

Electronic structure and optical properties of noncentrosymmetric LiGaSe₂: Experimental measurements and DFT band structure calculations



A.A. Lavrentyev^a, B.V. Gabrelian^a, V.T. Vu^a, L.N. Ananchenko^a, L.I. Isaenko^{b,c},
A.P. Yelisseyev^b, O.Y. Khyzhun^{d,*}

^a Department of Electrical Engineering and Electronics, Don State Technical University, 1 Gagarin Square, 344010 Rostov-on-Don, Russian Federation

^b Laboratory of Crystal Growth, Institute of Geology and Mineralogy, SB RAS, 43 Russkaya Street, 630090 Novosibirsk, Russian Federation

^c Laboratory of Semiconductor and Dielectric Materials, Novosibirsk State University, 2 Pirogova Street, 630090 Novosibirsk, Russian Federation

^d Frantsevych Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3 Krzhizhanivsky Street, UA-03142 Kyiv, Ukraine

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ABSTRACT

We report on measurements of X-ray photoelectron (XP) spectra for pristine and Ar⁺ ion-irradiated surfaces of LiGaSe₂ single crystal grown by Bridgman-Stockbarger method. Electronic structure of the LiGaSe₂ compound is studied from a theoretical and experimental viewpoint. In particular, total and partial densities of states of LiGaSe₂ are investigated by density functional theory (DFT) calculations employing the augmented plane wave + local orbitals (APW + lo) method and they are verified by data of X-ray spectroscopy measurements. The DFT calculations indicate that the main contributors to the valence band of LiGaSe₂ are the Se 4p states, which contribute mainly at the top and in the upper portion of the valence band, with also essential contributions of these states in the lower portion of the band. Other substantial contributions to the valence band of LiGaSe₂ emerge from the Ga 4s and Ga 4p states contributing mainly at the lower and upper portions of the valence band, respectively. With respect to the conduction band, the calculations indicate that its bottom is composed mainly from contributions of the unoccupied Ga s and Se p states. The present calculations are confirmed experimentally when comparing the XP valence-band spectrum of the LiGaSe₂ single crystal on a common energy scale with the X-ray emission bands representing the energy distribution of the Ga 4p and Se 4p states. Measurements of the fundamental absorption edges at room temperature reveal that bandgap value, E_g, of LiGaSe₂ is equal to 3.47 eV and the E_g value increases up to 3.66 eV when decreasing temperature to 80 K. The main optical characteristics of the LiGaSe₂ compound are clarified by the DFT calculations.

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1. Introduction

Ternary A^IB^{III}C^{VI} and A^{II}B^{IV}C^{VI} compounds have attracted significant attention from technological and scientific viewpoints as very promising optoelectronic materials because of the existence for many of them of both p- and n-type electrical conductivity [1–3] and visible light emission [4–7]. The A^IB^{III}C^{VI} and A^{II}B^{IV}C^{VI} compounds manifest optoelectronic applications as light emitting diodes, nonlinear optical (NLO) materials, solar energy and optical frequency convertors and detectors [8–12]. However, among a big

variety of the above-mentioned ternary compounds intensively investigated since the early 1960s, only several of them, namely AgGaS₂ and AgGaSe₂ (both belonging to the A^IB^{III}C^{VI} family) and ZnGeP₂ (a member of the A^{II}B^{IV}C^{VI} family), have been reported to get down to technological maturity [13,14]. The AgGaX₂ (X = S, Se) and ZnGeP₂ compounds crystallizing in the chalcopyrite-type structures [13], were recognized for many decades, beginning from 1970s [15–18], as the most appropriate NLO materials suitable for frequency conversion of customary lasers to midfar infrared (IR) wavelengths (3–20 μm range) for a number of practical military and civil applications like laser guidance, laser intrusion, atmospheric monitoring, etc. [14]. For many decades, the AgGaX₂ (X = S, Se) and ZnGeP₂ compounds, which possess large NLO coefficients and wide transparency regions in the IR range, have been treated as

* Corresponding author.

E-mail address: khyzhun@ipms.kiev.ua (O.Y. Khyzhun).

the benchmark IR NLO materials applied in different technologies and equipments [14]; however, they expose some disadvantages that confine substantially their practical application. Among them, it is worth mentioning low laser damage threshold values that are characteristic of the AgGaX_2 compounds and two phonon absorption (TPA) effects for ZnGeP_2 applied in the ordinary Nd:YAG and Yb:YAG laser pumping sources [19]. To resolve the mentioned problems, in particular, the replacement of Ag by Li in the AgGaX_2 compounds was found to be a proper way to enlarge their band gaps, thereby to enhance the laser damage thresholds of these materials that is a significant property of laser crystals, and to abolish TPA of the ordinary lasers emitting in the range from 1 to $1.55 \mu\text{m}$ [11,20]. For example, the band gaps have been reported to increase essentially in the sequence $\text{AgGaX}_2 \rightarrow \text{LiGaX}_2$ ($X = \text{S}, \text{Se}$): values of $E_g = 4.15 \text{ eV}$ for LiGaS_2 and $E_g = 3.34 \text{ eV}$ for LiGaSe_2 are essentially bigger than those of AgGaS_2 (2.64 eV) and AgGaSe_2 (1.80 eV) [21].

Among those compounds, lithium gallium diselenide, LiGaSe_2 (LGSe), is of particular concern. LiGaSe_2 crystallizes in the $\beta\text{-NaFeO}_2$ orthorhombic structure within $Pna2_1$ space group (SG), with unit cell parameters $a = 6.833 \text{ \AA}$, $b = 8.227$ and $c = 6.541 \text{ \AA}$, as evidenced from powder X-ray diffraction (XRD) patterns reported by Kuriyama and Nozaki [22]. These results were enforced lately in Ref. [23], where very close values of unit cell parameters, namely $a = 6.832 \text{ \AA}$, $b = 8.237$ and $c = 6.535 \text{ \AA}$, were derived for this compound based on the single-crystal X-ray analysis. In the LiGaSe_2 structure (Fig. 1), Li and Ga atoms are positioned at the two different 4a sites, while two nonequivalent 4a positions are distinctive for the Se atoms. The structure of the LiGaSe_2 compound can be discerned as a three-dimensional framework of the distorted LiSe_4 and GaSe_4 tetrahedra connected to each other by corner sharing. The Li–Se distances in the titled compound are within $2.49261\text{--}2.56508 \text{ \AA}$, while the Ga–Se distances range from 2.38861 to 2.40479 \AA in the case of the LiSe_4 and GaSe_4 tetrahedra, respectively (Fig. 2). The LiGaSe_2 structure is characterized by close hexagonal packing of anions yielding good chemical stability of the compound. The melting temperature of LiGaSe_2 was determined to be $846 \text{ }^\circ\text{C}$, and the compound under consideration reveals no phase transition above room temperature [22]. LiGaSe_2 crystals were found to possess wide transparency ranging from the UV–visible to the mid-IR spectral range ($0.37\text{--}13.2 \mu\text{m}$ at absorption level $\lambda = \text{cm}^{-1}$ [23]), and they reveal appropriate second harmonic generation (SHG) and superior thermo-mechanical properties, which induce them to be attractive for application in deep mid-IR nonlinear devices [13]. The NLO coefficient for LiGaSe_2 was determined as $d_{31} = 9.9 \text{ pm/V@}2.53 \mu\text{m}$, being somewhat bigger than that of LiGaS_2 ($d_{31} = 5.8 \text{ pm/V@}2.53 \mu\text{m}$) [24,25]. Further, possessing a high neutron capture cross section area, ^6Li is known to

have the potential of being a remarkable material for neutron detector production, thereby to make lithium containing semiconductors, especially LiGaSe_2 crystals, to be very promising for their application in thermal neutron detection [26,27].

The enlightenment of peculiarities of the electronic structure of solids and formation of the chemical bonding in them plays a decisive role in understanding and predicting their physical and chemical properties [28]. Therefore, band structure calculations based on density functional theory (DFT) [29] were performed in Refs. [30–33] to elucidate distinctions of filling the valence band and conduction band regions by electronic states associated with Li, Ga and Se atoms in LiGaSe_2 . These results allow for statement that the LiGaSe_2 compound is a direct band semiconductor in which the substantive contributions to the valence band emerge from the Se 4p states mainly in the upper portion of the band, while the bottom of the conduction band is dominated by the Ga 4s and Se 4p states. Further, the strong covalent bonds in the titled compound are formed among the Se 4p, Ga 4s and Ga 4p states [33]. In addition, DFT calculations of the elastic and piezoelectric properties of LiGaSe_2 indicate [33] that this compound is a very promising candidate for piezoelectric applications. Reshak et al. [34] have performed DFT calculations of nonlinear optical susceptibilities of LiGaSe_2 and concluded that lithium gallium diselenide is a good material to be used as matrices for transition metal doping. Moreover, the 2ω and 1ω interband/intraband contributions to the imaginary parts of the SHG tensor $\chi_{333}^2(\omega)$ was found to possess the opposite signs throughout the frequency range of LiGaSe_2 that is promising for application of the titled compound in molecular engineering of crystals with the desirable NLO susceptibilities [34].

Nevertheless, to the best of our knowledge, the electronic structure of LiGaSe_2 has not been studied yet experimentally. To fill this gap, we have made a complex study of the electronic structure and optical properties of the titled compound from both experimental and theoretical points of view. To gain the goals, we have used X-ray photoelectron spectroscopy (XPS) to determine the binding energies (BEs) of core-level electrons of atoms which constitute LiGaSe_2 as well as to measure the XPS valence-band spectrum of the compound under consideration. For this aim, we use optical quality inclusion-free LiGaSe_2 single crystal specially grown for the present experimental studies by the Bridgman-Stockbarger technique. In order to clarify the energy distribution of electronic states of different symmetries of atoms constituting the LiGaGe_2 crystal under study, we calculate total density of states (DOS) and partial densities of states (PDOS) employing the augmented plane wave + local orbitals (APW + lo) method as realized in the WIEN2k package [35]. With the aim of verifying results of the present APW + lo calculations of LiGaSe_2 , as well as those obtained for the titled compound in Refs. [30–33], we have adopted X-ray emission spectroscopy (XES). The latter method is applied to measure the X-ray emission Ga $K\beta_2$ and Se $K\beta_2$ bands giving information about the energy distribution of the valence p-states of Ga and Se, respectively. We have compared the XES Ga $K\beta_2$ and Se $K\beta_2$ bands of LiGaSe_2 on a common energy scale with its XPS valence-band spectrum. We have overseen also the impact of middle-energy Ar^+ ion-irradiation on the XPS spectra of the LiGaSe_2 single crystal surface because this surface treatment is generally applied in epitaxial technologies [36].

Furthermore, it should be indicated that the DFT band structure calculations of LiGaSe_2 were performed in Refs. [30–33] adopting for the exchange-correlation potential either local density approximation (LDA) [37] or generalized gradient approximation (GGA) [38]. It is well-known that band gaps of semiconductors and insulators estimated in DFT band structure calculations carried out within LGA and GGA are generally substantively smaller in comparison with the experimental data because of the discontinuity of

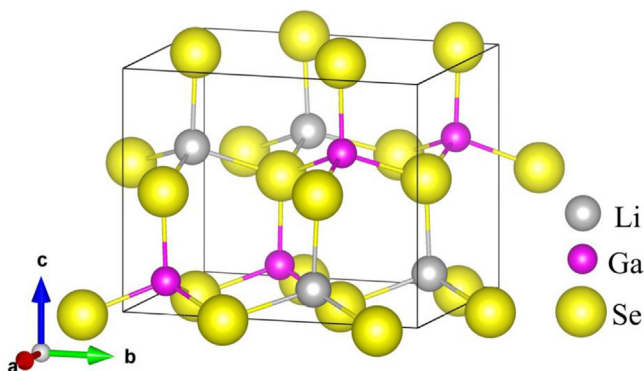


Fig. 1. Crystal structure of LiGaSe_2 (Note: Unit cell is outlined).

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