

Pressure-induced noncrystalline phase of LiKSO₄

Hema Sankaran, S. K. Sikka, Surinder M. Sharma, and R. Chidambaram
Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India
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Recent Raman scattering experiments on LiKSO₄ from room pressure to 10 GPa suggest three phase transitions in this region. We have performed a high-pressure energy-dispersive x-ray diffraction study of this compound, using a diamond-anvil cell, to pressures of about 15 GPa. We find that not all phase transitions indicated in the Raman study are associated with structural changes. The most interesting feature, however, is exhibited by this compound above 12 GPa. The diffraction peaks diminish in intensity and are replaced by a broad hump indicative of an amorphous phase. On release of pressure, the compound returns to a crystalline phase after several days.

I. INTRODUCTION

Lithium potassium sulphate (LiKSO₄) belongs to the structure family with the general formula $MNAX_4$ ($M = \text{Li}; N = \text{Na, K, Rb, Cs, NH}_4, \text{ and N}_2\text{H}_5; AX_4 = \text{SO}_4, \text{ BeF}_4$). This class of compounds has a "stuffed tridymite" structure with three-dimensional networks built up of six-membered rings of vertex-linked MX_4 and AX_4 tetrahedra with the N^+ ions in the large X interstices. It is well known that coordination polyhedra joined at vertices have several configurations, with different relative orientations of the polyhedra but with very nearly the same energy.^{1,2} This, coupled with the fact that the anion polyhedral network and the cation polyhedra may have largely varying compressibilities,³ explains the ease with which structural phase transitions may be brought about in these compounds by polyhedral tilting. LiKSO₄ is known to undergo several such phase transitions as a function of temperature.⁴ We wished to investigate the polyhedral tilt mechanisms in this compound as a function of pressure.

Though LiKSO₄ has been widely studied in various temperature regimes, its behavior under pressure is relatively less known. To date, only three such investigations have been reported. Fujimoto, Yasuda, and Hibino⁵ have measured the dependence of the dielectric constant of this material on temperature and hydrostatic pressure, and in the range of their investigations (temperatures between 150 and 320 K and pressures less than 0.6 GPa) have found two anomalies at 190 and 253 K. These shift to higher temperatures as pressure is increased. A triple point was also established at 0.43 GPa and 287 K.

Bhakay-Tamhane *et al.*⁶ have carried out differential thermal analysis (DTA) in a piston-cylinder apparatus to pressures of 0.3 GPa. The phase transitions at 740 K ($P6_3 \rightarrow$ incommensurate) and at 940 K (incommensurate $\rightarrow P6_3/mmc$) have been studied. Very recently Melo *et al.*⁷ have performed Raman scattering experiments on this compound to 10 GPa and have found evidence for three phase transitions at 0.9, 3.2, and 6.7 GPa. They report that the Raman spectrum of the β phase, existing between 0.9 and 3.2 GPa, shows a continuous qualitative

change with pressure over this region, and attribute this to an incommensurate structure. In order to get the crystallographic information on these phases, we have carried out energy dispersive x-ray powder diffraction studies on LiKSO₄ up to pressures of about 15 GPa at room temperature ($T = 297$ K).

II. EXPERIMENTAL

Powder particles of LiKSO₄ were obtained from a single crystal grown by Bansal (Nuclear Physics Division, Bhabha Atomic Research Centre) from an aqueous solution of equimolar proportions of Li₂SO₄ and K₂SO₄. These were contained in a gasket and subjected to pressure in a diamond-anvil cell fabricated from the design of Huber, Syassen, and Holzapfel.⁸ Gaskets were formed by preindenting foils of Inconel-600 to a thickness of 100 μm and drilling a hole of about 150- μm diameter in the center using a Nd-glass laser. The cavity was filled with the sample, and 16:3:1 methanol-ethanol-water mixture⁹ was used to ensure hydrostaticity. The pressure was estimated in some runs by monitoring the diffraction peaks of Au powder mixed with the sample. Conversion to pressure was carried out using the well-established equation of state¹⁰ of Au ($B_0 = 167 \pm 11$ GPa and $B'_0 = 5.5 \pm 0.8$ GPa at room temperature).

A continuous spectrum of x rays from a rotating copper anode x-ray generator, operating at 44 kV and 45 mA was used. The diffracted beam was collected over the full cone of Bragg angle 6.1°, by a large-area intrinsic germanium detector of 35-mm diameter.

III. RESULTS AND DISCUSSION

The diffraction patterns of LiKSO₄ at different pressures show that the compound undergoes very interesting structural transitions. Figure 1 shows the spectra recorded with no pressure calibrant, while Fig. 2 shows the patterns obtained with Au as a pressure marker. At ambient pressure [Fig. 1(a)] the pattern can be well explained by the known $P6_3$ structure.¹¹ At higher pressures the original diffraction peaks are accompanied by weak superlattice lines, shown by arrows in Fig. 1(b). However, since

the resolution of our apparatus does not permit accurate distinction of these weak peaks, indexing them is difficult. We cannot, therefore, distinguish between the incommensurate (β) or the lock-in (γ) phase, postulated in the Raman study. Further, no change in the diffraction pattern was discernible in the range of existence of the δ phase.

At still higher pressures a broad glassy background developed, with a simultaneous decrease of the strength of the Bragg peaks [Fig. 2(b)]. The diffraction peaks disappear completely at ~ 13 GPa, and the pattern recorded is that of an amorphous solid or a liquid [Figs. 1(c) and 2(c)].

This relatively unusual noncrystalline phase of LiKSO_4

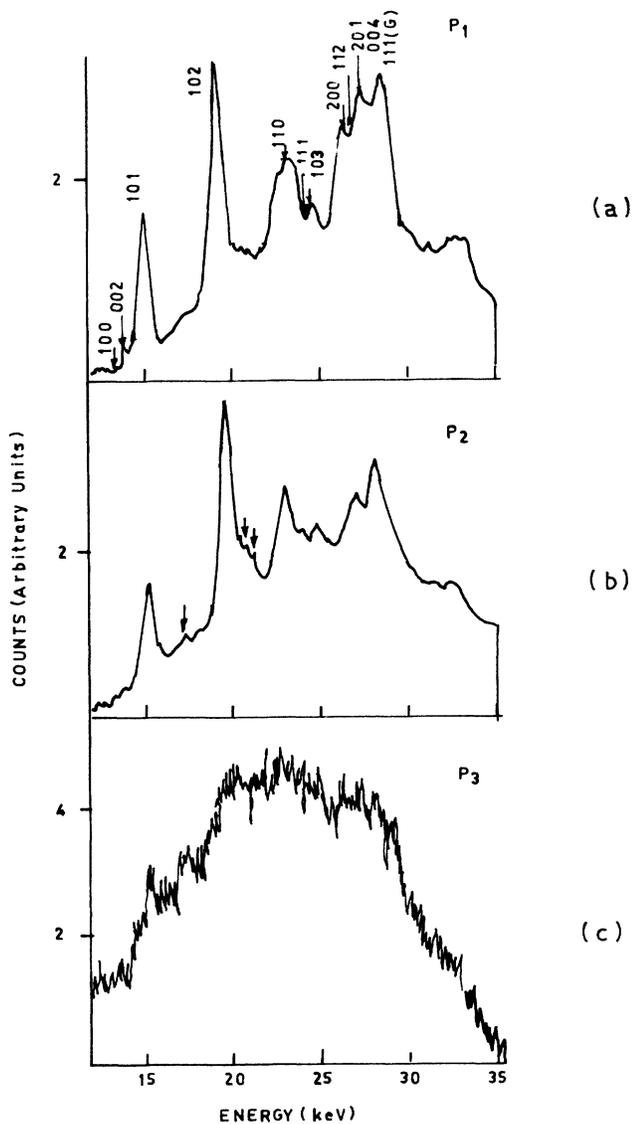


FIG. 1. Diffraction patterns of LiKSO_4 recorded at different pressures ($P_1 < P_2 < P_3$) without a pressure marker. G and E denote, respectively, gasket diffraction and escape peaks.

returned to a crystalline form on release of pressure, albeit slowly. It took nearly three days for diffraction peaks of significant strength to appear [Fig. 2(d)], and the pattern continued to evolve until the fifth day, when the experiment was terminated. The experiment was repeated several times with identical results.

Is this high-pressure noncrystalline phase of LiKSO_4 an amorphous solid? We resort to indirect reasoning to

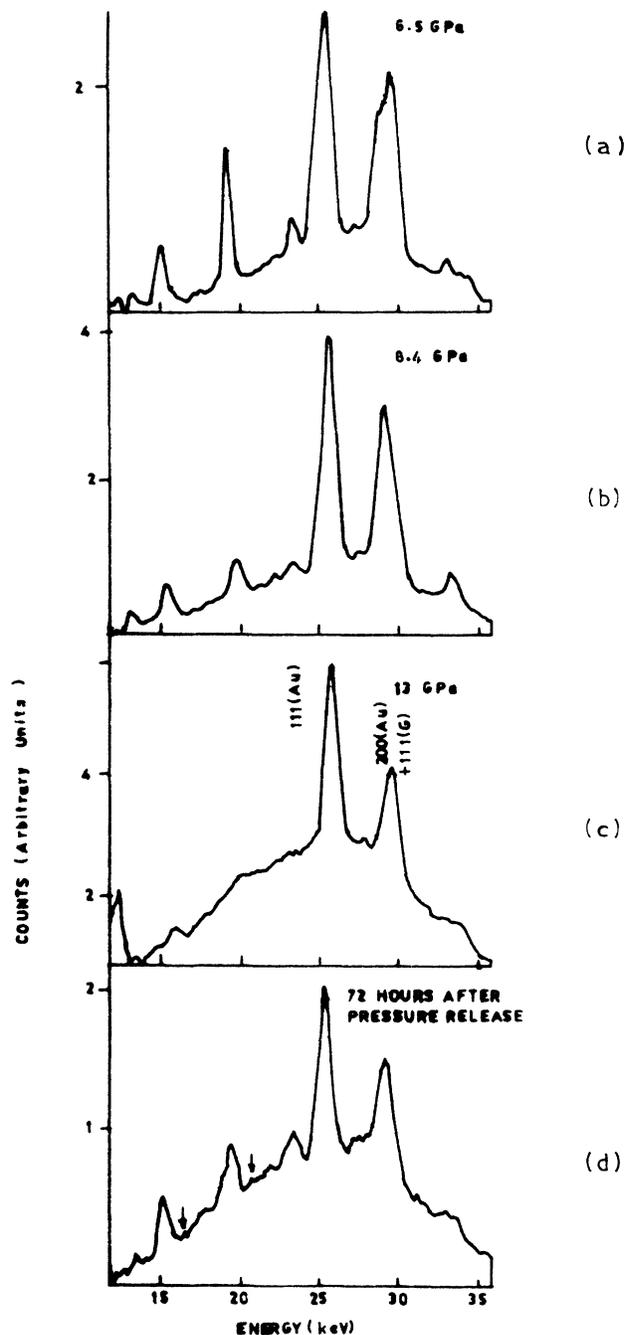


FIG. 2. Diffraction patterns of LiKSO_4 with *in-situ* Au marker: (a) at 6.5 GPa; (b) at 8.4 GPa; (c) at 13 GPa; and (d) 72 h after release of pressure.

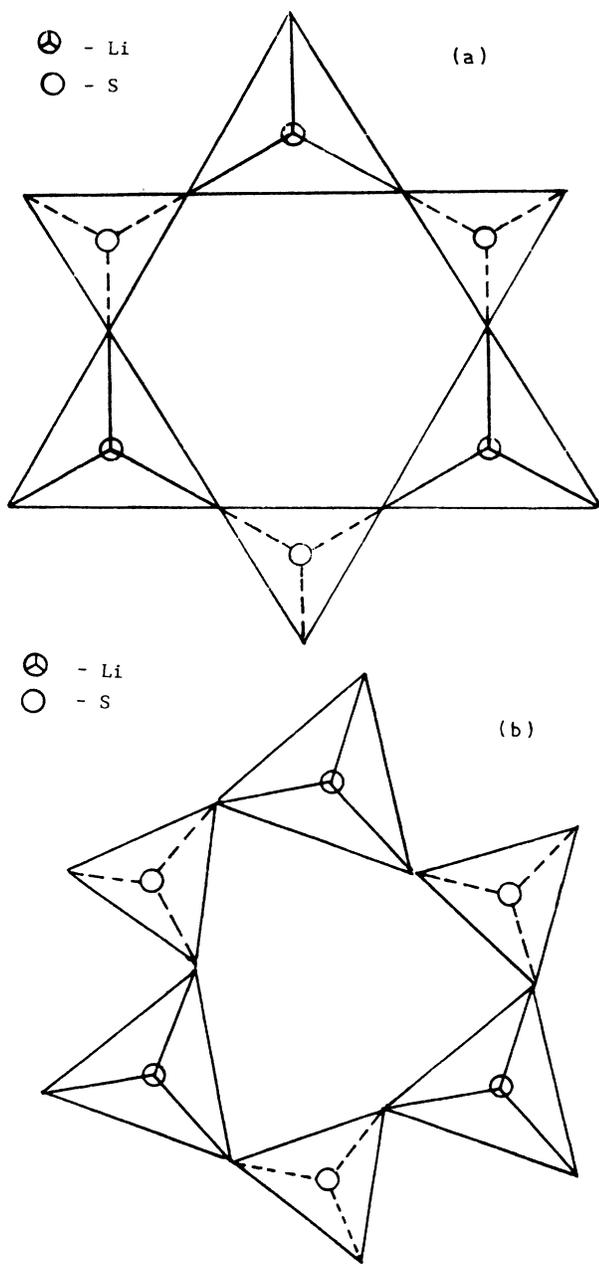


FIG. 3. The six-membered tridymitelike ring of LiO₄ and SO₄ polyhedra (dashed lines) (a) in the orthorhombic (*Pnma*) phase and (b) in the hexagonal (*P6₃*) phase.

eliminate several possibilities. The experiment was repeated without the pressure-transmitting alcohol mixture with the same results. This invalidates the suspicion that the solubility of LiKSO₄ in alcohol increases markedly with pressure and that the diffraction peaks disappear as the salt dissolves. It is unlikely that the sample has melted under pressure, as this would imply a shift of the melting temperature with pressure (dT_m/dP) of nearly 60 K/GPa. No melting signals were observed in the high-pressure DTA experiments of Bhakay-Tamhane *et al.* and therefore we cannot estimate dT_m/dP for LiKSO₄. The kinetics of the reverse noncrystalline-to-crystalline phase transition in LiKSO₄ is typical of a solid-solid transition, and is very similar to the other known solid-solid phase transitions of this compound which exhibit thermal hysteresis and extremely slow kinetics.¹²

Figure 3(a) shows the structure of LiKSO₄ in the orthorhombic high-temperature (740-K) phase.¹³ SO₄ and LiO₄ tetrahedra joined at corners form a network of six-membered rings with K⁺ ions in the large oxygen interstices. Figure 3(b) shows the ambient condition hexagonal phase of this compound, and it illustrates the extent to which the polyhedra have rotated over so small a temperature contraction (3.7% volume change). According to Kurzniski and Halawa,¹⁴ the variety of configurations due to the subtle tilting of polyhedra may give rise to structures belonging to as many as 25 different space groups. The random packing of tetrahedra in an amorphous structure is therefore not very surprising.

Very few cases of pressure-induced amorphization are known [SnI₄ (Ref. 15) and SiO₂ (Ref. 16)]. In connection with our experiment, it is worthwhile to look at the polymorphs of SiO₂ and other minerals with corner-linked coordination polyhedra. The volumes of these crystals are often reduced by changing the angles between the polyhedra rather than by significant reduction in the ionic bond lengths.¹ SiO₂ has a number of polymorphs—quartz, coesite, tridymite, cristobalite, and glass—which transform from one form to another by the tilt of the SiO₄ tetrahedra. Hemley *et al.*¹⁶ have recently demonstrated that quartz and coesite display, above 30 GPa, a pressure-induced transition to a glassy state. In analogy one is tempted to conclude that the high-pressure noncrystalline form of LiKSO₄ is amorphous. Further studies on other *MNAX₄* compounds are being carried out in order to understand the mechanism better.

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