

# Influence of rare-earth impurities on optical properties of As<sub>2</sub>S<sub>3</sub> glasses and KCl crystals

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**Abstract** - Optical transmission spectra of As<sub>2</sub>S<sub>3</sub> glass-like plates and nanolayers, undoped and doped with Sm<sup>2+</sup>, Sm<sup>3+</sup>, Dy<sup>3+</sup>, Pr<sup>3+</sup>, and Mn<sup>3+</sup> ions have been investigated. The spectral dependences of the refractive index and glass transmission spectra, registered in the configuration of crossed polarizers, were studied. The concentration of rare-earth ions in the matrix influences on the magnitude of refractive indices ( $n$ ,  $n^+$ ) of polarized light. The emission spectra of As<sub>2</sub>S<sub>3</sub> glasses, doped with rare-earth ions (Sm<sup>2+</sup>, Sm<sup>3+</sup>, Pr<sup>3+</sup>), as well as KCl crystals, doped with Sm<sup>2+</sup> ions, have been investigated for different temperatures in the range 300 - 10 K. A luminescence signal associated with recombination transitions of charge carriers from <sup>5</sup>D<sub>j</sub> and <sup>5</sup>L<sub>j</sub> levels to <sup>7</sup>F<sub>j</sub> levels of samarium ion was registered. A wide photoluminescence band was registered in the region 1.8 - 2.1 eV, which can be related to intercenter photoluminescence, and a number of narrow absorption bands were registered, which can be attributed to self-absorption process, determined by electronic transitions between the levels of samarium ions.

**Index Terms** – As<sub>2</sub>S<sub>3</sub> glasses; rare-earth elements; birefringence; interference spectra; ordinary and extraordinary waves;

## I. INTRODUCTION

Chalcogenide glass-like materials attract attention of many researchers for various applications in optoelectronics, in infrared spectroscopy, telecommunications and nonlinear optics [1]. The main advantages of chalcogenide glasses as materials for medium-IR optics are determined by a number of their specific properties: their high transparency in the spectral range 1 - 10 μm, high refractive indices, as well as the possibility for their modification [2].

The impact of various rare-earth elements and transition metals on the optical properties of glassy As<sub>2</sub>S<sub>3</sub> was investigated along the years in many details for a wide spectral range. Raman and IR spectroscopy, optical edge absorption technique, and X-ray spectroscopy were extensively used in order to obtain information on the behavior of impurities ions within the matrix of doped glass, to investigate associated changes in optical characteristics of the glasses [3]. While referring to the region of the fundamental absorption edge, incorporation of impurities in the glass matrix strongly affect

both the slope and the magnitude of the weak absorption tail from the very beginning of the absorption edge. It was established that introduction of specific impurities leads to suppressing of some absorption bands, associated with defects in the glass matrix, for a wide range of optical transmission spectra. This specific feature is an indication of the interaction of the rare-earth ions with the glassy matrix. Besides, one can observe a shift of some absorption maxima from the region near the absorption edge to short wave region (Dy, Sm doping) or to long wave region (Mn doping) [4].

In the present paper we investigate the induced optical activity (OA) **caused** by incorporation in the matrix of As<sub>2</sub>S<sub>3</sub> glass or KCl crystals of the ions of rare-earth elements - samarium (Sm), manganese (Mn), dysprosium (Dy), and praseodymium (Pr).

## II. EXPERIMENTAL METHODS

Bulk As<sub>2</sub>S<sub>3</sub> chalcogenide glasses were prepared from high purity (5N) elements As and S, through conventional method of melting the mixtures of constituent elements, and rapid quenching of the melt. For synthesis of chalcogenide glasses doped with rare-earth metals, small amounts of rare earth elements, such as samarium (Sm), manganese (Mn), dysprosium (Dy), praseodymium (Pr), or erbium (Er) were added to the initial glass material. The synthesis process was carried out in sealed quartz ampoules, previously evacuated to 10<sup>-4</sup>-10<sup>-5</sup> Torr, and placed in a horizontal or vertical furnace. The furnace was equipped with the mechanism for rotation of the ampoule around its axis, as well as with vibration mechanism. For different glass compositions the maximum synthesis temperature was varied in the range 700 °C - 1100 °C, and the synthesis duration varied from 24 to 72 hours. After completion of the synthesis process, the ampoule with the melted glass mixture was quenched by rapid cooling in air (cold water or liquid nitrogen). The nominal concentration of the metal ions in glasses was varied between 0.01 and 0.5%. The color of obtained glasses changed from yellow-red (pure As<sub>2</sub>S<sub>3</sub>), to dark-red for As<sub>2</sub>S<sub>3</sub>, doped with Dy or Sm, while As<sub>2</sub>S<sub>3</sub> glass doped with Mn exhibited a black color. Chalcogenide glass thin films of different thicknesses were

obtained by thermal evaporation on glass substrates in a vacuum.

### III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Fig. 1A illustrates a typical dependence of **one-photon absorption** coefficient  $K$  vs the photon energy  $h\nu$  near the edge of the fundamental absorption band for pure chalcogenide glasses  $As_2S_3$ , as well as for glass samples, doped with  $Sm^{3+}$  ions. The absorption coefficient varies over a wide range of magnitude,  $10 - 10^4 \text{ cm}^{-1}$ . For transmission ( $T$ ) spectra of thin film samples at the onset of absorption edge in the infrared region, a pronounced interference effect can be observed. Fig. 1B and Fig. 1C illustrate the absorption spectra in the regions of high and low absorption coefficients, respectively, for  $As_2S_3$  chalcogenide glass samples doped (0.1-0.5%) with various rare-earth metals (Mn, Sm, Dy, Pr). It should be noted, that thin film samples obtained by vacuum deposition, exhibited high absorption coefficients. In the region of high absorption coefficients, the doping impurities lead to a shift of the absorption edge toward lower energies. The higher doping concentration of metal is, the greater shift of the absorption edge occurs (Fig. 1C). In the region of low absorption coefficients such dopants, as Sm, Dy, and Pr, shift the absorption spectrum toward shorter wavelengths (Fig. 1B), while increasing the concentration of the dopant, results in a greater shift of the absorption edge (Fig. 1B).

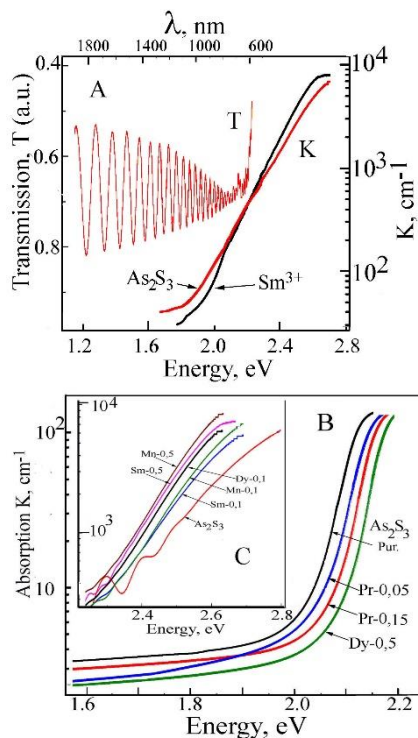


Fig. 1. Optical transmission ( $T$ ) and absorption ( $K$ ) spectra for pure and doped  $As_2S_3$  glass samples.

Doping of chalcogenide glasses with rare-earth elements affects the spectral dependences of the refractive index ( $n$ ), and

this is the case for  $As_2S_3$  glasses too (Fig. 2A, B and C). Figure 2A shows the spectral dependences of the refractive index ( $n^*$ ,  $n^{**}$ ) of pure  $As_2S_3$  and doped  $As_2S_3$  with samarium ions ( $Sm^{2+}$ ,  $Sm^{3+}$ ) at concentration 0.1% and 0.5%, derived from optical transmission spectra  $T$  ( $n^*$  - by the method described in [5],  $n^{**}$  - by the method described in [6]). The spectral dependences of the transmittance  $T$ , for  $As_2S_3$  layers doped with  $Sm^{3+}$ , and  $Sm^{2+}$  ions are represented in Fig. 2A. In the region of transparency one can observe the interference effect, as well as the shift of the absorption edge with increasing the concentration of the dopant. For thin films samples of pure  $As_2S_3$  the amplitude of interference maxima practically does not change until the onset of absorption edge. For thin layers with the concentration 0.1% and 0.5% of samarium, the amplitude of the interference bands decreases as the absorption edge is approached, and the decrease is larger for those layers with larger samarium concentration. This is due to the fact that the spectral dependence of the refractive index changes with the concentration of samarium dopant in the glass. From the refractive index spectra it can be seen that a small concentration of Sm dopant (0.1%) decreases the magnitude of the refractive index, while a higher concentration of 0.5% Sm dopant leads to an increase in the refractive index. A low concentration (0.1%) of Dy dopant, similarly to the case of low concentration of Sm dopant, also reduces the refractive index of  $As_2S_3$ . **The spectral dependences of the refractive index of  $As_2S_3$  glass doped with Mn ions (0.1% and 0.5%) change to a greater extent, while the features of  $\alpha$  and  $\beta$  appear as weak maxima.**

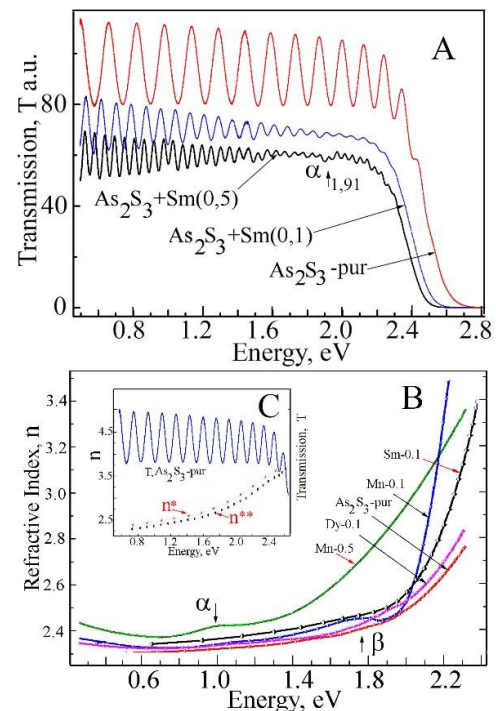
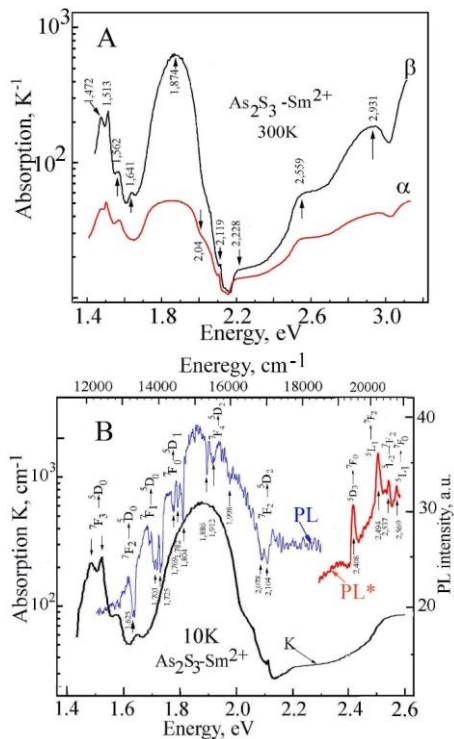


Fig. 2. Spectral dependences of the refractive index  $n$  of  $As_2S_3$  glasses, pure and doped with different elements, derived from the transmission spectra  $T$  ( $n^*$  - by the method [5],  $n^{**}$  - by the method [6]).

Absorption spectra of  $\text{As}_2\text{S}_3$  glass layers doped with Sm ions 0.1% ( $\alpha$ ) and 0.5% ( $\beta$ ) registered at 300 K exhibit an intense absorption band at 1.874 eV, four bands with a smaller half-width at lower energies and other four absorption bands in the region of the onset of absorption edge (Fig. 3A). In the case of glass samples with a higher concentration of samarium the absorption bands have higher magnitudes and are better resolved. Figure 3B shows the absorption (K) and luminescence (PL) spectra of  $\text{As}_2\text{S}_3$ -Sm (0.5%) thick plates registered at 10 K. The spectral dependence of the absorption coefficient at 10 K reveals almost the same absorption bands as for 300 K, with a more intense maximum at 1.886 eV. When a glass sample of  $\text{As}_2\text{S}_3$ -Sm (0.5%) is excited with a 457.9 nm  $\text{Ar}^+$ -laser beam at 10 K, a broad and intense luminescence band is observed at the same energy as the absorption band (1.886 eV). A weaker luminescence band appears in the region 2.5 - 2.6 eV. On the overall contour of the luminescence spectra a number of narrow lines are distinguished in the form of dips, which are marked by the arrows in Fig. 3B.



noted that with increasing the samarium concentration, the refractive index in the entire registered spectral region increases by approximately 0.1 - 0.2 (Fig. 4B). For glass samples with an increased samarium concentration (0.5%) a weak feature in the form of shoulder can be observed around 1.8 - 1.9 eV in the spectral dependence of the index of refraction. Figure 4B also illustrates the transmission spectra of  $\text{As}_2\text{S}_3$  glass plates (5 mm thick), undoped ( $T^*$ ), and doped with  $\text{Sm}^{2+}$  ( $T^{**}$ ), registered in the configuration of crossed polarizers (the inset in Fig. 4B). Undoped  $\text{As}_2\text{S}_3$  glass plates are almost opaque when placed between crossed polarizers, when the transmittance  $T^*$  does not exceed 1-2%. For  $\text{As}_2\text{S}_3$  glass plates doped with 0.5% samarium the transmittance  $T^{**}$  reaches about 60% around 1.8 - 1.9 eV (Fig. 4B).

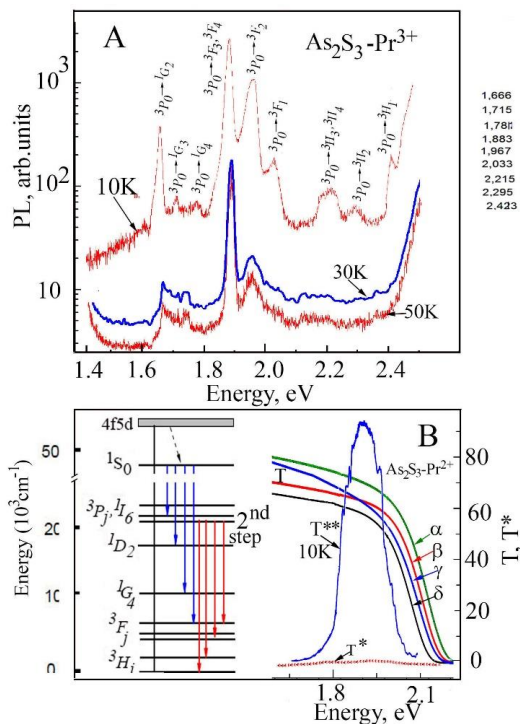


Fig. 5. A - Illustration of the luminescence spectra of  $\text{As}_2\text{S}_3$  plates doped with  $\text{Pr}^{3+}$  ions at different temperatures 50, 30 and 10 K under excitation of the  $\text{Ar}^+$ -laser line 457.9 nm; B - The energy diagram of  $\text{Pr}^{3+}$  levels in  $\text{As}_2\text{S}_3$  glass [9], transmission ( $T$ ) spectra of glass samples with the dopant content 0.5% ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) and 0.15% ( $\delta$ ), and the transmission spectra of undoped  $\text{As}_2\text{S}_3$  ( $T^*$ ), and doped 0.5%  $\text{Pr}^{3+}$  ( $T^{**}$ ), registered in the configuration of crossed polarizers.

The luminescence spectra of  $\text{As}_2\text{S}_3$  glass samples doped with  $\text{Pr}^{3+}$  ions, registered at different temperatures 50, 30, and 10 K, under intense  $\text{Ar}^+$ -laser lines excitation, exhibit a number of intensive emission bands in the region 1.6 - 2.4 eV (Fig. 5A). These **PL bands can be related to radiative transitions from the electronic levels of  $\text{Pr}^{3+}$  ions** [9], whose **emission scheme** is illustrated in Fig. 5B.

The same figure shows the transmittance spectra ( $T$ ) of glass samples with different content of  $\text{Pr}^{3+}$  ions, 0.5% ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) and 0.15% ( $\delta$ ). These transmission spectra of undoped  $\text{As}_2\text{S}_3$  ( $T^*$ ), and doped 0.5%  $\text{Pr}^{3+}$  samples ( $T^{**}$ ), were measured in

the configuration of crossed polarizers at 10 K. The spectral characteristics  $\alpha$ , were measured on the glass samples of the same thickness obtained from different technological batches. It can be seen from the transmission spectra, that absorption edge shifts to higher energies, when the concentration of  $\text{Pr}^{3+}$  ions increases. While measured in configuration of crossed polarizers, undoped  $\text{As}_2\text{S}_3$  glass plates are opaque ( $T^* \lesssim 1\%$ ). For glass composition containing 0.5%  $\text{Pr}^{3+}$  ions the glass samples with 3 mm thickness exhibit a transmission up to 90% with a maximum transparency in the region 1.91 eV (Fig. 5).

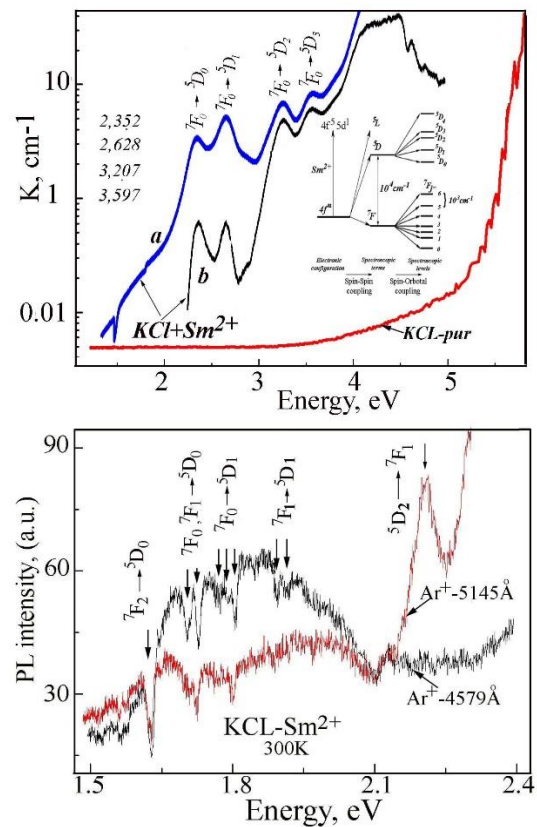


Fig. 6. A - Absorption spectra of KCl salt crystals, pure and doped with  $\text{Sm}^{2+}$  ions, and luminescence spectra of doped crystals upon excitation by the argon laser beam 514.5 nm or 457.9 nm.

In the case of pure crystals of KCl salt no absorption band was registered in the energy range up to 6 eV. On the other hand, absorption spectra of KCl samples doped with  $\text{Sm}^{2+}$  ions, exhibit a number of absorption bands, registered at 2.352 eV, 2.628 eV, 3.207 eV, and 3.597 eV, which can be associated with electron transitions between the energy levels of samarium ions,  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$ . In the energy range 4.1 - 4.6 eV, a broad absorption band is registered (Fig. 6A). The emission spectrum of KCl doped crystals, when excited by 514.5 nm or 457.9 nm argon laser beam, shows a broad luminescence band with narrow dips on the overall luminescence spectrum contour, as illustrated in Fig. 6B. These narrow dips on the **emission spectrum contour indicate on self-absorption of the radiated energy because of electronic transitions between samarium ion levels**. A

similar picture was discussed above for the luminescence spectra of As<sub>2</sub>S<sub>3</sub> glasses doped with samarium.

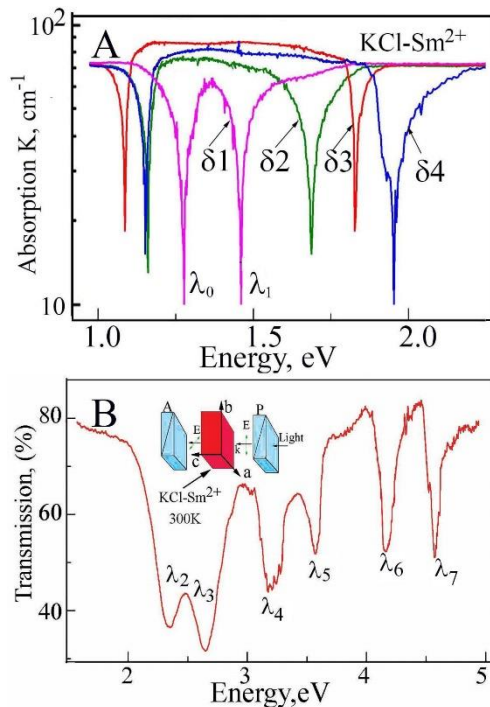


Fig. 7. Absorption spectra of crystals of KCl - Sm<sup>2+</sup> salt registered in the configuration of crossed polarizers (A), and in configuration of parallel polarizers (B) (the insert shows the crystal position in parallel polarizers).

This wide emission band is associated with the **defects-related inter-centre luminescence** of the KCl Sm-doped crystals. In the case of undoped KCl crystals no luminescence was observed. The narrow bands in the form of dips, which appear in the PL spectrum, are due to **self-absorption of emission energy (inter-center luminescence)**, determined by electronic transitions between the levels of samarium ions, from the **F**-state levels to the **D**-states levels (Fig. 3B). Higher in the energy region above 2.4 eV the PL spectra exhibit emission of the samarium energy levels, from **D**- and **L**-states levels to the **F**-state energy levels.

KCl crystal samples with different samarium content exhibited different **color** density. A higher color density corresponded to a larger concentration of samarium ions in the KCl salt crystals. Figure 7A shows the absorption spectra of KCl salt crystal samples (8 mm thick plates), with different color density (different samarium content), registered in configuration of crossed polarizers. When measured in crossed polarizer configuration, the transparency of undoped KCl crystals is almost zero,  $T < 0.1\%$ , (respectively the absorption coefficient  $K \approx 10^2 \text{ cm}^{-1}$ ), which corresponds to the transmission coefficient of crossed polarizers themselves. While measuring the absorption spectra of KCl crystals (8 mm thick) in crossed polarizer configuration, a number of absorption bands appear, for which the absorption coefficient varies by two orders of magnitude. Similarly, the transmittance of the samples measured in configuration of

crossed polarizers, varies at the same band energies by two orders of magnitude. For the crystals with a high color density, the transparency bands are observed at energies  $\lambda_0$  - 1.283 eV and  $\lambda_1$  - 1.460 eV. While increasing the color density, i.e. as the concentration of samarium impurities increases, these bands are shifted in different directions. The low-energy band ( $\lambda_0$ ) shifts toward lower energies and is registered at 1.156 eV (for the densities  $\delta_2$ ,  $\delta_3$ ), and at 1.086 eV for  $\delta_4$ . The high-energy band ( $\lambda_1$ ) shifts toward higher energies 1.691 eV ( $\delta_2$ ), 1.832 eV ( $\delta_3$ ) and 1.955 eV ( $\delta_4$ ). This indicates that circularly polarized light waves have different propagation velocities in the crystals with different samarium concentration. The light waves with right-hand and left-hand circular polarization have different refractive indices ( $n^-$  and  $n^+$ ), which vary with the concentration of the samarium ions impurity.

A number of other absorption bands are observed in the energy range  $E > 2 \text{ eV}$ . Figure 7B shows the absorption spectra of KCl crystal samples with the largest samarium content, while registered in the configuration of parallel polarizers. In the case of samples with large concentration of Sm impurity additional absorption bands  $\lambda_2 - \lambda_7$  at different energies are observed - 2.353 eV, 2.628 eV, 3.207 eV, 3.597 eV, 4.194 eV and 4.575 eV, respectively.

While measuring anisotropic crystals transmission in crossed polarizers configuration, a number of absorption bands are also registered, and these bands are associated to the fact that the light waves, with the polarization parallel and perpendicular to the anisotropy axis, have different refractive indices ( $n_o$  and  $n_e$ ). At some specific wavelengths these indices are equal ( $n_o = n_e$ ) and at these wavelengths the crystal becomes isotropic; respectively this wavelength is called “*the isotropic wavelength*” [10]. The light waves of right- and left-hand circular polarization at specific wavelengths have equal refractive indices ( $n^- = n^+$ ). At these wavelengths one can observe transparency bands in the crossed polarizers configuration, and absorption bands in the configuration of parallel polarizers. Since the concentration of the incorporated impurity affects the propagation velocity of circular polarized waves, one can achieve equality of the refractive indices for different wavelengths of propagating light waves ( $n^- = n^+$ ), i.e. one can obtain optical filters with “*band-pass*” characteristics [11], with required transmission bands for specific applications.

#### IV. CONCLUSIONS

Investigations of the emission spectra of As<sub>2</sub>S<sub>3</sub> glasses doped with rare-earth ions (Sm<sup>2+</sup> and Pr<sup>3+</sup>), as well as KCl crystals doped with Sm<sup>2+</sup> ions, carried out at different temperatures 300-10 K, have shown that the ions of rare-earth elements significantly affect optical characteristics of the **doped matrix**. A luminescence band was registered which is associated with recombination processes of charge carriers from the energy levels <sup>5</sup>D<sub>j</sub> and <sup>5</sup>L<sub>j</sub> to <sup>7</sup>F<sub>j</sub> levels of samarium ions. A wide emission band was registered in the region 1.8 - 2.1 eV, which is associated to **inter-center** photoluminescence, and a number of narrow absorption bands were registered, which can be attributed to **self-absorption process**,

determined by electronic transitions between the levels of samarium ions.

Optical transmission spectra of As<sub>2</sub>S<sub>3</sub> glass plates and nanolayers are significantly affected by doping with Sm<sup>2+</sup>, Dy<sup>3+</sup>, Pr<sup>3+</sup> and Mn<sup>3+</sup> ions. The concentration of incorporated rare-earth ions affects the refractive indices ( $n^-$  and  $n^+$ ) for circularly polarized light waves. The light waves of right-hand and left-hand circular polarization at some specific wavelengths have equal refractive indices ( $n^- = n^+$ ). At these wavelengths, a number of transparency bands are registered in the configuration of crossed polarizers, while absorption bands are registered in the configuration of parallel polarizers.

Variation of the concentration of incorporated impurity affects the propagation velocity of circular polarized wave, which makes it possible to obtain the equality of the refractive indices ( $n^- = n^+$ ) at different wavelengths of light wave, i.e. one can obtain optical “band-pass” filters with specific transmission bands for required application needs.

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