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Modified Bridgman growth and properties of mid-infrared $LiInSe_2$ crystal

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ABSTRACT

A mid-infrared $LiInSe_2$ (LISe) single crystal was successfully grown by the modified vertical Bridgman technique with dimensions of about ∅12 mm × 30 mm. A large amount of high purity polycrystalline LISe used for crystal growth was synthesized in one run by a novel two-step synthesis method. The thermal properties of the crystal were carefully investigated by measuring the melting point, specific heat, and thermal diffusivity, and deriving the thermal conductivity. The transmission spectrum showed that the 50% transmittance level extends from 0.65 to 12.6 μm. The excellent thermal conductivity and optical properties indicate that LISe is one of only a few promising candidates for high average power nanosecond OPOs pumped by ~1 μm lasers.

1. Introduction

Coherent and tunable mid-infrared (MIR) lasers are very important for the applications such as LIDAR, laser countermeasures, MIR spectroscopy, and environmental monitoring [1–3]. To achieve high average power and single pulse energy MIR lasers, nanosecond OPO is one of the most promising techniques. However, due to the limitations of phase-matching and transparency range, only a few MIR crystals, such as $AgGaS_2$ (AGS) [4–6], $HgGa_2S_4$ (HGS) [7,8], $LiInSe_2$ (LISe) [9,10], solid solution $Cd_xHg_{1-x}Ga_2S_4$ (CHGS) [11], $CdSiP_2$ (CSP) [12,13], etc., can be pumped by ~1 μm lasers to produce an MIR laser. Although $ZnGeP_2$ (ZGP) [14–16] and $AgGaSe_2$ (AGSe) [17,18] have larger nonlinearities coefficients, they either are not phase matchable for a pump wavelength of ~1 μm or exhibit severe two-photon absorption (TPA) due to their low energy gap. The new chalcopyrite CSP allows for noncritical phase matching with the maximum effective nonlinearity (84.5 pm/V) when pumped by a 1064 nm laser. However, intrinsic multi-photon absorption limits its useful transparency up to 6.5 μm. For lithium-containing chalcogenide NLO crystals, the lighter lithium ions in the structure enlarge the band gap and increase the frequency of the lattice vibrations and thus the Debye temperature, thereby improving the thermal conductivity. This situation favors an increased optical damage threshold, which is very important for high average power laser output. LISe is an excellent lithium-containing chalcogenide NLO crystal. It crystallizes in the β-$NaFeO_2$ structure with *mm*2 point group, and has a superstructure of the wurtzite type [19]. The crystal has excellent properties [20], such as large nonlinear coefficients (d_{33} = −16 pm/V), a wide transparency range (0.50–13 μm), nearly isotropic thermal expansion, large thermal conductivity ~5 $W\,m^{-1}\,K^{-1}$ (~3 times higher than in AGS), a high damage threshold and the ability to be phase-matched over a large wavelength range. Compared to commercially available AGS, the nonlinear coefficients of LISe turn out to be much larger. It is also worth noting that LISe can exhibit noncritical phase matching when pumped by a high power 1064 nm Nd:YAG laser without onset of TPA, which is a unique advantage of LISe for practical applications in MIR technology. Therefore, LISe is a promising candidate for 1.064 μm pumped MIR OPO operation with the advantages of a wider transparency range, larger effective nonlinear coefficient, higher thermal conductivity and larger damage threshold.

Until now, much research has been carried out on crystal growth and the NLO properties of LISe [9,10,21–24]. In order to replace or partly substitute for commercially available AGS for ~1 μm pumped high power nanosecond OPO, there is still a lot of work to be done on LISe. In this paper, the synthesis of polycrystalline LISe, the modified Bridgman growth and the properties of single crystal LISe were investigated. A two-step synthesis method using a high-temperature autoclave was used to synthesize polycrystalline LISe. This novel synthesis method avoids the possible explosion of the quartz ampoule, and a large amount of polycrystalline LISe can be efficiently obtained. The Bridgman growth process was also modified, including remelting at an early stage of crystal growth in order to eliminate extra growth nuclei and in-situ controlling of the growth interface to improve crystal quality.

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2. Experimental

2.1. Synthesis of polycrystalline LISe

Polycrystalline LISe was synthesized from high purity elemental Li (3 N), In (5 N) and Se (5 N) using a two-step synthesis method in the high temperature autoclave. In the first step, binary In_2Se_3 was synthesized by the stoichiometric reactions of elemental In and Se at 760 °C in a sealed silica tube evacuated to 1×10^{-3} Pa. In the second step, Li, In_2Se_3 and Se were used to synthesize LISe. The components were added in proportion to the stoichiometric ratio 1:1:2 with excess of 0.2% Li and 0.5% Se. The mixture of Li, In_2Se_3 and Se was ground and loaded into a specially-polished inner wall graphite crucible under Ar atmosphere in a glovebox. The crucible with charge was enclosed in the high temperature autoclave under a pressure of 1×10^{-3} Pa. The synthesis was carried out in a single-temperature-zone coil furnace, which was controlled by an FP23 temperature controller (SHIMANDEN). A stepwise heating program was designed with temperature maintained at 600 °C and 950 °C for 24 and 48 h, respectively. The crucible was then cooled down to room temperature at a rate of 50 °C/h. This method avoids crucible explosion during the synthesis process. As a result, polycrystalline LISe can be synthesized with high efficiency. In one run, 60–100 g LISe polycrystals were obtained. A synthesized LISe ingot is shown in Fig. 1. It was confirmed to be single-phase, high-purity polycrystalline LISe by XRD characterization.

2.2. Modified Bridgman growth of LISe

LISe single crystals were grown by the modified vertical Bridgman technique. The synthesized polycrystalline LISe powder was enclosed in the polished inner wall graphite crucible. In order to eliminate spurious nucleus formation, the growth crucible was designed with a sharp conical bottom. The charged crucible was then put into an inner carbon-coated quartz ampoule. During vacuum pumping, the quartz ampoule was heated to ~200 °C, in order to eliminate volatiles. The ampoule was sealed under a pressure of 1×10^{-3} Pa. The Bridgman furnace was divided into three zones, i.e. the upper (high-temperature) zone, the gradient zone and the lower (low-temperature) zone. The upper and lower zones were separated by a baffle to produce a temperature gradient. The gradient was controlled by adjusting the baffle and the temperatures of the upper and lower zones. During the growth of LISe, the gradient of the furnace was set to be ~15 °C/cm. The ampoule was initially supported by a silica holder in the hot zone of the furnace. The upper zone was gradually heated up to 950 °C, ~30 °C above the melting point of LISe. The lower zone was simultaneously heated to 850 °C. After the polycrystalline LISe was completely melted, the accelerated crucible rotation technique (ACRT) was used to make the melt homogenous. During crystal growth, one thermocouple was placed near the conical tip of the crucible and another near the LISe melt. Therefore, the crystal growth process could be observed and controlled in situ. This modification is very important for Bridgman crystal growth in an enclosed furnace. For the self-nucleation Bridgman technique, careful control of nucleation is very important in order to obtain a high quality crystal. The thermocouple near the conical tip was used to monitor the in situ nucleation. The process of multiple nuclei remelting was designed to optimize the nucleation, and so a single LISe crystal nucleus was obtained. The ampoule was pulled down at a rate of 0.5–1 mm/h. The growth was completed after the entire crucible had passed through the growth interface. The ampoule was then slowly cooled to room temperature. A LISe single crystal of about 12 mm diameter and 30 mm length was successfully removed from the ampoule. A photograph of typical as-grown crystals with a (020) cleaved facet is displayed in Fig. 2. The different coloring of the crystals is possibly due to different stoichiometric compositions. The colors of the as-grown LISe can vary from colorless to greenish, depending on the growth conditions and initial reagent composition. The color changes are attributed to the defects in crystals, which can be improved by annealing under suitable conditions [20,25].

2.3. Characterization

Single-crystal X-ray diffraction data were collected over the 2θ range from 3.89° to 32.27° using a Bruker APEX2 CCD area-detector diffractometer with graphite monochromated Mo Kα radiation ($\lambda=0.71073$ °) at 70 K. A LISe single crystal with dimensions of $0.23\times0.21\times0.10$ mm^3 was mounted on a glass fiber with epoxy. The structural model was refined using the SHELXL-97 routine. The final refinement included anisotropic displacement parameters and a secondary extinction correction.

The melting point of the LISe crystal was measured using a Mettler-Toledo TGA/DSC1/1600HT Thermal Analyzer in the range of 30–1000 °C. The LISe sample was placed in an Al_2O_3 crucible with Ar gas flowing at a rate of 60 ml/min to avoid oxidation at high temperatures. The heating rate was 10 °C/min.

The specific heat of LISe was measured between 30 °C and 200 °C at a heating rate of 10 °C/min. The thermal diffusivity was measured by the laser flash method using a laser flash apparatus (NETZSCH LFA 447 Nanoflash) over the range from 30 °C to 200 °C. The LISe samples were $4\times4\times1$ mm^3 in size and coated with

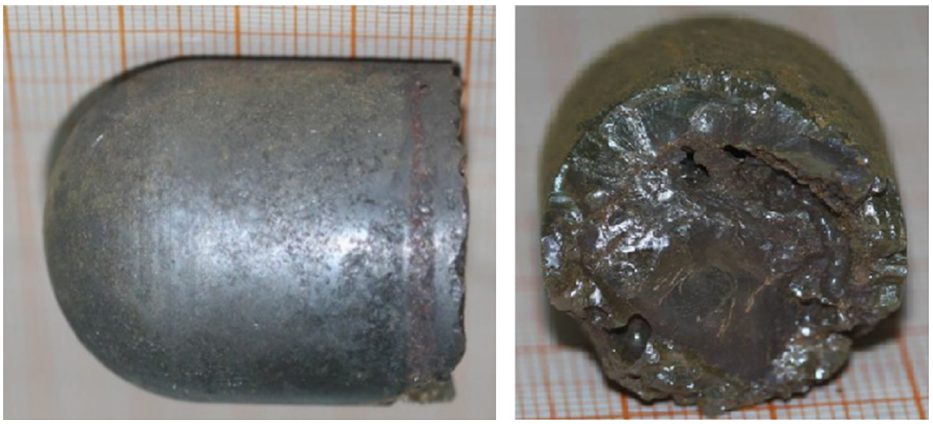

Fig. 1. Photograph of compact polycrystalline LISe ingot (left) and shining cross-section (right).