Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Thin Solid Films 483 (2005) 27–30

thin solid films

www.elsevier.com/locate/tsf

Pulsed laser deposition and characterization of europium borate glass films

A.S. Aleksandrovsky*, A.M. Potseluyko, V.A. Seredkin, A.I. Zaitsev, A.V. Zamkov

L. V. Kirensky Institute of Physics, Krasnoyarsk, Akademgorodok, Krasnoyarsk 660036, Russia

Received 2 March 2004; accepted in revised form 6 December 2004
Available online 22 January 2005

Abstract

Thin films of europium borate glass have been obtained by pulsed laser deposition. Optical spectra of these films show no indications of the presence of trivalent europium, contrary to the material of the target. Magneto–optical activity of the films is demonstrated with the help of magnetic circular dichroism spectra.

PACS: 81.15.Fg; 78.20.-e; 78.20.Ls
Keywords: Laser ablation; Optical properties; Europium

1. Introduction

Optical and magneto–optical properties of rare earth ions in different valences continue to be the subject of intense study [1–5], especially in various borate glasses and crystal environments [6–13]. In particular, borate glasses heavily doped with divalent europium ions are characterized as a magneto–optic material for the near ultraviolet (UV) region [6,13]. Rare earth doped glasses with their rather high Verdet constant give the possibility of creation of thin film magneto–optic elements and devices for UV. However, mechanical manufacturing of these devices seems to be sophisticated, and common thin film technologies must be developed for such materials. The pulsed laser deposition (PLD) attracts attention among these technologies because it allows one to find regimes of deposition where chemical content of the film closely follows that of the target, and often laser-deposited films have superior quality to ones obtained by other methods, as for example, in the case of superconducting and ferroelectric thin films. This may be important in case of europium borate glass since europium has two stable valence states, and for accurate characterization of UV magneto–optic properties of these materials it is necessary that most of the europium should be in the chosen valence state. Recently PLD of epitaxial europium doped strontium barium niobate thin films has been examined, and only Eu^{3+} ions were found in deposited films [14].

In the present paper the pulsed laser deposition of europium borate glass films is investigated, and absorption and magnetic circular dichroism spectra of the films are compared to those of bulk samples.

2. Europium borate glass preparation

Three kinds of europium containing borate glass were prepared during this work. The first two kinds of samples, further on referred to as samples A and B, contained europium at overall density 8×10^{20} cm^{-3}. They are used as reference samples for spectral measurements. The third kind of europium borate glass referred as sample C contains a total of 6.8×10^{21} cm^{-3} europium ions and was used as the target material for pulsed laser deposition.

Sample A was prepared from a mixture of SrB_4O_7, B_2O_3 and Eu_2O_3 taken in 0.9:0.2:0.05 molar ratio. The mixture was grounded with ethanol and heated up to 300 °C slowly. Then the charge was put into a platinum crucible, and the

---

* Corresponding author. Tel.: +7 3912 494613; fax: +7 3912 438923.
E-mail address: aleksandrovsky@kirensky.ru (A.S. Aleksandrovsky).

0040-6090/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2004.12.016

latter was placed into furnace and heated up to 1050 °C in air. The melt was kept during 5 h at this temperature and poured out into a glass carbon crucible. The glass annealing was carried out at 350 °C during 15 h in air.

Sample B was prepared from mixture SrB_4O_7, B_2O_3 and Eu_2O_3 taken in 0.9:0.2:0.05 molar ratio, that is, the composition is identical to that of sample A. The preparation procedure was analogous to that for sample A, but the melt was kept in a glass carbon crucible in an atmosphere N_2+5 vol.% H_2 during 12 h. This procedure should reduce europium to Eu^{2+} state. The cooling process was made in the same reducing conditions. The glass annealing was carried out analogously to the sample A, however, in N_2/H_2 ambience.

Sample C was prepared from a mixture of H_3BO_3 and Eu_2O_3 taken in 4:0.5 molar ratio correspondingly. The mixture was grounded and heated up to 300 °C slowly. Then the charge was put into a glass carbon crucible and heated up to 900 °C slowly in atmosphere N_2+5 vol.% H_2. The sample was kept 12 h under these conditions. Then the temperature was increased up to 1100 °C and the mixture entered the melting state. The melt was kept during 12 h. The cooling and the annealing were the same as for the sample B.

3. Pulsed laser deposition of europium borate glass films

Europium borate glass films were deposited with a XeCl laser onto fused quartz substrates of thickness 80–200 microns. The target used was europium borate glass with chemical content EuB_4O_{7+x} analogous to that used for bulk samples and prepared as described above. Since the starting materials for target preparation contained Eu in the form of Eu^{3+} ions, some amount of these ions might have been preserved in the material of target after the reduction procedure, as expressed by adding the notation x in the chemical formula above. Hence, monitoring of Eu^{3+} presence in the target is needed. As we have shown in Ref. [15], the most reliable way for monitoring of Eu^{3+} in borate glasses codoped with Eu^{2+} and Eu^{3+} ions at overall densities of Eu of order of 10^{21} cm^{-3} is the measurement of absorption at the f–f transition $^7F_0 \rightarrow {}^5D_2$ of Eu^{3+}. The absorption spectrum of the material of the target in this spectral region is presented in Fig. 1 (Sample C). The absorption of $Sr_{0.9}Eu_{0.1}B_4O_{7+x}$ glasses containing 100% of Eu^{3+}(Sample A) and 30% of Eu^{3+}(Sample B) are presented in the same graph. Absorption peaks are well seen both for the target material and reference materials in the area of the transition quoted above. Assuming that absorption cross section for Eu^{3+} ions is the same in the samples A and C, the value of x for the material of target is approximately 0.29. The latter assumption seems to be rather well grounded. The oscillator strength of f–f transitions is determined mainly by the absence of inversion symmetry of the crystal field produced by the nearest environment. The second coordination sphere of europium ions in glass is expected to be formed mainly by BO_4 groups. These groups partially isolate the environment of the trivalent europium ions from structural changes caused by replacing strontium ion (Sample A) with divalent and trivalent europium (Sample C). Of course, the limited accuracy of this reasoning limits, in its turn, the accuracy of the method used to determine trivalent europium content.

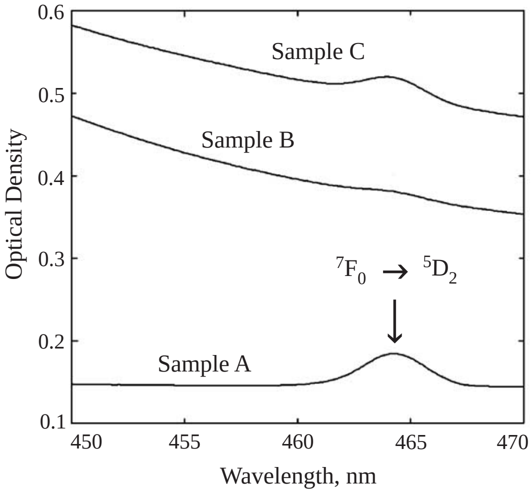

Fig. 1. Absorption spectra of the target material (Sample C, thickness 150 μm), strontium borate glass doped with trivalent europium (Sample A, thickness 1.29 mm) and strontium borate glass codoped with divalent (70%) and trivalent (30%) europium (Sample B, thickness 0.52 mm), in the region of the $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+}.

The deposition was performed at a laser pulse energy of 25–40 mJ at 10 Hz repetition rate. The wavelength of laser lies in the wing of the intense 4f–5d absorption band of divalent europium, rather far from the maximum of this band that gives the main contribution to the absorption of the target. The absorption coefficient of target material is 1800 cm^{-1} at 308 nm, which corresponds to an absorption depth of order 5 μm. This explains the rather high ablation threshold of 2 J/cm^2. The energy density during the deposition was 4–5 times above threshold. The pressure in the chamber during the deposition was 10^{-3} Pa. The ambience of oxygen for pulsed laser deposition of oxygen-containing compounds is common both for epitaxial superconducting and ferroelectric films, since otherwise the loss of oxygen in the process of deposition leads to a change of the structure of the growing film. This is not the case for the deposition of glass films. However, excessive loss of oxygen might lead to formation of non-ionized europium atoms inside the film. Nevertheless, we considered oxygen ambience unnecessary in order to avoid possible oxidation of europium in the film from divalent to trivalent state. Under these conditions Eu^{3+} content in the film is not expected to be higher than in the target, except for the case when the loss of europium during the deposition is higher than the loss of oxygen. The laser plume at 10^{-3} Pa has a characteristic greenish color, whereas at the residual air pressure above 10^{-1} Pa the color of the plume changes to slightly pink, giving a hint to the change of state of the europium ions inside the plume.

To achieve better adhesion and to obtain a higher density structure of the deposited film, the substrates were heated up to 500 °C. Various borate films produced by PLD are known to be strongly hygroscopic[16]. According to that, we observed that our films obtained at room temperature change their optical properties after the deposition. Contrary to this, the films obtained at the heater temperature of 400–500 °C are stable, though the deposition rate with a heated substrate is noticeably lower than with a cold substrate.

4. Absorption and magnetic circular dichroism spectra

The absorption spectra of films as well as those of reference samples are obtained using a Kontron Instruments UVIKON 943 Spectrophotometer with resolution 0.3 nm.

The typical thickness of deposited films measured with Linnik interferometer microscope is 300 nm. Absorption of the film in the UV is depicted in Fig. 2. In the same graph the absorption is presented of strontium borate glass containing 8×10^{20} cm^{-3} overall density of europium, 70% of which is in the divalent state and the rest is in trivalent state. The spectrum of strontium borate glass is used as the reference instead of the spectrum of the material of target since the strong absorption of the latter hinders obtaining it in the whole UV range. Both spectra are evidently formed by the contribution from Eu^{2+} ions. However, spectrum of the film is broadened with respect to the spectrum of diluted bulk material. Partially this may be connected with the increasing europium density in the film. Whilst the spectrum of bulk material is easily separated into e_g and t_{2g} components confirming cubic symmetry of the nearest environment of Eu^{2+} ions as first approximation [15], the spectrum of the film can hardly be definitely separated in the same way. A rather good fit can be obtained both for cubic and octahedral symmetry. We should also note that the longer wavelength wing of the spectrum is poorly described by Gaussian contours. This discrepancy can hardly be ascribed to the influence of increased europium density. Therefore, one can suspect stronger inhomogeneous spectrum broadening in the film with respect to the strontium-containing bulk material. The europium ions contributing to this part of spectrum are experiencing stronger crystal field than the typical value for bulk borate glasses. This, in our opinion, is connected with the conditions of deposition, namely, with the high energy of particles in the plume that leads to specific structural changes in the growing film. Another conclusion that can be outlined from the film spectrum in Fig. 2 is that even in heavily doped europium borate glasses the spectrum of these ions does not adjoin to conduction band of the material, which is formed by oxygen and boron transitions lying below 200 nm.

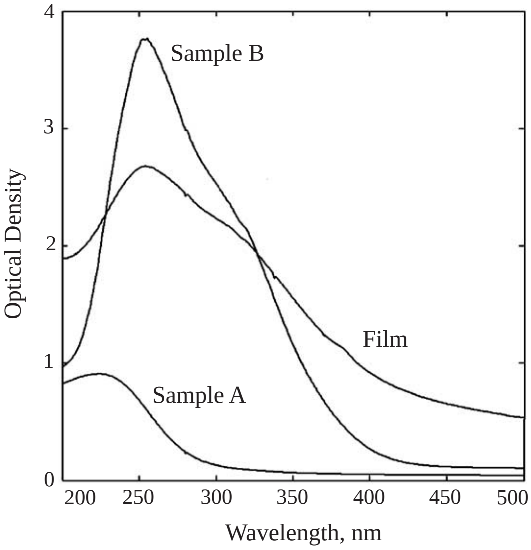

Fig. 2. UV absorption spectra of deposited film and of bulk strontium borate glasses doped with 100% trivalent europium (Sample A, thickness 49 μm) and codoped with divalent (70%) and trivalent (30%) europium (Sample B, thickness 19 μm).

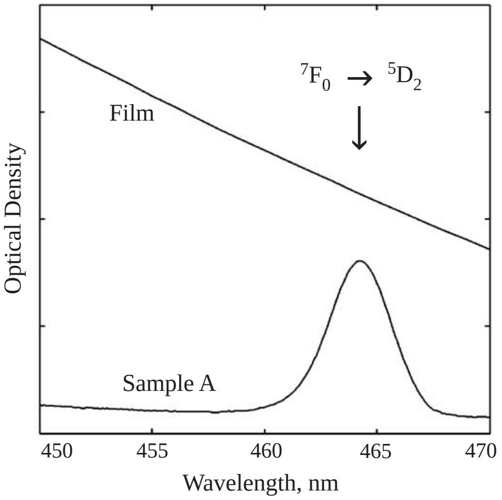

Fig. 3. Absorption spectra of deposited film and of bulk strontium borate glass doped with trivalent europium (Sample A, thickness 1.29 mm) in the region of the $^7F_0\rightarrow{}^5D_2$ transition of Eu^{3+}. The spectrum of the film is shifted down to reveal the absence of the Eu^{3+} peak.

The absorption of the film in the region of $^7F_0\rightarrow{}^5D_2$ of Eu^{3+} reveals no contribution from this ion (Fig. 3). Therefore, based on the presented absorption spectra we conclude that deposited films contain exclusively Eu^{2+}ions. However, we must emphasize it is more difficult to observe Eu^{3+} $^7F_0\rightarrow{}^5D_2$ absorption line in the film than in the bulk sample because of the broadening of the Eu^{2+} absorption spectrum. Therefore, a more reliable check of Eu^{2+} presence in the films must be magneto–optical measurements.

The magnetic circular dichroism (MCD) spectra of the films and of the reference samples were obtained using a traditional scheme involving polarization modulation and synchronous detection. In such a scheme the output signal of the synchronous detector is proportional to the difference

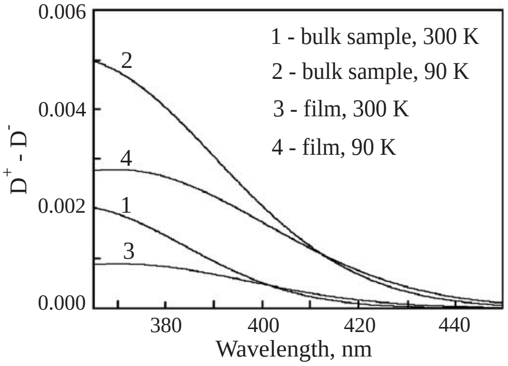

Fig. 4. Magnetic circular dichroism spectra of the bulk europium borate glass sample and of the film deposited on quartz.

of the optical densities for right circular (D+) and left circular (D^-) light. Spectra are taken in transmission geometry at 3.5 kOe magnetic field strength.

The MCD spectra of the bulk europium borate glass (Sample C) and of the film are presented in Fig. 4. The signal obtained from the film must be attributed to europium ions in the film but not to the substrate since MCD signal from the substrate is below the detection threshold of our apparatus. The spectral behavior of MCD for both samples is in general similar. The certain difference correlates with the changes in absorption spectrum at Eu^{2+} f–d transition and is, in our opinion, explained by shift and broadening of the transitions contributing to the formation of the MCD spectral profile.

We have not been able to detect Faraday rotation in the films, contrary to the bulk samples [13]. This is due to the thinness of the film and presence of an oppositely directed Faraday rotation in the quartz substrate. However, the presence of magneto–optic activity is obvious through the presence of MCD. One can expect that for films of higher thickness readily obtainable by the PLD method [17] Faraday rotation will be detectable. The spectral range of magneto–optic activity of the film obtained lies in the region of generation of such advanced light sources as GaN laser, and also near UV semiconductor lasers pumped with miniature electron guns. This fact presumes possible applications of the films under study. However, as one can understand from the absorption spectrum in Fig. 2, figure of merit for the films under study will be worse than for bulk samples, for deposition conditions used in this work. Hence, improvement of deposition technology is needed in order to decrease broadening of Eu^{2+} UV absorption spectrum in the films.

5. Conclusion

Thin films of europium borate glass were obtained with the help of pulsed laser deposition. Absorption spectra of these films show no signs of presence of trivalent europium, contrary to the material of target. However, they are broadened as compared to diluted bulk samples. Magneto–optical activity of the films is demonstrated with the help of magnetic circular dichroism spectra. The maxima of these spectra are shifted to longer wavelengths with respect to bulk samples.

Acknowledgements

This work was partially supported by Russian Foundation for Basic Research (Grant No. 02-02-16428), by Physical Sciences Department of Russian Academy of Sciences (Project 2.2.6.1) and by Siberian Branch of Russian Academy of Sciences (Project No.9). A. M. Potseluyko is grateful for the support from Russian Science Support Foundation.

References

[1] H. Ebendorff-Heidepriem, D. Ehrt, Opt. Mater. 15 (2000) 7.
[2] K. Binnemans, R. Van Deun, C. Gorller-Walrand, J. Adam, J. Non-Cryst. Solids 238 (1998) 11.
[3] H. Hosono, T. Kinoshita, H. Kawazoe, M. Yamazaki, Y. Yamamoto, N. Sawanobori, J. Phys.: Condens. Matter 10 (1998) 9541.
[4] M. Nogami, T. Yamazaki, Y. Abe, J. Lumin. 78 (1998) 63.
[5] X. Chen, T. Nguyen, Q. Luu, B. Di Bartolo, J. Lumin. 85 (2000) 295.
[6] K. Tanaka, K. Fujita, N. Soga, J. Qiu, K. Hirao, J. Appl. Phys. 82 (1997) 840.
[7] Z. Pei, Q. Zeng, Q. Su, J. Phys. Chem. Solids 61 (2000) 9.
[8] L. Huang, X. Wang, H. Lin, X. Liu, J. Alloys Compd. 316 (2001) 256.
[9] G. DasMohapatra, Mater. Lett. 35 (1998) 120.
[10] J. Ju, T. Kwon, S. Kim, J. Kim, M. Cha, S. Yun, Mater. Lett. 28 (1996) 149.
[11] O. Aloui-Lebbou, C. Goutaudier, S. Kubota, C. Dujardin, M. Cohen-Adad, C. Pedrini, P. Florian, D. Massiot, Opt. Mater. 16 (2001) 77.
[12] Q. Zeng, Z. Pei, Q. Su, S. Lu, J. Lumin. 82 (1999) 241.
[13] A. Potseluyko, I. Edelman, A. Malakhovskii, Y. Yeshurin, T. Zarubina, A. Zamkov, A. Zaitsev, Microelectron. Eng. 69 (2003) 216.
[14] H. Liu, S. Li, F. Fernandes, G. Liu, Thin Solid Films 424 (2003) 61.
[15] A. Aleksandrovsky, A. Krylov, A. Malakhovskii, A. Potseluyko, A. Zaitsev, A. Zamkov, J. Phys. Chem. Solids 66 (2005) 75.
[16] R. Xiao, L. Ng, P. Yu, G. Wong, Appl. Phys. Lett. 67 (1995) 305.
[17] A. Anderson, R. Eason, L. Hickey, M. Jelinek, C. Grivas, D. Gill, N. Vainos, Opt. Lett. 22 (20) (1997) 1556.