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Study on the structural properties and relaxation mechanisms in $\text{LiRb}_{1-x}(\text{NH}_4)_x\text{SO}_4$ ($x=0, 0.5, \text{ and } 1$) mixed crystals by ^1H , ^7Li , and ^{87}Rb nuclear magnetic resonance

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ABSTRACT

$\text{LiRb}_{1-x}(\text{NH}_4)_x\text{SO}_4$ ($x=0, 0.5, \text{ and } 1$) mixed crystals were grown using the slow evaporation method, and their lattice constants were determined by X-ray diffraction. The effects of replacing ammonium ions with rubidium on the phase transitions and dynamics of $\text{LiRb}_{1-x}(\text{NH}_4)_x\text{SO}_4$ mixed crystals were studied. We investigated the structural properties and phase transition temperatures of the $\text{LiRb}_{1-x}(\text{NH}_4)_x\text{SO}_4$ mixed crystals by performing ^1H , ^7Li , and ^{87}Rb NMR relaxation and DSC. When a fraction of rubidium ions in the pure LiRbSO_4 crystal is partially replaced by ammonium ions, we compare the structural properties for LiRbSO_4 , $\text{LiRb}_{0.5}(\text{NH}_4)_{0.5}\text{SO}_4$, and LiNH_4SO_4 single crystals. The ^1H , ^7Li , and ^{87}Rb NMR relaxation mechanisms of $\text{LiRb}_{0.5}(\text{NH}_4)_{0.5}\text{SO}_4$ are different from those of pure LiRbSO_4 and LiNH_4SO_4 ; the sequence of the structural phase transitions of $\text{LiRb}_{0.5}(\text{NH}_4)_{0.5}\text{SO}_4$ is different, which might be related to the dynamics and orientation of the sulfate tetrahedral groups in the crystal structure.

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1. Introduction

A large number of studies have examined the physical properties of lithium rubidium sulfate, LiRbSO_4 , and lithium ammonium sulfate, LiNH_4SO_4 ; these materials are interesting because of their ferroelastic and ferroelectric properties. LiRbSO_4 undergoes successive phase transitions at 477 K ($=T_{C1}$), 475 K ($=T_{C2}$), 458 K ($=T_{C3}$), and 439 K ($=T_{C4}$) [1,2]. The successive phases in order of decreasing temperature are referred to as I, II, III, IV, and V. Phases I and V are paraelectric [2]. Phases II and III are ferroelectric and antiferroelectric, respectively [3]. Further, phase III has been found to exhibit both antiferroelectric and ferroelastic characteristics. Microscopic observations have shown that phases IV and V are monoclinic and that the crystal system is orthorhombic above 458 K [4]. Ferroelectricity has been found in phase IV between 439 and 458 K [2,5]. The phase transitions of LiRbSO_4 can be approximately described as arising from changes of the orientations of the tetrahedral SO_4 groups. LiNH_4SO_4 undergoes several structural phase transitions with changes in temperature. A large number of studies have examined the properties of the different phases of LiNH_4SO_4 , with the ferroelectric behavior of the room temperature phase attracting particular attention. LiNH_4SO_4 is an extremely interesting material that undergoes four phase

transitions, at 459.5 K ($=T_{C1}$), 284.5 K ($=T_{C2}$), 133 K ($=T_{C3}$), and 27 K ($=T_{C4}$) [6–9]. These four transitions of LiNH_4SO_4 single crystals separate five phases denoted by I, II, III, IV, and V in order of decreasing temperature. The symmetry of the high temperature paraelectric phase above 459 K has been identified as orthorhombic. At room temperature the crystal displays orthorhombic symmetry, which differs from the space group of phase I, and has ferroelectric characteristics. The structure below 284.5 K has been described as monoclinic with both antiferroelectric and ferroelectric characteristics. Below 27 K, the space group is $C1c1$ [10]. Thus, the crystal structures of LiRbSO_4 and LiNH_4SO_4 in phase I are isomorphous and described by the space group $Pm\bar{c}n$, whereas the crystal structures of all the remaining phases show no mutual correspondence. LiRbSO_4 is pseudo-isostructural to LiNH_4SO_4 and the main difference between the two structures is in the orientations of the LiO_4 and SO_4 tetrahedra [11], as shown in Fig. 1.

Kawamura et al. [11] has studied the x - T phase diagrams of $\text{LiRb}_{1-x}(\text{NH}_4)_x\text{SO}_4$ mixed crystals in detail using X-ray diffraction. They investigated the influence of low concentrations of ammonium on the phase transitions in $\text{LiRb}_{1-x}(\text{NH}_4)_x\text{SO}_4$ ($0.0 \leq x \leq 0.2$) and the influence of low concentrations of rubidium on the phase transitions in $\text{LiRb}_{1-x}(\text{NH}_4)_x\text{SO}_4$ ($0.9 \leq x \leq 1.0$). The effects of replacing an ammonium ion with rubidium on the x - T phase diagram in the concentration range $0.5 \leq x \leq 1.0$ have been investigated using X-ray and neutron powder diffraction over a wide temperature range by Smirnov et al. [12]. It was shown that

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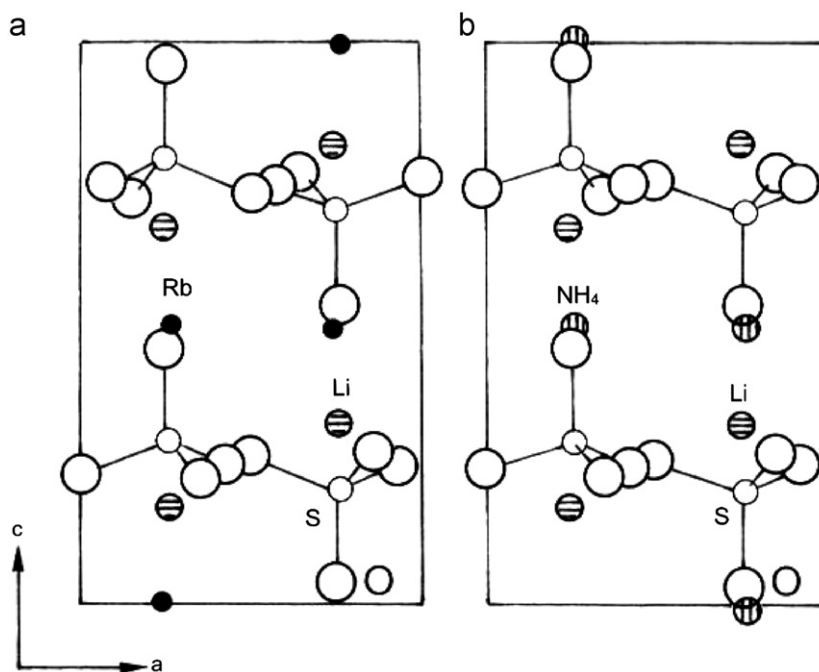


Fig. 1. Projection of the structures of (a) LiRbSO₄ and (b) LiNH₄SO₄ along [0 1 0] at room temperature.

a decrease in the ammonium concentration is accompanied by an increase in the temperature of the II–I phase transition and by the stabilization of phase II up to low temperatures.

In the present study, LiRb_{1-x}(NH₄)_xSO₄ ($x=0, 0.5$, and 1) mixed crystals were grown using the slow evaporation of aqueous solutions. The structures and the phase transition temperatures of these crystals were determined using X-ray diffraction and differential scanning calorimetry (DSC), respectively. Our aim was to study the phase transitions and the structural dynamics of LiRb_{1-x}(NH₄)_xSO₄ mixed crystals. Further, this study examined the effects of the random presence of electronically different cations of similar size. To probe the structural properties of the three single crystals, LiRbSO₄, LiRb_{0.5}(NH₄)_{0.5}SO₄, and LiNH₄SO₄, the measurement of the ¹H, ⁷Li, and ⁸⁷Rb relaxation times was preferred, because these relaxation times are likely to be very sensitive to changes in the symmetry of these crystals. The nuclear magnetic resonance (NMR) spectrum and spin-lattice relaxation times, T_1 , for ¹H, ⁷Li, and ⁸⁷Rb in LiRbSO₄, LiRb_{0.5}(NH₄)_{0.5}SO₄, and LiNH₄SO₄ single crystals were obtained. We use these results to compare the structural properties and relaxation mechanisms of the three single crystals.

2. Crystal structures

LiRbSO₄ has a monoclinic structure with four molecular formula units per unit cell. The space group is $P2_1/n$ and the lattice parameters of the monoclinic cell are $a=5.288$ Å, $b=9.105$ Å, $c=8.731$ Å, and $\gamma=90.09^\circ$ at room temperature [13]. The projection of the structure of LiRbSO₄ along [0 1 0] is shown in Fig. 1(a). The Rb⁺ ions are shown as dark circles. LiRbSO₄ has a pseudo-hexagonal network of six-membered rings of SO₄ and LiO₄, and the structure of LiRbSO₄ is characterized by the alternate rotation in opposite directions of each tetrahedron, layer by layer. The SO₄²⁻ anion is an almost regular tetrahedron, and each SO₄ tetrahedron shares all of its corners with distorted LiO₄ tetrahedra.

The structure of LiNH₄SO₄ is orthorhombic with the space group $P2_1cn$ and the lattice constants are $a=5.280$ Å, $b=9.140$ Å,

and $c=8.786$ Å in the temperature range $283 < T < 459$ K (Phase II) [14–16]. This structure consists essentially of six-membered rings typical of a tridymite framework that is made up of tetrahedral LiO₄ and SO₄ groups. In each ring, three adjacent tetrahedra have their vertices pointing up and down alternately around the ring. The six-membered rings are connected along the c -axis by an almost linear Li–O–S bond. The layers of the six-membered rings form channels along the axis in which the NH₄ groups are located. The NH₄ groups lie approximately at the centers of the large cavities in the tetrahedral framework. The structure of LiNH₄SO₄ is characterized by the alternate rotation in same directions of each tetrahedron, layer by layer, as shown in Fig. 1(b).

3. Experimental procedure

LiRb_{1-x}(NH₄)_xSO₄ ($x=0, 0.5$, and 1) mixed crystals were obtained by slow evaporation of aqueous solutions of Li₂SO₄, Rb₂SO₄, and (NH₄)₂SO₄ with the appropriate molar ratios at room temperature. The compositions of the resulting crystals differ from the initial compositions of the respective aqueous solutions. The compositions of the grown crystals were determined using chemical analysis. Three types of compounds were obtained: LiRbSO₄, LiRb_{0.5}(NH₄)_{0.5}SO₄, and LiNH₄SO₄. The crystals were transparent and colorless. The structures of the LiRb_{1-x}(NH₄)_xSO₄ ($x=0, 0.5$, and 1) single crystals at room temperature were determined with an X-ray diffractometer system (Bruker AXS GMBH) at the Korea Basic Science Institute. The structures and the lattice constants of the LiRbSO₄ and LiNH₄SO₄ crystals are consistent with previous results [13–16]. The LiRb_{0.5}(NH₄)_{0.5}SO₄ crystal has an orthorhombic structure with cell parameters $a=5.286$ Å, $b=8.755$ Å, and $c=9.110$ Å. These results are consistent with those of Smirnov et al. [12]. The phase transition temperatures were determined using a DuPont 2010 DSC instrument. Measurements were made at heating rate of 10 K/min. The phase transition temperatures of LiRbSO₄ and LiNH₄SO₄ are consistent with those previously reported [1,2,6–9], and only

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