

Hysteresis effect of ammonium and water protons by ^1H MAS NMR in $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$



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ABSTRACT

The chemical shifts, linewidths, and spin-lattice relaxation times for ammonium and water protons in $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ were investigated by ^1H magic angle spinning nuclear magnetic resonance (MAS NMR) with a focus on the roles of NH_4^+ and H_2O at high temperatures. The changes in the temperature dependence of the data near T_d (≈ 360 K) were related to variations of the H environments; the mechanism above T_d was related to hydrogen-bond transfer involving breakage of the weak part of the hydrogen bond. The hysteresis effects for the ammonium and water protons in $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ by MAS NMR were described with respect to heating and cooling.

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1. Introduction

Crystals of dihydrate tetrahalogen-metallates ($\text{Me}^I_2\text{Me}^{II}\text{X}_4 \cdot 2\text{H}_2\text{O}$) may contain the following ions: $\text{Me}^I = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$; $\text{Me}^{II} = \text{Cu}, \text{Mn}, \text{Ca}, \text{Ni}$; $\text{X} = \text{Cl}, \text{Br}$. Crystals from this group can be divided into two classes according to their symmetry and structure [1–5]. The first class includes compounds with Cu^{2+} ions, which crystallize at room temperature in a tetragonal symmetry with space group $P4_2/mnm$. The tetrahedrons surrounding the divalent metal ions placed at the corners of the unit cell are rotated exactly 90° with respect to the tetrahedron surrounding the ion at the center of the cell. The ions NH_4^+ are placed in the nearly cubic cavities formed by the tetrahedrons [6–8]. The crystal with Mn^{2+} , Ca^{2+} , and Ni^{2+} ions belong to the second class with triclinic symmetry and the space group $P1$. $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ is a member of the isomorphous family of $\text{Me}^I_2\text{CuX}_4 \cdot 2\text{H}_2\text{O}$, and it undergoes a weak second-order phase transition that changes the symmetry from $P4_2/mnm$ to $P42_1$ m at 158 K [9,10]. At room temperature, $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ forms a tetragonal structure with space group $P4_2/mnm$. The unit cell contains two formula units with lattice constants $a = b = 7.947$ Å, $c = 8.271$ Å [11,12]. The square planar

coordination of the copper atom is formed by the trans-situated Br atoms and water molecules, as shown in Fig. 1. The water molecules and the ammonium and Br(2) ions are involved in an intricate three-dimensional network of intermolecular $\text{O}-\text{H} \cdots \text{Br}$ and $\text{N}-\text{H} \cdots \text{Br}$ hydrogen bonds. $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$, which is different from isotropic $(\text{NH}_4)_2\text{MnBr}_4 \cdot 2\text{H}_2\text{O}$, has scarcely been investigated.

The present study examines $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ using differential scanning calorimetry (DSC) to obtain the phase transition temperatures above the room temperature. To understand the thermodynamic properties, the chemical shifts, linewidths, and spin-lattice relaxation times $T_{1\rho}$ were measured as a function of temperature in the rotating frame using ^1H magic angle spinning nuclear magnetic resonance (MAS NMR), focusing on the role of NH_4 and H_2O . In addition, the hysteresis effects for the ammonium and water protons in $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ were examined with respect to heating and cooling using MAS NMR. Our findings represent the first report of NMR characteristics of ^1H nuclei in $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$, and assist in understanding thermal dehydration.

2. Experimental methods

Single crystals of $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ were grown by slow evaporation of NH_4Br and $\text{CuBr}_2 \cdot 2\text{H}_2\text{O}$ aqueous solutions with molar ratios of 2:1. The obtained crystals were dark green. The

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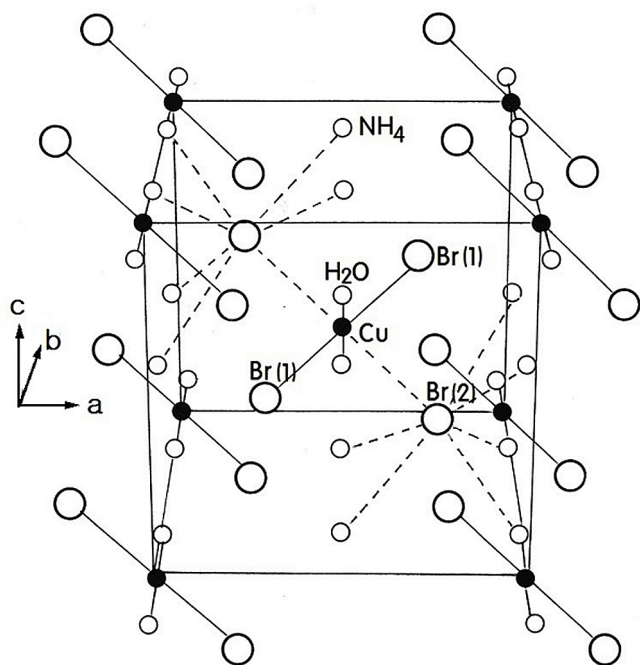


Fig. 1. The tetragonal structure of the $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ crystal.

phase transition temperature was determined using a Dupont 2010 DSC instrument. The rate of temperature change during heating and cooling was 10 K/min. The mass of the powdered samples used in DSC experiment was 10 mg.

^1H MAS NMR spectra of $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ were obtained using Bruker DSX 400 FT NMR spectrometer at the Korea Basic Science Institute, Western Seoul Center. The static magnetic field was 9.4 T. The central radio frequency was set at $\omega_{\text{H}}/2\pi = 400.13$ MHz for the ^1H nucleus, and the powdered samples were placed in a 4-mm cross polarization (CP)/MAS probe. The MAS rate was set to 10 kHz to minimize the overlap of the spinning sidebands. The spin-lattice relaxation times were measured using a saturation recovery pulse sequence called $\text{sat}-t-\pi/2$; the nuclear magnetizations of the ^1H nuclei were measured at time t after the sat pulse, and a combination of one hundred $\pi/2$ pulses were applied at regular intervals, which were determined following the $\pi/2$ excitation pulse. The width of the $\pi/2$ pulse was 2.4 μs for ^1H , and the temperature-dependent NMR measurements were conducted from 180 to 430 K. The samples were maintained at specific constant temperatures by controlling the helium gas flow and heater current, which yielded an accuracy of ± 0.5 K.

3. Experimental results

The structures of the $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ crystals at room temperature were determined by X-ray diffraction (PANalytical, X'pert Pro MPD) with a $\text{Cu-K}\alpha$ ($\lambda = 1.5418$ Å) radiation source at the Korea Basic Science Institute, Western Seoul Center. Measurements were taken in a $\theta - 2\theta$ geometry from 10° to 60° at 45 kV and a tube power of 40 mA. The $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ crystals have a tetragonal structure with lattice constants $a = b = 7.9520$ Å, $c = 8.2720$ Å, and $\alpha = \beta = \gamma = 90^\circ$. This result is consistent with those of previous studies [11,12]. The DSC analysis of $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ reveals three endothermic peaks during heating, and two exothermic peaks during cooling, as shown in Fig. 2. We checked for premelting and decomposition phenomena using thermogravimetric analysis

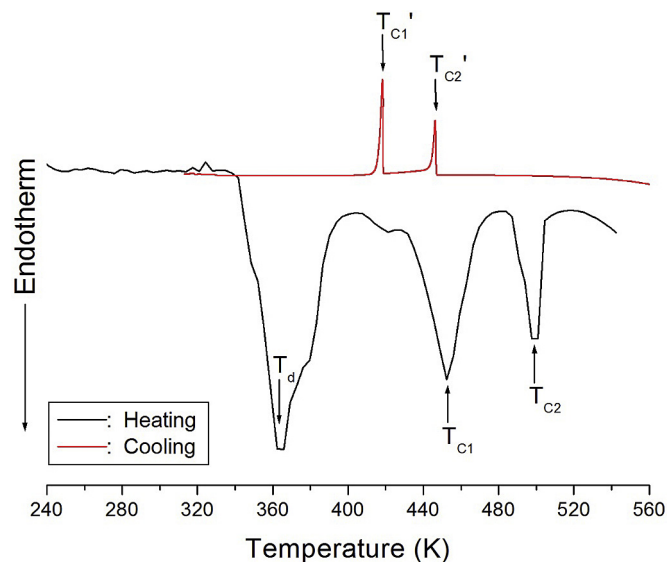


Fig. 2. DSC thermogram of $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ with respect to heating and cooling.

(TGA). Fig. 3 shows the thermogram of $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$; the mass of the powdered sample used in the TGA experiment was 14.88 mg. The TGA results show that the crystals decompose during dehydration of one molecule of crystalline water near 352 K. From the DSC and TGA results, the endothermic peak near 364 K ($=T_d$) in $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ is accompanied by the partial escape of H_2O . In addition, the DSC peaks at 452 K ($=T_{C1}$) and 500 K ($=T_{C2}$) are related to a chemical change through thermal dehydration from the TGA result, $\text{NH}_4\text{CuBr}_3 \cdot \text{H}_2\text{O}$ and NH_4CuBr_3 , respectively, and these results are supported by those of Tylczynski et al. [13] and Park et al. [14,15]. Two exothermic peaks are observed during cooling and are related to phase transitions: $T_{C2}' = 446$ K and $T_{C1}' = 418$ K. The mass of $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$ decreases at 352 K, which is interpreted as the onset of partial thermal decomposition. The weight loss in the sample observed in the TGA curve suggests that T_d , T_{C1} , and T_{C2} are not related to physical changes, such as structural phase transitions; rather, they are related to a chemical change through thermal dehydration. The temperature discrepancy for the DSC and TGA results are apparently caused by the different experimental humidity conditions. The transition corresponding to heating and

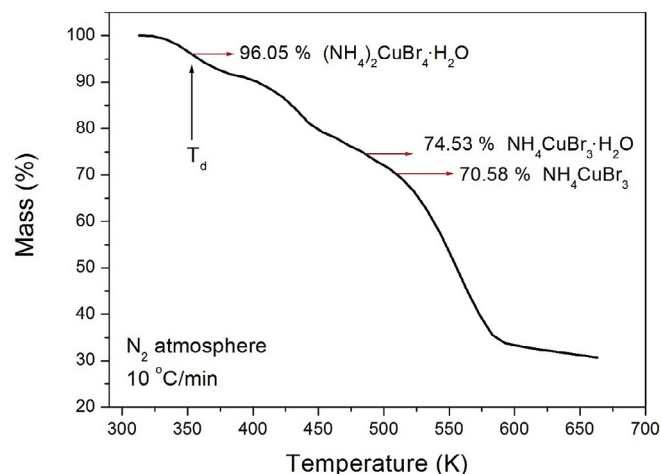


Fig. 3. Thermogravimetric analysis of $(\text{NH}_4)_2\text{CuBr}_4 \cdot 2\text{H}_2\text{O}$.

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