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# Photoluminescence properties and the influence of the Stark effect of a $ZnIn_2S_4$ crystal doped with Nd

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## Abstract

In this work, the photoluminescence properties of $ZnIn_2S_4$ chalcogenide crystals doped with $Nd^{3+}$ ions were investigated. As a result of spectral measurements carried out in the wavelength range of 550–930 nm, three main emission peak groups corresponding to the internal transitions of $Nd^{3+}$ ions $^4G_{5/2} \rightarrow {}^4I_{9/2}$, $^4F_{9/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ were identified. As a result of increasing the diffraction grating permittivity, a fine structure due to the Stark effect was observed in each of these peaks. Also, lowering the temperature weakened the effect of phonons, leading to a narrowing of the peaks and an increase in the emission intensity. The obtained results demonstrate the high sensitivity of $Nd^{3+}$ ions to crystal field and temperature variations and indicate the prospects of this material in photonic applications.

***Keywords*:** photoluminescence, rare-earth doping, chalcogenide, Stark effect.
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## 1. Introduction

Recently, ternary metal chalcogenide compounds, especially those of the $AB_2X_4$ type (where A and B are metal elements and X is a chalcogen element such as sulfur, selenium or tellurium), have attracted the attention of the scientific community due to their interesting optical and electronic properties. $CdIn_2S_4$, $ZnIn_2Se_4$, $CdGa_2S_4$, $ZnGa_2S_4$ and other similar materials belonging to this group have a wide range of applications and have high potential as semiconductors [1-10]. These compounds are of great importance, especially for use in photocatalysis, solar energy conversion, optoelectronics and sensor technologies. The tunable energy gaps, high photostability and environmental compatibility of these materials make them an alternative to traditional semiconductors [11-19]. One of the compounds belonging to this group, zinc indium sulfide ($ZnIn_2S_4$), occupies an important place due to its light absorption capacity in the visible light spectrum, high chemical stability and environmental safety. Due to its layered crystal structure, $ZnIn_2S_4$ provides effective charge separation and transport, which significantly improves its optical performance [5,18-25]. Optical properties of the $ZnIn_2S_4$ compound, such as light absorption behavior, photoluminescence properties and energy gap, determine the wide application of this material in light energy harvesting and photoelectronic technologies. In addition, the study of the structural structure, morphological features and the effect of external factors such as temperature and pressure on the optical properties of the $ZnIn_2S_4$ material is of great importance in terms of optimizing the functional applications of the $ZnIn_2S_4$ material [26-34]. On the other hand, as is known, rare earth ions have a developed system of electronic states associated with the ground state with forbidden transitions in crystal matrices. Often, such metastable states, which have a duration of milliseconds or more, allow the creation and maintenance of a significant part of the activating ions without resorting to particularly strong excitations. It is known that the photoluminescence of these compounds occurs due to the intra-center transitions of rare earth elements [34-40]. In this regard, $ZnIn_2S_4$:REE type ternary alkaline earth chalcogenide semiconductors are promising. In this research work, the emission properties of the neodymium-doped $ZnIn_2S_4$ compound are systematically investigated, the effect of the changes occurring under the influence of neodymium on the optical behavior is analyzed, and the potential of the material for application in modern optoelectronics is evaluated.

Layered metal chalcogenides show strong sensitivity of their electronic and luminescent properties to defects, impurities, and local crystal-field effects, making doping an effective approach for property modulation [41–48]. In particular, rare earth incorporation can introduce localized 4f states that alter recombination processes and generate additional emission channels [42,49–52]. In $ZnIn_2S_4$, rare earth ions are expected to modify the electronic structure and defect environment, leading to changes in emission intensity, spectral position, and carrier lifetime [53–60]. Neodymium is especially attractive due to its characteristic intra-4f transitions, which produce stable luminescence in the visible and near-infrared regions [35]. Therefore, investigating Nd-doped $ZnIn_2S_4$ provides insight into host–activator interactions and supports the development of efficient optoelectronic materials for light-emitting and energy-related applications.

## 2. Experimental method

Photoluminescence (PL) measurements were carried out using a PL/PLE/Raman spectrometer device manufactured in Japan. The emission of the samples was studied using lasers with different wavelengths: 532 nm (Nd- YAG) and 785 nm. Photoluminescence from the sample was scattered by a grating (100 g/mm−1) monochromator MS 5207 I and MS 3704 I (SOL Instruments, Inc), detected by a CCD multiplier DU 491A-1.7.

$ZnIn_2S_4$ single crystals were obtained by gas phase transport. The initial Zn, In, S and Nd elements (all 99.9% pure) were synthesized as reaction products and placed in a transparent quartz ampoule, which was sealed at a pressure of $1.3 \times 10^{-3}$ Pa. The ampoule was placed in a horizontal furnace, the growth zone was maintained at 940 °C, and the source zone was maintained at 830 °C. The transport process was carried out by diffusion, and the temperature was controlled by a platinum-rhodium thermocouple.

## 3. Results and discussion

In this work, the optical properties of $Nd^{3+}$ ions in a chalcogenide matrix and the factors affecting the internal transitions of these ions were systematically investigated. The photoluminescence (FL) spectra of the $Nd^{3+}$-doped $ZnIn_2S_4$ compound are given in figure 1. Spectral measurements were carried out in the wavelength range of 550–930 nm and three main emission peak groups were observed. These peaks are related to the characteristic 4f-4f $^4G_{5/2} \rightarrow {}^4I_{9/2}$, $^4F_{9/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{9/2}$ internal electronic transitions of $Nd^{3+}$ ions and cover the regions of 584–610 nm, 667–687 nm,880–920 nm, respectively [21,34].

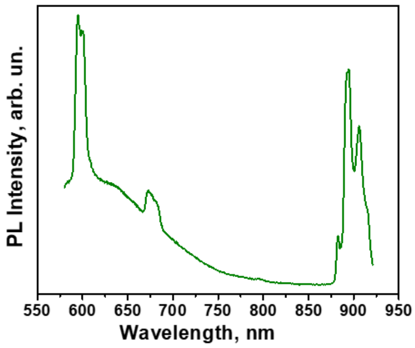

**Figure 1.** PL spectrum of $ZnIn_2S_4$:Nd at room temperature

Initially, the transitions were observed as two, one and three narrow peaks, respectively. As a result of increasing the resolution of the diffraction grating, the presence of a fine structure in each of these peaks became clearly visible. This is due to the splitting of energy levels due to the influence of the internal electric field created by the crystal field (Stark effect). When neodymium ions are located in a chalcopyrite crystal, the electric field there (asymmetric local field) can split the energy levels of the ion.

Figures 2a, 2b and 2c show the fine structure and temperature dependence of the photoluminescence peaks in the wavelength regions of 584–610 nm, 667–687 nm and 880–920 nm. Accordingly, the first peak is split into eight, the second peak into six and the third peak into seven fine peaks. These observations are the result of the interaction of $Nd^{3+}$ ions with local symmetry and defects in the crystal field. In particular, the presence of chalcogen vacancies and other structural defects in the material increases the depth of this splitting.

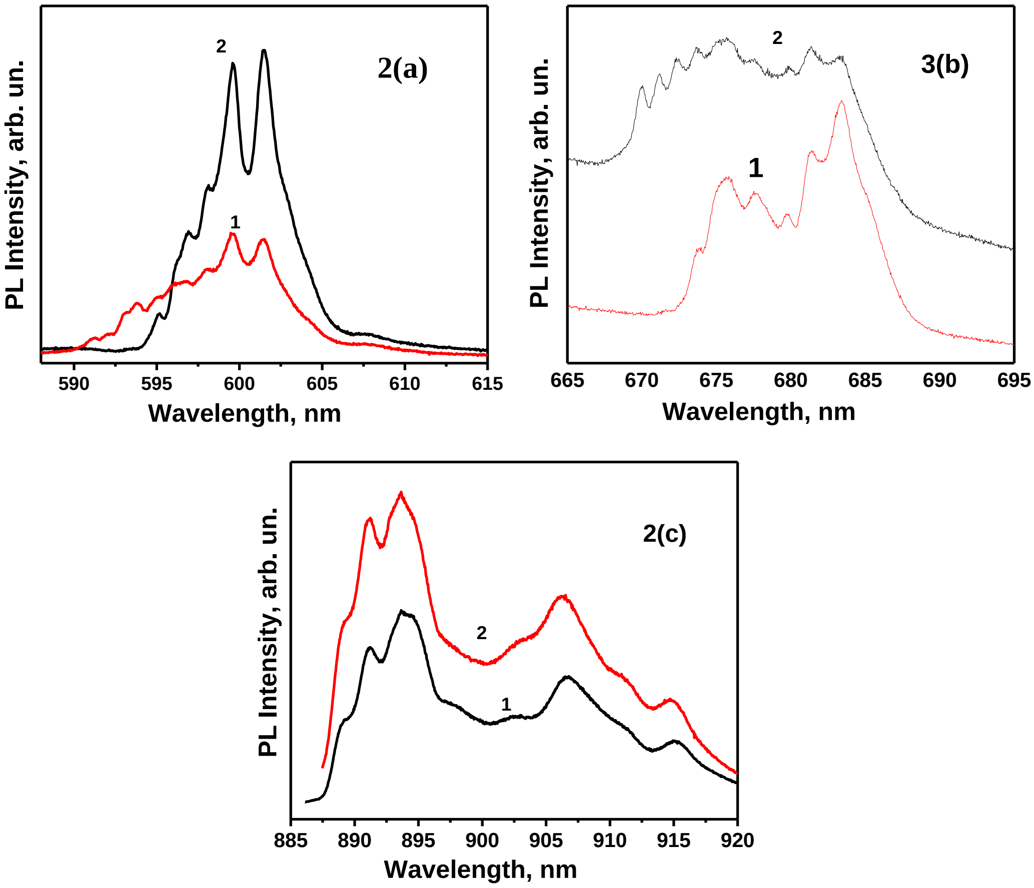

**Figure 2.** PL spectrum of $ZnIn_2S_4$:Nd at different temperature(1-50K, 2-300K)

In the next stage of the experiment, the effect of temperature on the photoluminescence peaks was investigated. Lowering the temperature reduces the number of phonons and weakens the radiationless relaxation processes, which resulted in further thinning of the peaks and an increase in the emission efficiency. All the observations noted indicate a high sensitivity of the energy levels of $Nd^{3+}$ ions in the $ZnIn_2S_4:Nd^{3+}$ system to both crystal field variations and temperature changes. These properties increase the importance of the material for potential laser, optoelectronic and other photonic applications.

## 4. Conclusion

Studies have shown that the fine structure of the photoluminescence peaks observed in $ZnIn_2S_4$ crystals doped with $Nd^{3+}$ ions is due to the Stark effect induced by the crystal field. The separation of the peaks into multiple fine components reflects the effects of local symmetry violations and defects. Lowering the temperature led to a narrowing of the peaks and an increase in the emission efficiency. These features indicate the prospects of the $ZnIn_2S_4:Nd^{3+}$ crystal for optoelectronics and photonic devices and open up the possibility of optimizing these properties in the future through ion concentration and crystal engineering.

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