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Optical Behavior of Boron Doped $GaSe$ Single Crystals in the Visible – NIR Region

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Abstract

Boron-doped $Ga_{1-x}B_xSe$ ($x = 0.3, 0.5\ and\ 1.0\%$) single crystals were successfully synthesized and their optical properties were investigated using UV–Vis spectroscopy. All samples exhibited a sharp absorption edge around $630 - 640\ nm$, indicating dominant band-to-band electronic transitions and preservation of the intrinsic optical characteristics of the $GaSe$ host lattice. The optical band gap values, determined from Tauc analysis assuming a direct allowed transition, showed a slight red shift with increasing boron content, decreasing from $1.963\ eV\ to\ 1.949\ eV$. This minor band gap narrowing is attributed to subtle lattice strain and defect-related effects induced by boron incorporation, while the overall band structure remains largely unchanged. Extinction coefficient analysis revealed low optical attenuation in the near-infrared region, with only weak composition-dependent variations related to sub-bandgap absorption. These results demonstrate that low-level boron doping provides an effective approach for fine-tuning the optical properties of $GaSe$, highlighting the potential of $Ga_{1-x}B_xSe$ crystals for optoelectronic and photodetector applications.

Keywords: solid solution, optical absorption edge, band-to-band electronic transitions, strain-engineered semiconductors.
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1. Introduction

Gallium selenide ($GaSe$) is a layered $III - VI$ semiconductor that has attracted significant attention due to its distinctive crystal structure, anisotropic electronic

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properties, and strong potential for optoelectronic applications [1-3]. $GaSe$ crystallizes in four polymorphic forms—β, γ, δ and ε —among which the $\varepsilon - GaSe$ polytype is thermodynamically stable under ambient conditions and exhibits superior optical characteristics. The $\varepsilon - GaSe$ phase possesses a hexagonal layered structure composed of $Se - Ga - Ga - Se$ atomic sequences within each layer, where strong covalent bonding exists in-plane, while adjacent layers are held together by weak van der Waals interactions. This structural anisotropy enables easy cleavage along the (0001) plane and facilitates the preparation of atomically thin layers suitable for two-dimensional ($2D$) device fabrication [4-8]. The layered nature of $GaSe$ results in pronounced optical and electrical anisotropy, making it one of the most promising candidates for nonlinear optics, photonics, and optoelectronic devices. Bulk $GaSe$ exhibits a moderate band gap of approximately $2.0 - 2.1\ eV$, which increases with decreasing thickness due to quantum confinement effects. Interestingly, unlike conventional transition metal dichalcogenides such as MoS_2 and WS_2, where the band gap narrows as the number of layers decreases, $GaSe$ demonstrates an opposite trend, with a widening of the band gap in its monolayer form. This unique behavior originates from its particular electronic band structure and reduced interlayer coupling, highlighting $GaSe$ as a highly tunable material platform for next-generation optoelectronic technologies. Due to these remarkable features, $\varepsilon - GaSe$ has been widely employed in various optoelectronic devices, including photodetectors, phototransistors, light-emitting devices, frequency converters, and nonlinear optical components. Its high absorption coefficient, large surface-to-volume ratio, excellent photoresponse, and strong second-harmonic generation efficiency make it particularly attractive for high-performance photodetectors operating in the visible and near-infrared spectral regions. Furthermore, the epitaxial compatibility of $\varepsilon - GaSe$ with other $2D$ materials enables the fabrication of ultrathin heterostructures, expanding its application potential in multifunctional optoelectronic systems [9-17].

Despite the outstanding intrinsic properties of $GaSe$, its optical and electronic characteristics can be further tailored through controlled external perturbations such as thickness reduction, mechanical strain, and chemical doping. Among these approaches, doping offers a powerful route for engineering the band structure, lattice dynamics, and carrier recombination processes without altering the fundamental layered framework. In particular, dopant-induced strain and defect modulation have been shown to significantly influence lattice coherence, phonon behavior, and optical absorption characteristics in van der Waals semiconductors [18 – 21]. Boron has emerged as a particularly promising dopant for $GaSe$ due to its exceptionally small atomic radius and strong covalent bonding nature compared to gallium [22]. The substantial size mismatch between boron and gallium atoms is expected to induce localized lattice contraction and internal strain, thereby modifying interlayer coupling and electronic structure without destroying the hexagonal symmetry of the host lattice. At low concentrations, boron incorporation can subtly perturb the crystal lattice, influence phonon dynamics, and introduce localized electronic states near the band edges, while avoiding the formation of secondary phases commonly associated with heavier dopants. Depending on synthesis conditions, boron atoms may substitute Ga sites or occupy interstitial positions, leading to observable changes in structural, vibrational, and optical properties. Although boron doping in $GaSe$ has not been extensively explored—particularly at low concentrations—recent studies on doped layered semiconductors suggest that light-element doping provides an effective strategy for strain-mediated tuning of optoelectronic properties. Most previous investigations of $GaSe$ modifications have focused on transition metal or chalcogen substitutions, leaving the influence of light dopants such as boron relatively unexplored. Addressing this gap is essential for developing a deeper understanding of dopant–lattice interactions in layered chalcogenides.

In this context, the present work focuses on the synthesis and optical characterization of boron-doped $Ga_{1-x}B_xSe$ ($x = 0.3, 0.5\ and\ 1.0\%$) single crystals, with particular emphasis on their UV–Vis optical properties. These compositions were deliberately chosen to remain within the solid solubility limit, ensuring minimal phase segregation while enabling the investigation of subtle compositional and strain-induced effects. UV–Vis spectroscopy was employed to analyze the absorbance behavior, determine the optical band gap using Tauc analysis, and evaluate the extinction coefficient as a function of wavelength. Through a systematic comparison of optical parameters, this study aims to elucidate how low-level boron incorporation influences the optical response of $GaSe$, providing valuable insights for optimizing $Ga_{1-x}B_xSe$ crystals for advanced photodetector and optoelectronic device applications.

2. Synthesis of $Ga_{1-x}B_xSe$ solid solution and Single Crystal Growth

High-purity gallium (99.999%), boron (99.999%), and selenium (99.999%) were used as starting materials. The elements were weighed in stoichiometric ratios corresponding to the nominal compositions $Ga_{1-x}B_xSe$ ($x = 0.3, 0.5$ and 1.0%), with a total batch mass of approximately $15\ g$, and sealed under high vacuum ($\sim 10^{-5}\ Pa$) in pre-cleaned quartz ampoules. The synthesis was carried out by direct melting of the constituent elements in a programmable furnace. To suppress selenium volatilization, a controlled temperature gradient was applied along the ampoule. The charge was gradually heated to $1100\ °C$ and maintained at this temperature for $4h$ to ensure complete melting and chemical homogeneity. After homogenization, the melt was cooled to room temperature at a rate of $50\ °C\ h^{-1}$, yielding dense and uniform polycrystalline ingots. Single crystals were subsequently grown using the horizontal Bridgman technique. The synthesized material was reloaded into evacuated quartz ampoules and directionally solidified at $1100\ °C$ with a translation rate of

$1\ mm\ h^{-1}$ under a temperature gradient of $20 - 25\ ^{\circ}C\ cm^{-1}$. After crystallization, the samples were slowly cooled to room temperature to minimize thermal stress. The obtained $Ga_{1-x}B_xSe$ single crystals exhibited a dark red color and a well-defined layered morphology characteristic of $GaSe$-based materials.

3. Results and discussions

3.1. Absorbance spectroscopy

The UV–Vis absorbance spectra of $Ga_{1-x}B_xSe$ single crystals with boron concentrations $x = 0.3\%, 0.5\%$ and 1.0% were recorded by Specord 250 Plus UV–Vis spectrophotometer across the spectral range of $190 - 1100\ nm$. As shown in Fig. 1(a–c), all samples exhibit high absorbance in the short-wavelength region below approximately $630\ nm$, followed by a sharp decrease in absorbance with increasing wavelength. This abrupt change corresponds to the fundamental optical absorption edge associated with band-to-band electronic transitions. Beyond the absorption edge, in the near-infrared (NIR) region ($\approx 650 - 1000\ nm$), the absorbance significantly decreases and remains at a low level with a weak wavelength dependence. This behavior indicates reduced optical absorption and minimal energy loss in the NIR region. Slight differences in the absorbance background are observed among the samples, suggesting composition-dependent variations in sub-bandgap absorption, which may originate from localized defect states, lattice imperfections, or disorder induced by boron incorporation. Nevertheless, the overall shape and position of the absorption edge remain nearly unchanged, implying that the fundamental optical properties of the $GaSe$ host lattice are preserved for low boron concentrations.

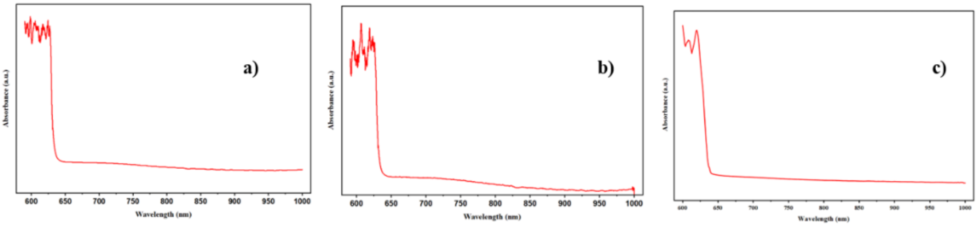

Fig.1. UV–Vis absorbance spectra of $\boldsymbol{Ga_{1-x}B_xSe}$ single crystals with different boron concentrations: (a) $\boldsymbol{x = 0.3\%}$, (b) $\boldsymbol{x = 0.5\%}$, and (c) $\boldsymbol{x = 1.0\%}$.

3.2. Band gap evaluation

The optical band gap (E_g) of $Ga_{1-x}B_xSe$ crystals was determined using the Tauc relation. The absorption coefficient (α) was calculated from the absorbance data, and the Tauc plots were constructed by assuming a direct allowed electronic transition, according to the relation

$$(\alpha h\nu)^2 \propto \left(h\nu - E_g\right), \tag{1}$$

where $h\nu$ is the photon energy. The plots of $(\alpha h\nu)^2$ versus $h\nu$ for all compositions are shown in Fig. 2 (a–c). The linear region near the absorption edge was extrapolated to the energy axis, and the intercept was taken as the optical band gap. The estimated band gap values are found to be $1.963\ eV$, $1.960\ eV$, and $1.949\ eV$ for $x = 0.3\%, 0.5\%$ and 1.0%, respectively. A slight red shift of the band gap with increasing boron content is observed, indicating a small narrowing of the optical band gap [23]. This behavior can be attributed to subtle modifications in the electronic structure caused by boron incorporation, such as local lattice strain, enhanced interlayer coupling, and the presence of defect-related states near the band edges. Despite this minor shift, the band gap values remain close to that of pristine $GaSe$, confirming that the overall band structure is retained at low boron concentrations.

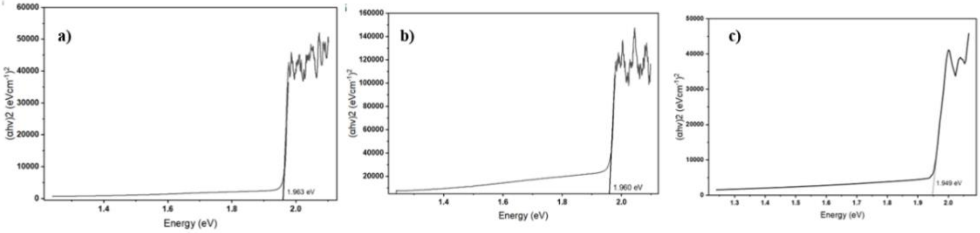

Fig. 2. Tauc plots $(\boldsymbol{\alpha h\nu})^2$ versus photon energy $\boldsymbol{h\nu}$ for $\boldsymbol{Ga_{1-x}B_xSe}$ single crystals with different boron concentrations: (a) $\boldsymbol{x = 0.3}\%$, (b) $\boldsymbol{x = 0.5}\%$, and (c) $\boldsymbol{x = 1.0}\%$.

3.3. Extinction coefficient analysis

The extinction coefficient (k), which represents the attenuation of electromagnetic waves inside the material due to absorption and scattering, was evaluated from the absorption coefficient using the relation

$$k = \frac{\alpha\lambda}{4\pi}, \tag{2}$$

where α is the absorption coefficient and λ is the wavelength of the incident radiation. The extinction coefficient spectra of $Ga_{1-x}B_xSe$ crystals are presented in Fig.3(a–c). For all compositions, relatively high k values are observed in the short-wavelength region below $\sim 630\ nm$, corresponding to strong optical absorption near the fundamental absorption edge. A pronounced decrease in k occurs around $630 - 640\ nm$, which is consistent with the sharp absorption edge observed in the absorbance spectra and confirms the onset of interband electronic transitions. In the NIR region ($\approx 650 - 1000\ nm$), the extinction coefficient reaches a minimum and exhibits a weak, gradual increase with wavelength. The low k values in this region indicate reduced optical losses and weak absorption, which are desirable characteristics for optoelectronic and photodetector applications. The residual extinction in the sub-bandgap region is attributed to localized states, defect-induced absorption, and Urbach tail effects arising from structural imperfections in the crystal lattice. A comparative analysis reveals that while the position of the absorption edge remains nearly unchanged for all boron concentrations, the magnitude of k in the NIR region shows slight composition-dependent variations. In particular, the $x = 0.5\%$ sample exhibits relatively higher k values, suggesting enhanced sub-bandgap absorption, possibly due to increased defect density or local disorder. In contrast, the $x = 0.3\%\ and\ x = 1.0\%$ samples show smoother and lower k profiles, reflecting reduced optical attenuation in the NIR range.

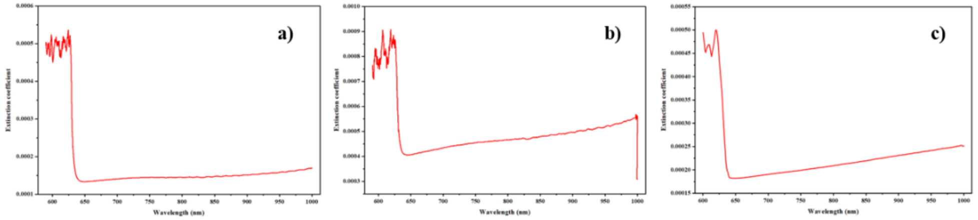

Fig.3. Extinction coefficient ($\boldsymbol{k}$) spectra of $\boldsymbol{Ga_{1-x}B_xSe}$ single crystals with different boron concentrations: (a) $\boldsymbol{x = 0.3}\%$, (b) $\boldsymbol{x = 0.5}\%$, and (c) $\boldsymbol{x = 1.0}\%$.

4. Conclusion

In this work, boron-doped $Ga_{1-x}B_xSe$ ($x = 0.3, 0.5\ and\ 1.0\%$) single crystals were successfully synthesized using the direct melting method followed by horizontal Bridgman crystal growth, and their optical properties were systematically investigated by UV–Vis spectroscopy. The obtained crystals exhibited a well-defined layered morphology characteristic of $GaSe$-based materials, indicating that low-level boron incorporation does not disrupt the intrinsic layered structure. UV–Vis absorbance measurements revealed a sharp optical absorption edge around $630 - 640\ nm$ for all compositions, corresponding to fundamental band-to-band electronic transitions. In the near-infrared region, the absorbance remained low with weak wavelength dependence, indicating reduced optical losses. Minor variations in the sub-bandgap absorbance background suggest the presence of localized defect states or disorder induced by boron incorporation, while the overall optical response of the $GaSe$ host lattice is preserved. The optical band gap values, evaluated using Tauc analysis assuming a direct allowed transition, were found to be $1.963\ eV, 1.960\ eV\ and\ 1.949\ eV\ for\ x = 0.3\%, 0.5\%\ and\ 1.0\%$, respectively. A slight red shift of the band gap with increasing boron concentration was observed, which can be attributed to subtle modifications in the electronic structure arising from local lattice strain, enhanced interlayer interactions, and defect-related states near the band edges. Despite this gradual narrowing, the band gap values remain close to that of pristine $GaSe$, confirming that boron acts as a gentle tuning element rather than a disruptive dopant. The extinction coefficient analysis further supported these findings, showing a pronounced decrease near the absorption edge and low k values in the near-infrared region. The reduced extinction coefficients indicate weak optical attenuation and minimal absorption losses, which are highly desirable for optoelectronic and photodetector applications. Slight composition-dependent variations in the extinction behavior, particularly for the $x = 0.5\%$ sample, were attributed to enhanced sub-bandgap absorption related to localized states and lattice disorder.

Overall, this study demonstrates that low-concentration boron doping provides an effective strategy for fine-tuning the optical properties of $GaSe$ without compromising its fundamental electronic structure. The combination of a well-defined absorption edge, tunable band gap, and low extinction in the near-infrared region highlights the potential of $Ga_{1-x}B_xSe$ single crystals for advanced optoelectronic and photodetector applications. The obtained results offer valuable insights into dopant-induced optical modulation in layered chalcogenides and contribute to the development of strain-engineered van der Waals semiconductors.

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