A study on structural, compositional, microhardness and dielectric properties of LiInS$_2$ crystal

A. Arunkumar, P. Vijayakumar, M. Magesh, P. Ramasamy, E. Nageswara Rao & S. Venugopal Rao

To cite this article: A. Arunkumar, P. Vijayakumar, M. Magesh, P. Ramasamy, E. Nageswara Rao & S. Venugopal Rao (2020) A study on structural, compositional, microhardness and dielectric properties of LiInS$_2$ crystal, Materials Research Innovations, 24:1, 8-17, DOI: 10.1080/14328917.2018.1540456

To link to this article: https://doi.org/10.1080/14328917.2018.1540456

Published online: 29 Oct 2018.

Submit your article to this journal

Article views: 20

View related articles

View Crossmark data

Citing articles: 1 View citing articles
A study on structural, compositional, microhardness and dielectric properties of LiInS₂ crystal

A. Arunkumar, P. Vijayakumar, M. Magesh, P. Ramasamy, E. Nageswara Rao, and S. Venugopal Rao

*Department of Physics, Aurora Scientific Technology and Research Academy, Hyderabad, India; †Centre for Crystal Growth, SSN College of Engineering, Chennai, India; ‡Department of Physics, Saveetha School of Engineering, Saveetha Institute of medical and technical science, Chennai, India; §Advanced Centre of Research in High Energy Materials, University of Hyderabad, Hyderabad, India

ABSTRACT

LiInS₂ material was synthesized with high purity elements in homemade graphite crucible using horizontal furnace. LiInS₂ single crystal was grown by Bridgman method with temperature gradient of 10–15°C cm⁻¹. The phase purity and cell parameters of grown LiInS₂ crystal were confirmed by powder x-ray diffraction and single crystal x-ray diffraction respectively. The freezing point and enthalpy of melting were found to be 977°C and 26.26 Jg⁻¹ respectively. The compositional analysis was made from inductively coupled plasma – optical emission spectrometry. Dielectric constant and dielectric loss was measured on (111) plane for various temperatures with frequency ranging from 50 Hz to 5 MHz. The hardness of the LiInS₂ single crystal in the (111) plane was assessed for different loads. The laser damage threshold was evaluated for single shot and multiple shot at 532 nm. The photocurrents were measured for various temperatures with different filters.

1. Introduction

Laser plays a very important role in the modern society; too many applications of laser in industry, medicine, military, and scientific research such as spectroscopy, microscopy, photochemistry, material processing, nuclear fusion, and so on. In order to extend laser frequency ranges, the important method, frequency conversion is often used, in which an efficient and stable frequency-shifting device, nonlinear optical (NLO) crystal is indispensable [1]. \( A^I \text{VI} C^V_2 \) and \( A^I \text{VII} C^V_2 \) chalcopyrite semiconductors with high NLO coefficients, such as AgGaS₂ (AGS) and ZnGeP₂ (ZGP), are well known commercially available materials for mid-IR nonlinear optics. However, these types of materials exhibit lower laser-induced damage threshold due to their narrow band gap, which limits their applications in optical parametric oscillator (OPO) and high power laser output [2–6]. Ternary chalcogenides with the general formula \( A^I \text{IV} B^\text{VI} C^V_2 \) \((A = Li, Na, Cu, Ag; B = Al, Ga, In; C = S, Se, Te)\) are of considerable interest because of their potential optoelectronic applications such as light emitting diodes (LED), NLO devices, detectors and solar energy converters [7]. Lithium containing semiconductors are used as promising candidates for neutron detection and are little known because of difficulties of crystal growth caused by the chemical activities of lithium [8]. Potential advantage of the LiInS₂ crystals is used in frequency conversion of femtosecond pulses over all known crystals both in the mid-IR region and in direct conversion of radiation of femtosecond Ti: sapphire (Ti:Al₂O₃) and Cr:forsterite(Cr: Mg₂SiO₄) lasers into the mid IR region [9]. So far, many works have been reported on crystal growth and its characterization [10–17]. However, growth of LiInS₂ crystal is very difficult because of Li interaction with crucible and difficulties in handling of lithium.

The objective of present study was to grow good quality crystal by Bridgman method using our own designed graphite crucible with stepper translation. The grown crystal was subjected to various characterizations such as powder X-ray diffraction, single crystal X-ray diffraction, differential scanning calorimetry, ICP-OES, dielectric measurements, hardness measurement, laser damage threshold and photoconductivity. This provides an opportunity to understand the basic property of the LiInS₂ single crystal.

2. Material and methods

2.1 Synthesis

High purity raw materials of 6N for In, 5N for S and 99.9 % for Li were used as starting elements for the synthesis. Excess of 5 % Li and 2 % S were taken for the compensation of high chemical activity of Li and evaporation loss of S at high temperature [17]. To avoid the interaction of Li with the quartz ampoule, synthesis was performed in a specially designed cylindrical shape pyrolytic carbon coated graphite crucible, having an inner diameter 12 mm, outer diameter 18 mm and length 140 mm which is shown in Figure 1. The starting charge materials were loaded into the graphite crucible using a homemade glove box under argon atmosphere condition with the humidity level of below 10%; then crucible was subsequently placed into a quartz ampoule. The crucible was sealed at residual pressure of \( 1.5 \times 10^{-6} \) Torr.

Figure 2 shows the temperature profile of the synthesis furnace with the sealed ampoule kept at 1080°C in the horizontal position. The furnace temperature was controlled by a Eurotherm PID controller with K-type thermo couple. To avoid the ampoule exploding, a stepwise temperature procedure was followed. The temperature was raised from room temperature to 400°C (just below the boiling point 444°C of...
sulfur) at a rate of 30°C/h and maintained for 12 hours, 400°C to 900°C at 20°C/h. The final temperature of 1080°C was reached at a rate of 8°C/h and maintained for 24 hours. At this stage ampoule was continuously rotated with help of motor. Then furnace temperature was reduced to 900 °C at a rate of 15°C/h, 900°C to 400°C at a rate of 5°C/h and finally 400°C to 35°C at a rate of 30°C/h. During the cooling process, ampoule exploded many times due to prolonged Li interaction with quartz ampoule. After several trial runs, the synthesis condition was optimized as ampoule hot end temperature at 1080ºC and ampoule cold end temperature at 310ºC. Finally polycrystalline material was successfully synthesized.

2.2 Growth of single crystal

For crystal growth, the polycrystalline material was loaded into bottom coned cylindrical graphite crucible under the argon atmosphere in the glove box.

The loaded graphite crucible was placed into the quartz crucible, evacuated upto 1.5 × 10⁻⁶ Torr and then sealed. LiInS₂ single crystals were grown by the modified Bridgman-Stockbarger method in a two-zone vertical tubular resistive heated furnace. In order to get the desired temperature gradient, a ceramic pad was introduced into the muffle. A temperature gradient of 10–15°C/cm⁻¹ was obtained and maintained during crystal growth. Figure 3 shows the temperature profile of growth furnace. The sealed ampoule was introduced inside the vertical furnace. The ampoule was rotated at a steady rate of 3–5 rpm and the ampoule was lowered at a rate of 6–12 mm/day using a stepper motor. Self nucleation started at bottom tip of graphite crucible and crystal was grown by lowering the ampoule. After complete growth, the furnace temperature was slowly cooled at a rate of 5°C/h to 900°C and then at the rate of 13°C/h to room temperature. A crystal of diameter 8 mm and length 30 mm was grown. Twenty days taken to complete the growth process. Many crystals were grown by the above processes. Diamond wheel crystal cutter was used to cut the grown LiInS₂ single crystal and polished with a 2 μm particle size alumina powder paste (made from a mixture of alumina powder and ethylene glycol solution). Figure 4 shows as grown and the cut and polished LiInS₂ crystal ingots.

3. Result and discussion

3.1 Powder and single crystal X-ray diffraction

X-ray powder diffraction (XRD) is a vital tool to confirming the identity of a solid material and determining crystalline and phase purity. The grown crystal was ground using an agate mortar and pestle. X-ray powder diffraction analysis was performed using a Rigaku powder X-ray diffraction system with the X-ray wavelength of 1.54178 Å (CuKα₁) with 2θ values from 10° to 80°. X-ray powder diffraction pattern of the synthesized LiInS₂ is shown in Figure 5. The peak positions are in good agreement with reported powder diffraction files (PDF00-036-1352) of LiInS₂.
The Cut and polished wafer, fabricated out of the grown LiInS$_2$ single crystal was subjected to Powder X-ray diffraction analysis. The recorded spectrum confirms the growth orientation to be $<$111$. The LiInS$_2$ single crystal structure was determined by using Enraf Nonius CAD4-MV31 Bruker Kappa Apex II single crystal diffractometer. The observed lattice parameter values are belongs to orthorhombic system are $a = 6.8912(10)$ Å, $b = 8.0591(9)$ Å.
Å, and c = 6.4820(11) Å which is closed to the literature [18]. Figure 6 gives details about unit cell structure of LiInS₂. This structure is formed by LiS₄ and InS₄ tetrahedrons, and the S²⁻ ions are arranged in hexagonal packing with tetragonal and octahedral cavities. It may be visualized as a distorted tetrahedral as shown in the ORTEP view in Figure 7. The crystallographic data and the refinement details for LiInS₂ are summarized in Table 1.

3.2 Thermo gravimetry and differential scanning calorimetry

DSC measurements are both qualitative and quantitative; provide information about physical and chemical changes involved. The thermal properties of crystal have a significant influence on crystal growth and application. The thermo gravimetry (TG) and differential scanning calorimetry were carried out using an NETZSCH STA 449F3 thermal analyzer in the range 30–1000 °C at a heating rate of 20 °C/min⁻¹ in the nitrogen atmosphere. In TG curve, there is no weight loss before the melting point but weight percentage was slightly increased which might be due to absorption of oxygen trace present in the gas used. The DSC heating and cooling curves for LiInS₂ sample are shown in Figure 8. From DSC, endothermic peak was observed at 1025 °C which is corresponding to the melting point of the LiInS₂. DSC cooling curves of LiInS₂ shows an exothermic sharp peak at 977°C which is corresponding to the crystallization or solidification of the sample. The area under the curve corresponds to 427.7 mJ. The enthalpy of melting was calculated to be 26.26 Jg⁻¹. The LiInS₂ material has a congruent melting point, determined by various authors as 880°C [19], 990°C [20,21], 980°C [22] 1030°C [23]. This difference in the melting point is due to the wide variation in composition of LiInS₂ crystal.

3.3 Inductively coupled plasma – optical emission spectrometry

ICP-OES is one of the most powerful and popular analytical tools for the determination of trace elements present in the crystal. For this analysis, the grown crystals were crushed into pieces and finely ground in an agate mortar. The powdered sample (16 mg) was transferred into a 25 mL volumetric flask with the help of a funnel and diluted with nitric acid + deionized water. This diluted sample was analyzed by ICP-OES system Perkin Elmer Optima 5300 DV spectrophotometer. The characteristic wavelengths are observed at 670.7 nm for Li, 230.6 nm for In and 181.9 nm for S. Further, these results indicate that the concentrations of various elements are as follows Li = 5.925 ppm, In = 94.54 ppm and S = 39.63 ppm. The atomic percent values of Lithium, Indium and Sulfur are 29.3%, 28.27% and 42.43% respectively. It was observed from ICP-OES analysis that the crystal has sulfur deficient. The grown crystal’s composition was Li₁₁.₁₁In₁₁.₁₁S₁₇.₇.

3.4 Dielectric measurements

For dielectric measurements, a good quality (111) plane LiInS₂ crystal of 2 mm thickness was electroded on either side with silver paste coating to make it behave like a parallel plate capacitor. The dielectric constant and the dielectric loss of LiInS₂ sample were evaluated using the conventional parallel plate capacitor method with the frequency range from 50 Hz to 5 MHz using the HIOKI 353250 LCR HI TESTER at temperature range 30º-250ºC.

The dielectric constant was calculated using the relation.

\[ \varepsilon' = \frac{C \delta}{A \varepsilon_0} \]  

(1)

\[ \varepsilon'' = \varepsilon' \tan \delta \]  

(2)

Where C is the capacitance of the parallel plate capacitor, \( \delta \) is the thickness of the crystal, A is the area of the crystal. \( \varepsilon_0 \) is the permittivity of free space (8.85 × 10⁻¹² C²N⁻¹m⁻¹). Figures 9 and 10 shows the variation of dielectric constant and dielectric loss with log frequency under different temperatures from 30º-250ºC. The dielectric constant decreases very rapidly at low frequencies and slowly at higher frequencies. The electronic exchange between the ions in the crystal causes local displacement of electrons in the direction of the applied field that causes polarization. This is a normal dielectric behavior that both dielectric constant and dielectric loss decrease with increase in frequency [24].
3.5 Mechanical hardness

The hardness of the material depends on different parameters such as lattice energy, Debye temperature, and heat of formation and inter atomic spacing [25]. During an indentation process, the external work applied by the indenter is converted to a strain energy component which is proportional to the volume of resultant impression and the surface energy component is proportional to the area of the resultant impression [26]. Microhardness is a general microprobe technique for assessing the bond strength, apart from being a measure of bulk strength. The hardness of a material is a measure of the resistance it offers to local deformation. It plays a key role in the device fabrication. The microhardness measurement was carried out on (111) plane by using Shimadzu HMV-2 Vickers indentation tester at room temperature, and the indentation time was kept as 5 s. The Vickers microhardness number $H_v$ was calculated using the relation [27]

$$H_v = \frac{1.8544P}{d^2} \text{ (MPa)}$$  \hspace{1cm} (3)
where $P$ – is the indenter load and $d$ – is the diagonal length of the impression.

The variation of Vickers micro hardness values with load on the grown crystal is shown in Figure 11. Initially hardness number increases as load increases. There was no crack observed up to a load of 300 g.

At a load of 500 g, a significant crack developed around the indentation mark, which may be due to the release of internal stresses generated at the corners of the indentation mark. The increase in microhardness (Hv) with increasing load is in agreement with the reverse indentation size effect (RISE). The RISE can be caused by the relative predominance of nucleation and multiplication of dislocations [28].

Various models like Mayer’s law, Hays and Kendall’s approach, elastic/plastic deformation model and proportional specimen resistance model (PSR) have been proposed to explain indentation size effect phenomenon. Using PSR model, several researchers [29,30] have proposed that the relation may describe the normal ISE behavior

$$P = ad + bd^2$$  \hspace{1cm} (4)

where the parameter $a$ characterizes the load dependence of hardness and $b$ is a load-independent constant. In Equation (4) when $P$ and $d$ are taken in N and µm, respectively, load-independent hardness Hv = 1.854b. In the present work applying the PSR model for LiInS$_2$ single crystal, we observed that the
plot of $P/d$ against $d$ gives a straight line (Figure 12). This linear relationship confirms that the PSR model is also applicable for explaining the reverse ISE behavior of LiInS$_2$ single crystal. The constants $a$ and $b$ are obtained from the plot of $P/d$ against $d$ for LiInS$_2$ single crystal. In the case of LiInS$_2$ single crystal, $a$ is $-0.007 \text{ N} \mu \text{m}^{-1}$. From the result of this analysis, the value of the correction factor $a$ is negative. This means that in the case of the reverse ISE a specimen does not offer resistance or undergo elastic recovery as postulated in the PSR model, but undergoes relaxation involving a release of the indentation stress away from the indentation site. This leads to larger indentation size and hence to a lower hardness at low loads [28].

### 3.6 Laser damage threshold

A nonlinear optical crystal’s ability to withstand very high power densities of laser energy is an important factor in various applications particularly that involves Q-switched lasers. Hence, the determination of the laser damage threshold for crystal is essential as this would decide the upper limit of the laser power density to which a crystal could be exposed. A linearly polarized second harmonic output 532 nm of a Q switch Nd:YAG laser was used for the laser damage threshold measurement. The laser was operated at a repetition rate of 10 Hz, pulse duration 7 ns and beam diameter 8 mm in TEM$_{00}$ Gaussian mode. The laser pulses were focused onto LiInS$_2$ sample by a 90 mm focal length lens, a 1 mm thick LiInS$_2$ sample was mounted on a computer-controlled motorized X-Y translation stage. The occurrence of laser damage was characterized by audible cracking and damage was confirmed at test site by microscope. The measurement was made in different sites on the crystal surface for single shot irrespective of whether damage had occurred on the surface or not.

![Figure 11](image1.png)

**Figure 11.** Variations of Vickers hardness number $H_v$ against applied load $P$.

![Figure 12](image2.png)

**Figure 12.** $P/d$ plotted against $d$ for test materials.
For multiple shot experiments, the same test position was continuously irradiated with repeated pulse of the same intensity. The number of pulses required to make damage on the crystal was recorded.

The diffraction limited spot diameter at focus was calculated using the formula [31]

$$W_0 = \frac{4M^2\lambda f}{\pi d}$$

(5)

where $M^2$ is the beam quality factor (which has a value equal to 1 for the laser used), $\lambda$ is the wavelength of the laser (532 nm), $f$ is the focal length of the lens (90 mm) and $d$ is the diameter of the laser beam (8 mm). At a distance before focus, beam spot size was calculated by

$$W(X) = W_0 \sqrt{1 + \left( \frac{Z}{Z_R} \right)^2}$$

(6)

$$Z_R = \frac{\pi W_0^2}{\lambda}$$

(7)

where $Z_R$ is Rayleigh length. The spot diameter was calculated to be 200 μm. The single shot surface damage threshold of LiInS₂ crystal was measured as 70 GW/cm². The multiple shot damage threshold value is 45.5 GW/cm². The multiple damage threshold value is found to be always lower than the single shot damage threshold value due to cumulative effects. Single shot and multiple shot damage pattern is shown in Figure 13. The star like image reflects the mirror symmetry of the plane of the damage. The dominant operating mechanism is dielectric breakdown. Moreover, at the power density value slightly above threshold there was distorted star pattern which is shown in Figure 14.

**3.7 Photoconductivity measurement**

The cut and polished sample was electroded with silver paste for photoconductivity measurement. LiInS₂ crystal was mounted in the sample holder. The photocurrent was measured from 100 to 400 K under the light illumination condition. As the temperature increases photocurrent also linearly increases which could be due to the generation of more number of free charge carrier is observed in Figure 15. Below 250 K, photocurrent is not much enhanced. The different filters were also employed to measure the maximum photocurrent present in the crystal. Photocurrent has high response over yellow color irradiation and corresponding energy is 2.1eV. This energy is enough to trigger maximum electron from valence band to conduction band. The same energy was observed in transmittance studies.

At room temperature resistivity and conductivity are calculated to be $1.7 \times 10^8$ Ω.cm and $5.88 \times 10^{-9}$ (Ω.cm)$^{-1}$ respectively. Figure 16 shows photocurrent for different filters.

**4. Conclusion**

The good quality IR transmittance LiInS₂ single crystal was successfully grown by modified Bridgman Stockbarger method. The powder X-ray diffraction confirmed that grown crystal possessed phase purity. Single crystal X-ray diffraction was used to study the cell parameters. The melting point (1025°C), crystallization point (977°C) and enthalpy of melting (26.26 Jg$^{-1}$) of the LiInS₂ single crystal were measured by DSC. From ICP-OES analysis, the crystal composition was found to be $Li_{1.17}In_{1.13}S_{1.7}$. The micro hardness value was obtained for various loads and found that LiInS₂ crystal undergoes reverse indentation size
The laser damage threshold value is calculated for single shot and multiple shots at 532 nm. Photoconductivity was measured for different filters and various temperatures.

Acknowledgments

The authors thank Dr. S. Kalainathan, VIT, Vellore for providing the dielectric facility and Dr. R. Gopalakrishnan, Anna University Chennai for giving the hardness facility. One of the authors P. Vijayakumar thanks SSN college of Engineering for senior research fellowship.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by DRDO-NRB under [Grant no. DNRD/05/4003/NRB/185].

References


