Pressure-Induced Changes of SO₄ Sites in LiNaSO₄ Crystal

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Hydrostatic pressure-dependent Raman scattering studies in the range 0.0 - 9.66 GPa were carried out in LiNaSO₄ at room temperature in order to investigate its phonon spectra in relation to the phase transition in the crystal. From the behavior of $\nu_1(\text{SO}_4)$ modes for A₁ species, we observe that the LiNaSO₄ undergoes two phase transitions: one at ~ 2 GPa and the other for $P > 5.5$ GPa.

[lithium sodium sulphate, phase transition, hydrostatic pressure, inelastic light scattering, stretching modes].

1. Introduction

The crystals of the family of LiASO₄ (A = Li, Na, K, Rb, Cs) have attracted a great number of investigation in the last years. This is because these crystals present very interesting characteristics, namely: (i) Some of them are fast-ionic (superionic) conductors when the material goes to high temperature and undergoes a phase transition [1]; (ii) some of them present ferroelectric and ferroelastic phases [2, 3] and (iii) in a general way they show a series of phase transitions both with temperature and pressure [4, 5], besides other interesting aspects.

LiNaSO₄ (LNS) is a very interesting material that exhibits a superionic phase transition at high temperature and for this reason a great number of works exist in the literature [6 - 9]. This material was isolated for the first time by Cavalca and Nardelli [10] and preliminary studies by nuclear magnetic resonance were carried out by Anderson in 1961 [11]. The structure of LNS was determined in a definitive way by X-ray diffraction study by Morosin and Smith in 1966 [12].

Here we present for the first time the Raman scattering studies of LNS at room temperature under hydrostatic pressure. Spectra were obtained for the Z(XX)Y scattering geometry. A careful analysis of the spectra shows that the symmetric stretching SO₄ Raman modes exhibit variations either in intensity or frequency, indicating that LNS undergoes two phase transitions for $P \sim 2$ GPa and for $P > 5.5$ GPa.

2. Experimental

To perform this work we used a membrane diamond anvil cell in order to utilise the liquid argon as a compression medium. This is because the common methanol - ethanol mixture used in diamond anvil cell can destroy the sample of LiNaSO₄. A 514.5 nm line of an Ar ion laser was used as excitation. Analysis was made with a Spex Triplemate 1877, a Hamamatsu R943-02

photomultiplier and a photon counting system. The slits were set for a typical spectral resolution of 1 cm⁻¹. Samples were thinned down to ~ 70 μm . A little ruby chip was used for pressure calibration. The pressure is expected to be accurate by ± 0.06 GPa by means of ruby R₁ luminescence line.

3. Results

At room temperature and atmospheric pressure the LNS belongs to space group P31c with six molecules per unit cell, $a = 0.7627$ nm and $c = 0.98579$ nm. Both the six Li and Na ions occupy sites of symmetry C₁ while the six SO₄ ions occupy three non-equivalent site of symmetry C₃. According to group theory analysis, the internal modes representation is given by:

$$\Gamma(\nu_1) = 9 A_1 + 9 A_2 + 18 E, \quad (1)$$

where A₁ and E species are both Raman and Infrared active.

Fig. 1. Raman spectra of LiNaSO₄ crystal .

In Fig. 1 we present the pressure dependent behavior of ν_1 (SO_4) modes in the range 1.22 - 9.66 GPa taken at $T = 300$ K. For unstressed crystal (not shown in Fig. 1) the ν_1 (SO_4) are observed at 974 cm^{-1} , 998 cm^{-1} and 1026 cm^{-1} . At $P = 2.39$ GPa the spectrum changes qualitatively. This can be seen in Fig. 1 where we observe, besides the variation in the frequency of the modes oscillating at 974 cm^{-1} and 998 cm^{-1} , the disappearance of the mode at 1026 cm^{-1} . By increasing the hydrostatic pressure up to 9.66 GPa we observe that two remaining modes collapse into just one mode oscillating at 1040 cm^{-1} . It seems reasonable to assume that the collapsing of these two peaks is related to another modification occurring in the crystal structure of LiNaSO_4 .

Summing up all the results obtained we can draw the pressure dependent behavior of the ν_1 (SO_4) modes frequency as shown in Fig. 2. The lines are guide to eyes. It is clear that for $P = 2.39$ GPa the LNS undergoes a phase transition. Before the transition the SO_4 ions occupy three non-equivalent sites of symmetry C_3 (phase α) while after the transition they occupy two non-equivalent site of symmetry (phase β). Also we observe that for $P > 5.5$ GPa it seems to be another phase transition and we arrive to a third phase (phase γ). In this last phase the SO_4 ions occupy just one site of symmetry C_3 . It should be remarked that the sites symmetry occupied by the SO_4 ions in phase β of LNS are similar to those ones occupied by the SO_4 ions in the $\text{LiNa}_3(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [13].

One thing to be investigated in the future is related to the observation of a hysteresis in LiNa SO_4 when pressure is decreased. This effect was already observed in KLiSO_4 [14], but it is not present neither in CsLiSO_4 [5] nor RbLiSO_4 [15]. Note the similarity between the hysteresis behavior of two $\text{A}'\text{LiSO}_4$ crystals with low ionic radius of A' ion ($\text{A}' = \text{K}, \text{Na}$) and that of two A' ion with high ionic radius ($\text{A}' = \text{Rb}, \text{Cs}$) where it is not observed the phenomenon. Such results can throw a light in the problem of the phase transition in ionic compounds with corner-linked rigid cation-anion groups. (Observe that although there is no hysteresis in both CsLiSO_4 and RbLiSO_4 , however do exist some difference in the behavior of the pressure-induced phase transitions in these materials. In the RbLiSO_4 it was observed an irreversible phase transition [15], while in CsLiSO_4 the observed transition for pressures up to 13.5 GPa, is reversible, rapid and preserve the single-crystal nature [5]).

The next measurement we are performing is the behavior of the material with x-ray technique in order to know the lattice parameter variation with hydrostatic pressure.

Fig. 2. Energy pressure dependence of symmetric stretching of LiNaSO_4 crystals.

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