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Elastic constant measurements of super ionic $LiKSO_4$:Na single crystals

G. Varughese*[1], A. Santhosh Kumar[2], J. Philip[3], and G. Louis[4]

[1] Department of Physics, Catholicate College, Pathanamthitta, Kerala, India
[2] SPAP, Mahatma Gandhi University, Kottayam, Kerala, India
[3] STIC, Cochin University of Science &Technology, Cochin-22, India
[4] Department of Physics, Cochin University of Science andTechnology, Cochin-22, India

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Elastic properties of sodium doped Lithium potassium sulphate, $LiK_{0.9}Na_{0.1}SO_4$, crystal has been studied by ultrasonic Pulse Echo Overlap [PEO] technique and are reported for the first time. The controversy regarding the type of crystal found while growth is performed at 35 °C with equimolar fraction of $Li_2SO_4H_2O$, K_2SO_4 and Na_2SO_4 has been resolved by studying the elastic properties. The importance of this crystal is that it exhibits pyroelectric, ferroelectric and electro optic properties. It is simultaneously ferroelastic and superionic. The elastic properties of $LiK_{0.9}Na_{0.1}SO_4$ crystal are well studied by measuring ultrasonic velocity in the crystal in certain specified crystallographic directions and evaluating the elastic stiffness constants, compliance constants and Poisson's ratios. The anisotropy in the elastic properties of the crystal are well explained by the pictorial representation of the surface plots of phase velocity, slowness and linear compressibility in a-b and a-c planes.

1 Introduction

Lithium potassium sulphate [LKS] is a very extensively studied super ionic crystal. It has potential use in [1] solid state batteries, super capacitors, sensors for medical application and aircraft designing and used as nanostructured material with ease in instruments. It exhibits a series of phase transition from 20 K to 998 K [2]. The importance of this crystal is that it shows pyroelectric, ferroelectric [2] and electro optic properties [4]. LKS is simultaneously ferroelastic and superionic. Lithium sodium potassium sulphate, $Li_2NaK(SO_4)_2$, [LSKS] was synthesized by Kitahama and Frech [5] by slow evaporation technique at 80 °C by equimolecular fraction of $Li_2SO_4H_2O$, K_2SO_4 and Na_2SO_4. Liang et al. [6], Ramkumar et al. [7] and Reddy et al. [8] have reported the synthesize of the same orthorhombic crystal grown at 35 °C. But Pimenta et al. [8] have reported that the crystal grown at 35 °C with equimolecular fraction of $Li_2SO_4H_2O$, K_2SO_4 and Na_2SO_4 is an hexagonal crystal with composition $LiK_{0.9}Na_{0.1}SO_4$. The crystal, $LiK_{0.9}Na_{0.1}SO_4$, comes under the space group C_{6h}^2 [Pb_3/m] and hexagonal in symmetry. The lattice parameters are a = 5.1421 Å, c = 8.602 Å. The melting point [9] of this crystal is 650 °C and this is intermediate between Lithium potassium sulphate and Lithium sodium sulphate.

In this study elastic property of sodium doped LKS crystal is reported. The aim of this investigation is to check what type of crystal is found to be grown at 35 °C with equimolecular fraction of $Li_2SO_4H_2O$, K_2SO_4 and Na_2SO_4 since there is a controversy regarding the symmetry of crystal found while growth is performed at 35 °C.This checking is performed using the measurement of interfacial angles, XRD, density and measurement of elastic constants using ultrasonics. So far no information is found in the literature about the elastic properties of this crystal.

* Corresponding author: e-mail: gvushakoppara@yahoo.co.in

2 Experimental

Large single crystals of Li $K_{0.9}$ Na $_{0.1}$ SO_4 of size (30×25×16) mm^3 have been grown from super saturated aqueous solution by slow evaporation technique at 323 K for 60 days. The solution has been prepared by equimolecular fraction of $Li_2SO_4H_2O$, K_2SO_4 and Na_2SO_4. The photograph and morphology of the crystal are as shown in figures 1 and 2.

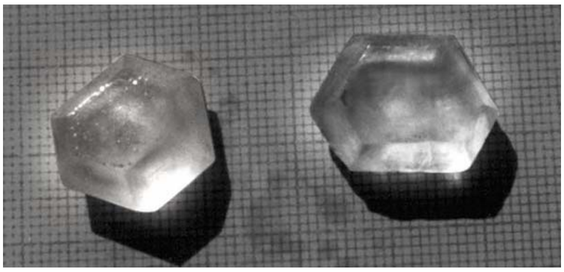

Fig. 1 Photograph of grown $LiKSO_4$:Na crystal.

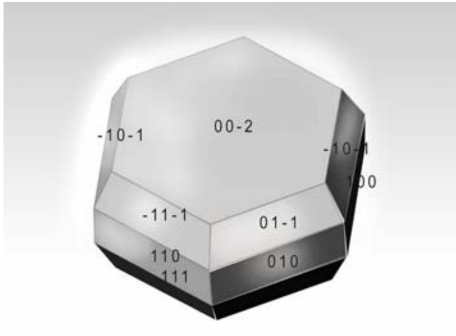

Fig. 2 Morphology of $LiKSO_4$:Na crystal.

We have examined the presence of metallic element and their % composition using Atomic Absorption Spectroscopy and flame test. The crystal structure of sodium doped LKS has been again examined by Powder X- ray Diffraction method (Fig. 3). FTIR spectrum (Fig. 4) of the material confirms the presence of SO_4 group in the crystal. Stereographic projection of the natural faces of the crystal was computed using the lattice parameters obtained by Pimenta et al. [9] The measured interfacial angles of natural faces of the grown crystal are measured using an accurate contact goniometer. Thus the natural faces of the sample have been identified [10] by comparing the measured interfacial angle with that from computed stereographic projection of the crystal planes.

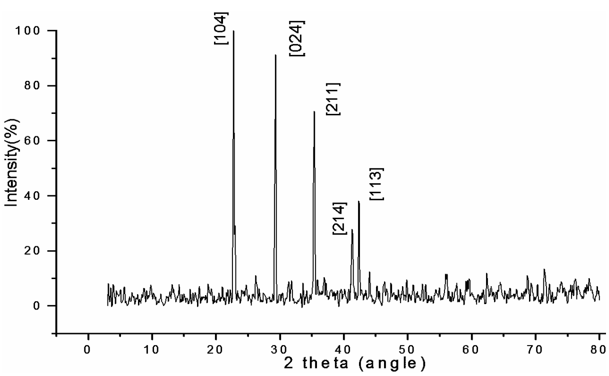

Fig. 3 XRD of LiKSO4:Na crystal.

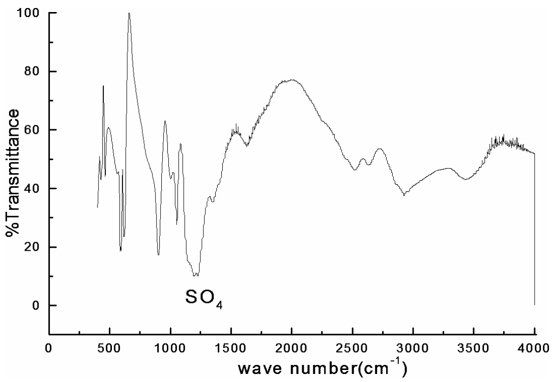

Fig. 4 FTIR spectrum of the crystal.

Bulk samples have been cut using a slow speed diamond wheel saw so as to have propagation directions along a- and c-axes. The misorientation is less than 1°. The samples are well polished by using Cerium oxide powder. The ultrasonic velocities are measured using the Pulse Echo Overlap (PEO) technique [11,12] and details of this technique ere explained. The basic experimental set up used for the measurement consists of MATEC model 7700 pulse modulator and receiver system with its associated subunits have been used for the velocity measurements. Hexagonal crystal has five-second order elastic stiffness constants.

3 Results and discussion

Elastic stiffness constant measurement Single crystals of Li $K_{0.9}$ Na $_{0.1}$ SO_4 have been grown by slow evaporation of saturated aqueous solution containing equimolar fractions of $Li_2SO_4H_2O$, K_2SO_4 and Na_2SO_4 at

35 °C. Earlier workers [6-8] conducted their work on growth using the same reagents at 35 °C and the grown crystal was reported to be Lithium sodium potassium sulphate, $Li_2NaK(SO4)_2$. The powder X-ray diffraction pattern of this crystal has been compared with JCPDS files of orthorhombic Li_2 Na $K(SO_4)_2$ [14] and that of hexagonal $LiKSO_4$ [15]. Intensity peaks positions of LSKS and the present crystal are entirely different, whereas they are almost identical with that of LKS. Additional peaks are found in the XRD of the present crystal in addition to the peaks of LKS. Besides, the density Li $K_{0.9}Na_{0.1}SO_4$ (2.469 g/cm^3) shows that the value lies between those of $LiKSO_4$ (2.396 g/cm^3) and lithium sodium sulphate (2.599 g/cm^3) and not of $Li_2NaK(SO_4)_2$ (2.2 g/cm^3). From the density measurement it is found that doped LKS is a different crystal. Measurement of interfacial angles is a very effective tool for identifying the symmetry of a crystal. The interfacial angles of grown crystal are measured with an accurate contact goniometer and compared it with computed value, which indicated that the symmetry of the grown crystal is hexagonal. From the above findings it is found that the presently grown crystal is Li $K_{0.9}Na_{0.1}SO_4$ as found by Pimenta et al. [9]. Hexagonal crystal has five second order elastic constants whereas orthorhombic crystals are having nine. We have measured ultrasonic velocity in [100], [010], and [001] directions. We have noticed that velocity along [100] and [010] have the same value and hence the crystal has only five elastic constants.

Table 1 Velocity of ultrasonic modes in Li $K_{0.9}Na_{0.1}SO_4$ at 300 K. L, T and QL represent longitudinal, transverse and quasi-longitudinal modes respectively

Mode	Direction of propagation	Direction of polarization	Measured mode velocity (m/s)	Mode velocity-elastic constant relation
L	[100]	[100]	$V_1 = 5200 \pm 5$	$C_{11} = C_{22} = \rho V_1^2$
T	[100]	[100]	$V_2 = 2477 \pm 2$	$C_{66} = \rho V_2^2$
T	[100]	[010]	$V_3 = 2914 \pm 3$	$C_{44} = C_{55} = \rho V_3^2$
L	[001]	[001]	$V_4 = 5132 \pm 5$	$C_{33} = \rho V_4^{\ 2}$
T	[001]	[100]	$V_5 = 3004 \pm 3$	$C_{44} = C_{55} = \rho V_5^2$
T	[001]	[010]	$V_6 = 2856 \pm 3$	$C_{44} = C_{55} = \rho V_6^2$
QL	[101]	QL	$V_7 = 5160 \pm 5$	$^*C_{13} = C_{23} = f_{ac}$

Hexagonal crystal has the following five second order elastic stiffness constants $C_{11} = C_{22}$, C_{33}, $C_{44} = C_{55}$, C_{66} and $C_{13} = C_{23}$

$$f_{ac} = {}^*C_{13} = f_{ac} = \left\{ \frac{1}{c^2 s^2} [(s^2 C_{11} + c^2 C_{55} - \rho\ \ v^2)(s^2 C_{44} + c^2 C_{33} - \rho\ \ v_7^{\ 2})] \right\}^{1/2} - C_{44}, \tag{1}$$

where s = sin θ c = cos θ where v is the velocity of propagation of respective mode; where θ=28° from a-c plane. ρ = 2.464 g/cm^3.

The diagonal elastic constants C_{11}, C_{33}, C_{44} and C_{66} have direct relationship with the suitable ultrasonic mode velocity given by $C_{ij} = \rho v^2$. Relationship between elastic constants in relevant ultrasonic wave velocity for the Hexagonal system are discussed in the literature [10]. The off diagonal constant C_{13} is estimated by measuring the velocity in [101] direction. The velocity measurements are tabulated in table 1. The McSkimin Δt Criterion [12,13] has been applied to correct for the phase lag introduced by the bonding medium on the RF echoes. From the above results it is proved that crystal synthesized with equimolecular fraction of $Li_2SO_4H_2O$, K_2SO_4 and Na_2SO_4 grown at 35 °C is Hexagonal, $LiK_{0.9}Na_{0.1}$ SO_4 and not orthorhombic as reported by Liang et al. [6]. The second order elastic stiffness constants and the corresponding compliance constants and Poisson's ratios are calculated from mode velocities tabulated in table 2.

Table 2 Elastic stiffness constant, Elastic compliance constant, and Poisson's ratio of sodium doped Lithium Potassium Sulphate at 300 K.

Sl. No	Elastic stiffness constant (GPa)	Compliance constant ($\times 10^{-10} N^{-1} m^2$)	Poisson's ratio
1	$C_{11} = C_{22} = 68.86 \pm 0.14$	$S_{11} = 0.21$	
2	$C_{33} = 64.89 \pm 0.13$	$S_{33} = 0.173$	
3	$C_{44} = C_{55} = 23.45 \pm 0.046$	$S_{44} = 0.426$	$\upsilon_{13} = 0.179$
4	$C_{66} = 15.94 \pm 0.03$	$S_{66} = 0.627$	$\upsilon_{31} = 0.148$
5	$C_{12} = 37.06 \pm 0.7$	$S_{12} = -0.104$	
6	$C_{13} = 19.25 \pm 0.4$	$S_{13} = -0.031$	

Table 3 Comparison of elastic stiffness constant LiKSO4:Na and Lithium potassium sulphate (LKS).

Elastic stiffness constants	
$LiK_{0.9}Na_{0.1}SO_4$ Crystal (GPa)	LKS Crystal (GPa)
$C_{11} = C_{22} = 68.86 \pm 0.14$	57.24
$C_{33} = 64.89 \pm 0.13$	67.45
$C_{44} = C_{55} = 23.45 \pm 0.046$	21.51
$C_{66} = 15.94 \pm 0.03$	14.29
$C_{12} = 37.06 \pm 0.7$	28.66
$C_{13} = 19.25 \pm 0.4$	22.37

The elastic constants of $LiK_{0.9}Na_{0.1}SO_4$ and LKS are compared in table 3. The elastic constants have substantial difference. The difference in density and velocity of ultrasonic waves through these samples are responsible for this difference. Constants C_{12} (23%), C_{13} (16%) and C_{11} (16%) have exhibited large deviation than constants C_{33} (4%) and C_{55} (9.8%) and C_{66} (11.3%).

Surface plots of phase velocity, slowness and linear compressibility The anisotropy of elastic wave propagation in this crystal can be made clear by drawing surface plots of the linear compressibility [18] in the a-b and a-c planes and phase velocity a-b plane following a well known procedure [16,18]. Figures 5 and 6 show the linear compressibility and phase velocity surfaces in the plane; The slowness surfaces plotted in the a-b, a-c planes are shown in figures 7 and 8. The Poisson's ratios [17] and volume compressibility have been evaluated. The Bulk modulus is evaluated as 30.959 GPa.

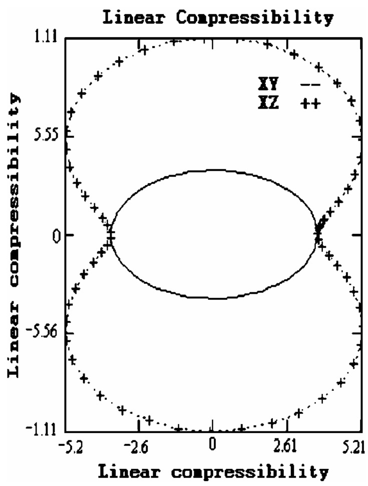

Fig. 5 Surface plot of linear compressibility.

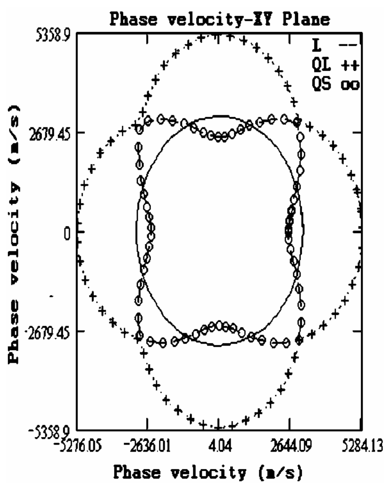

Fig. 6 Surface plot of phase velocity in the XY plane.

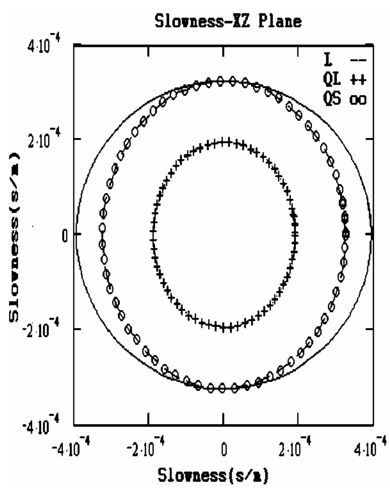

Fig. 7 Surface plot of slowness in the XZ plane.

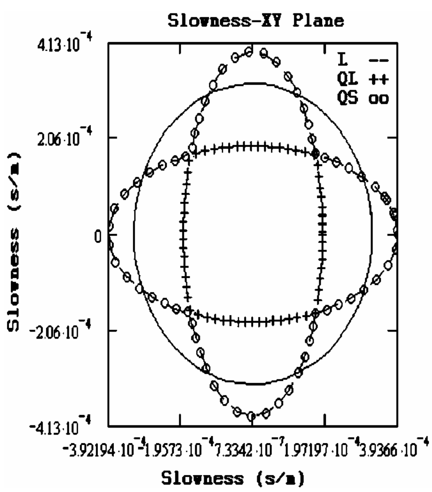

Fig. 8 Surface plot of slowness in the XY plane.

4 Conclusions

This study undoubtedly proved that crystal synthesized with equimolecular fraction of $Li_2SO_4H_2O$, K_2SO_4, and Na_2SO_4 grown at 35 °C is hexagonal $LiK_{0.9}Na_{0.1}SO_4$ not $Li_2NaK(SO_4)_2$ as reported earlier [6-8]. Hexagonal crystal has five second order elastic constants whereas orthorhombic crystals are having nine. For this doped crystal there are only five elastic constants. All the elastic stiffness constants, compliance constants, and Poisson's ratios have been measured. The anisotropy in the elastic properties have been demonstrated using the surface plots of phase velocity, slowness and linear compressibility in a-b, and a-c planes.

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