

Visual observation of phase transitions in LiKSO_4 under pressure

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Abstract. Phase transitions in LiKSO_4 have been visually observed in a diamond-anvil cell up to 16 GPa. The observations confirm a symmetry change at 0.9 GPa and a solid-state crystal to amorphous transition at 12 GPa. The crystal exhibits a memory across the crystalline transitions. Interesting microstructural features were observed in the range of the amorphous phase.

Keywords. High pressure; diamond-anvil cell; LiKSO_4 ; phase transitions; pressure-induced amorphization; visual observations.

1. Introduction

LiKSO_4 undergoes a large number of phase transitions as a function of temperature and pressure (Bansal 1984; Melo *et al* 1987). Three transitions at 0.9, 3.2 and 6.7 GPa (from ambient α (P6_3) phase to hitherto undetermined crystal structures β , γ and δ) have been observed in high pressure Raman experiments (Melo *et al* 1987). The high pressure X-ray diffraction experiments of Sankaran *et al* (1988) confirmed the transition at 0.9 GPa and reported a novel solid-state crystal-to-amorphous transition at 12–15 GPa. This was later also seen in Raman scattering experiments (Arora and Sakuntala 1990). To understand these transitions better we have studied single crystals of LiKSO_4 , which are transparent to visible light, visually under a magnification of 500, while at high pressures in a diamond-anvil cell. The experiments were carried out at the Institute of Geology and Geophysics, Novosibirsk, USSR.

2. Experiment and observations

A single crystal of LiKSO_4 and a speck of ruby were contained in a diamond-anvil cell. A methanol-ethanol mixture (4:1) was used as the pressure-transmitting medium. Pressure was measured by the nonlinear ruby fluorescence scale. Photographs were taken at various stages, both while increasing and decreasing pressure, with the sample being viewed through one of the diamonds. Some of these are shown here.

In one of the runs, pressure was increased in steps, up to 5.2 GPa and then gradually released. It was seen that the crystal, which appears quite clear under crossed Nicols up to pressures just less than 0.9 GPa (figure 1) developed distinct

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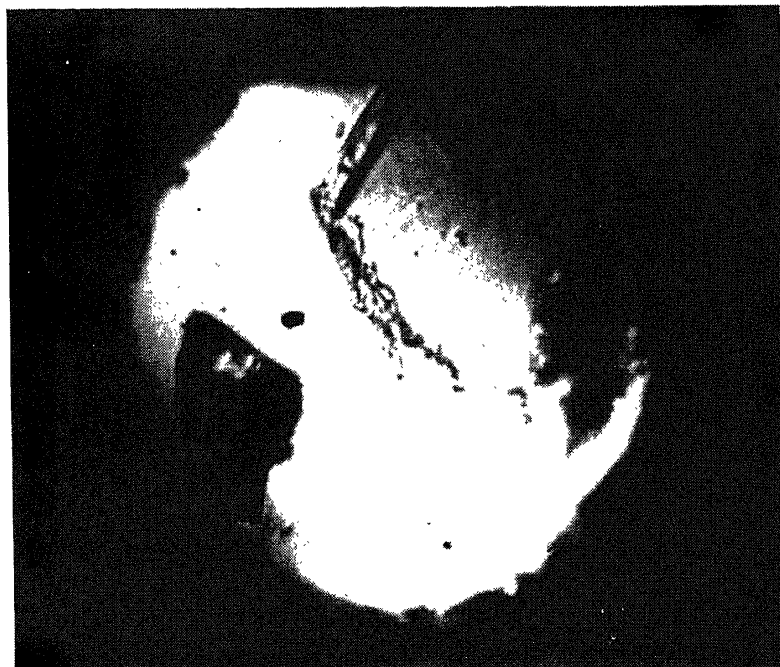


Figure 1. A single crystal of LiKSO_4 (top right) and a ruby (left) at 0.9 GPa in a diamond-anvil cell. The sample cavity is $\sim 100 \mu\text{m}$ in diameter and $\sim 20 \mu\text{m}$ in thickness.

domain walls as the pressure was increased slightly beyond this. This corresponds to the $\alpha \rightarrow \beta$ transition seen both in the Raman and X-ray diffraction experiments. Figure 2 shows the crystal at 1.3 GPa. The 30° and 60° domain walls suggest a loss of six-fold symmetry.

A further increase in pressure caused only an increase in the density of the domain walls (figure 3 at 5.2 GPa). On unloading, the twin walls disappeared at 0.7 GPa, showing a small hysteresis in the $\alpha \leftrightarrow \beta$ phase change. The original single crystal was recovered intact (figure 4 at ~ 0.7 GPa), indicating that for the $\alpha \leftrightarrow \beta$ and $\beta \leftrightarrow \gamma$ transitions, the crystal has a memory. This memory effect is similar to that for the low-temperature changes ($\text{PI} \leftrightarrow \text{PII} \leftrightarrow \text{PIII}$) observed by Bhakay-Tamhane (1988).

In another run, the pressure was increased to 15.8 GPa. Figure 5 shows the sample (without crossed Nicols) at this pressure, where the single crystal specimen appears very finely-grained and turbid). The turbidity may be an indication that the sample has turned amorphous. On the complete release of pressure, crystallites were seen to form out of this mass (figure 6).

3. Discussion

The extensive fracturing observed here upon amorphization of the crystal was also seen in ice ($I_h \rightarrow$ amorphous, Hemley *et al* 1989). It may be argued that the crystal did not undergo amorphization but rather shattered into nanocrystals. This can,



Figure 2. The sample at 1.3 GPa shows microstructural twinning indicating a structural phase transition.

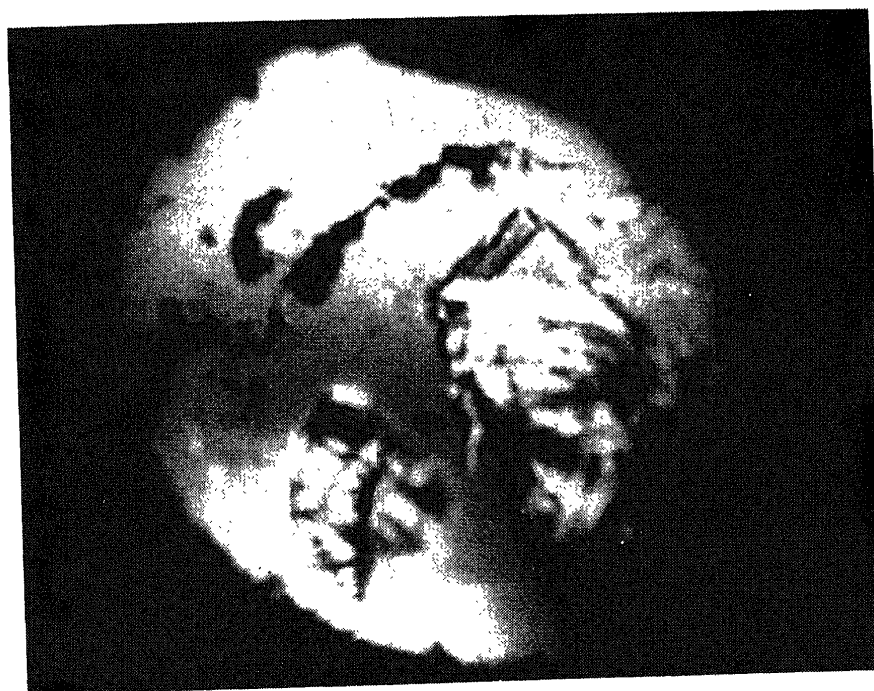


Figure 3. The sample at 5.2 GPa. Note the increase in density of the domain walls.

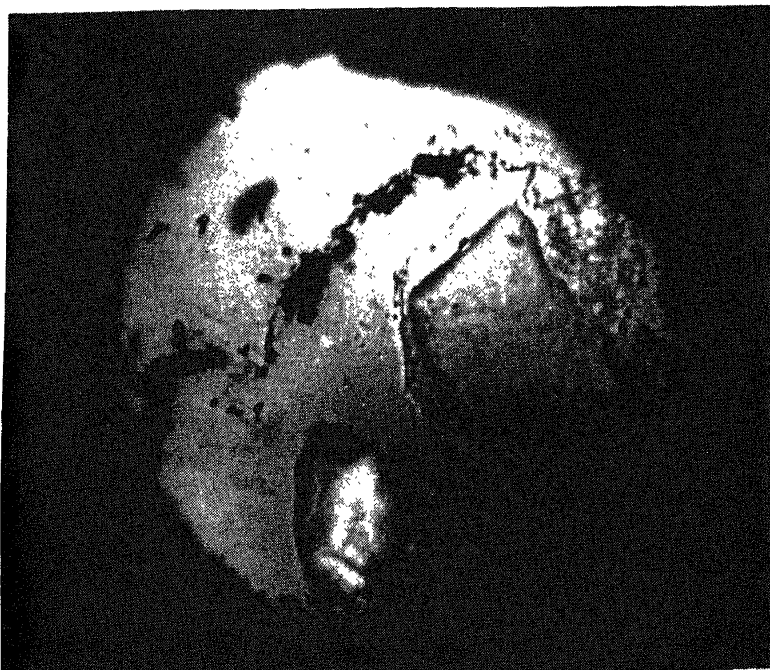


Figure 4. Pressure released to 0.7 GPa. The twinning has disappeared and the original single-crystal is recovered intact.

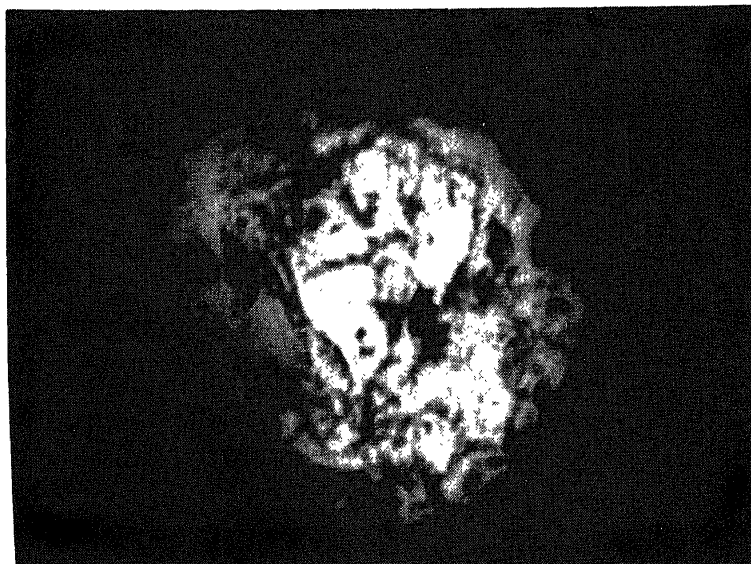


Figure 5. LiKSO_4 at 15.8 GPa in second run. The crystal is now completely shattered.

however, be ruled out by noting that in not only our present studies but also in our earlier X-ray studies and also the Raman work of Arora and Sakuntala (1990) the phase change was reversible.

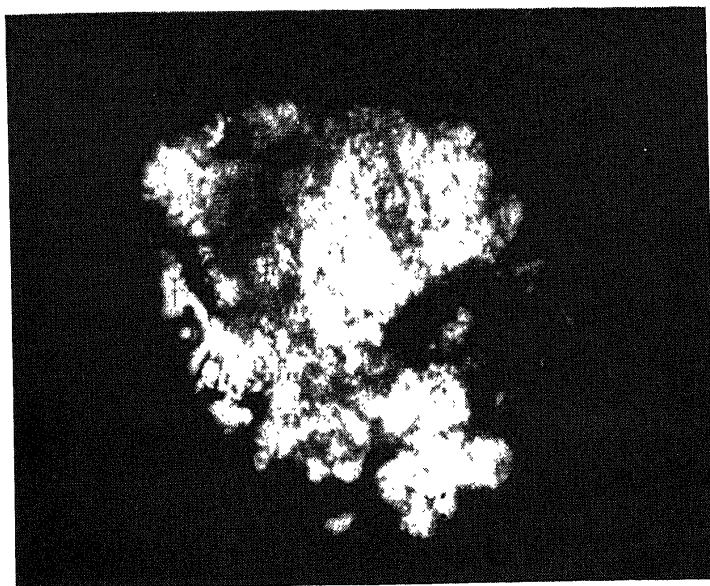


Figure 6. Complete release of pressure. Small crystallites are seen to form. This indicates the reverse amorphous to crystalline transition on pressure release.

Recent studies (see, for example, Hemley *et al* 1988, 1989) have shown that pressure-induced amorphization in ice and SiO_2 polymorphs can be understood in terms of the thermodynamics and elastic properties of various phases. As the crystal in phase I is subjected to increasing pressure, it may at some juncture transform to another crystalline phase II. These phase changes are usually accompanied by a decreasing shear constant. Further, the new phase has a higher coordination of the basic structural unit (e.g. in ice VII, the coordination of the oxygen atoms increases from 4 to 8, Kuhs *et al* 1984; the structural unit in SiO_2 changes from SiO_4 at ambient conditions to SiO_6 in the high-pressure high-temperature stishovite phase, Stishov and Popova 1961). It so happens that the kinetics preclude the transition from I \rightarrow II, and thus the crystal phase I becomes metastable in the high pressure range. However, this metastability cannot be maintained beyond the pressure where the shear constant vanishes (Born and Huang 1962; Hsich and Yip 1987) and the crystal fractures, and undergoes a catastrophic transition to an amorphous state. It may be noted here that a glass is characterized by a shear modulus that is zero in the static limit and non-zero at high frequencies (Wolf *et al* 1990). Since the process of solid-state amorphization is governed by phonon instabilities, the structural change is homogenous and instantaneous (10^{-12} s), unlike conventional thermodynamic melting which is heterogenous and takes place over a time governed by the thermal-activated diffusion.

LiKSO_4 is likely to behave in a fashion similar to ice and SiO_2 . It has the stuffed tridymite (a polymorph of SiO_2) structure at ambient conditions. Our recent molecular dynamics studies (Chaplot and Sikka 1990) show that the LiO_4 tetrahedra change into a nearly octahedral coordination units in the high pressure amorphous phase. In addition, our visual observations on fracturing of this compound show a behaviour similar to ice at high pressures.

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