Phase transitions in $A_4\text{Li(HSO}_4)_3\text{(SO}_4)_4$; $A = \text{Rb, K}$: Single crystal X-ray diffraction studies¶

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Abstract. The crystal structure of ferroelastic $\text{Rb}_4\text{Li(HSO}_4)_3\text{(SO}_4)_4$ has been determined at two temperatures, which indicates a structural phase transition, tetragonal $P4_1$ with $a = 7.629(1)$ Å, $c = 29.497(2)$ Å at 293 K and monoclinic $P2_1$ with $a = 7.583(3)$ Å, $b = 29.230(19)$ Å, $c = 7.536(5)$ Å, $\beta = 90.14(1)^\circ$ at 90 K. The crystal structure of $\text{K}_4\text{Li(HSO}_4)_3\text{(SO}_4)_4$ has also been determined at two temperatures, tetragonal $P4_1$ with $a = 7.405(1)$ Å, $c = 28.712(6)$ Å at 293 K and tetragonal $P4_1$ with $a = 7.371(5)$ Å, $c = 28.522(5)$ Å at 100 K. The overall coordination features in both the structures have been analysed in terms of bond valence sum calculations.

Keywords. Phase transition; ferroelastic; cryo-crystallography; crystal structure.

1. Introduction

Ferroelastic materials have been extensively reviewed$^1$ – $^3$ and they find application in the design of acoustic delay lines, transducers, optical shutters, modulators and as shape-memory materials. Compounds belonging to the family with general formula $A_4\text{Li(HSO}_4)_3\text{(SO}_4)_4$ where $A = \text{K, Rb}$ exhibit ferroelastic properties$^4$. These compounds at room temperature are generally found to display prototype tetragonal symmetry and undergo phase transitions at low temperatures and exhibit ferroelastic behaviour. Extensive physical studies including elastic, pyroelectric, dielectric and thermal measurements of this family of compounds suggest$^5$ that the pathway for phase transition from room temperature to low temperature could be either $4 \rightarrow 2$ type or $4 \rightarrow 2$ mm type. $\text{Rb}_4\text{Li(HSO}_4)_3\text{(SO}_4)_4$, hereafter RLHS and $\text{K}_4\text{Li(HSO}_4)_3\text{(SO}_4)_4$ hereafter KLHS have also been subjected to linear birefringence measurements$^6$ and EPR measurements.$^7$ In all these studies RLHS shows a well defined phase transition at $T_c \approx 122$ K (tetragonal to monoclinic) while the corresponding studies on KLHS though indicating the onset of transition at 110 K, does not exhibit recognizable changes in lattice parameters.$^4$ Also, thermal expansion studies on KLHS show no anomalies and the phase transition appears to be non ferroelastic.$^8$

Single crystal studies on RLHS at room temperature (293 K) reported earlier$^5$ showed that the crystals are optically laevorotatory and belong to the enantiomorphous space group $P4_1$. However, an analysis of the diffraction data based on the value of enantiomorph polarity parameter during refinement suggested that the sample is 87% $P4_1$ and 13% $P4_3$. Initial photographic studies at 100 K, points to a reduction of symmetry from

$^4$Dedicated to Professor C N R Rao on his 70th birthday
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tetragonal to monoclinic system, if the transition is of ferrodistortive type within the framework of Landau theory.\textsuperscript{5}

In order to ascertain the phase transition in RLHS unambiguously and to unequivocally establish the non-ferroelastic nature of the phase transition in KLHS, we have carried out detailed single crystal diffraction experiments. We describe here the details of these studies on RLHS and KLHS at room temperature (293 K), at 90 K for RLHS and at 100 K for KLHS respectively.

2. Experimental

Single crystals of both RLHS and KLHS were grown by slow evaporation at 313 K from an aqueous solution containing stoichiometric amounts of $\text{Rb}_2\text{SO}_4:\text{Li}_2\text{SO}_4$ and $\text{K}_2\text{SO}_4:\text{Li}_2\text{SO}_4$ in excess $\text{H}_2\text{SO}_4$ respectively. Beakers containing the solution (5 ml) were tightly corked to slow down the evaporation rate at this temperature. The crystals obtained were transparent, colourless and showed sharp optical extinction. The composition of the crystals was confirmed by preliminary powder X-ray diffraction as well as by EDAX measurements. The presence of the lithium ion was confirmed by qualitative chemical analysis. A variable temperature powder X-ray diffraction data collected on a STOE STADI-P diffraction system in the range 298 to 100 K using an Oxford cryosystem nitrogen open-flow cryostat confirmed the phase transition for RLHS. The corresponding studies on KLHS show no change in the powder pattern in this range.

![Figure 1. Powder X-ray diffraction pattern of RLHS at 298 and 107 K.](image-url)