



Thermodynamic properties and structural geometry of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystals

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Abstract The thermodynamic properties and structural geometry of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ were investigated using thermogravimetric analysis, differential scanning calorimetry, and nuclear magnetic resonance. The initial mass loss occurs around 351 K ($=T_d$), which is interpreted as the onset of partial thermal decomposition. Phase transition temperatures were found at 435 K ($=T_{C1}$) and 481 K ($=T_{C2}$). The temperature dependences of the spin-lattice relaxation time T_1 for the ^1H nucleus changes abruptly near T_{C1} . These changes are associated with changes in the geometry of the arrangement of octahedral water molecules.

Keywords $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$, Thermodynamic property, Nuclear magnetic resonance, Phase transition

Introduction

Many double salts of the type $\text{M}'\text{X} \cdot \text{MgX}_2 \cdot 6\text{H}_2\text{O}$ ($\text{M}' = \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$; $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) have been investigated using differential thermal analysis (DTA) and thermogravimetric analysis (TGA).¹⁻⁶ Among the double salts that were investigated, the main interest and focus of this study was on the hydrated mineral carnallite $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystals. At surface pressure, the decomposition of

carnallite proceeds in two steps: from $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ to $\text{KMgCl}_3 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}$ at 353 K, and from $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ to $\text{KMgCl}_3 + 6\text{H}_2\text{O}$ above 393 K.⁷ Moreover, Popp and Ken⁷ reported that thermal dehydration reactions were characterized by the values obtained using the combined measurements of electrical conductivity and elastic wave velocities. Single crystals of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ have orthorhombic structure with space group $Pnna$ and lattice parameters $a = 16.28 \text{ \AA}$, $b = 22.83 \text{ \AA}$, and $c = 9.59 \text{ \AA}$, with $Z = 12$.⁸ The crystal structure of carnallite comprises a network of face-sharing KCl_6 octahedra and isolated $\text{Mg}(\text{H}_2\text{O})_6$ octahedra occupying the openings in the KCl network, wherein the water molecules act as charge transmitters between the Mg^{2+} and Cl^- ions. The interatomic distances in the octahedra are 2.027–2.053 \AA for $\text{Mg}-\text{OH}_2$ and 3.154–3.321 \AA for $\text{K}-\text{Cl}$, and the interatomic distances between the $\text{H} \cdots \text{Cl}$ hydrogen bonds are in the range 2.255–2.429 \AA .

The hydrogen bond protons in $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ crystals are expected to play a dominant role in the physical properties and phase transition mechanisms of the crystals. The relationship between the loss of water protons and structural phase transitions is a subject of keen interest to researchers. To probe the variations in the physical properties of

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$\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ crystals with temperature, studying the ^1H NMR spectrum and relaxation times is preferable because they are likely to be very sensitive to changes in the symmetry of the crystal. Currently, a detailed research or study into the structural properties and molecular motions of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ crystals is not available in literature.

This paper discusses the thermodynamic properties of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ crystals on the basis of differential scanning calorimetry (DSC) and TGA measurements. In addition, the temperature dependences of the spin–lattice relaxation time for the ^1H and ^{39}K nuclei in $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystals were investigated using a pulse nuclear magnetic resonance (NMR) spectrometer to obtain detailed information about the structural geometry. This is the first investigation into the structural changes in $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ crystals, and we use the obtained results to analyze the environments of their ^1H and ^{39}K nuclei.

Experimental Methods

Single crystals of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ were grown by slow evaporation of an aqueous KMgCl_3 solution at 293 K. The resulting single crystals were transparent and colorless, with a size of approximately $3 \times 3 \times 2 \text{ mm}^3$.

The NMR spectrum and the spin–lattice relaxation time T_1 for ^1H and ^{39}K nuclei in the $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystals were measured using the Varian 200 MHz NMR and Bruker 400 MHz NMR spectrometer at the Korea Basic Science Institute Seoul Western Center. The static magnetic field and central radio frequency was 4.7 T and 200.13 MHz, 9.4 T and 18.67 MHz for ^1H and ^{39}K , respectively. The spin–lattice relaxation time was measured using a saturation recovery pulse sequence, $(\pi/2)_{\text{sat}} - \tau - \pi/2$; the nuclear magnetizations of the ^1H nuclei at time τ after the *sat* pulse were determined following the $\pi/2$ excitation pulse. The width of the π pulse was 2.5 μs for ^1H and 25 μs for ^{39}K . Temperature-dependent

NMR measurements were conducted at temperature ranges between 200 to 400 K. The sample temperature was maintained at the required constant value with an accuracy of $\pm 0.5^\circ\text{C}$ by controlling the helium gas flow and heater current.

Results and Discussion

To determine the structure of a $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystal, X-ray diffractometry was performed using the Bruker AXS GMBH instrument with a Cu target, at the Korea Basic Science Institute Seoul Western Center. The single crystals were mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation source. Data collection and integration were performed at 298 K by using SMART (Bruker, 2000) and SAINT-Plus (Bruker, 2001).⁹ The crystal structure was orthorhombic, and the obtained lattice constants were $a = 16.199 \text{ \AA}$, $b = 22.577 \text{ \AA}$, and $c = 9.545 \text{ \AA}$. These results were consistent with the data previously reported by Weck et al.⁸

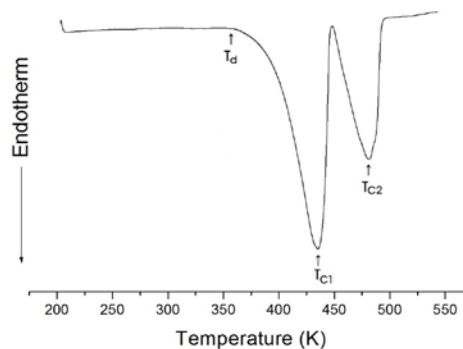


Fig. 1. Differential scanning calorimetry (DSC) thermogram of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ crystal.

In addition, in order to determine the phase transition temperatures, DSC was carried out on the crystals by using a Dupont 2010 DSC instrument. The DSC measurements revealed two endothermic peaks at 435 K and 481 K, as shown in Fig. 1. To determine

whether these high-temperature transformations are structural phase transitions, optical polarizing microscopy was conducted, and based on the obtained results, we concluded that the two endothermic peaks were related to phase transitions.

TGA was then used to determine whether these high-temperature transformations are structural phase transitions or chemical reactions. The thermogram of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ is shown in Fig. 2. Initial mass loss begins at around 351 K and the mass loss is 20 % of the total mass as $\text{KMgCl}_3 \cdot 3\text{H}_2\text{O}$ nears 394 K. Near 440 K, the thermal decomposition enters a new stage, and the residue of the final products reaches a value of 61%, accompanied by the escape of H_2O . The bulk mass of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ decreases at 351 K (T_d), which is interpreted as the onset of partial thermal decomposition, and is thermally decomposed completely into KMgCl_3 at around 440 K. These results are not consistent with the data previously reported by Popp and Ken.⁷ The DSC and TGA results for $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ crystals show that the mass loss around 351 K (T_d) is due to the onset of partial thermal decomposition. The transformation anomaly at 435 K (T_{C1}) is related to phase transitions from $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ to KMgCl_3 . Moreover, the endothermic peak at 481 K (T_{C2}) is confirmed as the phase transition temperature by optical polarizing microscopy.

The NMR spectra for the ^1H nuclei in a $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystal were obtained at several temperatures. Additionally, the ^1H spin-lattice relaxation time T_1 in the laboratory frame for a $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ crystal was obtained at a frequency of 200.13 MHz, and the magnetic field was applied along the crystallographic *c*-axis of the crystal. The saturation recovery curves of the magnetization of ^1H were measured at several different temperatures. The measured magnetization recovery curves were found to be satisfactorily fitted with the single exponential

function $[M(\infty) - M(t)]/M(\infty) = \exp(-Wt)$, where $M(t)$ is the nuclear magnetization at time t , and W is the transition probability corresponding to $\Delta m = \pm 1$. The relaxation time is given by $T_1 = 1/W$.¹⁰ The ^1H relaxation time was obtained in terms of W , and the spin-lattice relaxation time T_1 was found to have strong temperature dependence, as shown in Fig. 3.

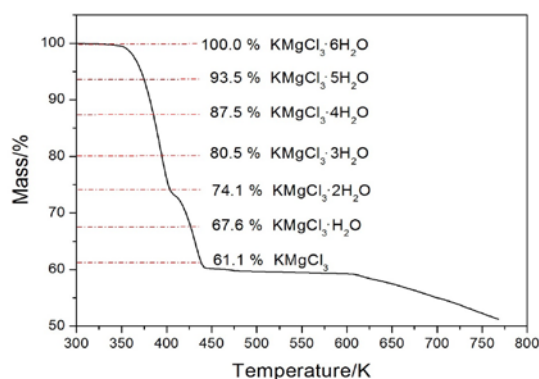


Fig. 2. Thermogravimetric (TG) analysis of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ crystal.

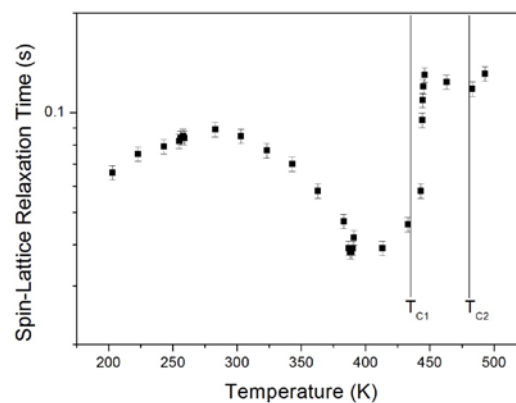


Fig. 3. Temperature dependence of spin-lattice relaxation time T_1 for the ^1H nuclei in $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystal.

The change in the temperature dependence of T_1 near T_{C1} (435 K) is related to the loss of H_2O ; the forms of the octahedra of water molecules surrounding Mg^{2+} were probably disrupted by the loss of H_2O . Moreover, the T_1 near T_{C2} (481 K) has more or less

continuously values. The T_1 near 390 K has a minimum value, and this temperature is consistent with the $\text{KMgCl}_3 \cdot 3\text{H}_2\text{O}$ state determined by TGA.

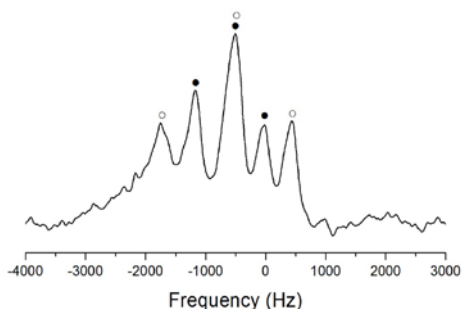


Fig. 4. ^{39}K NMR spectra of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystal at room temperature

On the other hand, two groups of ^{39}K ($I=3/2$) resonance lines were obtained instead of one group of three resonance lines, which is a characteristic of ^{39}K nuclei, as shown in Fig. 4. Two different three-line groups of K resonances are visible (● and ○ groups). From these results, we can conclude that two types of magnetically inequivalent K nuclei exist in the unit cell. The zero point of the frequency-axis in Fig. 4 is the resonance frequency, 18.67 MHz, of the ^{39}K nucleus. The ^{39}K spin–lattice relaxation time T_1 was obtained for a $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ crystal at a frequency of 18.67 MHz. The saturation recovery traces of the magnetization of ^{39}K were measured at several different temperatures. When only the central line is excited, the magnetization recovery traces of ^{39}K with dominant quadrupole relaxation in $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ do not resemble a single exponential function, but instead, they can be represented by a combination of two exponential functions: $[M(\infty)-M(t)]/M(\infty) = 0.5\exp(-2W_1t) + 0.5\exp(-2W_2t)$.¹⁰⁻¹³ Here, $M(t)$ is the nuclear magnetization at time t , and W_1 and W_2 are the transition probabilities for $\Delta m = \pm 1$ and $\Delta m = \pm 2$, respectively. Thus, the spin-lattice relaxation time T_1 is given by $T_1 = 5/[2(W_1+4W_2)]$. The slopes of the

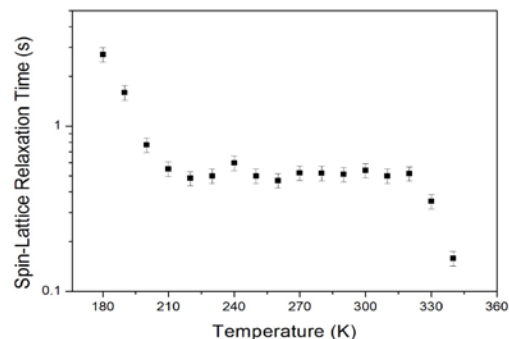


Fig. 5. Temperature dependence of spin–lattice relaxation time T_1 for ^{39}K nuclei in $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystal.

recovery traces at each temperature are different. The ^{39}K relaxation time was obtained in terms of W , and the spin–lattice relaxation time T_1 was found to have temperature dependence, as shown in Fig. 5. T_1 at low temperatures abruptly decreases with increasing temperature, and T_1 between 200 and 320 K is nearly constant. However, the NMR spectrum for ^{39}K above 340 K cannot be detected by the broadening of line width, and thus, T_1 is not obtained at high temperatures.

Conclusion

The thermodynamic properties of $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ were investigated, and phase transitions were observed at 435 K and 481 K. The crystal loses its water of hydration with increasing temperature. The first mass loss occurs near 351 K (T_d), which is interpreted as the onset of partial thermal decomposition. The transformation anomalies at 435 K (T_{C1}) are related to phase transitions from $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ to KMgCl_3 . From the T_1 for ^1H , determined by NMR experiment, we can conclude that the changes in the temperature dependence of T_1 near T_{C1} are associated with structural phase transitions, which are due to the loss of H_2O , and indicate that the forms of the octahedra of water molecules surrounding Mg^{2+} might be disrupted. This

transformation is due to proton hopping and the breaking of hydrogen bonds. The abrupt change in T_1 near T_{C1} is the only detectable result of the structural transformation. Near T_{C1} , the T_1 for ^1H increased abruptly, whereas that for ^{39}K decreased abruptly. This implies that the increasing value of T_1 for ^1H in

$\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ is due to the loss of H_2O , and the decreasing value of T_1 for ^{39}K is due to the increased the loss of H_2O . Consequently, the thermodynamic properties and structural geometry of the $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystals were studied by analyzing these environments.

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