Investigations on synthesis, growth, electrical and defect studies of lithium selenoindate single crystals

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LiInSe2 polycrystalline material was successfully synthesized from melt and temperature oscillation method (MTO). The crystalline phase was confirmed by powder X-ray diffraction pattern. Crack free LiInSe2 single crystal of size 12 mm diameter and 32 mm length was grown using two zone tubular resistive heated furnace by modified vertical Bridgman–Stockbarger method with steady ampoule rotation. The grown LiInSe2 crystal was subjected to single crystal XRD, inductively coupled plasma-optical emission spectroscopy (ICP-OES), positron annihilation spectroscopy (PAS), Hall effect and dielectric measurements. Single crystal XRD measurement confirms the orthorhombic crystal system. ICP-OES analysis gives the crystal composition as Li0.81In1.01Se2.18. The average lifetime 278.03 ps in PAS measurements corresponds to vacancy clusters present in LiInSe2 crystal. Hall effect measurement confirms the n-type semiconductor nature. The dielectric permittivity and dielectric loss were obtained to be 9.8 and 0.108 respectively by capacitance measurements at room temperature for the frequency of 2 MHz.

1. Introduction

Crystal materials which can work efficiently on the widely tunable coherent mid-infrared laser sources in the range of 3–20 μm, specially in the band of 3–5 μm and 8–14 μm of the three atmospheric transparent windows, a spectral range of importance for infrared (IR) laser technology [1], remains a continuing challenge. Ternary chalcogenides with the general formula A1B2Cn2 (A=Li, Na, Cu, Ag; B=Al, Ga, In; C=S, Se, Te) are of considerable interest because of their potential optoelectronic applications as light emitting diodes (LED), nonlinear optical (NLO) devices, detectors and solar energy converters [2]. Recently, most reports are focused on the chalcopyrite type Cu- or Ag-analogs in A1B2Cn2 families. However, the chalcopyrite is structurally uniaxial and therefore bears some limitations in thermal properties, such as low thermal conductivity and larger coefficient of thermal expansion anisotropy. The lithium-containing A1B2Cn2-type semiconductors are little known because of difficulties of crystal growth caused by the chemical activities of lithium. However, lithium alkali metal ternary semiconductors are of interest because they have larger band gaps than the corresponding noble-metal compounds. There is a reason that makes the Li-based crystals very attractive for nonlinear optics, Ag-ion replaced by lighter Li-ion results in the increase in the frequencies in the crystal lattice vibrations and on Debye temperature. It increases the thermal conductivity, which in turn, is accompanied by an increase in optical damage threshold. Also lithium containing semiconductors are used as promising candidates for neutron detection [3]. The advantage of the LiInSe2 crystals is the possibility of creating mid-IR parametric light oscillators pumped by radiation of near-IR solid-state lasers, in particular, Nd:YAG lasers, with more than doubled efficiency as compared to that of AgGaS2 and LiInS2 crystals used. It is also worth noting the potential advantage of the LiInSe2 crystals 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 [4]. Most recently, nuclear radiation detection device was fabricated using vertical Bridgman method grown LiInSe2 single crystal [3]. Many authors [5–7] have investigated the conditions of growth of these crystals by directional solidification technique [8–10]. Badikov [7] and his co-workers reported growth of LiInSe2 and LiInS2 crystals by vertical Bridgman–Stockbarger method using thin pyrolytic carbon coated silica ampoule. They reported that due to reactivity of lithium with silica ampoule walls cracked many times, but they grew crystals successfully. Based on this, we tried to synthesize LiInSe2 polycrystalline material, but all the times coated ampoule exploded. So, we tried to use graphite crucible, while using graphite crucible due to the porosity nature of the graphite crucible lithium leaks from the graphite at an elevated temperature. To get zero porosity, pyrolytic carbon coating was done inside of the walls of synthesized and
grown graphite crucibles. This pyrolytic carbon coating has reduced leakage thus reducing the reaction of Li with the quartz ampoule walls. LiInSe2 was synthesized and growth was successfully completed using a graphite crucible with pyrolytic carbon coating.

Positron annihilation spectroscopy, due to its sensitivity and selectivity of vacancy defects, is a powerful tool to investigate the presence of stoichiometric defects in the crystals [11,12]. A difficulty is the large number of intrinsic defects in ternary compounds. The positron annihilation spectroscopy, a well-established method to study vacancy like defects in solids, can yield valuable information on the structure of vacancies. Positrons may be trapped in open-volume defects and change their annihilation characteristics significantly. Because of their positive charge, positrons are sensitive to different charge states of a vacancy in semiconductors, and thus, they represent a selective tool for their identification. The electrical measurements in LiInSe2 may be able to clarify the nature of chalcogen atom vacancies. These vacancies will play an important role for the optical applications in infrared and/or near visible region in LiInSe2 [13]. The authors of reference [13] reported high resistivity in the order of $2 \times 10^{11} \Omega$ cm with bandgap of 1.8 eV. Presence of point defects can strongly influence its electrical and optical properties, which play a crucial role when used as gas sensors.

Many reports are available for synthesis, growth and characterization of LiInSe2 crystal, but there is no report on the stoichiometry and defect studies of grown LiInSe2 crystal. In the present investigation, we tried for reproducibility of LiInSe2 single crystals using low cost, homemade instruments and made several changes in synthesis part, furnace and ampoule design. Here we discuss the synthesis, crystal growth and characterizations like powder X-ray diffraction (PXRD), single crystal X-ray diffraction (SXRD), inductively coupled plasma-optical emission spectroscopy analysis (ICP-OES), positron annihilation spectroscopy analysis (PAS), Hall effect and dielectric measurements of LiInSe2 crystals.

2. Experimental section

2.1. Synthesis

4N purity of lithium (Li) and 6N purity of indium (In) and selenium (Se) elements were weighed in accordance with the stoichiometry of 1:1:2 and an excess of 5 wt% Li and 2 wt% Se were taken for the complication of high chemical activity of Li and evaporation loss of Se [9]. For avoiding the interaction of Li with the quartz ampoule, synthesis was performed in a specially designed graphite crucible, having an inside diameter 12 mm and length 140 mm. The starting materials were loaded into a quartz ampoule, synthesis was performed in a specially designed Bridgman–Stockbarger method in a two-zone vertical tubular resistive heated furnace. In melt growth the solid–liquid interface shape is a key factor to determine the quality of growth. In order to get the desired temperature gradient, the ceramic pad was introduced in the muffle and the thickness of the pad was adjusted. The temperature gradient of 10 °C/cm was achieved. The vertical two zone resistive heated furnace, translational and rotational assemblies were fabricated in our laboratory. To adjust two zone temperature set values, the maximum temperature of the furnace was slowly raised to 960 °C at a rate of 15 °C/h, and then maintained for complete growth run. The growth furnace temperature profile is shown in Fig. 1. The translation and rotation rates play an important role in deciding the nature of the crystal growth. The ampoule was rotating at a steady rate of 3–5 rpm and the ampoule was mechanically descended at a rate of 7–12 mm/day using stepper motor. When the whole LiInSe2 melt was solidified, the furnace temperature was slowly cooled at a rate of 13 °C/h to 800 °C and then at the rate of 2 °C/min to room temperature. A crystal of diameter 12 mm and length 32 mm was grown using conically tapered graphite crucible with spontaneous nucleation. Fig. 2(a) shows the grown LiInSe2 single crystal for different run. The grown LiInSe2 single crystal was cut using a diamond wheel crystal cutter and polished with a 2 μm particle size alumina powder and a paste made from a mixture of alumina powder and ethylene glycol solution. Fig. 2(b) shows the fabricated LiInSe2 wafer.

2.2. Crystal growth

For the crystal growth process, the pre-synthesized LiInSe2 polycrystalline material was loaded into a specially designed pyrolytic carbon coated conically tapered graphite crucible, which was inserted into a quartz ampoule. Ampoule was sealed under vacuum at $2 \times 10^{-6}$ mbar. LiInSe2 single crystals were grown by the modified Bridgman–Stockbarger method in a two-zone vertical tubular resistive heated furnace. In melt growth the solid–liquid interface shape is a key factor to determine the quality of growth. In order to get the desired temperature gradient, the ceramic pad was introduced in the muffle and the thickness of the pad was adjusted. The temperature gradient of 10 °C/cm was achieved. The vertical two zone resistive heated furnace, translational and rotational assemblies were fabricated in our laboratory. To adjust two zone temperature set values, the maximum temperature of the furnace was slowly raised to 960 °C at a rate of 15 °C/h, and then maintained for complete growth run. The growth furnace temperature profile is shown in Fig. 1. The translation and rotation rates play an important role in deciding the nature of the crystal growth. The ampoule was rotating at a steady rate of 3–5 rpm and the ampoule was mechanically descended at a rate of 7–12 mm/day using stepper motor. When the whole LiInSe2 melt was solidified, the furnace temperature was slowly cooled at a rate of 13 °C/h to 800 °C and then at the rate of 2 °C/min to room temperature. A crystal of diameter 12 mm and length 32 mm was grown using conically tapered graphite crucible with spontaneous nucleation. Fig. 2(a) shows the grown LiInSe2 single crystal for different run. The grown LiInSe2 single crystal was cut using a diamond wheel crystal cutter and polished with a 2 μm particle size alumina powder and a paste made from a mixture of alumina powder and ethylene glycol solution. Fig. 2(b) shows the fabricated LiInSe2 wafer.

2.3. Instrumentation for characterization

The synthesized LiInSe2 polycrystalline material’s phase formation was identified by powder X-ray diffraction (PXRD) method using a XPert pro analytical diffractometer using nickel-filtered Cu-Kα radiation ($\lambda=0.15418$ nm) as source and operated at 40 kV and 30 mA. The sample was scanned in the 2θ range from 10° to 80° at room temperature. Single crystal XRD data of the grown LiInSe2 crystal was obtained using Bruker Kappa APEXII single

Fig. 1. Axial temperature profile of the growth furnace.
crystal X-ray diffractometer. The composition of LiInSe₂ was determined using an ICP-OES analysis. ICP-OES was done using Perkin Elmer Optima 5300 DV spectrophotometer. A 15 mg of grown single crystal portion was dissolved in 1 ml of HNO₃ acid and to make 25 ml solution using deionized H₂O. Positron annihilation measurements were carried out using ²²Na source in a sandwich geometry using two identical samples. Positron lifetime measurements involve a coincidence setup of two BaF₂ detectors to measure the time difference between the 1.27 MeV gamma ray and the 511 keV annihilation gamma ray. The fast-fast lifetime spectrometer has a time resolution (FWHM) of 250 ps and a total counts of 1×10⁶ were acquired for the lifetime spectrum. The acquired spectrum was analyzed using LT program [14] to deconvolute into various components. The Doppler spectrum was measured using a 25% efficient intrinsic germanium detector having an energy resolution of 1.4 keV at 662 keV. From the Doppler spectrum a defect sensitive line shape S-parameter is deduced which is defined as the ratio of the counts in the central region (511 ± 1 keV) to the total counts under the peak (511 ± 10 keV). Since S-parameter is very sensitive to open-volume defects, the presence of the vacancy defects results in an increase in the S-parameter value [11,12]. The electrical parameters were measured using Hall measurements in van der Pauw configuration (ECOPA-HMS 3000) at room temperature with a permanent magnet of 0.57 T. The dielectric constant was measured using an Agilent E4980A. Capacitance and dielectric loss studies were performed on LiInSe₂ single crystals using an LCR meter in the frequency range 1 kHz–2 MHz and temperature range RT to 240 °C. The opposite parallel faces of the crystals were coated with high-grade silver paste placed between the two copper electrodes and thus a parallel plate capacitor was formed. The dielectric constant was calculated, which is based on observed capacitance, electrode area and sample thickness.

3. Result and discussion

3.1. Powder XRD

The powder X-ray diffraction pattern of the synthesized LiInSe₂ polycrystalline material is shown in Fig. 3(a). The peak positions are in good agreement with the powder diffraction files (PDF card no. 04-009-0089). The result shows that LiInSe₂ belongs to the orthorhombic crystal system with Pna2₁ space group. The powder X-ray diffraction pattern of the fabricated wafer out of the grown LiInSe₂ single crystal is shown in Fig. 3(b). The single peak confirms the growth orientation to be ⟨231⟩ direction.

3.2. Single crystal XRD

From the single crystal X-ray diffraction studies, it is observed that LiInSe₂ single crystal belongs to the orthorhombic crystal system with noncentrosymmetric space group Pnma and the cell parameters are (a=6.788(8) Å, b=7.166(9) Å, c=8.398(10) Å and volume V=408.5 (9) Å³) in close agreement with the reported values [15].

3.3. ICP-OES

ICP-OES analysis is a powerful approach to the accurate and direct determination of metals in crystal sample. The presence of the wavelengths 670.78 nm, 230.606 nm and 196.26 nm confirmed the presence of lithium, indium and selenium respectively and their concentrations are 17.74(0.274), 365.3(2.8) and 543.2 (5.34) mg/l. The atomic percent values of lithium, indium and selenium are 20.26%, 25.22% and 54.53% respectively. It is seen from ICP-OES analysis that the crystal is Li deficient, indium is slightly rich and Se rich. It gives the grown single crystal’s composition as Li₀.₈₁In₁.₀₁Se₂.₁₈. Since the size of the trivalent In (0.66 Å) and monovalent Li (0.59 Å) ions are close, the cation–cation replacement with Se shift into the position which is closer.
to center of the empty tetrahedron is possible. In LiInSe₂ such antisite defects are In ions in the Li position, Inₐ. Their formation is caused by an Li deficiency as well as by its strong shift in the tetrahedron. Isaenko et al. had reported the same antisite defects (Inₐ) in LiInSe₂ single crystal [6]. Therefore, it is deduced that intrinsic defects such as Li vacancy (Vₐ), Se interstitials (Sei) and In atom in the Li sites (Inₐ) exist in the LiInSe₂ crystal. The Inₐ donor-type defects may lead to an enhancement in electrical conductivity in the LiInSe₂ crystal because the LiInSe₂ indicates n-type conductivity when examined by Hall measurement. The deviation between starting composition and crystal composition is due to Li vapors penetrating into the pyrolytic carbon coated graphite walls and reacting with the quartz ampoule walls. Thus Li deficiency leads to stochiometric deviation, even though excess of Li was taken. LiInSe₂ single crystal has high Li vacancy sites compared to indium and selenium, because lithium might participate only weakly in the covalent bonding [16].

3.4. Positron annihilation studies (PAS)

Positron lifetime and Doppler broadening measurements were carried out on LiInSe₂ crystal. From the observed experimental spectrum two positron lifetime components i.e., first component \( \tau_1 \approx 238.3 \text{ ps (bulk annihilation)} \) with 73.7% intensity \( (I_1) \) and second component \( \tau_2 \approx 389.4 \text{ ps with 26.3% intensity (I}_2 \) (nominally associated with defects) were observed. The second component with considerable intensity corresponds to presence of vacancy clusters in the sample. The mean lifetime is calculated as \( \tau_m \approx 278.03 \text{ ps using the equation [17]} \)

\[
\tau_m = (\tau_1 I_1 + \tau_2 I_2) / (I_1 + I_2)
\]

An average lifetime \( \tau_m \approx 278.03 \text{ ps} \) is indicative of a strong presence of vacancy defects (bulk annihilation lifetime for common semiconductors is in the order of \( \approx 200 \text{ ps} \) [11]). Doppler broadening S-parameter value is found to be \( 0.6425 \times 10^{-3} \) and W-parameter is \( 0.0484 \times 10^{-4} \).

3.5. Hall measurements

The bulk resistivity of LiInSe₂ crystal at room temperature is an important property for neutron detector fabrication [3,18]. Kurijama et al. grew LiInSe₂ crystals using directional solidification and obtained high resistivity in the order of \( 2 \times 10^{11} \text{Ω cm} \) at room temperature [9,11]. Tupitsyn et al. grew LiInSe₂ single crystal using vertical Bridgman method and they reported the resistivity to be \( 6.5 \times 10^{11} \text{Ω cm} \) and \( 3.17 \times 10^{11} \text{Ω cm} \) for 20°C and 40°C, respectively [3]. In present investigation, middle portion of the (231) face LiInSe₂ crystal wafer of 1.45 mm thickness was used for electrical measurements. The negative sign of the Hall coefficient confirms the n-type conductivity. The measured parameters are Hall coefficient \( (-6.36 \times 10^3 \text{cm}^2/\text{V s}) \), resistivity \( (3.43 \times 10^{10} \text{Ω cm}) \), mobility \( (1.85 \times 10^{-2} \text{cm}^2/\text{V s}) \), bulk concentration \( (-9.81 \times 10^9 \text{cm}^3) \), sheet concentration \( (-1.42 \times 10^9 \text{cm}^2) \), magneto-resistance \( (2.02 \times 10^4 \Omega) \) and conductivity \( (2.91 \times 10^{-11} \text{Ω cm}) \) of the grown LiInSe₂ wafers. The occupation of the Li sites by trivalent In results in increase of electrical conductivity and thus resistivity decreases. Due to the antisite defect (Inₐ) resistivity value decreases compared to the previous reports [3,9,11].

3.6. Dielectric studies

Dielectric properties are correlated with the electro-optic property of the crystals [19]. Optical quality crystals with good transparency were selected for dielectric studies. The cut and polished (231) face was selected and the opposite faces were coated with a high grade silver paste after lapping and polishing with a 2 μm particle size alumina powder. The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystals. From Fig. 4(a) and (b), it is found that the values of dielectric permittivity and dielectric loss increase with the increase in temperature over the range 30–150°C, after that suddenly increases till 200°C and saturates. The dielectric permittivity and dielectric loss were obtained to be 9.8 and 0.108 respectively by capacitance measurements at room temperature for the frequency of 2 MHz. The dielectric constant has a higher value in the higher temperature region (240°C) and it then decreases with the applied lower temperature (30°C). The dielectric constant of materials is due to the contribution of electronic, ionic, dipolar and space charge polarizations which depend on the frequencies. At low frequencies, all these polarizations are active [20,21]. The space charge polarization is generally active at low
frequencies and high temperature. In order to get the reproducibility the above experiment was repeated several times and the same results were obtained. The reproducibility was observed clearly. The dielectric loss has a high value of 4.3 at 240 °C and decreases to 0.1 at 30 °C. The obtained values are in good agreement with the reported values [22,23]. The low value of dielectric loss indicates that the modified Bridgman–Stockbarger method grown LiInSe2 crystal is reasonably good in quality.

From Fig. 4(c), it is found that the values of AC conductivity increase with the increase in temperature over all the range. The conductivity of the crystals in high temperature region is mainly determined by the intrinsic defect caused by the thermal fluctuations in the crystal [24]. The defect concentration will increase exponentially with temperature and consequently the electrical conduction also increases.

4. Conclusion

High purity LiInSe2 polycrystalline material was synthesized successfully using MTOM. The synthesized LiInSe2 materials were characterized by powder XRD. Crack free LiInSe2 single crystals of size 12 mm diameter and 32 mm length were grown using a steady ampoule rotation by modified vertical Bridgman–Stockbarger method. The orientation of the as grown LiInSe2 single crystal is obtained to be [231] direction. The structure of the grown LiInSe2 crystal was confirmed by the single crystal XRD analysis. ICP-OES analysis confirms the presence of Li, In and Se and the crystal composition as LiInSe2. Positron lifetime measurements on LiInSe2 crystals indicate the strong presence of vacancy defects. The measured electrical properties of LiInSe2 wafers at room temperature are resistivity (3.43 × 1010 Ω cm), Hall coefficient (−6.36 × 10⁸ cm²/C) and conductivity (2.91 × 10⁻⁷/Ω cm). Dielectric study showed that the higher dielectric constant and lower value of dielectric loss are due to less defects present in the grown LiInSe2 crystal.

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