Proceedings of the International Conference on Oxide Materials for Electronic Engineering, May 29–June 2, 2017, Lviv

Physical Properties of the $(Ga_{70}La_{30})_2S_{300}$, $(Ga_{69.75}La_{29.75}Er_{0.5})_2$ S_{300} Single Crystals

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Using solution-melt method two single crystals, $(Ga_{70}La_{30})_2S_{300}$, $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$, were grown. The maxima of the luminescent radiation in the photoluminescence spectrum of the $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$ single crystal correspond to the intracentric transitions in the erbium ions: $^2H_{11/2} \rightarrow {}^4I_{15/2}$ (525 nm) and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (545 nm).

DOI: 10.12693/APhysPolA.133.994

PACS/topics: 61.82.Fk, 71.20.Eh, 78.20.–e, 78.55.–m

1. Introduction

The current research in the field of solid state chemistry follows the scheme:

composition → structure → properties → composition,

as modern technical progress requires the constant search for new materials that satisfy the demands of modern technology. Scientists are paying special attention to the properties of crystalline and amorphous media that are able to consistently show high-intensity conversion and up-conversion photoluminescence (PL) and non-linear optical (NLO) properties [1, 2]. That is why we are interested in the Ga_2S_3–La_2S_3 system, because ternary semiconductors are formed in it and there is also a region of glass forming there [3]. Previous investigations of the Ga_2S_3–La_2S_3 system found two ternary compounds, $GaLaS_3$ and $Ga_{1.67}La_3S_7$. $GaLaS_3$ forms in a peritectic reaction $L+Ga_{1.67}La_3S_7 \leftrightarrow GaLaS_3$ at 1223 K, crystallizes in the monoclinic structure, S.G. $P2_1/c$, $a = 1.517(8)$ nm, $b = 1.056(4)$ nm, $c = 1.282(6)$ nm, $\beta = 137.70$ (α-$GaLaS_3$) [3] or in the orthorhombic structure, S.G. $Pna2_1$, $a = 1.0405(1)$ nm, $b = 2.1984(2)$ nm, $c = 0.60565(5)$ nm (β-$GaLaS_3$) [4]. Electronic structure calculations of $GaLaS_3$ indicate that β-type is an indirect and α-type is a direct band gap semiconductor. The weak NLO response of β-$GaLaS_3$ has been detected [4]. The insertion of dopants like rare earth metals Pr^{3+}, Nd^{3+}, Dy^{3+}, Er^{3+} [1, 5–9] to binary or ternary compounds, is a condition for the production of media for laser technology and telecommunications.

2. Material and equipment

The single crystals of the $(Ga_{70}La_{30})_2S_{300}$, $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$ compositions were grown by solution-melt method from the primary crystallization range of the $GaLaS_3$. The compositions and the growth conditions were selected using the Ga_2S_3–La_2S_3 phase diagram [3]. The supercooling of the solid solution was 70 K as determined from the cooling thermograms of the samples. The synthesis of the starting alloy at maximum temperature 1200 K and the crystal growth was performed in the same evacuated quartz container with a conical bottom. The growth process was performed in a vertical two-zone furnace. The temperature gradient at the solid-melt interface was 20 K/cm. After melting the batch, the ampoule was lowered at a rate of 5 mm/day. Immediately after the crystallization of 10 mm along the ampoule, we followed by remelting 6.0–8.0 mm of the crystallized portion. Then the ampoule was annealed for 100 h. After that, the crystal growth was performed at a rate of lowering of 5 mm/day. At the end of the process, both furnaces were cooled to 820 K at a rate of 50–70 K/day, and then cooled to room temperature with the furnaces switched off. The grey-yellow single crystals (in case of the $(Ga_{70}La_{30})_2S_{300}$ colour was grey-pink) with a diameter of 10–13 mm and a length of 23–25 mm were obtained (Fig. 1). The photoluminescence spectra were investigated using an MDR-206 monochromator

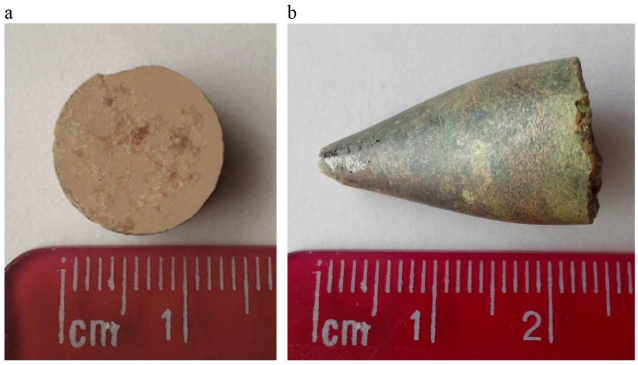

Fig. 1. Obtained $(Ga_{70}La_{30})_2S_{300}$ (a), $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$ (b) single crystals.

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at room temperature. The signal was registered by Si and PbS photosensors. The luminescence excitation was performed by a 400 mW laser at 810 nm wavelength.

3. Results and discussion

The single crystals $(Ga_{70}La_{30})_2S_{300}$, $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$ were indexed in the orthorhombic structure, S.G. $Pna2_1$, $a = 1.0412(2)$ nm, $b = 2.1966(4)$ nm, $c = 0.6052(3)$ nm for $(Ga_{70}La_{30})_2S_{300}$ with good agreement with [4] and $a = 1.0419(1)$ nm, $b = 2.1975(2)$ nm, $c = 0.6057(3)$ nm for $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$ (Fig. 2).

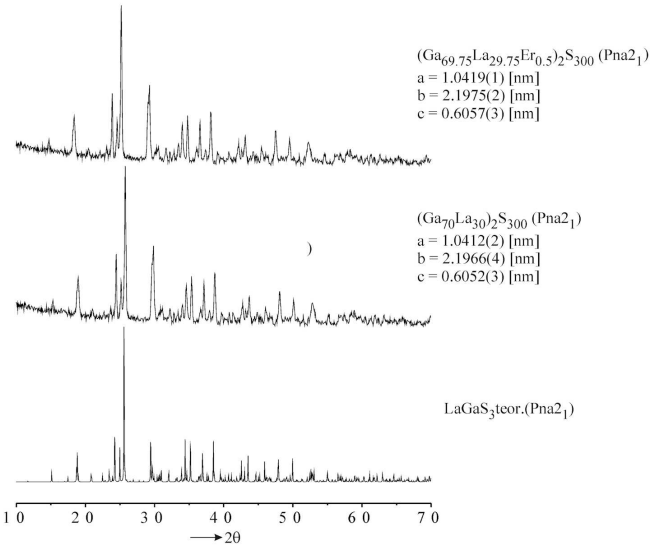

Fig. 2. Diffraction patterns of the obtained single crystals.

Up-conversion PL spectrum in the spectral range 510–560 nm (Fig. 3) consists of two peaks at 525 and 545 nm, with the ratio of the intensity at their maxima being $I_{545/525} = 4.2$. Characteristic narrow maxima and PL absence in the $(Ga_{70}La_{30})_2S_{300}$ crystal means that the emission in the $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$ single crystal is caused by the intra-center transitions in Er^{3+} ions, namely $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ for 525 and 545 nm, respectively. The absorption of IR quanta (810 nm) yields green luminescence, with higher energy quanta. Such a phenomenon (so called up-conversion photoluminescence) is especially common in erbium-doped chalcogenide glasses [10]. This can occur by sequential absorption of two photons with 810 nm wavelength; or when one erbium ion is in excited $^4I_{9/2}$ state, energy is transferred to another $^4I_{9/2}$-excited ion nearby

$$^4I_{15/2} + h\nu_{810} \rightarrow {}^4I_{9/2} + h\nu_{810} \rightarrow^2 H_{9/2},$$

$$^4I_{9/2} +^4 I_{9/2} \rightarrow {}^4I_{15/2} +^2 H_{9/2}.$$

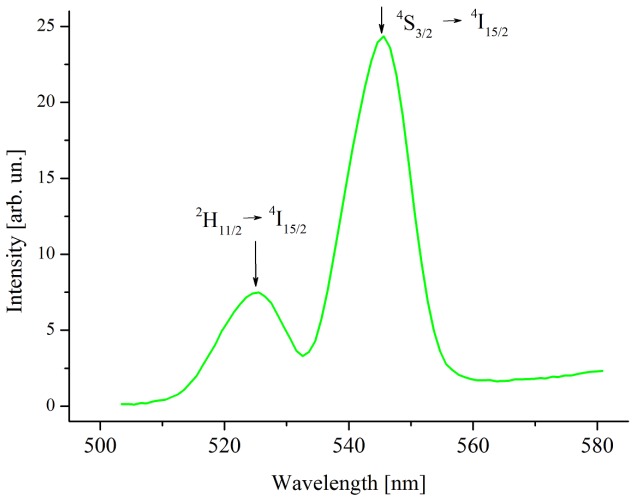

Fig. 3. Photoluminescence spectrum of the $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$ single crystal at 300 K.

The next step is non-radiative relaxation of erbium ions to the lower energy states or cross-relaxation involving $^2H_{11/2}$ and $^4S_{3/2}$ states. Thus, a high concentration of erbium ions in the $^2H_{11/2}$ to $^4S_{3/2}$ states is obtained through which PL radiation is emitted. This type of radiation is particularly promising for the manufacture of up-converters from infrared to visible light.

4. Conclusions

The single crystals of the $(Ga_{70}La_{30})_2S_{300}$, $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$ compositions were grown by solution-melt method from the primary crystallization range of the $GaLaS_3$. Both samples were indexed in the orthorhombic structure, S.G. $Pna2_1$, $a = 1.0412(2)$ nm, $b = 2.1966(4)$ nm, $c = 0.6052(3)$ nm for $(Ga_{70}La_{30})_2S_{300}$ and $a = 1.0419(1)$ nm, $b = 2.1975(2)$ nm, $c = 0.6057(3)$ nm for $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$. In the spectral range 510–560 nm the luminescence excitation was performed by a 400 mW laser at 810 nm wavelength led to photoluminescence in the $(Ga_{69.75}La_{29.75}Er_{0.5})_2S_{300}$ single crystal. The maxima of the luminescent radiation (525; 545 nm) correspond to the intracentric transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ in the erbium ions, respectively.

Acknowledgments

This work was partially supported by the Project of Ministry of Education and Science of Ukraine (No. 0115U002348).

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