Anisotropic Thermal Expansion and Electronic Structure of LiInSe

Victor V. Atuchin 1,2,3,4,*, Ludmila I. Isaenko 6,7, Sergei I. Lobanov 6,7, Alina A. Goloshumova 6,7, Maxim S. Molokeev 8,9,10, Zhaoming Zhang 11, Xingyu Zhang 12, Xingxing Jiang 12 and Zheshuai Lin 12,13

Abstract: Optical quality cm-sized LiInSe 2 crystals were grown using the Bridgman–Stockbarger method, starting from pure element reagents, under the conditions of a low temperature gradient of 5–6 degrees/cm and a slight melt overheating. The phase purity of the grown crystal was verified by the powder XRD analysis. The thermophysical characteristics of LiInSe 2 were determined by the XRD measurements in the temperature range of 303–703 K and strong anisotropy of the thermal expansion coefficients was established. The following values of thermal expansion coefficients were determined in LiInSe 2: \( \alpha_x = 8.1 \) (1), \( \alpha_y = 16.1 \) (2) and \( \alpha_z = 5.64 \) (6) MK\(^{-1}\). The electronic structure of LiInSe 2 was measured by X-ray photoelectron spectroscopy. The band structure of LiInSe 2 was calculated by ab initio methods.

Keywords: LiInSe 2; crystal growth; thermal expansion; band structure; XPS; DFT

1. Introduction

Complex chalcogenide compounds have interesting structural, chemical, and physical properties, and the materials are widely applied in modern optical and electronic technologies [1–10]. Among such compounds, the crystals with general composition LiMX 2 (M = Al, In, Ga; X = S, Se, Te) have attracted particular research interests because of their valuable combination of optical and electronic characteristics, including thermal and chemical stabilities, wide transparency range, appropriate nonlinear optical coefficients, birefringence values and optical damage thresholds [2,11–18]. From the structural point of view, two main structure types are known for compounds LiMX 2, as listed in Table 1 [19–25]: type I, space group \( Pna2_1 \), is observed in sulfides and selenides and type II, space group \( I-42d \), is common in tellurides. Moreover, the formation of trigonal high-temperature modification, space group \( P3m1 \), was detected for LiAlTe 2 [25]. All these structures are without inversion center, and accordingly, the materials are characterized by valuable combinations of attractive physical properties [26]. As of now, the LiMX 2 crystals are widely applied for...
the optical frequency conversion in visible-IR spectral ranges [2,15,27–34] and as a working medium in neutron detectors [35–39]. Accordingly, high-quality single crystals are urgently needed and the growth technology should be further developed to provide large-sized low-defect LiMX₂ materials.

Table 1. Structural types known in compounds LiMX₂ (M = Al, In, Ga; X = S, Se, Te).

| M   | S   | Se   | Te   |
|-----|-----|------|------|
| In  | P21nb (Pna₂₁) [19] | Pna₂₁ [23] | I-42d [24] |
| Ga  | Pna₂₁ [20,21] | Pna₂₁ [21,22] | I-42d [21] |
| Al  | Pna₂₁ [25] |  | I-42d and P3m1 [25] |

The thermal and thermophysical characteristics of LiMX₂ materials are of great importance in the single crystal growth to avoid crystal cracking and defect generation [12,17,18,40–42]. However, such information is scarce in the literature and, in some cases, is doubtful. The thermophysical parameters earlier reported for LiMX₂ crystals are summarized in Table 2 [43–46]. As it is seen, the behavior of type I and type II crystals is principally different, and in tellurides, the thermal expansion along crystallographic direction c is negative on heating. Comparatively, in sulfides and selenides, thermal expansion is positive in all crystallographic directions with increasing temperature. However, a detailed analysis of the thermophysical parameters is complicated by the following obstacles. As for the practically valuable LiInSe₂, the thermal expansion coefficients were measured only in one study and a contradiction is found in the reported values [43]. The possible error ranges given in Figure 5 of [43] are above the integrated effect over the considered temperature range. At the same time, the possible error ranges reported for the numerical values of thermal expansion coefficients seem to be reasonable (Table 2). Moreover, the atomic mechanism of the thermal expansion in type I LiMX₂ crystals has not been considered up to now. To avoid the uncertainty, the present work is aimed at the precise determination of the structural parameters of LiInSe₂ on temperature using both experimental and theoretical methods, including a detailed analysis of thermal expansion mechanism. To attain this, a high-quality single crystal of LiInSe₂ was grown by the developed technology and its structural parameters and electronic structure were determined. The electronic structure was observed in parallel by X-ray photoelectron spectroscopy (XPS) and theoretical methods, where XPS is extremely sensitive to the chemical state of the crystal surface and the theoretical model is a powerful tool to consider the relations between the crystal structure and physical properties.

Table 2. Thermal expansion coefficients of LiMT₂ (M = Ga, In; T = Se, Te) crystals.

| Compound   | Type | αₐ MK⁻¹ | αₐ MK⁻¹ | α₉ MK⁻¹ | αV MK⁻¹ | Reference |
|------------|------|---------|---------|---------|---------|-----------|
| LiGaTe₂    | II   | 19.1    | 19.1    | −8.6    | 29.4    | [45]      |
| LiGa₀.₅₅In₀.₄₅Te₂ | II   | 18.9    | 18.9    | −5.7    | 32.3    | [46]      |
| LiGa₀.₅₄In₀.₄₆S₂ | I    | 11.7    | 15.8    | 12.7    |         | [44]      |
| LiInS₂     | I    | 8.9     | 16.1    | 6.6     |         | [2]       |
| LiInSe₂    | I    | 11.5 ± 1.7 | 20.4 ± 2.4 | 8.9 ± 2.4 |         | [43]      |
| LiInSe₂    | I    | 8.1 (1) | 16.1 (2) | 5.64 (6) | 29.9 (3) | This work |

2. Experimental Methods

LiInSe₂ crystals were grown using the Bridgman–Stockbarger method, as described in [12]. Li (3N, Novosibirsk Chemical Concentrates Plant, Novosibirsk, Russia), In (5N, Alfa Aesar GmbH, Haverill, MA, USA), and Se (5N, Rechem, Moscow, Russia) were used as starting materials. The melting point of the batch was about 915 °C. Since chalcogenide compounds contain volatile components and chemically aggressive lithium, the synthesis and growth were carried out in glass-graphite containers. In the process of chalcogenide compound synthesis and crystal growth, incongruent evaporation takes place at tempera-
tures above the melting point [47–50]. As a result, there is a deviation of the composition from the stoichiometric one, but it can be reduced under the conditions of a low temperature gradient at the crystallization front and a small excess pressure in the ampoule. Deviation from stoichiometry is the cause of spot defects and changes in the LiInSe$_2$ sample color from greenish and yellow to red with the variation of cell parameters [51]. In the first group, the crystal composition is close to stoichiometric composition with lithium and selenium vacancies ($V_{Li}$, $V_{Se}$). The presence of $In_{Li} + 2V_{Li}^-$ interatomic substitution with a charge compensator and interstitial Se$_i$ atoms leads to an increase in red color intensity [52]. In this work, in contrast to the methodology described in [12], the crystals were grown under the conditions of a low gradient of 5–6 degrees/cm and a slight melt overheating (no more than 50 degrees above the melting point). The grown boules were annealed at 800 °C for 2 h. As a result, yellowish single crystals up to 17 mm in diameter 40 mm long of high optical quality were obtained (Figure 1). The applied method of crystal growth under the low thermal gradient conditions makes it possible to improve the crystal homogeneity along the ingot length and reduce the number of inclusions in the crystal volume. At the 5 cm$^{-1}$ absorption level, the transparency range for the crystal is 0.47–13 µm.

![Figure 1. Digital image of the LiInSe$_2$ crystal.](image)

The powder diffraction data of LiInSe$_2$ were collected at room temperature with a Bruker D8 ADVANCE powder diffractometer (Cu-Kα radiation) and a linear VANTEC detector. The step size of 2θ was 0.016°, and the counting time was 1.5 s per step. The 2θ range of 10–70° was measured with a 0.6 mm divergence slit, while the 2θ range of 70–140° was measured with a 2 mm divergence slit. Larger slits allow a noticeably increased intensity of high-angle peaks without the loss of resolution because the high-angle peaks are broad enough not to be affected by a more diverged beam. The esd’s σ ($I_i$) of all points on patterns were calculated using intensities $I_i$: \[ \sigma (I_i) = I_i^{1/2} \]. The intensities and obtained esd’s were further normalized: \[ I_{norm} = I_i \times 0.6/(slit \ width), \sigma_{norm} (I_i) = \sigma (I_i) \times 0.6/(slit \ width), \] taking into account the actual divergence slit width value, which was used to measure each particular intensity $I_i$, and saved in xye-type file. Such transformed powder XRD patterns can be viewed in the whole 2θ range of 10–140°, but all high-angle points have small esd’s. To prepare the powder sample for the XRD measurements, a piece of LiInSe$_2$ crystal was ground with the help of mortar and pestle.

The XPS analysis was performed in ultra-high vacuum with a VGESCALAB 220i-XL system employing a monochromatic Al Kα (1486.6 eV) X-ray source. The X-ray gun was operated at 120 W, and the spectrometer pass energy was set at 20 and 100 eV for regional and survey scans, respectively. The diameter of the area under analysis was approximately
500 µm, and the probed surface layer thickness was ~5 nm. A low-energy electron flood gun was used to neutralize the surface charge buildup. The binding energies (BEs) were calibrated by fixing the saturated hydrocarbon component of the C 1s peak at 285.0 eV. The peak fitting of the overlapping Li 1s and Se 3d region was performed using the CasaXPS software package [53]. The XPS measurements were carried out for a single crystal sample.

3. Computation Methods

First-principles band structure and lattice dynamics properties were calculated to analyze the thermal behavior of LiInSe$_2$. The calculation was carried out by CASTEP [54], a package based on the plane-wave pseudopotential density functional theory [55]. The functions developed by the Perdew, Burke, Emzerhof (PBE) [56] in the form of generalized gradient approximation (GGA) [57] were chosen to describe the exchange-correlation interaction, and optimized norm-conserving pseudopotentials [58] were adopted to model the effective interaction between the atomic cores and the valence electrons. To guarantee the precise calculation, the cutoff energy was set as 800 eV and the energy convergence tolerance for a self-consistent field calculation was set as $1 \times 10^{-8}$ eV/atom. The intensive Monkhorst–Pack k-point meshes [59] spanning less than 0.07 Å$^{-3}$ were chosen. The phonon characters were calculated by the linear response mechanism [60]. To get the phonon modes contribution to the thermal expansion of the respective axis, the phonon frequency was first calculated on the optimized structure with the cell parameter fixed on the experimental values at 303 K. Then, the respective axis was stretched to the experimental values at 703 K, and the phonon frequency was calculated. Finally, the Gruneisen parameter (g) was calculated by the formula $g = (V/\Delta V) \times (\Delta \omega / \omega)$.

4. Results and Discussion

Rietveld refinement was performed by using TOPAS 4.2 [61] which accounts esd’s of each point by a special weight scheme. All peaks were indexed by an orthorhombic cell (Pnma2$_1$) with parameters close to those previously reported for LiInSe$_2$ [23], and the refinement was stable resulting in low R-factors (Table 3, Figure 2). The obtained coordinates of atoms and main bond lengths are listed in Supplementary Materials, Tables S1 and S2, respectively, and the crystal structure is presented in Figure 3. To get the information on the temperature dependence of the unit cell parameters (Figure 4), 22 X-ray patterns in the 2θ range of 5–120° were collected from 303 to 723 K with 20 K step: (303, 323, 343, 363, 383, 403, 423, 443, 463, 483, 503, 523, 543, 563, 583, 603, 623, 643, 663, 683, 703, and 723 K) spending 35 min for each pattern (Figure S1). At each selected point, the temperature was fixed and controlled with precision of ±0.2 °C during the pattern measurement. The powder pattern recorded at 723 K showed a large amount of impurity and pattern intensities were not stable during the experiment. So, we stopped at this temperature because the sample decomposition was observed. Almost all peaks of all patterns were indexed by LiInSe$_2$, besides small amount of impurity peaks (Figure S1) marked by asterisk (appeared at 623 K and increased their intensities under further heating) and arrow (appeared at 503 K and disappeared at 663 K). These impurity phases were not identified, but their appearance did not influence the main phase cell parameter refinement. One can see that all $a$, $b$, and $c$ cell parameters and the cell volume of the main phase LiInSe$_2$ increase upon heating. Therefore, LiInSe$_2$ has thermal expansion behavior along all crystallographic directions. The related thermal expansion coefficients of LiInSe$_2$ are reported in Table 2. As it is seen in Figure 5, the thermal expansion coefficients of LiInSe$_2$ remain nearly constant with increased temperature. It should be pointed that the thermal expansion of LiInSe$_2$ is strongly anisotropic, and the ratio $\alpha_b / \alpha_c$ is as high as ~2.9.
Table 3. Main parameters of processing and refinement of the LiInSe₂ sample.

| Compound | LiInSe₂ |
|----------|---------|
| Sp. Gr.  | Pna2₁   |
| a, Å     | 7.20442 (7) |
| b, Å     | 8.42826 (8) |
| c, Å     | 6.80491 (6) |
| V, Å³    | 413.199 (7) |
| Z        | 4       |
| 2θ-range, ° | 10–140   |
| R exp, % | 5.63    |
| R p, %   | 4.71    |
| R exp, % | 2.67    |
| χ²       | 2.11    |
| R B, %   | 2.16    |

Figure 2. Observed, calculated (using the Rietveld method) and difference XRD patterns obtained for the LiInSe₂ sample.

Figure 3. Crystal structure of LiInSe₂. Unit cell is outlined. Lone atoms are omitted for clarity.
Figure 4. Cell parameter dependence on temperature: (a) $a(T)$, (b) $b(T)$, (c) $c(T)$, and (d) $V(T)$. 
Figure 5. Thermal expansion coefficient dependence on temperature.

The X-ray photoelectron survey spectrum recorded from LiInSe$_2$ is shown in Figure 6. Besides the photoemission and Auger lines of the constituent elements, two low intensity C1s and O1s peaks were also detected. These “foreign” species are attributed to the presence of adventitious hydrocarbons and hydroxyl groups adsorbed from the ambient environment and the results of surface chemical reaction with oxygen-bearing components of the air. The detailed regional spectra were measured for the valence band and all elemental core levels detected in the survey spectrum. The overlapping spectral region of the Li 1s core level and the Se 3d doublet is shown in Figure 7. Comparing our results with those published for LiGaSe$_2$ [62] and LiGa$_{0.5}$In$_{0.5}$Se$_2$ [63], it is obvious that the spectral resolution in the current study is much better as the overlapping peaks are partially resolved in our study in contrast to the single symmetric peak observed in the previous studies. Owing to the superior resolution, it is possible for us to determine the BE values of the Li 1s, Se 3d$_{5/2}$, and 3d$_{3/2}$ components by employing the curve fitting procedure in CasaXPS [53]. After background subtraction, all three components were fitted with a mixed 50% Gaussian—50% Lorentzian peak. To improve the reliability of curve-fitting, the intensity ratio of the two Se spin-orbit splitting peaks, I (3d$_{5/2}$)/I (3d$_{3/2}$), was fixed to the theoretical value of 1.5 (i.e., ratio of the respective degeneracies 2j + 1), and the amount of the spin-orbit splitting was fixed to be 0.85 eV (based on the value reported in a high resolution XPS study of a single crystal CuInSe$_2$ [64]), but no other constraints were imposed. The In 3d doublet region is presented in Figure 8. The energy positions of the constituent element core levels and Auger lines observed for LiInSe$_2$ are presented in Table 4 (based on the C 1s level being fixed at 285.0 eV). In Table 5, our XPS results of LiInSe$_2$ are compared to those of the representative LiMX$_2$ crystals, with their electronic structures reported in the literature [45,62,63,65]. As mentioned above, the overlapping peaks of Li 1s and Se 3d were not resolved for LiGaSe$_2$ [62] or LiGa$_{0.5}$In$_{0.5}$Se$_2$ [63]. Therefore, the reported BE for the combined Li 1s/Se 3d peak is an overestimation for the actual value of Se 3d and underestimation of the actual value of Li 1s in [62,63]. Nevertheless, a reasonable agreement is evident, especially given the possibility of differential charging effects.

The experimental XPS spectrum obtained for the valence band of LiInSe$_2$ is displayed in Figure 9. For comparison, the first-principles electronic density of state (DOS) and partial density of state (PDOS) projected in the electronic orbitals of the constituent atoms are also shown. Because the inner-shell electrons were excluded in the electronic structure calculations, the XPS spectrum and DOS/PDOS are exhibited only for the valence electrons. A good agreement is reached between the experimental and calculated spectra, especially for the energy position of the respective electronic orbitals, indicating the validity of the plane-wave pseudopotential method for the studied crystal. The measured spectrum is slightly broadened compared to the calculated results, which might be attributed to the thermal effect, as well as instrumental broadening associated with the experiment. From the calculated PDOS, the feature of anionic crystal for LiInSe$_2$ can be clearly deduced: almost all the electronic orbitals are strongly localized and the hybridization with the others is very small.
Figure 6. Survey X-ray photoelectron spectrum of LiInSe₂.

Figure 7. Detailed XPS spectrum of the Se 3d and Li 1s region in LiInSe₂.

Figure 8. Detailed XPS spectrum of the In 3d doublet in LiInSe₂.
Table 4. Core level binding energies and Auger lines in LiInSe$_2$.

| Line                  | Binding Energy, eV |
|-----------------------|--------------------|
| In 4d$_{5/2}$         | 18.06              |
| In 4d$_{3/2}$         | 18.93              |
| Se 3d$_{5/2}$         | 54.04              |
| Se 3d$_{3/2}$         | 54.89              |
| Li 1s                 | 54.97              |
| Se L3M45M45           | 179.95             |
| C 1s                  | 285.0 (fixed)      |
| O 1s                  | 531.46             |
| In 3d$_{5/2}$         | 444.60             |
| In 3d$_{3/2}$         | 452.15             |
| In M4N45N45           | 1078.70            |

Table 5. BE values of representative core levels measured in LiMX$_2$ materials.

| Crystal         | Ga 3d | Li 1s | In 3d$_{5/2}$ | S 2p | Se 3d$_{5/2}$ | Te 3d$_{5/2}$ | Ref.     |
|-----------------|-------|-------|---------------|------|---------------|---------------|----------|
| LiGaS$_2$       | 20.1  | 55.3  | -             | 162.0| -             | -             | [65]     |
| LiGaSe$_2$      | 19.72 | 54.23 | *             | -    | 54.23 *       | -             | [62]     |
| LiGaTe$_2$      | 19.3  | 55.0  | -             | -    | -             | 572.3         | [45]     |
| LiGa$_{0.5}$In$_{0.5}$Se$_2$ | 18.26 | 54.23 | *             | 444.82| 54.23 *       | -             | [63]     |
| LiInSe$_2$      | -     | 54.97 | 444.60        | -    | 54.04         | -             | This study |

* superposition (Li 1s + Se 3d). ** superposition (Ga 3d + In 4d). Note that values reported in [45] were shifted by +0.2 eV due to their C 1s level being fixed at 284.8 eV, and values in [62,63,65] were shifted by +0.4 eV because their C 1s level was fixed at 284.6 eV.

Figure 9. Comparison of the experimental XPS spectrum and ab initio calculated distributions of electronic states.

The anharmonicity of lattice vibration phonon is the principal source of thermal expansion of solids. To shed light on the mechanism of the thermal expansion anisotropy in LiInSe$_2$, Grüneisen constant, the parameter that characterizes the phonon anharmonicity was calculated. Accordingly, no imaginary frequency is observed in the phonon spectrum, which demonstrates the dynamical stability of LiInSe$_2$. According to the Grüneisen–constant-colored phonon dispersion, one can see that for all the three axes, the phonon modes in the range of 250–300 cm$^{-1}$ have the maximum Grüneisen constants (Figure 10a–c), i.e., maximum phonon anharmonicity. This suggests that these phonon modes make the major contribution to the thermal expansion along all the three modes. By subtracting the Grüneisen constants along the maximum (c-axis) and minimum (a-axis) thermal expansion
coefficient, the phonon modes accounting for the thermal expansion anisotropy can be obtained. Accordingly, as shown in Figure 10d, the modes with the largest Grüneisen constant difference are mainly located around 260 cm\(^{-1}\). Atomic vibrational assignment reveals that these modes mainly arise from the vibration of lithium atoms, and this demonstrates that lithium atoms play a key role in determining the thermal expansion anisotropy in LiInSe\(_2\).

**Figure 10.** (a–c) The phonon dispersion of the structure with the perturbation of axes \(a\), \(b\), and \(c\), respectively, in which the Grüneisen values of different vibration mode were presented by the color from blue to red. (d) The phonon dispersion of the structure at 303 K, in which the subtracted Grüneisen values of \(a\)-axis and \(c\)-axis were presented by the color from blue to red. The inset in (d) is the graphic vibration mode of around 260 cm\(^{-1}\), and the vibration vectors are shown as blue arrows.

5. Conclusions

In this study, a big-sized high-quality LiInSe\(_2\) crystal was grown by the developed Bridgman–Stockbarger method. The anisotropic thermal expansion behavior of the LiInSe\(_2\) crystal was measured for the first time. Combining the experimental characterization and theoretical calculations, the huge thermal expansion anisotropy was attributed to the vibration of lithium atoms. In addition, the electronic structure of LiInSe\(_2\) crystal was measured by XPS and the recorded valence band is in a good agreement with the theoretical electronic density of states. Moreover, the Grüneisen parameters were also calculated in the theory to reveal the dominant source of the thermal expansion anisotropy. These results indicate that LiInSe\(_2\), besides its well-known pronounced linear and nonlinear optical properties in the IR spectral range, possesses specific structural effects.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27165078/s1, Figure S1: X-ray patterns collected from 303 to 703 K. The major impurity peaks appeared under heating are marked by asterisk and arrow; Table S1: Fractional atomic coordinates and isotropic displacement parameters (Å\(^2\)) of LiInSe\(_2\); Table S2: Main bond lengths (Å) of LiInSe\(_2\).
Author Contributions: Conceptualization, V.V.A. and X.J.; methodology, L.I.I., S.I.L. and X.Z.; software, M.S.M., X.Z. and X.J.; formal analysis, M.S.M., Z.Z., X.Z. and X.J.; investigation, S.I.L. and A.A.G.; data curation, M.S.M. and Z.Z.; writing—original draft preparation, V.V.A., L.I.I., M.S.M., Z.Z. and X.Z.; writing—review and editing, V.V.A., L.I.I. and X.J.; supervision, Z.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was partly supported by the Ministry of Education and Science of the Russian Federation (grant FSUS-2020-0036), state assignment of IGM SB RAS (preliminary crystal charge composition analysis), Russian Science Foundation (grants #19-12-00085-P, crystal growth, and 21-19-00046, conceptualization), National Scientific Foundations of China (Grants 51702330, 11974360 and 51872297), the Young Elite Scientist Sponsorship Program by CAST (YESS), and the CAS Project for Young Scientists in Basic Research (Grants YSBR-024) and the Government of the Russian Federation (075-15-2022-1132). The XPS measurements were carried out at the Surface Analysis Laboratory of the University of New South Wales, Sydney, Australia.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are available on request to authors.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds are not available from the authors.

References

1. Ohmer, M.C.; Goldstein, J.T.; Zelmon, D.E.; Saxler, A.W.; Hegde, S.M.; Schunemann, P.G.; Pollak, T.M. Infrared properties of AgGaTe2, a nonlinear optical chalcopyrite semiconductor. J. Appl. Phys. 1999, 86, 94–99. [CrossRef]

2. Fossier, S.; Salaün, S.; Magin, J.; Bidault, O.; Theotoul, L.; Zondy, J.-J.; Chen, W.; Rotermund, H.; Petrov, V.; Petrov, P.; et al. Optical, vibrational, thermal, electrical, damage, and phase-matching properties of lithium thiostannate. J. Opt. Soc. Am. B 2004, 21, 1981–2007. [CrossRef]

3. Yin, W.; Feng, K.; He, R.; Mei, D.; Lin, Z.; Yao, J.; Wu, Y. BaGa2MO6 (M = Si, Ge; Q = S, Se): A new series of promising IR nonlinear optical materials. Dalton Trans. 2012, 41, 5653–5661. [CrossRef] [PubMed]

4. Reshak, A.H.; Kityk, I.V.; Parasyuk, O.V.; Kamarudin, H.; Auluck, S. Influence of replacing Si by Ge in the chalcogenide quaternary sulfides AgGa2Si(Ge)Se4 on the chemical bonding, linear and nonlinear optical susceptibilities, and hyperpolarizability. J. Phys. Chem. B 2013, 117, 2545–2553. [CrossRef] [PubMed]

5. Coughlan, C.; Ibañez, M.; Dobrozhano, O.; Singh, A.; Cabot, A.; Ryan, K.M. Compound Copper Chalcogenide Nanocrystals. Chem. Rev. 2017, 117, 5865–6109. [CrossRef] [PubMed]

6. Sengar, B.S.; Garg, V.; Kumar, A.; Awasthi, V.; Kumar, S.; Atuchin, V.V.; Mukherjee, S. Band alignment of Cd-free (Zn, Mg)O layer with Cu2ZnSn(S,Se)4 and its effect on the photovoltaic properties. Opt. Mater. 2018, 84, 748–756. [CrossRef]

7. Yelisseyev, A.P.; Molokeev, M.S.; Jiang, X.; Krinis, P.G.; Isaenko, L.I.; Lin, Z. Structure and Optical Properties of the Li2In2Se6 Crystal. J. Phys. Chem. C 2018, 122, 17413–17422. [CrossRef]

8. Yelisseyev, A.; Lobanov, S.; Molokeev, M.; Zhang, S.; Pugachev, A.; Lin, Z.; Vedenyapin, V.; Kurus, A.; Khamoyam, A.; Isaenko, L. A new nonlinear optical selenide crystal AgLiGa2Se4 with good comprehensive performance in mid-infrared region. Adv. Opt. Mater. 2020, 9, 2001856. [CrossRef]

9. Azarapin, N.O.; Aleksandrovsky, A.S.; Atuchin, V.V.; Gavriloa, T.A.; Krylov, A.S.; Molokeev, M.S.; Mukherjee, S.; Oreshkov, A.S.; Andreev, O.V. Synthesis, structural and spectroscopic properties of orthorhombic compounds BaLnCuS2 (Ln = Pr, Sm). J. Alloy. Compd. 2020, 832, 153134. [CrossRef]

10. Garg, V.; Sengar, B.S.; Siddharth, G.; Kumar, S.; Atuchin, V.V.; Mukherjee, S. Insights into the sputter-instigated valence plasmon oscillations in CIGSe thin films. Surf. Interfaces 2021, 25, 101146. [CrossRef]

11. Petrov, V.; Yelisseyev, A.; Isaenko, L.; Lobanov, S.; Titov, A.; Zondy, J.-J. Second harmonic generation and optical parametric amplification in the mid-IR with orthorhombic biaxial crystals LiGaSe2 and LiGaAs2. Appl. Phys. B 2004, 78, 543–546. [CrossRef]

12. Isaenko, L.; Vasilyeva, I.; Merkulov, A.; Yelisseyev, A.; Lobanov, S. Growth of new nonlinear crystals LiMX2 (M = Al, In, Ga; X = S, Se, Te) for the mid-IR optics. J. Cryst. Growth 2005, 275, 217–223. [CrossRef]

13. Andreev, Y.; Atuchin, V.; Lanskiy, G.; Pervukhina, N.; Popov, V.; Trocenco, N. Linear optical properties of LiIn(S1−xSex)2 crystals and tuning of phase matching conditions. Solid State Sci. 2005, 7, 1188–1193. [CrossRef]

14. Isaenko, L.; Krinis, P.; Vedenyapin, V.; Yelisseyev, A.; Merkulov, A.; Zondy, A.J.-J.; Petrov, V. LiGaTe2: A New Highly Nonlinear Chalcopryite Optical Crystal for the Mid-IR. Cryst. Growth Des. 2005, 5, 1325–1329. [CrossRef]

15. Petrov, V.; Zondy, J.; Bidault, O.; Isaenko, L.; Vedenyapin, V.; Yelisseyev, A.; Chen, W.; Tyazhev, A.; Lobanov, S.; Marchev, G.; et al. Optical, thermal, electrical, damage, and phase-matching properties of lithium selenoindate. J. Opt. Soc. Am. B 2010, 27, 1902–1927. [CrossRef]
16. Kato, K.; Petrov, V.; Umemura, N. Sellmeier and thermo-optic dispersion formulas for LiInSe2. *Appl. Opt.* 2014, 53, 1063. [CrossRef]

17. Drebushchak, V.A.; Isaenko, L.I.; Lobanov, S.I.; Kriutsyn, P.G.; Grazhdannikov, S.A. Experimental heat capacity of LiInSe2, LiGaSe2, and LiGaTe from 180 to 460 K. *J. Therm. Anal.* 2017, 129, 103–108. [CrossRef]

18. Kure, A.; Yelisseyev, A.; Lobanov, S.; Pulyusin, P.; Molokeev, M.; Solovyev, L.; Samoshkin, D.; Stankus, S.; Melnikova, S.; Isaenko, L. Thermophysical properties of lithium thiogallate that are important for optical applications. *RSC Adv.* 2021, 11, 39177–39187. [CrossRef]

19. Kish, Z.Z.; Kanishecheva, A.S.; Mikhailov, Y.N.; Lazarev, V.B.; Semrad, E.E.; Peresh, E.Y. Synthesis and crystal structure of lithium thiogallate. *Dokl. Akad. Nauk. SSSR* 1985, 280, 398–401.

20. Leal-Gonzalez, J.; Melibary, S.; Smith, A. Structure of lithium gallium sulfide, LiGaS2. *Appl. Phys. Lett.* 2010, 96, 201102. [CrossRef]

21. Isaenko, L.; Yelisseyev, A.; Lobanov, S.; Titov, P.; Petrov, V.; Zonyd, J.-D.; Kriutsyn, P.; Merkulov, A.; Vedenyapin, V.; Smirnova, J. Growth and properties of LiGa2X (X = S, Se, Te) single crystals for nonlinear optical applications in the mid-IR. *Cryt. Res. Technol.* 2003, 38, 379–387. [CrossRef]

22. Kuriyama, K.; Nozaki, T. Single-crystal growth and characterization of LiGaSe2. *J. Appl. Phys.* 1981, 52, 6441–6443. [CrossRef]

23. Neumann, H.; Hönle, W.; Kuhn, G. Die Kristallstruktur von LiInSe2. *Z. Anorg. Allg. Chem.* 1986, 543, 161–168.

24. Kühn, G.; Schumann, B.; Oppermann, D.; Neumann, H.; Sobotta, H. Preparation, structure, and infrared lattice vibrations of LiInTe2. *Z. Anorg. Allg. Chem.* 1985, 531, 61–66. [CrossRef]

25. Kim, J.; Hughbanks, T. ChemInform Abstract: Synthesis and Structures of New Ternary Aluminum Chalcogenides: LiAlSe2, α-LiAlTe2, and β-LiAlTe2. *ChemInform* 2000, 39, 3092–3097. [CrossRef]

26. Kidyarov, B.I.; Atuchin, V.V. Universal crystal classification system “Point symmetry—Physical property”. *Ferroelectrics* 2007, 360, 96–99. [CrossRef]

27. Huang, J.-J.; Atuchin, V.; Andreev, Y.M.; Lanskii, G.; Pervukhina, N. Potentials of LiGa(S2-xSe2x)2 mixed crystals for optical frequency conversion. *J. Cryst. Growth* 2006, 292, 500–504. [CrossRef]

28. Tyazhev, A.; Marchev, G.; Vedenyapin, V.; Kolker, D.; Yelisseyev, A.; Lobanov, S.; Isaenko, L.; Zonyd, J.; Petrov, V. LiInSe2 nanosecond optical parametric oscillator tunable from 4.7 to 8.7 μm. *Proc. SPIE* 2010, 7582, 75820E.

29. Takeya, K.; Takemoto, Y.; Kawayama, I.; Murakami, H.; Matsukawa, T.; Yoshimura, M.; Mori, Y.; Tonouchi, M. Terahertz emission from coherent phonons in lithium ternary chalcopyrite crystals illuminated by 1560 nm femtosecond laser pulses, EPL 91, *Eur. Lett.* 2010, 91, 20004. [CrossRef]

30. Beutler, M.; Rimke, I.; Büttner, E.; Petrov, V.; Isaenko, L. Femtosecond mid-IR difference-frequency generation in LiInSe2. *Opt. Mater. Express* 2013, 3, 1834–1838. [CrossRef]

31. Isaenko, L.; Yelisseyev, A.; Lobanov, S.; Vedenyapin, V.; Kriutsyn, P.; Petrov, V. Properties of LiGa0.5In0.5Se2: A Quaternary Chalcogenide Crystal for Nonlinear Optical Applications in the Mid-IR. *Crystals* 2016, 6, 85. [CrossRef]

32. Wang, S.; Dai, S.; Jia, N.; Zong, N.; Li, C.; Shen, Y.; Yu, T.; Qiao, J.; Gao, Z.; Peng, Q.; et al. Tunable 7–12 μm picosecond optical parametric amplifier based on a LiInSe2 mid-infrared crystal. *Opt. Lett.* 2017, 42, 2098–2101. [CrossRef] [PubMed]

33. Dai, S.-B.; Jia, N.; Chen, J.-K.; Shen, Y.; Yang, S.; Li, Y.-J.; Liu, Q.; Yang, F.; Zong, N.; Wang, Z.-M.; et al. Picosecond mid-infrared optical parametric amplifier based on LiInSe2 with tenability extending from 3.6 to 4.8 μm. *Opt. Express* 2017, 25, 12860–12866. [CrossRef]

34. Kata, K.; Petrov, V.; Miyata, K. Phase-matching properties of LiIn(S2-xSe2x)2. *Proc. SPIE* 2020, 11264, 112641W.

35. Tupitsyn, E.; Bhattacharya, P.; Rowe, E.; Matei, L.; Groza, M.; Wiggins, B.; Burger, A.; Stowe, A. Single crystal of LiInSe2 semiconductor for neutron detector. *Appl. Phys. Lett.* 2012, 101, 202101. [CrossRef]

36. Egner, J.C.; Groza, M.; Burger, A.; Stassun, K.G.; Buliga, V.; Matei, L.; Bodnarik, J.G.; Stowe, A.C.; Prettyman, T.H. Integration of a 6LiInSe2 thermal neutron detector into a CubeSat instrument. *J. Astronom. Telescopes Instrum. Syst.* 2016, 2, 046001. [CrossRef]

37. Belushkin, A.V.; Bogdzel, A.A.; Goloshumova, A.A.; Isaenko, I.L.; Lobanov, S.I.; Milkov, V.M.; Tarasova, A.Y.; Yelisseyev, A.P. Study of LiInSe2 Single Crystals for the Thermal Neutron Detection. *Synchrotron Neon Tech.* 2020, 48, 1–14. [CrossRef]

38. Lukosi, E.; Hamm, D.; Preston, J.; Hausladen, P.; Brune, C.; Massey, T.; Jacobs, D.; Burger, A.; Stowe, A. First evaluation of fast neutron imaging with LiInSe2 semiconductors. *Nucl. Phys. Methods Res. Sect.* 2020, 200, 976, 164254. [CrossRef]

39. Matei, L.; Hawrami, R.; Buliga, V.; Babolola, S.; Duff, M.C.; Inabnet, L.; Baldwin, T.; Janeska, A.; Burger, A. Lithium indium diselenide—An advanced material for neutron detection. *Nucl. Instrum. Methods Phys. Res. Sect.* 2021, 2020, 165898. [CrossRef]

40. Jia, N.; Wang, S.; Gao, Z.; Wu, Q.; Cai, Z.; Zhang, X.; Yu, T.; Lu, Q.; Tao, X. Optimized Growth of Large-Sized LiInSe2 Crystals and the Electric–Elastic Properties. *Cryst. Growth Des.* 2017, 17, 5875–5880. [CrossRef]

41. Grazhdannikov, S.A.; Kriutsyn, P.G.; Kurus’, A.F.; Isaenko, L.I.; Yelisseyev, A.P.; Molokeev, M.S. LiGaTe2 (LGT) nonlinear crystal: Synthesis and crystal growth processes exploration. *Mater. Sci. Semicond. Process.* 2017, 72, 52–59. [CrossRef]

42. Jia, N.; Xiong, X.; Wang, S.; Yu, T.; Han, B.; Qiao, J.; Li, C.; Tao, X. Optimized oriented seed growth and optical properties of high-quality LiInSe2 crystals. *CrytEngComm* 2018, 48, 7802–7808. [CrossRef]

43. Yelisseyev, A.P.; Drebushchak, V.; Titov, A.S.; Isaenko, I.L.; Lobanov, S.I.; Lyapunov, K.M.; Gruzdev, V.A.; Komarov, S.G.; Petrov, V.; Zonyd, J.-J. Thermal properties of the midinfrared nonlinear crystal LiInSe2. *J. Appl. Phys.* 2004, 96, 3659–3665. [CrossRef]

44. Yang, L.; Jiang, X.-M.; Guo, G.-C. LiGa0.5In0.4S2: A new infrared nonlinear optical material with large laser damage threshold designed by gallium substitution in LiInS2. *Inorg. Chem. Commun.* 2020, 115, 107852. [CrossRef]
45. Atuchin, V.V.; Liang, F.; Grazhdannikov, S.; Isaenko, I.I.; Krinitsin, P.G.; Molokeev, M.S.; Prosvirin, I.P.; Jiang, X.; Lin, Z. Negative thermal expansion and electronic structure variation of chalcopyrite type LiGaTe2. RSC Adv. 2018, 8, 9946–9955. [CrossRef] [PubMed]

46. Krinitsin, P.; Yelisseyev, A.; Jiang, X.; Isaenko, L.; Molokeev, M.; Lin, Z.; Pugachev, A. Growth, structure, and optical properties of nonlinear LiGa0.55In0.45Te2 single crystals. Cryst. Growth Des. 2019, 19, 1805–1814. [CrossRef]

47. Andreev, Y.M.; Atuchin, V.V.; Lanskii, G.V.; Morozov, A.N.; Pokrovsky, L.D.; Sarkisov, S.Y.; Voevodina, O.V. Growth, real structure and applications of GaSe1−xSx crystals. Mater. Sci. Eng. B 2006, 128, 205–210. [CrossRef]

48. Atuchin, V.V.; Golyashov, V.A.; Kokh, K.A.; Korolkov, I.V.; Kozhukhov, A.S.; Kruchinin, V.N.; Makarenko, S.V.; Pokrovsky, L.D.; Prosvirin, I.P.; Romanyuk, K.N.; et al. Formation of inert Bi2Se3(0001) cleaved surface. Cryst. Growth Des. 2011, 11, 5507–5514. [CrossRef]

49. Kokh, K.A.; Atuchin, V.V.; Adichtchev, S.V.; Gavrilova, T.A.; Bakhadur, A.M.; Klimov, A.O.; Korolkov, I.V.; Kuratieva, N.V.; Mukherjee, S.; Pervukhina, N.V.; et al. Cu2ZnSnS4 crystal growth using an SnCl4 based flux. CrystEngComm 2021, 22, 1025–1032. [CrossRef]

50. Vasilyeva, I.G.; Nikolaev, R.E. Non-stoichiometry and point native defects in non-oxide non-linear optical large single crystals: Advantages and problems. CrystEngComm 2022, 24, 1495–1506. [CrossRef]

51. Siemek, K.; Yelisseyev, A.; Horodek, P.; Lobanov, S.; Goloshumova, A.; Belushkin, A.; Isaenko, L. Optical and positron annihilation studies of structural defects in LiInSe2 single crystals. Opt. Mater. 2020, 109, 110262. [CrossRef]

52. Cui, Y.; Bhattacharya, P.; Buliga, V.; Tupitsyn, E.; Rowe, E.; Wiggins, B.; Johnstone, D.; Stowe, A.; Burger, A. Defects in 3LiInSe2 neutron detector investigated by photo-induced current transient spectroscopy and photoluminescence. Appl. Phys. Lett. 2013, 103, 092104. [CrossRef]

53. Fairley, N.; Fernandez, V.; Richard-Plouet, M.; Guillot-Deudon, C.; Walton, J.; Smith, E.; Flahaut, D.; Greiner, M.; Biesinger, M.; Tougaard, S.; et al. Systematic and collaborative approach to problem solving using X-ray photoelectron spectroscopy. Appl. Surf. Sci. Adv. 2021, 5, 100112. [CrossRef]

54. Clark, S.J.; Segall, M.D.; Pickard, C.J.; Hasnip, P.J.; Refson, K.; Payne, M.C. First Principles Methods Using CASTEP. Z. Krist.-Cryst. Mater. 2005, 220, 567–570. [CrossRef]

55. Kohn, W.; Sham, L.J. Self-consistent equations including exchange and correlation effects. Phys. Rev. 1965, 140, A1133–A1138. [CrossRef]

56. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865. [CrossRef]

57. Perdew, J.P.; Chevary, J.A.; Vosko, S.H.; Jackson, K.A.; Pederson, M.R.; Singh, D.J.; Fiolhais, C. Atoms, molecules, solids, and surfaces—Applications of the generalized gradient approximation for exchange and correlation. Phys. Rev. B 1992, 46, 6671–6687. [CrossRef]

58. Hamann, D.R.; Schlüter, M.; Chiang, C. Norm-conserving pseudopotentials. Phys. Rev. Lett. 1979, 43, 1494–1497. [CrossRef]

59. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. Phys. Rev. B 1976, 13, 5188. [CrossRef]

60. Baroni, S.; de Gironcoli, S.; Corso, A.D.; Giannozzi, P. Phonons and related crystal properties from density-functional perturbation theory. Rev. Mod. Phys. 2001, 73, 515–562. [CrossRef]

61. Bruker AXS. TOPAS V4: General Profile and Structure Analysis Software for Powder Diffraction Data—User’s Manual; Bruker AXS: Karlsruhe, Germany, 2008.

62. Lavrentiev, A.; Gabrelian, B.; Vu, V.; Ananchenko, L.; Isaenko, L.; Yelisseyev, A.; Khyzhun, O. Electronic structure and optical properties of noncentrosymmetric LiGaSe2: Experimental measurements and DFT band structure calculations. Opt. Mater. 2017, 66, 149–159. [CrossRef]

63. Lavrentiev, A.; Gabrelian, B.; Vu, T.V.; Isaenko, L.; Yelisseyev, A.; Khyzhun, O. Electronic structure and optical properties of LiGa0.55In0.45Se2 single crystal, a nonlinear optical mid-IR material. Opt. Mater. 2018, 80, 12–21. [CrossRef]

64. Sobol, P.E.; Nelson, A.J.; Schwertfeger, C.R.; Stickle, W.F.; Moulder, J.F. Single crystal CulnSe2 analysis by high resolution XPS. Surf. Sci. Spectra 1992, 2, 1, 393. [CrossRef]

65. Atuchin, V.; Isaenko, L.; Kesler, V.; Lobanov, S. Core level photoelectron spectroscopy of LiGaS2 and Ga–S bonding in complex sulfides. J. Alloy. Compd. 2010, 497, 244–248. [CrossRef]