

Optical properties of As_2S_3 glasses doped with Dy

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An effect of introduced dysprosium impurity and temperature on absorption spectra of As_2S_3 glasses is investigated. Absorption lines due to the electron transitions between dysprosium levels were observed in absorption (K), wavelength modulated transmission ($\Delta T/\Delta \lambda$) and photoluminescence (PL) spectra at temperatures range 10 - 300 K. It was established that in $\text{As}_2\text{S}_3:\text{Dy}$ glasses light waves of right and left circular polarization have different refractive indices ($n^- \neq n^+$). The circularly polarized waves propagate with different velocities and interfere. Values of n^- , n^+ and $\Delta n = n^+ - n^-$ were determined from interference fringes.

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1. Introduction

Chalcogenide glasses are the prospective material for different optical devices used in optoelectronics and waveguide optics. The glasses are the convenient matrices for investigations of optical transitions in impurity centers and of luminescence in the infrared region [1, 2]. They have attractive properties such as the wide transparency region (from visible to middle infrared) depending from glass composition, the high refractive index and the high values of nonlinear susceptibility. The main part of chalcogenide glasses possesses a good chemical resistivity especially to atmospheric moisture. Synthesis of glasses with a wide range of optical and technological properties is possible by changing the composition.

Chalcogenide glassy materials attract the attention of many researchers and are introduced as elements of optoelectronics into systems of analytical remote sensing IR spectroscopy, in the field of telecommunication and nonlinear optics [1-5]. The main advantages of chalcogenide glasses as materials for mid-IR optics are relatively high transparency (low losses of light energy) in the spectral range from 1 to 10 μm , corresponding and variable refractive indices [3-6]. An interest to glassy chalcogenides is great and researchers investigate them by different methods. These studies show that chalcogenides are used in both visible and infrared regions. Of greatest interest is the study of the properties of glasses doped with various rare earth elements [5-11]. At the same time it should be mentioned that a lack of information about the energy states of both rare-earth ions and their influence on the optical characteristics, including on the refractive indices. The information about the induced optical activity does not exist.

In the present work, high-resolution optical spectroscopy was used to study the energy states of electron transitions in As_2S_3 glasses doped with Dy^{3+} ions. The problems of the optical activity appearance due to introduced dysprosium impurity and the effect of impurity

levels on the absorption and luminescence spectra are considered.

2. Experimental methods

The bulk chalcogenide As_2S_3 glasses were grown from the initial elements As and S of high purity (5N) by the traditional method of component melting with subsequent quenching. For synthesis of chalcogenide glasses doped with impurities the rare-earth ligand (dysprosium) is added into the initial components composition. The synthesis process takes place in sealed quartz ampoules, pre-evacuated until 10^{-4} - 10^{-5} Torr and deposited in a horizontal or vertical furnace, equipped with mechanisms of vibration and rotation of the ampoule around its axis. The temperature range for compound synthesis is 700 - 1100 $^{\circ}\text{C}$ and the synthesis duration is 24 - 72 hours, depending on the compound composition. After the synthesis process the ampule with liquid compound is rapid cooled (quenching process) in atmosphere, in cold water or in liquid nitrogen. The nominal concentration of dysprosium in the glass-like samples varies from 0.01% to 0.5%. The samples have a color differentiation from yellow-red for undoped As_2S_3 to dark-red for Dy doped As_2S_3 . The thin films of the glasses were received by the vacuum thermal deposition on glass plates.

The low-temperature optical spectra of samples deposited in closed helium cryosystem (LTS-22 C 330) were measured on the spectrometer MDR-2 (light getting power 1:2 and linear dispersion 7 $\text{\AA}/\text{mm}$). The photoluminescence measurements were performed on the double Raman spectrometer DFS-32 (light getting power 1:5 and linear dispersion 5 $\text{\AA}/\text{mm}$). The entrance and exit slits of spectrometers do not exceed 30 μm i.e. measurements resolution is ~ 0.5 meV. The luminescence spectra are also measured on the double spectrometer SDL-1 (light getting power 1:2 and linear dispersion 7 $\text{\AA}/\text{mm}$).

3. Experimental results and discussion

Fig. 1 shows the spectral dependences of absorption coefficient (K) in the region of edge fundamental absorption for undoped and doped with dysprosium ions As₂S₃ glasses. The absorption coefficients for investigated plates are changed in the interval $10^2 - 10^3 \text{ cm}^{-1}$. The high absorption magnitude was received on the thin vacuum deposited on glass substrates As₂S₃ films. Fig. 1A illustrates the absorption spectra of As₂S₃ chalcogenide glasses doped by Dy of 0.05 – 0.5% concentration range.

Interference in transparency region and edge shift are observed with Dy concentration increasing. The amplitude of interference fringes are practically unchanged until the edge absorption. In the case of samples doped by Dy 0.1% and 0.5% at the absorption edge achieving the amplitude of interference bands are decreased and this drop is more for the higher concentration of dysprosium.

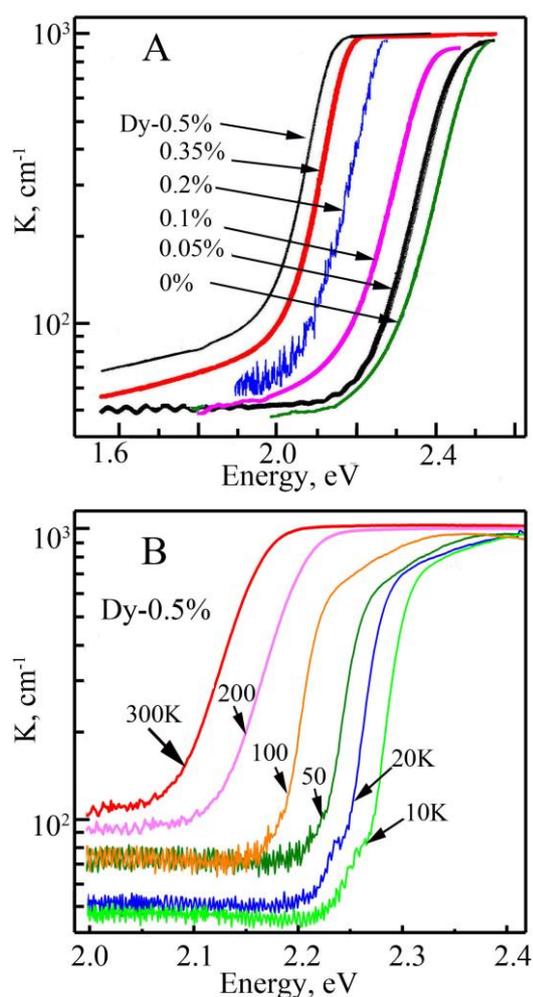


Fig. 1. A – Absorption (K) spectra of As₂S₃ glasses doped with Dy of different concentrations.
B – Temperature dependence of absorption for As₂S₃ glass doped with 0.5% Dy

It is well known that the common property of edge absorption for all amorphous semiconductors is the presence of the Urbach tail, which is associated with localized states in the band gap. In chalcogenide glasses the Urbach tail transfer in a region of slowly decreasing absorption (weak absorption tail) at photon energy decreasing. The introduction of some impurities in glass matrix leads to ordering of a glass structure in the region of valence and conduction bands edges, leads to a decrease in absorption bands blurring, as well as to the shift of the absorption edge to the shorter wavelengths. In the region of high absorption coefficients the energy levels of incorporated dopants predominate. For the investigated glasses with dysprosium impurity the concentration growth affects to the absorption edge shift toward long wavelengths. The maximal shift (0.2 eV) is observed for samples with 0.5% Dy. Fig. 2B illustrates absorption spectra of chalcogenide doped by Dy (0.5%) measured in temperature range 10 -300 K. With temperature decreasing from 300 K down to 10 K the absorption edge shifts toward higher energies on 0.15 eV. And the change in the slope of the characteristic in the region of high absorption coefficients takes place.

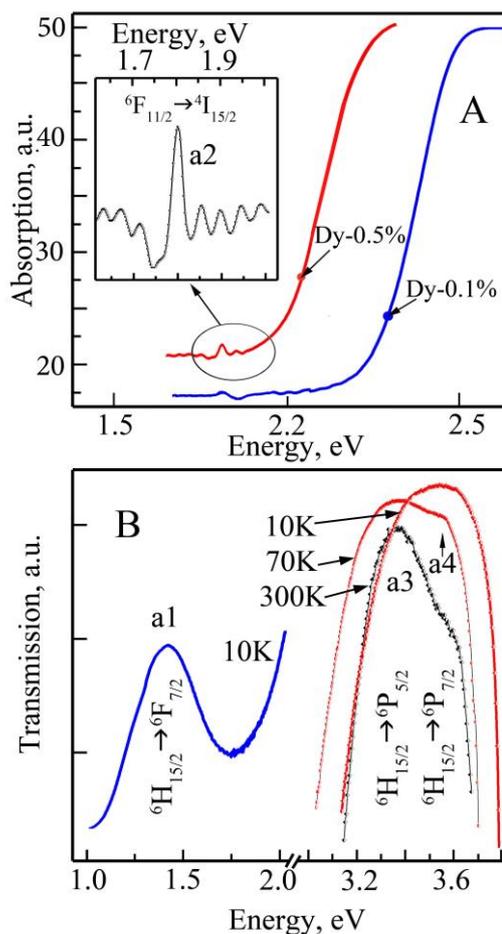


Fig. 2. A – Absorption spectra of 1.1 mm thickness samples doped with Dy of 0.1% and 0.5% concentrations. B – Transmission spectra measured at different temperatures

Fig. 2A shows the absorption spectra of As_2S_3 glasses plates of 1.1 mm thickness doped by Dy of concentrations 0.15 and 0.5%. The typical interference picture with well pronounced maximum a2 at 1.8 eV is found out in long-wavelength part of absorption (transmission) spectra of thin films. The fragment of these spectra is shown in Fig. 2A. The observed absorption maximum a2 can be associated with electron transitions from levels ${}^6F_{11/2}$ to levels ${}^4I_{15/2}$, the energy interval between these levels according data of Ref. [11, 12] is equal to 1.801 eV. Fig. 2B illustrates absorption spectra of plates of 2.1 mm thickness with 0.5% Dy concentration. The absorption band a1 at 1.404 eV is observed in the absorption spectra and it can be attributed to the transitions between levels ${}^6H_{15/2}$ and ${}^6F_{7/2}$. This energy interval according data of Ref. [11] is 1.377 eV. Transmission (absorption) spectra at higher energies were measured from samples in form of thin films. The maximum a3 at energy 3.372 eV and the weak shoulder a4 at 3.523 eV are observed at energies 3.2 – 4 eV in spectra measured at room temperature. At temperature decreasing down to 70 K the intensity of absorption band is changed and the short-wavelength part a4 increases. The maximum of absorption band (a4) is observed at energy 3.523 eV than temperature reaches 10 K. The absorption band at 3.372 eV is more probably caused by electron transitions ${}^6H_{15/2} \rightarrow {}^6P_{5/2}$ and the band at 3.523 eV is due to transitions ${}^6H_{15/2} \rightarrow {}^6P_{7/2}$ whose intensity increases with temperature decrease.

For receiving information about dysprosium levels in the glass matrix $\text{As}_2\text{S}_3:\text{Dy}$ lying higher than 2 eV it is necessary to weaken absorption by sample thickness reduction. It was used the standard methodic (vacuum deposition) for receiving the $\text{As}_2\text{S}_3:\text{Dy}$ thin films on glass substrates. The absorption spectra of As_2S_3 layers (5.65 μm) in high energy ($E > 2$ eV) range are shown in Fig. 3A, B. On thin samples (layers) in energy range less than 2 eV the interference fringes takes place in transmission (absorption) spectra (Fig. 3A, graph α). The interference can deform measured spectra of thin layers and in higher energy range. To avoid this, the layers with weak interference effect are used for these measurements (see Fig. 3 graph β). On these layers the transmission (absorption) spectra in region $E > 2$ eV (Fig. 3A) and in region 1.5 – 4.3 eV (Fig. 3B) were measured. The absorption band (c1) at energy 2.145 eV is observed in spectra and the maximal absorption reaches magnitude of 10^4 cm^{-1} . This absorption band is due to electron transitions ${}^6H_{11/2} \rightarrow {}^4G_{11/2}$. According Refs [11, 12] this energy interval is 2.14 eV. A weaker absorption band c2 at 2.582 eV is observed in these spectra. This band is associated with electron transitions between levels ${}^6H_{15/2} \rightarrow {}^4F_{9/2}$. The absorption band c3 at 3.502 eV due to electron transitions ${}^6H_{15/2} \rightarrow {}^6P_{5/2}$ or ${}^6H_{15/2} \rightarrow {}^6P_{7/2}$ is appeared in the highest energy range. According literature data [11, 12] this interval is equal to 3.373 eV and 3.543 eV, respectively.

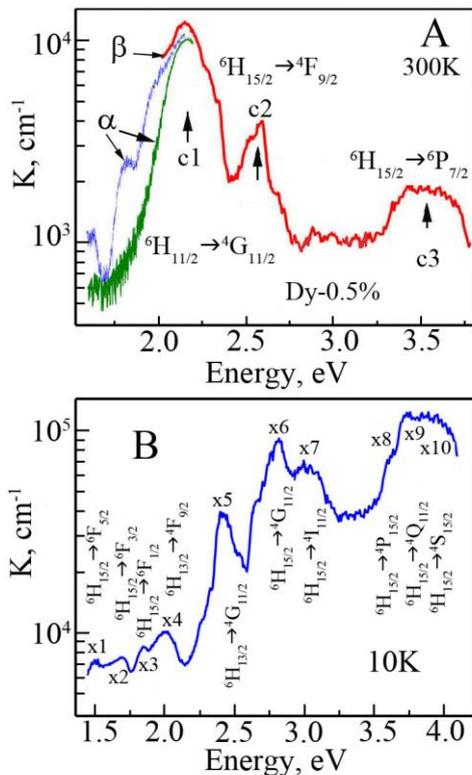


Fig. 3. Absorption spectra measured in interval 1.5 – 4 eV of thin film of 6.65 μm at temperatures 300 K (A) and 10 K (B)

Table 1. Energy positions of absorption lines and respective transitions between levels of dysprosium ions in As_2S_3 glasses

Lines	Lines energy, eV		Transition
	Present work	Ref. [12]	
a1	1.458	1.377	${}^6H_{15/2} \rightarrow {}^6F_{7/2}$
x1	1.512	1.509	${}^6H_{15/2} \rightarrow {}^6F_{5/2}$
x2,	1.680	1.612	${}^6H_{15/2} \rightarrow {}^6F_{3/2}$
a2, x3,	1.822; 1.845	1.687	${}^6H_{15/2} \rightarrow {}^6F_{11/2}$
c1,	2.145	2.145	${}^6H_{11/2} \rightarrow {}^4G_{11/2}$
x4	2.081	2.152	${}^6H_{13/2} \rightarrow {}^4F_{9/2}$
x5, b1	2.426; 2.435	2.441	${}^6H_{13/2} \rightarrow {}^4G_{11/2}$
c2	2.582	2.576	${}^6H_{15/2} \rightarrow {}^4F_{9/2}$
x6, b2	2.862; 2.919	2.865	${}^6H_{15/2} \rightarrow {}^4G_{11/2}$
x7, b3	3.051; 3.051	3.072	${}^6H_{15/2} \rightarrow {}^4I_{11/2}$
a3	3.402	3.373	${}^6H_{15/2} \rightarrow {}^6P_{5/2}$
c3	3.504	3.509	${}^6H_{15/2} \rightarrow {}^6P_{7/2}$
a4	3.527	3.543	${}^6H_{15/2} \rightarrow {}^6P_{7/2}$
x8	3.64		${}^6H_{15/2} \rightarrow {}^6P_{15/2}$
x9	3.75		${}^6H_{15/2} \rightarrow {}^6Q_{11/2}$
x10	3.92		${}^6H_{15/2} \rightarrow {}^4S_{15/2}$

Fig. 3B shows absorption spectra of same layers measured at temperature 10 K. The much more absorption maximums (x1 – x10) are observed in spectral interval 1.5 – 4.3 eV of these spectra. The weak observed band x1 at 1.512 eV is very close by energy to transitions ${}^6H_{15/2} \rightarrow {}^6F_{5/2}$. The weak band x2 is observed at energy 1.680 eV. This feature is most likely due to electronic transitions

${}^6H_{15/2} \rightarrow {}^6F_{1/2}$ and has an interval 1.70 eV according Ref [11, 12]. Absorption bands $x3$ (1.845 eV) and $x4$ (2.008 eV) is observed at higher energies (Fig. 3B). These absorption bands are better accorded by energies with transitions ${}^6H_{15/2} \rightarrow {}^6F_{9/2}$ and ${}^6H_{15/2} \rightarrow {}^4I_{15/2}$. The absorption maximum $c1$ observing at room temperature (see Fig. 3A) is not recognized at temperature 10 K. In the case of low temperatures at energy 2.426 eV the maximum $x5$, for our opinion associated with transitions ${}^6H_{13/2} \rightarrow {}^4G_{11/2}$, is observed. Absorption maximums $x6$ (2.862 eV) and $x7$ (3.051 eV) are associated with transitions ${}^6H_{15/2} \rightarrow {}^4G_{11/2}$ and ${}^6H_{15/2} \rightarrow {}^4I_{11/2}$. Weak features $x8$, $x9$ and $x10$ are observed in energy interval 3.5 – 4.2 eV, and possible transitions associated with these bands are shown in Table 1. Table 1 is also shown the energy position of observed features and corresponding transitions between dysprosium ions levels.

To clarify the influence of dysprosium ligand on the refractive index spectral dependences, measurements of thin glasses layers with pronounced interference fringes were carried out. The interference in the region $E < 2.3$ eV is observed on all As₂S₃ glassy films deposited on glass plates (see insert of Fig. 4A). The insert of figure 4A shows the typical transmission interference spectrum of As₂S₃ thin film and refractive index spectrum calculated from this interference. For each concentration the refractive indices were calculated by two methods described in Refs. [13] and [14]. For clarity, the refractive index spectral dependences of chalcogenide As₂S₃ glasses with a dysprosium concentration of 0.2%, 0.3%, and 0.5% are shifted vertically by 0.1, 0.2, and 0.3, respectively. No pronounced features in the refractive index spectral dependences were found. The thicknesses of measured As₂S₃ films are in interval 1.62- 5.65 μm . The magnitude of refractive index decreases from 2.4 to 3.6 at achieving to the absorption edge, Fig. 4A. The curves of refractive index spectral dependences shift towards lower energies with increasing dysprosium concentration in measured layers. This dependence on the nature and shift value coincides with the edge absorption shift abovementioned in Fig. 1.

Fig. 4B illustrates the transmission spectrum of glass plate of 1.2 mm thickness with 0.5% Dy concentration. One can see the interference fringes in this spectrum, but the plate thickness does not imply interference. Nevertheless the characteristic narrow interference fringes are observed in this transmission spectrum (see Fig. 4B). The density of narrow interference lines is decreased in the energy regions marked as $b1$, $b2$, and $b3$. The spectral dependence of refractive index (n) is calculated from the interference of measured transmission spectra. The features $b1$, $b2$ and $b3$ are found out in this dependence. Positions of these bands ($b1$, $b2$ and $b3$) are coincided with the regions where the density of interference fringes is minimal. The energy positions of these bands $b1$, $b2$ and $b3$ are coincided with the electron transitions between levels ${}^6H_{13/2} \rightarrow {}^4G_{11/2}$, ${}^6H_{15/2} \rightarrow {}^4G_{11/2}$ and ${}^6H_{15/2} \rightarrow {}^4I_{11/2}$, respectively.

In an isotropic non-gyrotropic medium, when birefringence does not occur, normal waves in any

directions are right and left circularly polarized. These waves have same velocities and respectively same refractive indices. Thus a linearly polarized wave during propagation does not rotate its polarization plane. An example of such material is glass-like semiconductor As₂S₃ materials. In optically isotropic mediums an induced optical activity can appear at some desymmetry creation i.e. creating conditions for the absence of a symmetry center. This condition, i.e. desymmetry changes (the gyrotropy appearance) are transition metal ions incorporation [15 - 19]. In the free state, the electron shells of transition metals atoms have a center and planes of symmetry, and therefore they are optically inactive. In complexes of coordination compounds of these metals with organic ligands, where they enter in the form of ions, optical activity induced by an asymmetric field of ligands appears on the absorption bands [15 - 19].

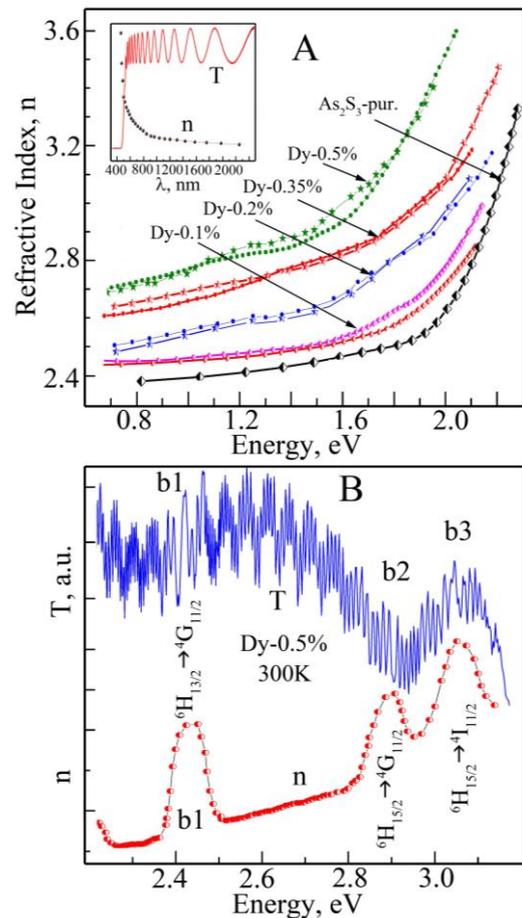


Fig. 4. A – Spectral dependences of refractive indices of As₂S₃ chalcogenide glasses for undoped and doped with dysprosium of various concentrations (the curves of 0.2%, 0.3% and 0.5% Dy are shifted up on 0.1, 0.2 and 0.3, respectively). Insert shows a typical interference transmission spectra of As₂S₃ thin film and calculated from this interference refractive index. B – The interference transmission spectra of As₂S₃ plate doped with 0.5% Dy and calculated refractive index

In glass-like As_2S_3 materials the doping by rare-earth element (Dy) leads to an appearance of optical activity in the molecular level. Most likely, the ion rare-earth element Dy plays the role of an asymmetric center in As_2S_3 glass or the implanted elements introduce asymmetry into the glass matrix. In such medium, normal waves with circular polarization have slightly different velocities and, accordingly, different refractive indices (n^- and n^+). Therefore, a linearly polarized wave will experience a rotation of the polarization plane during its propagation. The light wave rotation angle determined per unit path depends on the asymmetry created by the incorporated rare-earth ion and its concentration.

Namely, different velocities and, accordingly, different refractive indices (n^- and n^+) predetermine the interference appearance not related to the interaction of the waves reflected from the first and second surfaces of the measured structure (Fabry-Perot interference). Fig. 4B shows the thin interference modulated by the broad one which distance between neighboring interference fringes are much more than it for thin interference. According to the refractive indices calculations for thin films it was determined that the refractive index magnitude at energy 2.2 eV is equal to 3.6 (see Fig. 4A). Taking into account this refractive index value and a distance between interference extreme shown in Fig. 4B the thickness of layers where such interference can happen was estimated. For dense interference the thickness is 0.06 μm and for broad interference it is around 0.03 μm . But the thickness of measured samples is 1.2 mm consequently the interference occurs inside the plate due to interaction of circularly-polarized light waves. And appearance of these waves is associated with dysprosium ions levels. The broad interference appearance is due to birefractive effects associated with propagation velocities difference for left- and right-circularly polarized light waves. Taking into account the energy position of the broad interference maximums, the estimated value of refractive index difference ($\Delta n = n^+ - n^-$) is 0.001.

4. Conclusions

The incorporated dysprosium impurity shifts the edge absorption to the long-wavelengths. With temperature decreasing from 300 K to 10 K the edge absorption shifts toward higher energies. Absorption bands associated with transitions between dysprosium levels are detected in measured spectra.

Detected interference unrelated to the interaction of waves reflected from the first and second surfaces of the structure being measured. In As_2S_3 :Dy glasses, the light waves of the right and left circular polarization have unequal refractive indices ($n^- \neq n^+$). Different velocities and, accordingly, different refractive indices (n^- and n^+) predetermine the appearance of interference due to both n^- , n^+ and $\Delta n = n^+ - n^-$.

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