

Linear optical properties of $\text{LiIn}(\text{S}_{1-x}\text{Se}_x)_2$ crystals and tuning of phase matching conditions

Yu.M. Andreev^a, V.V. Atuchin^{b,*}, G.V. Lanskii^a, N.V. Pervukhina^c,
V.V. Popov^d, N.C. Trocenco^d

^a Laboratory of Ecological Devices, Institute of Monitoring of Climate and Ecological Systems, SB RAS, Tomsk, 634055, Russia

^b Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk, 630090, Russia

^c Laboratory of Crystal Chemistry, Institute of Inorganic Chemistry, SB RAS, Novosibirsk, 630090, Russia

^d Research Division, FGUP GOKB Ametist, 46a, 9 May str., Krasnodar, 350059, Russia

Received 21 January 2005; received in revised form 26 May 2005; accepted 26 May 2005

Available online 15 July 2005

Abstract

LiInSe_2 and mixed $\text{LiIn}(\text{S}_{0.5}\text{Se}_{0.5})_2$ crystals have been grown by vertical Bridgman–Stockbarger method. Optical properties of deep red LiInSe_2 and orange $\text{LiIn}(\text{S}_{0.5}\text{Se}_{0.5})_2$ crystals have been evaluated. The dispersion of refractive indices has been measured and the Sellmeier coefficients have been calculated for LiInSe_2 and $\text{LiIn}(\text{S}_{0.5}\text{Se}_{0.5})_2$ crystals. Linear dependence of the refractive indices on $\text{Se}/(\text{S} + \text{Se})$ ratio has been found in $\text{LiIn}(\text{S}_{1-x}\text{Se}_x)_2$ compounds. The ranges of phase matching possible in $\text{LiIn}(\text{S}_{1-x}\text{Se}_x)_2$ solid solutions for main crystal planes have been calculated with using Sellmeier equations specified for the compounds.

© 2005 Elsevier SAS. All rights reserved.

PACS: 42.70.Mp; 78.20.Ci; 81.10.Fq

Keywords: Refractive index; Sulfide; Selenide; Nonlinear optics

1. Introduction

Orthorhombic crystals LiInS_2 and LiInSe_2 are characterized by very wide transparency range 0.34–13.2 and 0.45–14 μm at zero level, relatively high nonlinear coefficients $d_{31} = 6.2$, $d_{32} = 5.4$ and $d_{31} = 12.2$, $d_{32} = 10.8$ pm/V, reasonable birefringence 0.044 and 0.053 and are promising for effective nonlinear optical interactions in visible—middle infrared (IR) range [1–4]. The compounds are semiconductors with energy band gap strongly dependent on synthesis and growth conditions, for example, the values reported in literature for LiInSe_2 scatter over the range 1.1–2.87 eV according to crystal quality [3,5–7]. Great progress in growing technology during few last years

enables the growth of LiInS_2 and LiInSe_2 crystals with optical quality and dimensions enough for determination of linear and nonlinear optical properties [3,4,8,9]. This opens the possibility for experiments on frequency conversion in the materials [10–14]. Although several nonlinear optical processes have been effectively realized, many characteristics and limitations of LiInS_2 and LiInSe_2 crystals have not been sufficiently explored. In some instances the equations reported for refractive indices dispersion contradict with phase-matching conditions determined in frequency conversion experiments.

In the recent time, for several solid solutions, for example $\text{AgGa}_x\text{In}_{1-x}\text{Se}_2$ and $\text{Hg}_{1-x}\text{Cd}_x\text{Ga}_2\text{S}_4$, the pronounced ability has been demonstrated for tuning such properties as phase matching, thermo-optical properties, damage thresholds, and second order nonlinear susceptibilities by variation of chemical composition [12,13,15–20]. In such a way the conditions of three-wave interactions may be tuned to

* Corresponding author. Institute of Semiconductor Physics, Novosibirsk, 630090, Russia. Tel.: +7 (3832) 343889, Fax: +7 (3832) 332771.

E-mail address: atuchin@thermo.isp.nsc.ru (V.V. Atuchin).

optimum condition with great benefit in frequency conversion efficiency. The solid solutions $\text{LiIn}(\text{S}_{1-x}\text{Se}_x)_2$ are also promising for such tuning effects because, for example, the refractive indices of the edge compounds are strongly different, the values are higher in LiInSe_2 , and the continuous variation of phase matching conditions may be achieved by changing $\text{Se}/(\text{S} + \text{Se})$ ratio in the crystal. In this work we intend to grow the representative compounds from the $\text{LiIn}(\text{S}_{1-x}\text{Se}_x)_2$ family and define the dependence of refractive indices as a function of $\text{Se}/(\text{S} + \text{Se})$ ratio for the solutions. With using the results, the three-wave phase matching will be calculated for several configurations and possible tuning ranges will be estimated.

2. Crystal structures of LiInS_2 and LiInSe_2

Only end members of the family $\text{LiIn}(\text{S}_{1-x}\text{Se}_x)_2$, $x = (0 \div 1)$, LiInS_2 and LiInSe_2 , had been synthesized and observed up to now. Crystal structure of LiInS_2 , space group $\text{P2}_1\text{nb}$, $a = 647.1(1)$ pm, $b = 688.7(1)$ pm and $c = 805.0(1)$ pm, has been determined by single crystal X-ray study [21]. Structure refinement of LiInSe_2 has been produced few later in $\text{Pna}2_1$ space group, $a = 718.3(2)$ pm, $b = 839.8(3)$ pm and $c = 678.1$ pm [22]. From the comparison of the results it is evident that the LiInS_2 and LiInSe_2 crystals are isostructural. As an example, the structure of LiInS_2 is shown in Fig. 1. The structures of both crystals are made of the chains of closely packed InS_4 (InSe_4) and LiS_4 (LiSe_4) tetrahedrons that, seemingly, defines good chemical stability of the compounds. The In–S and Li–S bond lengths are in the ranges 243.7(2)–246.3(2) pm and 237.3(2.5)–259.3(6.7) pm and In–Se and Li–Se bond lengths lie in the ranges 255.5(3)–257.7(3) pm and 249.1(5.4)–262.2(3.6) pm in LiInS_2 and LiInSe_2 respectively. So, the complete substitution of Se for S in the compounds results only in some swelling of the basic building units without principal transformation of the crystal lattice framework. This feature gives

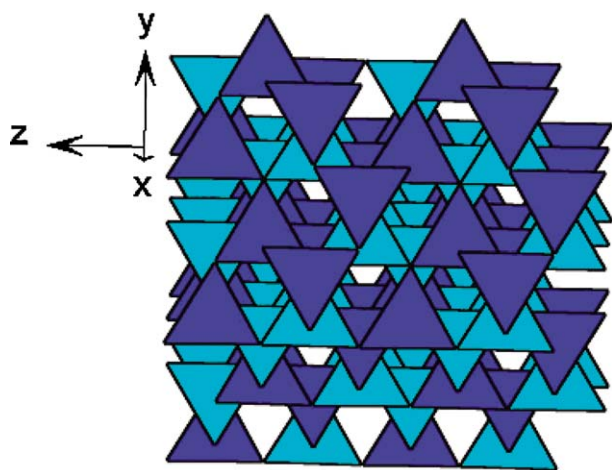


Fig. 1. Crystal structure of LiInS_2 . Alternating InS_4 and LiS_4 tetrahedrons are shown by light and dark colours.

reasonable promise for existence of a continuous set of the solid solutions $\text{LiIn}(\text{S}_{1-x}\text{Se}_x)_2$, $x = (0 \div 1)$, without loss of optical quality for intermediate compositions.

3. Crystal growth and experimental methods

The single crystals $\text{LiIn}(\text{S}_{1-x}\text{Se}_x)_2$, $x = 0.5, 1$, have been grown by vertical Bridgman–Stockbarger method. The elementary reagents were used for starting charge preparation. The purity of starting chemicals was 99.999% for S, Se and 99.9% for In and Li. Elementary S and Se were initially purified by distillation and metallic Li and In were purified by directed crystallization. Weight ratios of the charges were prepared with some difference from the stoichiometric composition. Excess quantity of Li was added into the charge to compensate losses of the element during subsequent post-growth annealing in Se vapor. The charges were capsulated into fused silica ampoules, protected by pyrolytic carbon layer on the inner side to guard against the contact with the melt. The crystals were grown in the ampoules 18 mm in diameter. During $\text{LiIn}(\text{S}_{0.5}\text{Se}_{0.5})_2$ growth the temperature gradient in the furnace was $12^\circ\text{C}/\text{cm}$ and pulling rate was kept as 0.5 mm/day. For LiInSe_2 the parameters were $20^\circ\text{C}/\text{cm}$ and 6 mm/day. Under the conditions the optical grade crystals with the length up to 50 mm were yielded. The color of the resulted crystals was deep red for LiInSe_2 and light-orange for $\text{LiIn}(\text{S}_{0.5}\text{Se}_{0.5})_2$.

The dispersion of the refractive indices n_i ($i = x, y, z$) has been evaluated with minimum deviation method in the spectral range $0.5\text{--}12\ \mu\text{m}$ [23,24]. The prisms with working faces of 10×10 mm and refractive angles $17\text{--}25^\circ$ were used for the measurements. As a result, the Sellmeier equations have been obtained for LiInSe_2 and mixed $\text{LiIn}(\text{S}_{0.5}\text{Se}_{0.5})_2$ crystals. The dispersion of principle refractive indices was fitted by the polynomial $n^2 = A_1 + \sum A_{2j+1}/(A_{2j} - \lambda^2)$ ($j = 1, 2$) where λ is a wavelength taken in micrometers.

4. Results and discussion

Transparency spectrum of $\text{LiIn}(\text{S}_{0.5}\text{Se}_{0.5})_2$ crystal is shown in Fig. 2. The transparency range measured for LiInSe_2 crystal has been reported earlier [25]. The Sellmeier parameters evaluated for $\text{LiIn}(\text{S}_{1-x}\text{Se}_x)_2$, $x = 0.5, 1$, together with available literature results are shown in Table 1. Up to now three different sets of Sellmeier's equations has been defined for LiInS_2 . The most accurate set seems to be reported in Ref. [14], when two-pole dispersion equations were refitted with accounting experimental phase matching conditions. Also three different sets of Sellmeier's parameters are presently known for LiInSe_2 . The reasonable source of the difference may be small variations in stoichiometry of the crystals grown by different manufacturers. This effect has been earlier detected and discussed for both LiInS_2 and LiInSe_2 [9,28]. To define the optimal set of dispersion equations for LiInSe_2 , it is reasonable to compare theoretical phase matching diagrams with available experimental

Download English Version:

<https://daneshyari.com/en/article/10636798>

Download Persian Version:

<https://daneshyari.com/article/10636798>

[Daneshyari.com](https://daneshyari.com)