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Short Note

Eu^{3+} LUMINESCENCE IN As_2S_3 DOT NETWORK

S. GEORGESCU[a], M. POPESCU[b], F. SAVA[b], A. VELEA[b*], G. PAVELESCU[c]
[a]*National Institute of Lasers, Plasma and Radiation Physics, 409 Atomistilor Street, P. O. Box MG. 36, RO-77125 Magurele Romania*
bNational Institute of Materials Physics, 105 bis Atomistilor Str., P.O. Box MG 7, RO-77125 Măgurele, Romania
[c]*National Institute of Research & Development for Optoelectronics, INOE2000, 409 Atomistilor Street, P.O. Box MG-5, RO-77125, Magurele, Romania*

Thin films of As_2S_3 doped with Eu^{3+} were prepared by vacuum evaporation. It was measured the fluorescence spectra before and after a heat treatment at 180 ºC for 45 minutes in inert atmosphere. After the heat treatment the transitions $^5D_1 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ were evidenced in the luminescence spectrum.

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In two recent papers [1, 2], the luminescence of Eu^{3+} in samples of chalcogenide glass As_2S_3 was discussed. The luminescence was excited at ~ 400 nm, corresponding to the Eu^{3+} transition $^7F_0 \rightarrow {}^5L_6$. In one experiment, a network of As_2S_3 dots was prepared by vacuum evaporation of As_2S_3 and Eu_2O_3 [2] on a glass substrate. In the as prepared sample, a very weak luminescence, characteristic to Eu^{3+}, was observed. After thermal treatments at moderate temperatures, a rather strong luminescence was observed. Besides, as a result of the annealing, the position of the luminescence band shifts toward shorter wavelengths (see Fig. 1).

In this note, we propose an explanation of the observed increase and "blue" shift of the Eu^{3+} luminescence in the network of As_2S_3 dots obtained by evaporation.

As a result of the vacuum evaporation of As_2S_3, the arsenolite (cubic As_2O_3) phase was obtained, as can be seen in the XRD patterns (Fig. 1, Ref. [2]). No phase transformation was observed as a result of the thermal treatment; only an increase of the size of the arsenolite crystallites can be noted (the diffraction lines became narrower).

In the as prepared sample (circles in Fig. 1, this paper), two weak luminescent lines, at ~ 612 nm and at ~ 525 nm can be seen. These lines correspond to the Eu^{3+} transitions $^5D_0 \rightarrow {}^7F_2$ and $^5D_1 \rightarrow {}^7F_1$. Besides, a shoulder at ~ 590 nm (corresponding to the magnetic-dipole transition $^5D_0 \rightarrow {}^7F_2$ is also observed). We consider that the Eu_2O_3 phase still exists in the as prepared sample, though, due to its low concentration, the characteristic diffraction lines are not observed in the XRD pattern. In Eu_2O_3 (cubic phase) there are two nonequivalent Eu^{3+} positions: ¾ Eu^{3+} ions lies in C_2 position (low symmetry). This implies an intense hypersensitive forbidden electric-dipole transition $^5D_0 \rightarrow {}^7F_2$ (at ~612 nm), much more intense than the allowed magnetic-dipole transition $^5D_0 \rightarrow {}^7F_1$. The remaining Eu^{3+} ions (1/4 from the total number of europium ions) in S_6 position (with inversion symmetry) contribute only to the magnetic-dipole transition $^5D_0 \rightarrow {}^7F_1$.

As noted in [1, 2], due to the absorption edge of the as prepared samples at long wavelengths, pumping at 400 nm is very inefficient, resulting in a very weak luminescence. We suppose that, as a result of the annealing, beside the increase of the size of the arsenolite crystallites, Eu^{3+} enter in the As_4O_6 cages, the local symmetry being high (T_d point symmetry [3, 4]).

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*Corresponding author: alin.velea@infim.ro

As a result, the intensity of the forbidden electric-dipole $^5D_0 \rightarrow {}^7F_2$ transition is substantially diminished, the allowed magnetic-dipole transition $^5D_0 \rightarrow {}^7F_1$ (at ~588 nm) becomes dominant.

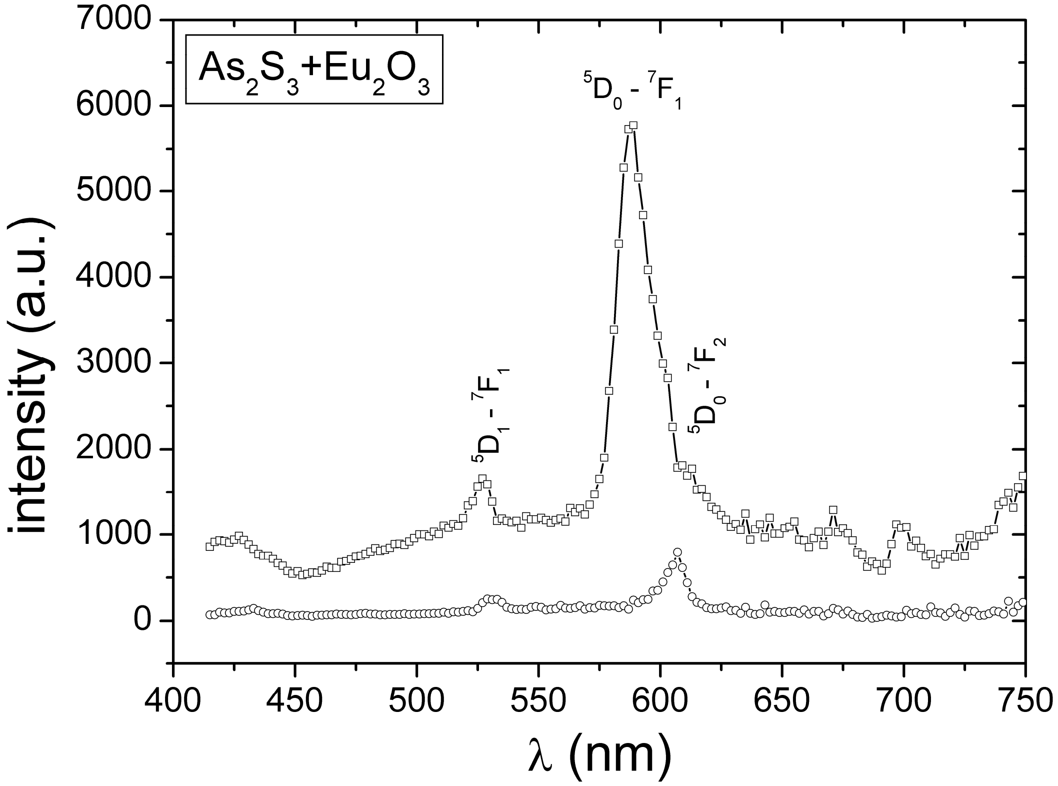

Fig. 1. Luminescence of Eu^{3+} in the dot network prepared by simultaneous evaporation of As_2S_3 and Eu_2O_3; circles – as prepared sample, squares – after the thermal treatment.

The emission line at ~525 nm is allowed magnetic-dipole transition ($^5D_1 \rightarrow {}^7F_1$). Since, as a result of the thermal treatment, the absorption edge shifts toward shorter wavelengths [1, 2], the pump becomes more efficient, explaining the increase of the luminescence intensity. The change of the dominant luminescent transition from $^5D_0 \rightarrow {}^7F_2$ (at ~ 612 nm) to $^5D_0 \rightarrow {}^7F_1$ (at ~588 nm) explains the observed 'blue' shift of the luminescence.

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