals split into 16 resonance lines. The number of resonance lines varied near the phase transition temperature, which indicates the ferroelastic twin characteristic.

Figure 9. (a) *In-situ* ^{14}N NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0.5$). (b) Resonance frequency of the ^{14}N NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0.5$).

Figure 10. (a) *In-situ* ^{14}N NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0.7$). (b) Resonance frequency of the ^{14}N NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0.7$).

On the other hand, the patterns of the resonance frequencies for $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ with $x=1$ changed abruptly at the phase transition temperature, as shown in Fig. 11(a and b). Between T_{C2} and T_{C1} , the two lines were due to N(1) and N(2) in $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ ions, respectively. In the low-temperature region below T_{C3} , the ^{14}N NMR signals were split into approximately 16 resonance lines. The ^{14}N NMR spectra were split into several lines for the signals arising from $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$. Although the unit cell at all temperatures had $Z=4$, the ^{14}N resonance lines showed several resonance lines at low temperature.

Consequently, the splitting of several resonance lines near the phase transition temperatures in the $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ indicated that a phase transition into a new phase with monoclinic symmetry occurred at this temperature, which corresponded to symmetry reduction from orthorhombic symmetry. Temperature-dependent changes in the ^{14}N resonance frequency are generally due to a change in structural geometry. The electric field gradient (EFG) tensor at the N sites varied, which reflects configuration changes of atoms neighboring the ^{14}N nuclei. Near the phase transition temperature, the splitting of several resonance lines of the ^{14}N NMR lines for $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ were due to a ferroelastic twin domain with different orientations.

In order to confirm the ferroelastic property, the domain wall orientations were evaluated according to the spontaneous strain tensors given by Aizu²⁵ and Sapriel²⁶. In the transition from an orthorhombic structure with the point symmetry group mmm to monoclinic with the point symmetry group $2/m$, the domain wall orientations are expressed by the following equations: $x=0, z=0$. These equations of the twin boundaries indicate the $mmm/2/m$ ferroelastic species. During the phase transition, the point group symmetry in the crystal changed from mmm (phase I in case of $x=0, 0.5$, and 0.7 ; phase III on case of $x=1$) to $2/m$ (phase II in case of $x=0, 0.5$, and 0.7 ; phase IV in case of $x=1$). Consequently, the NMR spectra of $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x=0, 0.5, 0.7$, and 1) at low temperature were attributed to the ferroelastic property, respectively.

Figure 11. (a) *In-situ* ^{14}N NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 1$). (b) Resonance frequency of ^{14}N NMR spectrum as a function of temperature for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 1$).

Discussion and Conclusion

The variation in the structural geometry as a function of the impurity concentration in the mixed system was considered according to differences in the size and electron structure between the host and impurity ions. The local structures in pure $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ and $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ crystals were investigated for the effect of the random presence of a cation with a similar size. After the partial replacement of Zn^{2+} ions with Cu^{2+} ions, the Cu^{2+} ions occupied the same locations in the lattice as the Zn^{2+} ions did. The structures and phase transition temperatures of the perovskite-type $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) mixed crystals were almost unchanged when $[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$ crystals were doped with Cu^{2+} ions. The environments for the local structures in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) were understood by considering the differences in chemical shifts of the ^1H MAS NMR and ^{13}C CP/MAS NMR spectra. The chemical shifts for ^1H nuclei in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ varied according to the concentration of Cu^{2+} ions, whereas those for ^{13}C nuclei did not change for mixed crystals with $x = 0.5$ and 0.7 when Cu^{2+} ions were added. In addition, the two crystallographically inequivalent kinds of $\text{N}(1)(\text{CH}_3)_4$ and $\text{N}(2)(\text{CH}_3)_4$ in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) were identified by using ^{13}C CP/MAS NMR. The ^1H and ^{13}C spin-lattice relaxation times $T_{1\rho}$ were obtained with varying concentrations of Cu^{2+} ions in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$. The $T_{1\rho}$ values for ^1H and ^{13}C nuclei were not governed by the same mechanism for a given amount of paramagnetic impurity Cu^{2+} .

The roles of $\text{N}(\text{CH}_3)_4$ for the mixed systems containing the paramagnetic Cu^{2+} impurity were explained based on the ^1H MAS NMR, ^{13}C CP/MAS NMR, and ^{14}N NMR data for $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$. The NMR spectra and $T_{1\rho}$ for ^1H and ^{13}C nuclei near the phase transition temperature were not affected when Zn^{2+} ions were substituted with Cu^{2+} ions. However, the ^{14}N NMR spectra were affected near the phase transition temperature. Consequently, the main indicators of the phase transition in $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_{1-x}\text{Cu}_x\text{Br}_4$ ($x = 0, 0.5, 0.7$, and 1) were related to the ferroelastic characteristic with different orientations.

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Additional Information

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