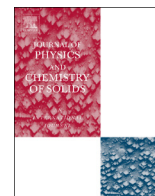




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Study on ethyl groups with two different orientations in $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CuBr}_4$

Ae Ran Lim ^{a,b,*}^a Department of Science Education, Jeonju University, Jeonju 560-759, South Korea^b Department of Carbon Fusion Engineering, Jeonju University, Jeonju 560-759, South Korea

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ABSTRACT

The crystal structure and phase transition temperature of $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CuBr}_4$ are studied using X-ray diffraction and differential scanning calorimetry (DSC); measurements revealed a tetragonal structure and the two phase transition temperatures T_c of 204 K and 255.5 K. The structural geometry near T_c is discussed in terms of the chemical shifts for ^1H magic angle spinning (MAS) nuclear magnetic resonance (NMR) and ^{13}C cross-polarization (CP)/MAS NMR. The two inequivalent ethyl groups are distinguishable by the ^{13}C NMR spectrum. The molecular motions are discussed in terms of the spin–lattice relaxation times $T_{1\rho}$ in the rotating frame for ^1H MAS NMR and ^{13}C CP/MAS NMR. The $T_{1\rho}$ results reveal that the ethyl groups undergo tumbling motion, and furthermore that the ethyl groups are highly mobile.

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1. Introduction

Crystals with the formula A_2BX_4 (B=Mn, Co, Cu, Zn, Cd; X=Cl, Br) often exhibit phase transitions leading to a ferroelectric or ferroelastic ordering. $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{BX}_4$ crystals are characterized by their ability to undergo a complicated sequence of phase transitions that depend on both the B ion and the transformations that occur as these crystals grow [1–8]. Some of them undergo one or two structural phase transitions to phases of lower symmetry. $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{BX}_4$ crystals have a tetragonal structure with space group $\text{P4}_2/\text{nmc}$ at room temperature. More specifically, each tetraethylammonium $[\text{N}(\text{C}_2\text{H}_5)_4]^+$ cation is located at the center of a cavity formed by BX_4 ions [9,10]. Many of these crystals exhibit phase transitions connected with a rearrangement of BX_4 and the $[\text{N}(\text{C}_2\text{H}_5)_4]$ groups [11]. These phase transitions have been related to the orientational ordering of tetraethylammonium $[\text{N}(\text{C}_2\text{H}_5)_4]^+$ [12,13]. The organic groups and the anion tetrahedron are disordered at room temperature. These compounds at room temperature have a common space group $\text{P4}_2/\text{mmc}$ and similar cell parameters – namely, $a=b=9 \text{ \AA}$ and $c=15 \text{ \AA}$ [6]. The $[\text{N}(\text{C}_2\text{H}_5)_4]^+$ molecular structure, as it appears in $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{NiCl}_4$, is shown in Fig. 1 [14], and the two possible orientations of the ethyl groups are clearly visible. The $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CuBr}_4$ crystal is interesting on

account of its phase transitions, although detailed structural studies have not yet been reported.

In order to obtain information regarding the structural changes that occur as a result of the phase transitions, the chemical shifts of ^1H magic angle spinning (MAS) nuclear magnetic resonance (NMR) and the ^{13}C cross-polarization (CP)/MAS NMR spectrum for $[\text{N}(\text{C}_2\text{H}_5)_4]^+$ cations in $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CuBr}_4$ were measured a function of temperature. Moreover, the spin–lattice relaxation time in the rotating frame, $T_{1\rho}$, in $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CuBr}_4$ was determined as a function of temperature in order to provide insight into the molecular motions. From these results, the two inequivalent $[\text{N}(\text{C}_2\text{H}_5)_4]$ groups in $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CuBr}_4$ were distinguished. This investigation therefore focuses on the molecular motions and the changes in the local structure of $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CuBr}_4$ near the phase transition temperature.

2. Experimental methods

Single crystals of $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CuBr}_4$ were grown from saturated aqueous solution by slow evaporation at 303 K. The starting materials were CuBr_2 and $[\text{N}(\text{C}_2\text{H}_5)_4]\text{Br}$. The single crystals took on the shape of square plates perpendicular to the tetragonal axis. The color of the $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CuBr}_4$ crystals was dark brown.

The MAS NMR spectrum and the spin–lattice relaxation time $T_{1\rho}$ in $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CuBr}_4$ were measured for ^1H and ^{13}C using the Bruker 400 MHz NMR spectrometers at the Korea Basic Science Institute,

* Corresponding author at: Department of Science Education, Jeonju University, Jeonju 560-759, South Korea.

E-mail addresses: ae.ranlim@hanmail.net, arlim@jj.ac.kr

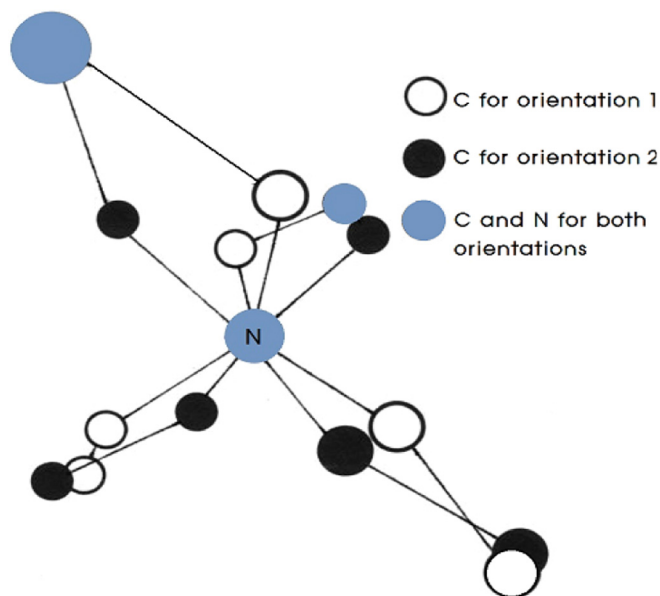


Fig. 1. The two different orientations of the $N(C_2H_5)_4$ group in $[N(C_2H_5)_4]_2CuBr_4$ [14].

Seoul Western Center. The 1H MAS NMR measurement was performed at a Larmor frequency of 400.13 MHz; the ^{13}C CP/MAS NMR measurement was performed at a Larmor frequency of 100.61 MHz. Sample powders were placed in a 4 mm CP/MAS probe, and the MAS rate was set to 10 and 5 kHz for 1H MAS and ^{13}C CP/MAS, respectively, in order to minimize spinning-sideband overlap. The $T_{1\rho}$ values for 1H were measured using $\pi/2-t$ acquisition by varying the duration of the spin-locking pulses. The $\pi/2$ pulse width used for the $T_{1\rho}$ of 1H and ^{13}C was 5 μs according to the spin-locking field at 50 kHz. In addition, $T_{1\rho}$ was measured by varying the duration of a ^{13}C spin-locking pulse applied after the CP preparation period. The $T_{1\rho}$ value for ^{13}C was obtained using CP- t acquisition, and the spin-locking field was set at 50 kHz. The sample temperatures were held constant by controlling the helium gas flow and heater current, thus achieving an accuracy of ± 0.5 K. The temperature-dependent NMR measurements were carried out in the temperature range of 180–430 K.

The $[N(C_2H_5)_4]_2CuBr_4$ crystal structure at room temperature was determined with an X-ray diffraction system (Bruker AXS GMBH) at the Korea Basic Science Institute, Seoul Western Center. The single crystal was mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated $Mo\ K\alpha$ ($\lambda=0.71073$ Å) radiation source. Data collection and integration were performed at 298 K with a SMART (Bruker, 2000) and SAINT-Plus (Bruker, 2001) [15]. In addition, the phase-transition temperatures of the crystal were determined by differential scanning calorimetry (DSC) measurements with a DuPont 2010 DSC instrument at a heating rate of 10 °C/min.

3. Experimental results and analysis

The unit cell parameters at room temperature were found to be $a=b=9.029$ Å, $c=15.875$ Å, and $\alpha=\beta=\gamma=90^\circ$, thus evidencing a tetragonal lattice from the X-ray diffraction (XRD) data; these values are consistent with the data previously reported on $[N(C_2H_5)_4]_2CuCl_4$ crystals by Mahoui et al. [13]. The DSC measurements show three endothermic peaks at 203 ($=T_{C2}$), 255.5 K ($=T_{C1}$), and 451 K ($=T_m$), as shown in Fig. 2. The two endothermic peaks at 203 and 255.5 K are related to the phase transitions, whereas the endothermic peak at 451 K is defined as the melting temperature by optical polarizing microscopy.

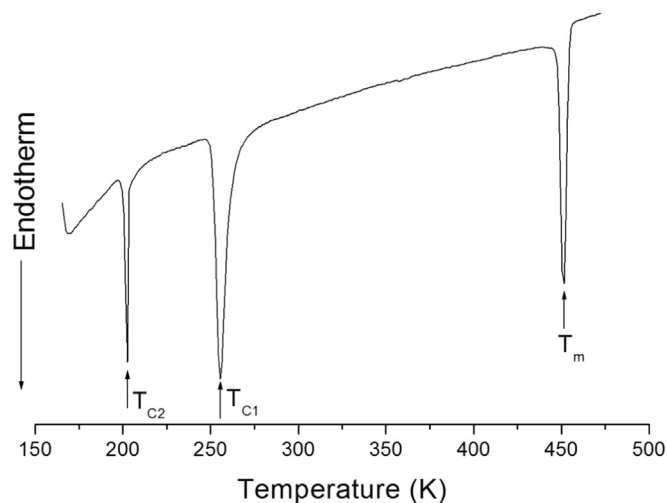


Fig. 2. Differential scanning calorimetry (DSC) thermogram of $[N(C_2H_5)_4]_2CuBr_4$.

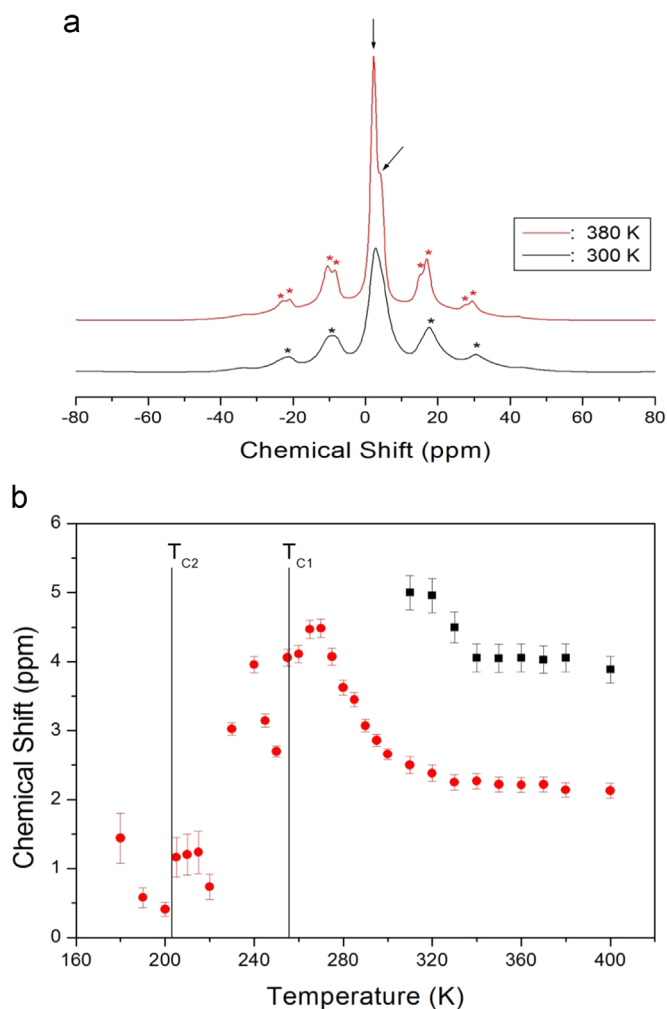


Fig. 3. (a) 1H magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectrum for $[N(C_2H_5)_4]_2CuBr_4$ at 300 K and 380 K. (b) Chemical shifts of the 1H MAS NMR spectrum for $[N(C_2H_5)_4]_2CuBr_4$ as a function of temperature.

The 1H MAS NMR spectrum in $[N(C_2H_5)_4]_2CuBr_4$ was measured in order to perform the structural analysis. The chemical shifts at 300 and 380 K are shown in Fig. 3(a). At 300 K, the NMR spectrum consists of only one peak at chemical shift of $\delta=2.28$ ppm, whereas the NMR spectrum at 380 K contains two peaks at

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