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PROSPECTS FOR THE USE OF ZnSe <Te> CRYSTALS IN HYPERSPETRAL OPTICAL SYSTEMS

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Abstract. The prospects for the use of molten ZnSe <Te> crystals after their additional doping with rare-earth elements to create hyperspectral optical elements with elevated temperature and radiation resistance are discussed.

Key words: zinc selenide, temperature and radiation resistance, transmission, rare-earth elements.

Анотація. Обговорюються перспективи використання розплавних кристалів ZnSe<Te> після їх додаткового легування рідкісноземельними елементами для створення гіперспектральних оптичних елементів з підвищеною температурною та радіаційною стійкостями.

Ключові слова: селенід цинку, температурна та радіаційна стійкості, пропускання, рідкісноземельні елементи

Аннотация. Обсуждается перспективы использования расплавных кристаллов ZnSe<Te> после их дополнительного легирования редкоземельными элементами для создания гиперспектральных оптических элементов с повышенными температурной и радиационной стойкостями.

Ключевые слова: селенид цинка, температурная и радиационная стойкости, пропускание, редкоземельные элементы.

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INTRODUCTION

One of the possible ways to improve the physical and technical parameters and operational capabilities of optoelectronic systems is to use materials with a wide spectral bandwidth. These include, in particular, zinc selenide, which has a high melting point, resistance to the action of the atmosphere, mechanical strength and significant (50–60%) optical transmission T_λ in a wide (0.5–20 μm) wavelength range [1, 2]. We also pay attention to the fact that the transparency of ZnSe in the visible range greatly simplifies the alignment of optical systems with elements based on it in comparison with similar devices based on GaAs and CdTe.

Meanwhile, the noted high optical characteristics are peculiar only to high-purity zinc selenide single-crystal, which, unfortunately, has very low resistance to the various types of ionizing radiation and high-power laser fluxes. It can be significantly improved by doping the material with an isovalent impurity, which was successfully implemented for ZnSe<Te> crystals. They are characterized by high thermal (~ 500 K) and radiation ($\sim 10^7$ rad) resistance, time stability, and high efficiency ($\sim 30\%$ at 300 K) radio luminescence, which, in fact, determined their widespread use as scintillators [3, 4].

The disadvantage of these crystals is the practical absence of transmission at $\lambda \approx 6 \mu\text{m}$ (Fig. 1), which makes it impossible to use them in wide-band, so-called hyperspectral optical systems [2]. Let's mention that the elements of such systems should have significant transmission in a wider range ($>0.5\text{--}20 \mu\text{m}$). In this paper, the possibilities of expanding the transparency region of ZnSe <Te> crystals while maintaining their thermal and radiation resistance are discussed.

SAMPLES AND INVESTIGATION TECHNIQUES

Despite the large number of methods for producing poly- and single-crystal zinc selenide, only a few of them are used in the synthesis of material suitable for the manufacture of hyperspectral optical elements. At

present, the Bridgman-Stockbarger method is the most popular, allowing one to grow pure and doped ZnSe bulk crystals of sufficiently good structural quality with a diameter of up to 120 mm [5].

In the present work, similar crystals were used, which were grown from a melt under the pressure of an inert gas and doped during growth with an isovalent Te impurity [3, 4]. The plates cut out from the bulk ZnSe <Te> crystal of the 5x5x1 mm³ size underwent stepwise mechanical and chemical polishing in a C2O3: HCl = 2: 3 solution, thorough washing in distilled water and finishing drying. The quality of surface treatment was monitored visually by the appearance of the bulk orange luminescence characteristic of ZnSe <Te> crystals [3], which was excited by an N2 laser. The optical transmission spectra of the objects of research were measured in the spectral range of 1–25 μm using a NICOLET 6700 IR Fourier spectrophotometer. A typical optical transmission spectrum of ZnSe <Te> crystals, represented by curve 1 in Fig. 1. limited to the wavelength range of ~ 0.5-6 microns, which makes them unsuitable for use in hyperspectral systems.

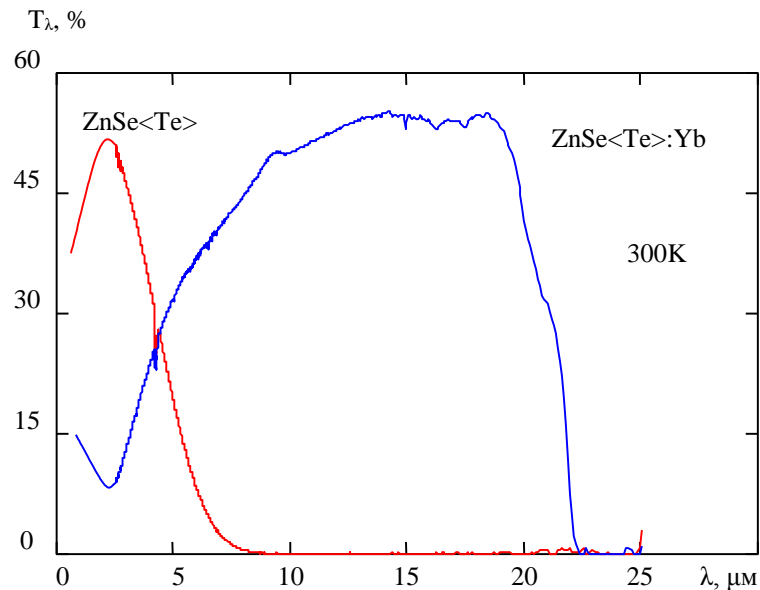


Fig. 1 Optical transmission spectrum of research objects

The practical absence of transmission at $\lambda \approx 6 \mu\text{m}$ is apparently caused by transitions of electrons from the valence band to levels with an ionization energy of $E_u \approx 0.2 \text{ eV}$. This value is close to the depth of negative single-charged zinc vacancies V_{Zn}' whose concentration in ZnSe<Te> crystals is rather high $\sim 10^{22} \text{ cm}^{-3}$ [6]. Transformed from a single-charge to a double-charged zinc vacancy V_{Zn}'' , the latter can combine with a positive single-charge selenium vacancy V_{Se}^* to form associates $(V_{\text{Zn}}'' V_{\text{Se}}^*)$ responsible for the orange luminescence band of zinc selenide [3,6]. The foregoing implies that in order to increase the transmission in the IR region, it is necessary to reduce the concentration of zinc vacancies, mainly single-charged ones.

One of the possible ways to reduce vacancies is their doping with rare earth elements (REE). Thus, in the article [7], it is convincingly shown that the introduction of REE into crystals or epitaxial films of III-V compounds in the process of their growth leads to an effective cleaning of them from background impurities, and the phenomenon is called the “purification” effect. We also observed a similar effect after doping of ZnSe crystals with ytterbium impurity Yb from the vapor phase in a closed volume [8]. The advantage over the method used in [7] is the possibility of its use for already grown crystals or layers and containing various impurities.

In this paper, doping of ZnSe <Te> substrates with Yb impurity prepared according to the previously described technology, was carried out in a pumped out to 10^{-4} Torr and a sealed quartz ampoule. To prevent erosion of the surface of the plates, the weighed elemental selenium was also loaded together with Yb. In addition, Se prevents entering of REE into the anion sublattice, thus increasing the probability of filling zinc vacancies (cation sublattice). Note that it is precisely this substitution scheme that leaves atoms of an isovalent Te impurity in the anionic sites without affecting the thermal and radiation resistance of the material caused by it. During the diffusion, the substrate and diffusant (selenium and crushed REE) were located at different ends of the ampoule, and the process is carried out under isothermal conditions at 1400 K for 3 hours, which is sufficient for doping the entire substrate volume.

CONCLUSIONS

Thus, the presented results indicate that it is possible in principle to significantly expand the transmission spectrum of ZnSe <Te> substrates due to their additional doping with rare-earth ytterbium impurity. A further increase in the spectral region and absolute transmittance values is possible by choosing the type of rare earth element and the optimal doping modes.

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