Chalcogenide Letters Vol. 8, No. 11, November 2011, p. 699 - 702

LUMINESCENCE OF EUROPIUM IN ARSENIC SULPHIDE MATRIX

M. POPESCU, A. LŐRINCZI, A. VELEA, I. D. SIMANDAN, F. SAVA, G. PAVELESCU[1], G. H. NICIU, D. O. NICIU, I. N. MIHAILESCU[2], G. SOCOL[2], N. STEFAN[2]
National Institute of Materials Physics, 105 bis Atomistilor Str., P.O. Box MG 7, RO-77125 Măgurele, Romania
[1]National Institute of Research & Development for Optoelectronics, INOE2000, 409 Atomistilor Street, P.O. Box MG-5, RO-77125, Magurele, Romania
[2]National Institute of Lasers, Plasma and Radiation Physics, 409 Atomistilor Street, P. O. Box MG. 36, RO-77125 Magurele Romania

Thin films of arsenic sulphide have been obtained by Pulsed Laser Deposition from bulk As_2S_3. A very thin layer of Eu_2O_3 was deposited by PLD from a different target in the next deposition process. After a heat treatment at 180 ºC for 45 minutes in inert atmosphere a structural transformation of the amorphous As_2S_3 to realgar (As_2S_2) occurred and the film develops a strong luminescence effect.

(Received 18 November 18, 2011; accepted November 23, 2011)

Keywords: Chalcogenide, Europium, Luminescence

1. Introduction

The developing of optoelectronic materials resulted in an increased interest in special glasses, in particular chalcogenide glasses with the aim to use them as matrix material for doping with rare earth ions. Investigations have shown that chalcogenide glasses appear to be very suitable materials for this purpose. A main characteristic of these glasses is the high transparency in the IR spectral range. The transparency of matrix with no absorption transitions in IR region is of special importance since this is exactly the region in which rare-earth ions exhibit emission transitions [1, 2]. The interest is primarily related to the transitions within the 4f orbital of the rare-earth ion, which appear in the near or middle range of IR spectrum [3]. Chalcogenide glasses doped with erbium (Er^{3+}) and europium (Eu^{3+}) are used in optical fibers, as passive fibers, in the power transmission systems, but also as active fibers in laser YAG: Er (λ = 2.97 μm). The breakthrough made in the area of these wavelengths is of great importance in optoelectronics and it is thought the chalcogenide glasses doped with rare-earths will take the leading role of optical amplifiers similar to the one that transistor had in the era of electronics. Some glasses in the system As-S-Ge with Er^{3+} have been synthetized [4]. The up-conversion luminescence properties of Erbium doped GeS_2-Ga_2S_3.KCl has been recently observed by J. Zhang, H. Tao and X. Zhao [5]. No information exists about of development of systems that transforms the excitation radiation in the UV range into luminescent radiation in red range to be used in optoelectronic devices.

In the paper by Kozyukhin et al [6] it is demonstrated that the use of rare-earth complexes to modify the chalcogenides is a promising approach which makes it possible to raise the rare-earth concentration in amorphous matrices. The fact that arsenic sulphide films with Eu exhibit room temperature luminescence suggests that complexes are incorporate into the glass without destruction of the glass network. The introduction of different rare-earth complexes allows the optical characteristics of amorphous films to be varied, which probably is associated with changing in the degree of disordering.

2. Experimental

2.1 Preparation of thin films

The films of amorphous chalcogenides have been deposited by Pulsed Laser Deposition (PLD) methods. As support for the deposition was used ordinary glass plates of size 25 x 25 mm^2 cleaned in potassium di-chromate solution in water and washed finally in double distilled water. The deposition was carried out from two different targets As_2S_3 and Eu_2O_3 and a sandwich of two layers was obtained: arsenic sulphide (~µm) and Eu_2O_3 (~nm).

The luminescence was stimulated by a special thermal annealing in nitrogen atmosphere at 180 ºC for 45 minutes. The second annealing was carried out in order to saturate the luminescence effect. The deposited material exhibits light yellow colour.

2.2 Characterization of thin films

The chalcogenide films were characterized by X-ray diffraction, optical microscopy, and optical spectroscopy.

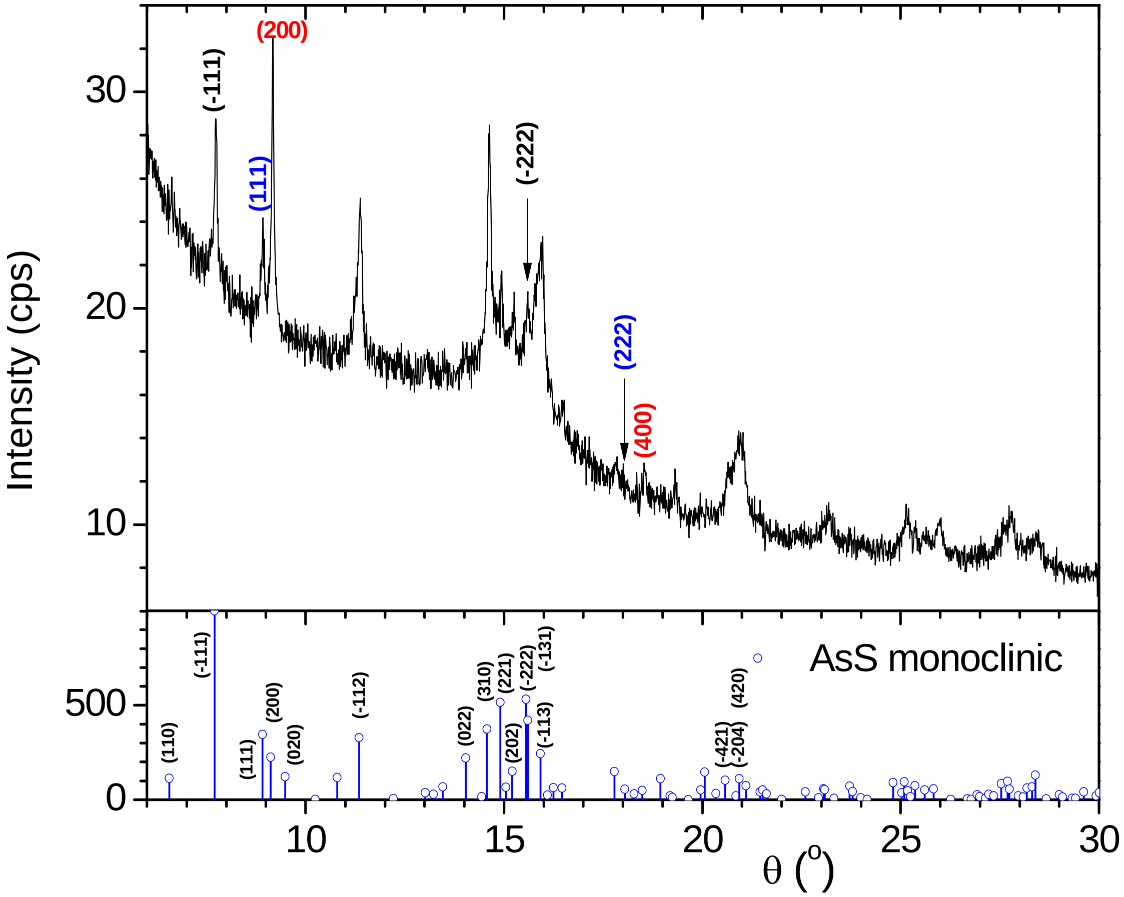

Fig. 1. X-ray diffraction diagram of the luminescent material after first annealing 45 minutes at 180 ºC. There is a polycrystalline phase of AsS base-centered monoclinic (according to File No. 89-1371 data sheet).

The X-ray pattern of the As_2S_3/Eu_2O_3 after heat treatment is shows in Fig. 1. The amorphous matrix of As_2S_3 is transformed into realgar (As_4S_4) as a consequence of a significant loss of sulphur. In the same time the surrounding of Europium is reorganized in the material.

The optical absorbtion spectra measured on initial and in hear treated ones are shown in Figure 2. It can be seen the shift of the absorption edge to smaller wavelength when the sample is annealed in the conditions described above.

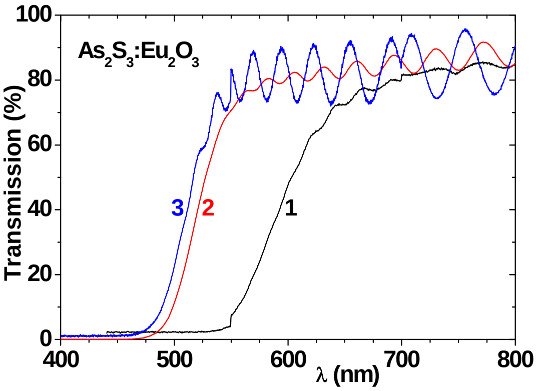

Fig. 2. The spectra of optical absorption measured on the sandwich of two layers of As_2S_3/ Eu_2O_3 *before and after thermal annealing:*

1. *initial;*
2. *after first annealing 45' at 180 ºC;*
3. *after second annealing 45' la 180 ºC.*

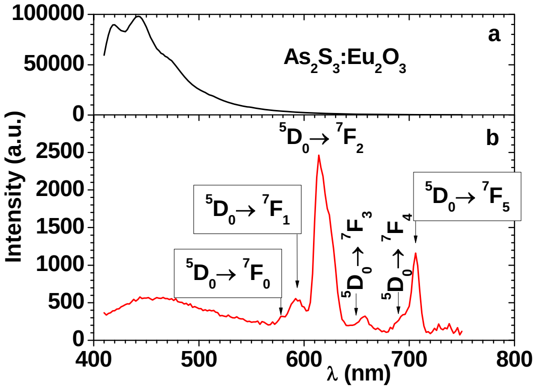

Fig. 3. Luminescence spectra of the sandwich of two layers of As_2S_3/ Eu_2O_3 *before and after thermal annealing the irradiation was made by monochromatic light (λ = 400 nm):*

a) *initial;*
b) *after first annealing 45' at 180 ºC.*

The luminescence of the initial and heat treated sample is shown in Figure 3 a, b. The excitation of the luminescence was performed at the wavelength of 400 nm. After annealing in inert atmosphere the element obtained reacts to light radiation λ = 400 nm emitting orange-red light (λ =614 nm) and red light (λ = 705 nm). Fluorescence spectrum (Fig. 3b) clearly shows the high intensity fluorescent emission of Eu^{3+} ions.

3. Discussion

In the initial sample, during PLD deposition, most of Europium oxide diffused in As_2S_3. Due to the unfavorable surrounding of Europium and due to the matrix of amorphous As_2S_3, whose absorption edge covers the excitation domain and the main luminescence line, the effect of luminescence of Eu cannot be evidenced.

The position of the absorbtion edge in As_2S_3 is situated at λ_{edge} (initial) = 587 nm ± 5 nm (2.112 ± 0.018) eV (see Figure 2). After the first annealing the absorption edge is shifted towards smaller wavelengths: λ_{edge} (after first annealing) = 517 nm (2.398 eV). By repeating the annealing in identical regime was reached the saturation of the shift to lower wavelengths: λ_{edge} (after second annealing) = 504 nm (2.460 eV). In the same time the intensity of the emission line increases.

Thus we got a strong luminescence at the wavelengths of around 614 nm, corresponding to the emission line of Europium $^5D_0$ -$^7F_2$.

4. Conclusions

Strong luminescence in Eu doped Arsenic sulphide was obtained in PLD deposited films annealed at 180 ºC for 45 minutes. The appearance of luminescence is due to the modification of the arsenic sulphide matrix in realgar crystalline form of the material by some loss of sulphur. The enhancing of luminescence of the Europium atoms is due to the change of the atomic configuration around the Europium atoms followed by the shift of the absorption edge of the films.

Acknowledgement

The authors kindly acknowledge for the financial support of the Ministry of the Education, Research, Youth and Sports in the frame of the Project CNMP no. 12089/2008.

References

[1] G. Liu (Editor), B. Jacquier (Editor), „Spectroscopic Properties of Rare Earths in Optical Materials", Springer Series in Materials Sciences and Tsinghua University Press, Beijing, vol. **83** (2005).

[2] D. Lezal, J. Optoelectron. Adv. Mater. **5**(1), 23 (2003).

[3] M. Letz, U. Peuchert, B. Schreder, K. Seneschal, R. Sprengard, J. S. Hayden, Journal of Non-Crystalline Solids **351,** 1067 (2005).

[4] V. B. Petrović, D. D. Štrbac, I. O. Gut, S. R. Lukić, J. Optoelectron. Adv. Mater., **11**(12), p. 2035 (2009).

[5] J. Zhang, H. Tao, X. Zhao, Rare Metals, 30(1), 18 (2011).

[6] S. A. Kozyukhin, N. A. Markova, A. R. Fairushin, N. F. Kuzmina, E. N. Voronkov, Inorganic Materials, **40(**8), 908 (2004).