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

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ABSTRACT

$LiInSe_2$ polycrystalline material was successfully synthesized from melt and temperature oscillation method (MTOM). The crystalline phase was confirmed by powder X-ray diffraction pattern. Crack free $LiInSe_2$ 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 $LiInSe_2$ 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 $Li_{0.81}In_{1.01}Se_{2.18}$. The average lifetime 278.03 ps in PAS measurements corresponds to vacancy clusters present in $LiInSe_2$ 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 $A^IB^{III}C_2^{VI}$ (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 $A^IB^{III}C_2^{VI}$ 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 $A^IB^{III}C_2^{VI}$-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 $LiInSe_2$ 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 $AgGaS_2$ and $LiInS_2$ crystals used. It is also worth noting the potential advantage of the $LiInSe_2$ 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:Al_2O_3) and Cr:forsterite (Cr:Mg_2SiO_4) lasers into the mid IR region [4]. Most recently, nuclear radiation detection device was fabricated using vertical Bridgman method grown $LiInSe_2$ 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 $LiInSe_2$ and $LiInS_2$ 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 $LiInSe_2$ 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

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grown graphite crucibles. This pyrolytic carbon coating has reduced leakage thus reducing the reaction of Li with the quartz ampoule walls. $LiInSe_2$ 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 $LiInSe_2$, 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 $LiInSe_2$ [13]. The authors of reference [13] reported high resistivity in the order of 2×10^{11} Ω 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 $LiInSe_2$ crystal, but there is no report on the stiochometry and defect studies of grown $LiInSe_2$ crystal. In the present investigation, we tried for reproducibility of $LiInSe_2$ 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 $LiInSe_2$ 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 compensation 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 graphite crucible using a homemade glove box under argon atmosphere with humidity level of below 10%, which was subsequently loaded into a quartz ampoule. Ampoule was sealed under vacuum at 2×10^{-6} mbar. It was then placed into a horizontal furnace, where the components were reacted according to the MTOM. The furnace temperature was controlled by a Eurotherm PID controller. To avoid the ampoule exploding, a stepwise temperature procedure was designed. The temperature gradient of the synthesis furnace is 8 °C/cm. The temperature was raised from room temperature to 680 °C (just below the boiling point 685 °C of selenium) at a rate of 55 °C/h and maintained for 12 h, to avoid boiling of unreacted selenium. The maximum temperature of 960 °C was reached at a rate of 8 °C/h and maintained for 24 h and reduced to 800 °C at a rate of 13 °C/h. Temperature oscillation between 800 °C and 900 °C was executed. Homogenization of synthesized $LiInSe_2$ polycrystalline material increases with increasing number of oscillations. The temperature oscillation was executed 8 times, each oscillation has 14 h and then the melt was slowly cooled at a rate of 9 °C/h to 680 °C, then to room temperature at a rate of 60 °C/h. The synthesized $LiInSe_2$ polycrystalline material was harvested and no reaction between polycrystalline material and graphite crucible was observed.

2.2. Crystal growth

For the crystal growth process, the pre-synthesized $LiInSe_2$ 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 2×10^{-6} mbar. $LiInSe_2$ 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 $LiInSe_2$ 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 $LiInSe_2$ single crystal for different run. The grown $LiInSe_2$ 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 $LiInSe_2$ wafer.

2.3. Instrumentation for characterization

The synthesized $LiInSe_2$ polycrystalline material's phase formation was identified by powder X-ray diffraction (PXRD) method using a X'Pert pro panalytical diffractometer using nickel-filtered Cu-Kα radiation (λ=0.15418 nm) as source and operated at 40 kV and 30 mA. The sample was scanned in the 2θ ranging from 10° to 80° at room temperature. Single crystal XRD data of the grown $LiInSe_2$ crystal was obtained using Bruker Kappa APEXII single

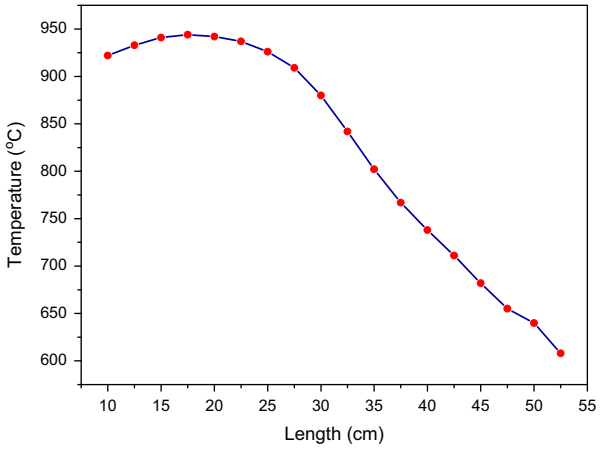

Fig. 1. Axial temperature profile of the growth furnace.