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ADP012643

TITLE: Characterization of LiInS₂ and LiInSe₂ Single Crystals for Nonlinear Optical Applications

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Characterization of LiInS_2 and LiInSe_2 single crystals for nonlinear optical applications

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ABSTRACT

X-ray structural analysis, nuclear magnetic resonance, optical spectroscopy and second harmonic generation were used to characterize the new nonlinear crystals LiInS_2 and LiInSe_2 which possess maximum band gap (3.59 and 2.86 eV at 300 K, respectively) among ternary chalcogenides. As grown crystals are only slightly colored while color change after annealing is due to native point defects.

INTRODUCTION

Only few suitable nonlinear crystals are available for generation of coherent radiation tunable in the mid-IR (3 to 20 μm), a spectral region of great importance for vibrational molecular spectroscopy and atmospheric sensing. An active search for new nonlinear crystals for this region is in progress now. The new materials that can be successfully added to this limited list of crystals are LiInS_2 and LiInSe_2 (further LIS, LISe, respectively). The first one was first studied by Boyd and co-workers in the 70-ies [1], and has recently enjoyed renewed interest because of its attractive optical properties, such as the large transparency range from 0.35 to 13 μm and the high (estimated at 10.6 μm [1]) nonlinear susceptibility $d_{33}=15.8 \text{ pm/V}$. No information about the nonlinearity of LISe was available, but it was expected to be higher. Problems with growth of the LiInS_2 and LiInSe_2 crystals were solved recently and large crystals of high optical quality became available [2,3]. One of the typical features of ternary compounds is considerable variation of their color depending on growth or annealing conditions. Taking into account that such coloration can be due to phase transitions and affect strongly the main output parameters including nonlinear efficiency, we studied LIS and LISe samples of different color using several structurally sensitive techniques: X-ray structural analysis, nuclear magnetic resonance (NMR), frequency conversion (nonlinear susceptibility and phase-matching conditions) and optical spectroscopy and showed that color variations can be due to point defects.

EXPERIMENTAL DETAILS AND DISCUSSION

Samples: Crystal growth and annealing

The bulk LIS and LISe crystals were grown by the Bridgman-Stockbarger technique on (001) and (010) seeds. Details of LIS growth were given in [2], the growth techniques for LISe is very similar. Special attention is paid to ratios between components in the charge. A correction of the stoichiometric $\text{Li:In:S (Se)}=1:1:2$ ratios is made taking into account different stability of the

elements to weight loss during the runs because of volatilization and interaction between melt and container walls. An additional post-growth thermal treatment in chalcogen vapor at temperature close to melting point is performed to remove the small opaque inclusions of different phases. The as-grown samples are almost colorless for LIS or yellow to greenish for LISe. For as-grown samples chemical analysis indicates 1 to 3% deficit of chalcogen relative to metals (Li+In), on the other hand there is 2 to 4% Li deficit relative to In [2]. There are a lot of small inclusions inside as-grown LIS and LISe crystals which make them milky and one uses a high temperature annealing in chalcogen vapor to make samples highly transparent. It is a wide-spread technological treatment which is used for other crystals such as AgGaS_2 or AgGaSe_2 . Indeed, chemical analysis shows up to 3% surplus S or Se [2] after annealing, but in contrast to the mentioned compounds LIS and LISe change their color considerably: Annealed LIS is rose and LISe becomes dark red to opaque. Since the phase diagram can be very complicated for ternary compounds and the area of homogeneity related to a certain phase is sometimes only about 1 w.% in width, it is necessary to verify that the crystal structure remains unchanged after annealing. Thus as-grown and annealed samples of LIS and LISe were compared using different structurally sensitive techniques.

The X-ray structural analysis

The crystal structure determination for different LIS and LISe samples was performed using CAD4 diffractometer along with the SHELXL97 structure determination/refinement program. For all samples investigated identical structure (space group $\text{Pna}2_1$, wurtzite- type lattice) was established, but lattice parameters somewhat varied: they increased in line with color intensity (Table 1).

Table I. Lattice parameters for LiInS_2 and LiInSe_2 single crystals of different color determined in the present work and comparison with Ref.[1,4]

Crystal	LiInS_2			LiInSe_2			
Color	Colorless	Yellowish	Rose	Yellow	Greenish	Rose	Dark red
Space group	$\text{Pna}2_1$	$\text{Pna}2_1$	$\text{Pna}2_1$	$\text{Pna}2_1$	$\text{Pna}2_1$	$\text{Pna}2_1$	$\text{Pna}2_1$
a [Å]	6.874(1) 6.894 [1]	6.890(1)	6.896(1)	7.1917(8)	7.192	7.1939(8)	7.1934(10) 7.218 [4]
b [Å]	8.0332 8.064 [1]	8.053(1)	8.058(2)	8.4116(10)	8.412	8.4163(10)	8.4159(11) 8.441 [4]
c [Å]	6.462(1) 6.485 [1]	6.478(2)	6.484(4)	6.7926(8)	6.793	6.7926(8)	6.7971(9) 6.772 [4]
V [Å ³]	356.82 360.5 [1]	359.43	360.3	410.90(8)	410.97	411.27(8)	411.49(9) 412.6 [4]

Nuclear Magnetic Resonance: LiInSe_2

Both ^7Li ($I=3/2$) and ^{115}In ($I=9/2$) are quadrupole nuclei: their NMR line shape is sensitive to the variations of the structure of compound and to existing defects. Single crystals of LISe $3.5 \times 3.5 \times 5 \text{ mm}^3$ in size were placed into an NMR coil of 5 mm in diameter. The powder samples were prepared also from the same crystals. The ^7Li and ^{115}In spectra were measured with a Tecmag pulse

NMR spectrometer in the applied magnetic field of 8.0196 T (at resonance frequencies 132.68 and 74.84 MHz for ^7Li and ^{115}In nuclei, respectively), using Fourier transformation of the spin echo signals accumulated with the 16-phase cycled sequence. The length of $\pi/2$ pulse was 4 μs for ^7Li and 5 μs for ^{115}In . Angular dependence was measured when the crystals were rotated around their c -axis, which was perpendicular to the applied magnetic field. All samples exhibited very long spin-lattice relaxation time (around 1 h) which is characteristic for high purity compounds.

^7Li and ^{115}In NMR spectra of LiSe single crystals and powders are given in Fig. 1A and Figs. 1B-1C, respectively. Both ^7Li and ^{115}In should show quadrupolar perturbed NMR signals. In single crystal, the NMR spectrum of ^7Li nucleus with $I=3/2$ consists of three lines. Besides a single resonance at Larmor frequency ν_0 , two satellites with the first-order shift of

$$\nu_1 = e^2qQ(3\cos^2\theta - 1)/4h \quad (1)$$

occur. Here q is the electric field gradient (EFG), Q is the quadrupole moment of the nucleus, θ is the angle between applied magnetic field and the principal axis of the EFG tensor, and h is the Planck's constant. The aforementioned satellites are clearly seen in the ^7Li spectrum of single crystal (Fig. 1A). In the powder (Fig. 1B), the central line and the satellites are almost unresolved due to the overlap caused by angular dependence of the resonance frequency given by Eq.(1). For ^{115}In nucleus with $I=9/2$, nine satellites should occur. However, they are hardly excited with our $\pi/2$ pulse, and thus we show and analyze only the central line corresponding to $S \rightarrow -S$ transition.

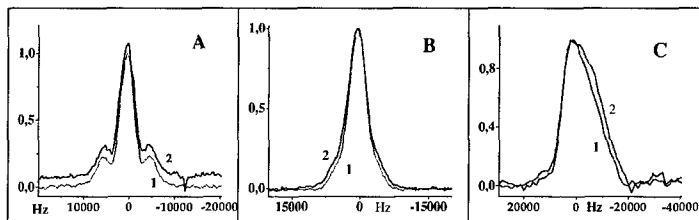


Fig. 1: A. Room temperature ^7Li NMR spectra of single crystal LiInSe_2 corresponding to the maximal splitting of the lines. Orientation of external magnetic field B_0 is: $B_0 \perp c$, angles $(B_0, a) = 22.5^\circ$, $(B_0, b) = 67.5^\circ$ (with accuracy about $2\text{--}3^\circ$). For as-grown (1) and annealed (2) samples, the spectrum of the latter is shifted upwards for clarity. B and C: Room temperature ^7Li and ^{115}In NMR spectra for as-grown (1) and annealed (2) powder LiInSe_2 , respectively.

Line width of the quadrupolar perturbed NMR signals is caused by dipole-dipole interaction of nuclei and distribution of electric field gradients existing in an imperfect crystal. The nearest neighbors of In and Li atoms are Se atoms. Due to the low natural abundance of ^{77}Se isotope (7.6%) having nuclear spin and rather large Li-Li, In-In and Li-In distances (around 4.1 Å), the dipole-dipole interactions among nuclei are weak; their contribution into the second moment of the resonance line is calculated to be around 1 kHz^2 for both ^7Li and ^{115}In . Moreover, the dipole-dipole interactions should be the same for the as-grown and annealed samples. Thus the main contribution to the line width results from the distribution of EFGs, and the difference in the line width is caused by the variation of this distribution in annealing. From Fig. 1B-C, one can see that the powder ^7Li

and ^{115}In NMR spectra of as-grown and annealed LISe are very similar, though the resonance of the annealed sample is a little bit broader. Two reasons are suggested: 1. The EFG distributions on Li and In nuclei are broader in the annealed sample, which is less perfect than the as-grown one. It may be, for example, because surplus Se atoms occupy the unfilled tetra- or octahedral sites of the lattice. Such an imperfection of the crystal creates an additional electric field gradient at nucleus; these gradients vary from site to site and yield additional line broadening. 2. The structural parameters of the two samples are a little bit different, resulting in EFG values larger in the annealed sample than in the as-grown one. Such effect would lead to a difference in the quadrupole splitting of the NMR spectra of the two crystals, which is not obtained in the single crystalline spectra (Fig.1A). Thus one can conclude that both as-grown and annealed LiInSe_2 samples have identical crystal structure and the negligible differences in NMR spectra can be related to point defects such as surplus Se ions in different positions in crystal lattice.

Optical absorption spectroscopy

Optical transmission spectra in the whole transparency region were recorded, using Shimadzu UV-3101 UV/VIS/NIR and Bomem FTIR spectrometers(Fig.2). Both shortwave and longwave

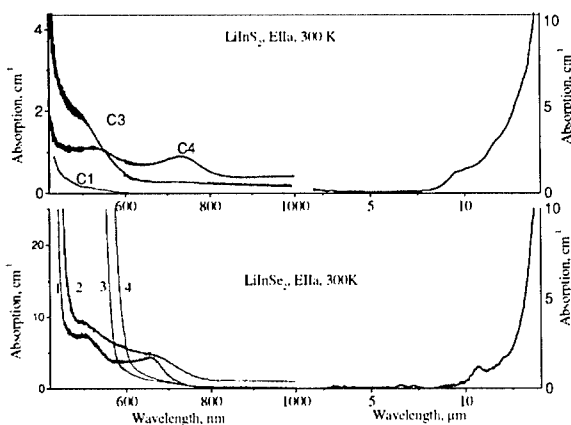


Fig.2 Absorption spectra for LIS(A) and LISe(B). In A: C1 and C4 are as-grown LIS samples; C3 was annealed [2]. In B spectra 1,2 were obtained for yellow as grown LISe and 3,4 correspond to a dark red sample. Spectra 1,3 and 2,4 were recorded at 80 K and 300 K, respectively.

edges of transparency region are important for crystal characterization. The latter is determined by lattice vibrations and one can see in Fig.2 that both for LIS and LISe it is identical in shape and position for as-grown and annealed crystals. The shortwave absorption edge characterizes band-to-band electronic transitions: in real crystals the near-edge absorption bands due to native defects mask it usually and this is the reason why thin samples, less than 0.1 mm thick are studied. For LIS this work has been reported in [2]. In both as-grown colorless and annealed rose samples the absorption spectra were found to become straight lines in $(\alpha \cdot h\nu)^2 = f(h\nu)$ coordinates and to lead

to identical band gap: $E_g = 3.72$ and 3.59 eV at 80 and 300K, respectively. The rose color of thick annealed LIS samples was due to broad bands at 420 and 540 nm [2]. For as-grown LISe the same approach gave $E_g = 3.04$ and 2.86 eV at 80 and 300K [5], respectively, but for annealed samples some additional intense bands with maxima in the 500 to 550 nm range superimpose the fundamental edge even at 0.1 mm thickness and it was necessary to decrease the thickness further. As a result annealed thin plate is red in color. It is important to note that illumination by a visible light with $\lambda \sim 400$ -500 nm from 1kW Xe lamp through MDR2 diffraction monochromator was found to remove the red color of annealed LiInSe_2 crystals and to make them yellow, the effect being reversible. Such effects are typical of the recharge of point defects in solids.

Refractive indices, phase-matching and nonlinearity

For yellow and rose LIS samples tensor components of $d_{15} = 8.35$ pm/V and $d_{24} = 8.3$ pm/V were deduced both from precise gaussian beam analysis of the SHG process and also by relative measurements [6]. These values are only slightly lower than estimations based on non-phase matched methods presented in [1] at $10.6 \mu\text{m}$ ($d_{31} = 9.9$ pm/V and $d_{32} = 8.6$ pm/V, $d_{31} = d_{15}$ and $d_{32} = d_{24}$ under Kleinman symmetry). Study of the second harmonic generation for LIS showed practically identical phase-matching conditions for as-grown and annealed samples (Fig.3) which confirms that refractive indices and their dependence on wavelength are similar for these samples. Thus their structure is also the same. Some difference from [1] is likely to be due to variations in growth conditions and differences in real structure.

Refractive indices of as-grown and annealed LISe samples were measured for n_x and n_z using conventional technique of minimum deviation angles with one and the same prism which was

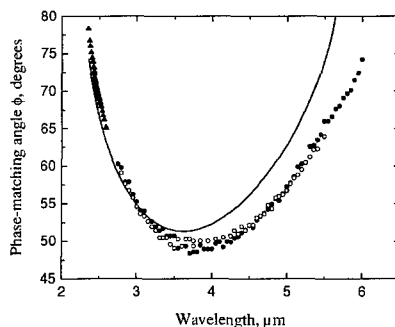


Fig.3 Measured internal phase-matching angles for the as-grown (open dots) and annealed LIS (solid dots), obtained using a free electron laser [6]. The solid triangles were measured for annealed, rose LIS with a nanosecond OPO as the pump source. The line is the calculated phase-matching curve based on Boyd's refractive index data [1].

annealed after the first stage of experiments. The indices obtained before and after annealing are given in Table 2 and one can see that they are identical within the experiment accuracy. Nonlinear parameters were measured only for as-grown LISe samples to date: they are 1.26-1.56 times higher

than those for LIS [3]. Investigation of LISe phase-matching conditions and nonlinear parameters is in progress.

Table II. Comparison of refractive indices for LiInSe₂

λ , nm	Yellow-greenish LiInSe ₂		Dark red LiInSe ₂	
	n_x	n_z	n_x	n_z
700	2.3627	2.4215	2.3615	2.4219
800	2.3341	2.3886	2.3347	2.3752
900	2.3130	2.3656	2.3138	2.3662
1000	2.3004	2.3507	2.3006	2.3513
1500	2.2704	2.3188	2.2709	2.3186
1900	2.2619	2.3082	2.2619	2.3090

CONCLUSIONS

Combined investigation of as-grown and colored annealed LIS and LISe crystals using X-ray structural analysis, NMR, optical absorption spectroscopy, refractive indices and phase matching conditions showed the identity of their structure and of main physical properties, which allows to associate the coloration at annealing in chalcogen vapor with native point defects: Both as-grown and annealed samples are feasible for nonlinear optical applications.

ACKNOWLEDGEMENTS

This work was partially supported by the European Community INCO-COPERNICUS program (grant No ERBIC15-CT98 0814), ISTC and CRDF (grant RE2-2222, proposal 6410).

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