^{27}Al and ^{87}Rb Nuclear Magnetic Resonance Study of the Relaxation Mechanisms of RbAl(CrO$_4$)$_2$·2H$_2$O Single Crystals

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Abstract: The spin-lattice relaxation times, T_1, and spin-spin relaxation times, T_2, of the ^{27}Al and ^{87}Rb nuclei in RbAl(CrO$_4$)$_2$·2H$_2$O crystals were investigated. The presence of only one resonance line for the ^{27}Al nuclei indicates that the results in a dynamical averaging of the crystal electric field that produces a cubic symmetry field. The changes in the temperature dependence of T_1 are related to variations in the symmetry of the octahedra of water molecules surrounding Al$^+$ and Rb$^+$. The T_1 values for the ^{27}Al and ^{87}Rb nuclei are different due to differences in the local environments of these ions. We also compared these ^{27}Al and ^{87}Rb NMR results with those obtained for RbAl(SO$_4$)$_2$·12H$_2$O crystals. The relaxation mechanisms of RbAl(XO$_4$)$_2$·nH$_2$O (X=Cr and S) crystals are characterized by completely different NMR behaviors.

INTRODUCTION

Considerable attention is currently focused on the development of materials suitable for storing the energy absorbed by solar collectors. For domestic heating and hot-water supplies, this energy

might be stored chemically in reversible reactions or thermally in the phase changes and/or temperature increases of storage materials. Some inorganic salt hydrates have suitable melting temperatures and high enthalpies of fusion, and so are among the most promising materials.[1] Therefore, further studies of the thermodynamic properties of such salt hydrates are needed. The alums can be represented with the general formula $M^+Me^{3+}(XO_4)_2 \cdot nH_2O$, where M is a monovalent cation such as Na, K, Rb, Cs, or NH$_4$, and Me is a trivalent cation such as Al, Fe, or Cr;[2,3] X is S, Se, or Cr. It is well known that there are a considerable number of alums $M^+Me^{3+}(XO_4)_2 \cdot nH_2O$ that exhibit ferroelectric activity.[4] KAl(CrO$_4$)$_2$·2H$_2$O is an alum in the $M^+Me^{3+}(XO_4)_2 \cdot nH_2O$ family; its crystals are monoclinic with space group C2/m and its lattice parameters are a=10.785 Å, b=5.403 Å, c=10.293 Å, and β=138.19°. The AlO$_4$·2H$_2$O octahedra are linked by CrO$_4$ tetrahedra to form $n[Al(CrO_4)_2 \cdot 2H_2O]^-$ chains parallel to the b-axis. These chains are held together by the potassium ions.[5, 6] Of the $M^+Al(CrO_4)_2 \cdot 2H_2O$ family,[7-9] KAl(CrO$_4$)$_2$·2H$_2$O has the most symmetrical structure; NaAl(CrO$_4$)$_2$·2H$_2$O crystallizes in the space group C2/c and has a less symmetrical structure. Although the crystal structures for KAl(CrO$_4$)$_2$·2H$_2$O and NaAl(CrO$_4$)$_2$·2H$_2$O at room temperature have been reported, sufficient research has not yet been conducted into the physical properties and phase transition temperatures of RbAl(CrO$_4$)$_2$·2H$_2$O, which is another member of the $M^+Al(CrO_4)_2 \cdot 2H_2O$ family.

In the present study, the nuclear magnetic resonance (NMR) spectra, spin-lattice relaxation times, T$_1$, and spin-spin relaxation times, T$_2$, for ^{27}Al and ^{87}Rb in RbAl(CrO$_4$)$_2$·2H$_2$O single crystals were obtained. To probe the phase transitions and the relaxation processes that occur in RbAl(CrO$_4$)$_2$·2H$_2$O

single crystals, the measurement of the ^{27}Al and ^{87}Rb relaxation times was preferred, because these

relaxation times are likely be very sensitive to changes in the symmetry of these crystals. This is the

first time that the relaxation processes of $RbAl(CrO_4)_2 \cdot 2H_2O$ crystals have been investigated, and we

use these results to analyze the environments of their Al and Rb nuclei. These observations also

enhance our understanding of the relaxation processes of similar crystals.

EXPERIMENTAL METHODS

Single crystals of $RbAl(CrO_4)_2 \cdot 2H_2O$ were prepared by carrying out the slow evaporation of

aqueous solutions. The $RbAl(CrO_4)_2 \cdot 2H_2O$ single crystals are hexagonal and dark blue.

The NMR signals of the ^{27}Al and ^{87}Rb nuclei in the $RbAl(CrO_4)_2 \cdot 2H_2O$ single crystals were

measured by using the Bruker DSX 400 FT NMR spectrometers at the Korea Basic Science Institute.

The static magnetic field was 9.4 T, and the central radio frequency was set at $\omega_o/2\pi$=104.26 MHz for

the ^{27}Al nucleus and at $\omega_o/2\pi$=130.92 MHz for the ^{87}Rb nucleus. The spin-lattice relaxation times

were measured by applying pulse sequences of π–t–$\pi/2$ and $\pi/2$–t–$\pi/2$, respectively. The nuclear

magnetizations S(t) of the ^{27}Al and ^{87}Rb nuclei at time t after the π and $\pi/2$ pulses, respectively, were

determined from the inversion and saturation recovery sequence following each pulse. The width of

the π pulse was 5 μs for ^{27}Al and the width of the $\pi/2$ pulse was 5 μs for ^{87}Rb. In addition, T_2 was

measured by using the solid echo method. The temperature-dependent NMR measurements were

obtained over the temperature range 180–430 K. Unfortunately in the present study the relaxation

time in the laboratory frame could not be determined above 430 K because the NMR spectrometer

did not have adequate temperature control at higher temperatures. The samples were maintained at constant temperatures by controlling the nitrogen gas flow and the heater current.

EXPERIMENTAL RESULTS AND ANALYSIS

The single crystal was mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo Kα (λ=0.71073 Å) radiation source. Data collection and integration were performed at room temperature with SMART (Bruker 2000) and SAINT-Plus (Bruker 2001) [10]. The structure of the RbAl(CrO$_4$)$_2$·2H$_2$O single crystals at room temperature was determined with an X-ray diffractometer system at the Korea Basic Science Institute. The RbAl(CrO$_4$)$_2$·2H$_2$O crystals have hexagonal symmetry with cell parameters a=b=11.982 Å, c=12.804 Å, and β=120°.

In addition, in order to determine the phase transition temperatures, differential scanning calorimetry (DSC) was carried out on the crystals with a DuPont 2010 DSC instrument. These measurements were performed at a heating rate of 10ºC/min under N$_2$ flow. An endothermic peak was found for RbAl(CrO$_4$)$_2$·2H$_2$O at 550 K (see Fig. 1), indicating the occurrence of a phase transition.
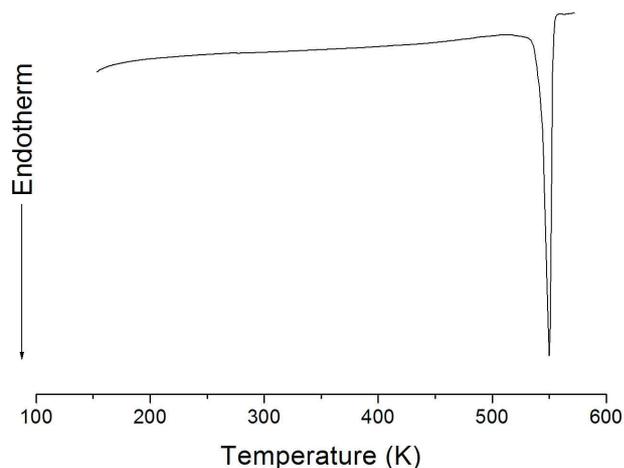
Figure 1. The differential scanning calorimetry (DSC) thermogram for RbAl(CrO$_4$)$_2$ ·2H$_2$O.

The natural abundance of ^{27}Al (I=5/2) is 100%. The magnetization recovery of ^{27}Al for the central resonance line does not follow a single exponential, but can be represented by a combination of three exponential functions:[11]

$$[S(\infty) - S(t)] / 2S(\infty) = 0.06\exp(-4/5W_1t) - 0.85\exp(-3/2W_1t) - 0.09\exp(-33/10W_1t) \qquad (1)$$

where W_1 is the ^{27}Al transition probability corresponding to the $\Delta m=\pm1$ transition when $W_1=W_2$, S(t) is the nuclear magnetization at time t after saturation, and W_1 is the inverse of the spin-lattice relaxation time, T_1. The magnetization recovery of ^{87}Rb (I=3/2) was also measured. When only the central transition is considered, the recovery law for quadrupole relaxation in ^{87}Rb nuclear spin systems can be represented by a nonexponential function: [11, 12]

$$[S(\infty) - S(t)] / S(\infty) = 0.5\exp(-2W_1t) + 0.5\exp(-2W_2t) \qquad (2)$$

where W_1 and W_2 are the ^{87}Rb spin-lattice transition rates corresponding to the $\Delta m=\pm1$ and $\Delta m=\pm2$ transitions respectively and S(t) is the nuclear magnetization corresponding to the central transition at time t after saturation. The spin-lattice relaxation time is given by $T_1 = 5 / [2(W_1 + 4W_2)]$.[11-13]

The NMR spectrum of ^{27}Al (I=5/2) usually consists of a central line and four satellite resonance lines. However, the ^{27}Al NMR spectrum of RbAl(CrO$_4$)$_2$·2H$_2$O single crystals contains only resonance line instead of five resonance lines in all directions. This indicates that the Al^{3+} in RbAl(CrO$_4$)$_2$·2H$_2$O is surrounded by the four oxygen atoms and two H$_2$O molecules in a symmetric arrangement, specifically a regular octahedral configuration.

The nuclear magnetization recovery traces of the ^{27}Al nuclei were measured at several temperatures, and the spectra at room temperature for the ^{27}Al nuclei are shown in Fig. 2 for delay times ranging from 0.001 ms to 700 ms. The inversion recovery traces of ^{27}Al do not follow a single exponential. T_1 was determined directly from the slope of a plot of log $[S(\infty) - S(t)]/2S(\infty)$ versus time t. The ^{27}Al spin-lattice relaxation time, T_1, and the spin-spin relaxation time, T_2, were measured in the temperature range 240–400 K. The temperature dependence of the spin-lattice relaxation time, T_1, for ^{27}Al in this single crystal is very strong, as shown in Fig. 3. Here, the trend of T_1 is similar with that of T_2. And, T_1 and T_2 at high temperature are very short values and has nearly same values.
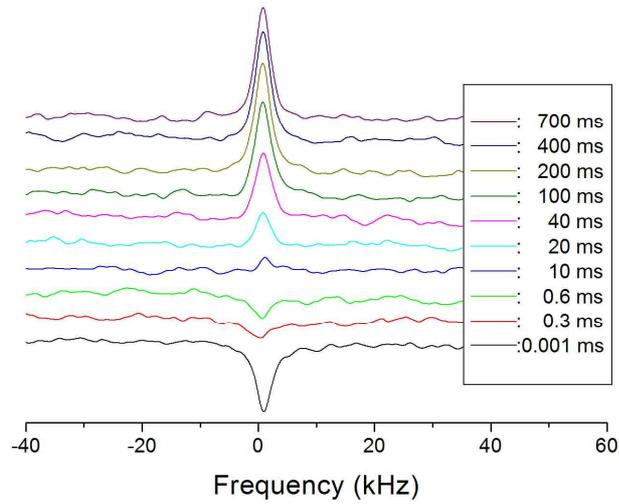
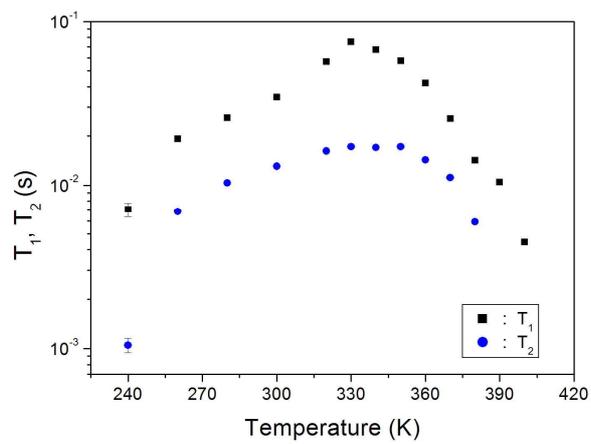**Figure 2.** Inversion recovery traces for ^{27}Al as a function of the delay time at room temperature.

Figure 3. Temperature dependences of the spin-lattice relaxation time, T_1, and the spin-spin relaxation time, T_2, of ^{27}Al nuclei in a RbAl(CrO$_4$)$_2 \cdot$2H$_2$O single crystal

The NMR spectrum of ^{87}Rb (I=3/2) in RbAl(CrO$_4$)$_2$·2H$_2$O was obtained at the frequency $\omega_o/2\pi$=130.92 MHz. When such crystals are rotated about the crystallographic axis, crystallographically equivalent nuclei would be expected to give rise to three lines: one central line and two satellite lines. The magnitudes of the quadrupole parameters of ^{87}Rb nuclei are of the order of megahertz, so only central lines are usually obtained. Instead of one central resonance line, four central resonance lines are obtained for the RbAl(CrO$_4$)$_2$·2H$_2$O crystal, as shown in Fig. 4. This result points to the presence of magnetically inequivalent Rb nuclei, Rb(1), Rb(2), Rb(3), and Rb(4).
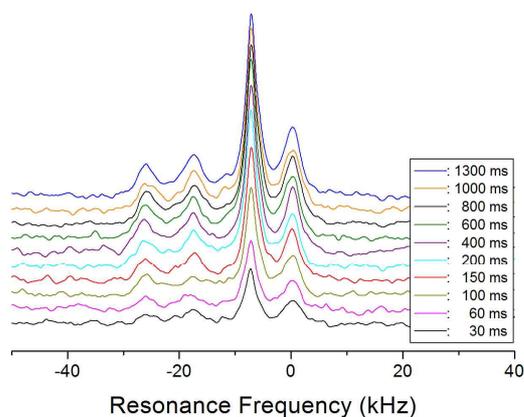

Figure 4. The saturation recovery traces for ^{87}Rb as a function of the delay time at room temperature.

The saturation recovery curves were obtained at room temperature in the range 30 to 1300 ms, as shown in Fig. 4. The recovery traces for the central Rb(1), Rb(2), Rb(3), and Rb(4) lines of RbAl(CrO$_4$)$_2$·2H$_2$O can be represented by a combination of two exponential functions, as in Eq. (2).

We determined the variations with temperature of the relaxation times of the four central lines for Rb. T_1 for ^{87}Rb was obtained in terms of W_1 and W_2, and the temperature dependences of T_1 and T_2 for the four Rb nuclei in RbAl(CrO$_4$)$_2$·2H$_2$O are shown in Fig. 5. The T_1 values for the four resonance lines are the same within experimental error. The T_1 values decrease with increasing temperature, and are very short, on the order of 10^{-1} to 10^{-3}. In addition, the spin-spin relaxation time, T_2, was found to depend on temperature. As shown in Fig. 5, T_2 decreases with increasing temperature, with T_1 and T_2 taking on similar values (i.e. of the order of milliseconds) near 400 K. The changes in the geometry around the Rb nuclei play an important role at high temperatures.
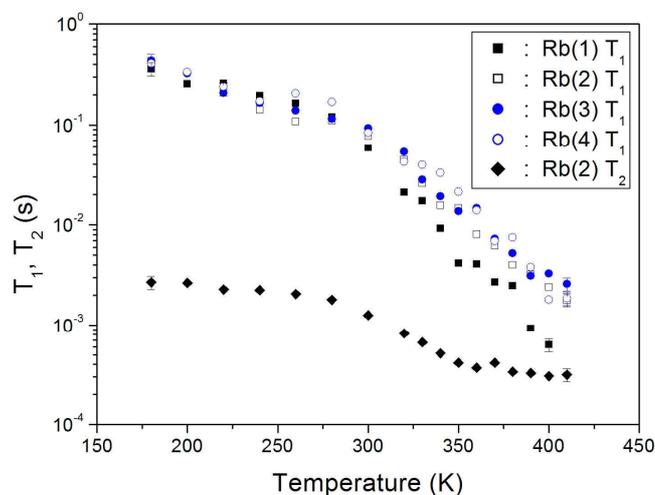

Fig. 5. Temperature dependences of the spin-lattice relaxation time, T_1, and the spin-spin relaxation time, T_2, of ^{87}Rb nuclei in a RbAl(CrO$_4$)$_2$·2H$_2$O single crystal.

DISCUSSION AND CONCLUSION

The physical properties and relaxation mechanisms of RbAl(CrO$_4$)$_2$·2H$_2$O single crystals grown with the slow evaporation method were investigated. A phase transition was found at 550 K, and we investigated the behaviors of T$_1$ and T$_2$ of the ^{27}Al and ^{87}Rb nuclei by using FT NMR spectrometry. The presence of only one resonance line for the ^{27}Al nucleus indicates that the results in a dynamical averaging of the crystal electric field that produces a cubic symmetry field. The relaxation times for ^{27}Al and ^{87}Rb have different temperature dependences; at room temperature, the ^{27}Al T$_1$ is 30 ms, whereas the ^{87}Rb T$_1$ is 60–90 ms. The changes in the temperature dependence of T$_1$ are related to variations in the symmetry of the octahedra of water molecules surrounding Al$^+$ and Rb$^+$. The T$_1$ values for the ^{27}Al and ^{87}Rb nuclei are different due to differences in the local environments of these ions. The differences between the T$_1$ for the two nuclei are also due to their different Larmor and quadrupole frequencies, amongst other factors.

We compared these ^{27}Al and ^{87}Rb NMR results with those obtained for RbAl(SO$_4$)$_2$·12H$_2$O crystals. The temperature dependences of the spin-lattice relaxation times of ^{27}Al and ^{87}Rb NMR in RbAl(SO$_4$)$_2$·12H$_2$O crystals are reported previously.[14] The T$_1$ values for the ^{87}Rb nuclei in RbAl(CrO$_4$)$_2$· 2H$_2$O were found to decrease with increasing temperature, whereas the opposite trend was observed for the compound RbAl(SO$_4$)$_2$·12H$_2$O. This result means that the T$_1$ of the ^{87}Rb nucleus in these crystals is dependent on the local environment of Rb. Although the RbAl(CrO$_4$)$_2$·2H$_2$O and RbAl(SO$_4$)$_2$·12H$_2$O crystals both have the formula M$^+$Me^{3+}(XO$_4$)$_2$·nH$_2$O, their ^{87}Rb T$_1$ have different temperature dependences. These differences between the ^{87}Rb T$_1$ of the members of this series could be due to differences between the chemical properties of the CrO$_4$ and SO$_4$ ions. Therefore, the

relaxation mechanisms of the RbAl(XO$_4$)$_2$·nH$_2$O (X=Cr and S) crystals are characterized by completely different NMR behaviors.

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