

RE containing glasses as effective magneto-optical materials for 200–400 nm range

A. Potseluyko^a, I. Edelman^{a,*}, A. Malakhovskii^b, Y. Yeshurun^c, T. Zarubina^d,
A. Zamkov^a, A. Zaitsev^a

^a*L.V. Kirensky Institute of Physics, Russian Academy of Sciences-SB, Akademgorodok, 660036 Krasnoyarsk, Russia*

^b*Department of Chemistry, Bar-Ilan University, 52900 Ramat-Gan, Israel*

^c*Department of Physics, Bar-Ilan University, 52900 Ramat-Gan, Israel*

^d*S.I. Vavilov Optical State Institute, 193117 St. Petersburg, Russia*

Abstract

Magneto-optical Faraday rotation (FR), optical absorption and magnetization of oxide glasses with high concentration of rare earth (RE) ions (up to 25 mol.% of R_2O_3 , R: Pr^{3+} , Dy^{3+} , Eu^{2+}) are investigated. These glasses had a good transparency and high value of Verdet constant simultaneously. They can be considered as materials of high magneto-optical quality in the wavelength range 200–400 nm.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Rare-earth glasses; Faraday rotation; Magneto-optical figure of merit

Glasses activated by rare earth (RE) elements have attracted considerable attention of scientists and engineers during several last decades because of their numerous applications in optically pumped solid-state lasers, optical modulators, switches, etc. Optical and magneto-optical properties of RE ions that depend on their environment in glasses are also interesting from the fundamental point of view and were studied in a great number of works [1–8]. The appearance of a new generation of lasers for the ultraviolet spectral (UV) region gave a new impetus to the study of these kind of materials because of the necessity to create effective magneto-optical elements for UV. The main difficulty in achieving high magneto-optical quality in UV range is that Faraday

rotation (FR) which increases with the increase of light quanta energy is usually accompanied by considerable rise of optical absorption. Earlier we have shown [7] that the formation of RE clusters can cause an increase of UV absorption in glass, which is absolutely undesirable from the viewpoint of glass applications. Thus, the clarification of clustering mechanism is of primary importance for glass technology. Valuable information on the problem can be obtained with the help of magnetic measurements. Magneto-optical properties of RE compounds are closely connected with their magnetic properties. This connection was first considered by Van Vleck and Hebb [9]. Though many authors dealt with magnetic properties of RE compounds, in general, the investigations of magnetic properties of RE doped glasses started quite recently [10–14]. The comparative study of magnetic, magneto-optical and

*Corresponding author. Fax: +7-3912-43-8923.

E-mail address: ise@iph.krasn.ru (I. Edelman).

optical properties of different glass matrices with various RE ion concentrations can promote obtaining new information on RE cluster formation and studying their influence on magneto-optical quality of glasses.

In the present work we will show spectral dependencies of FR and optical absorption and temperature dependencies of magnetic susceptibility of several RE containing glasses which have not been studied before from this viewpoint.

Three glass compositions were investigated: (a) $\{x(\text{Pr}_2\text{O}_3 + \text{La}_2\text{O}_3) + (100-x)(\text{SiO}_2 + \text{P}_2\text{O}_5 + \text{GeO}_2)\}$, (b) $\{x(\text{Dy}_2\text{O}_3 + \text{La}_2\text{O}_3) + (100-x)(\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3 + \text{SiO}_2 + \text{GeO}_2)\}$ and (c) EuB_4O_7 . Glasses containing praseodymium were prepared from the mixture of reagents H_3PO_4 , SiO_2 , GeO_2 and Pr_6O_{11} in a resistance furnace in quartz or platinum 100 ml crucibles at 1300–1500 °C. During this process Pr^{4+} from the compound of mixed valency was reduced to Pr^{3+} . Glasses containing dysprosium were prepared from the corresponding oxides as starting materials. La_2O_3 was added so that the total molar concentration of $(\text{R}_2\text{O}_3 + \text{La}_2\text{O}_3)$ was 15 and 25% for Pr and Dy, correspondingly. The melts were vitrified by rapid cooling to 350–400 °C, and then the glasses obtained were annealed at 300 °C. The total impurity levels in all the samples were 0.12 mass% of Pr_6O_{11} , 2×10^{-3} mass% of R_2O_3 , and 10^{-4} mass% of some

other uncontrolled impurities. Glass samples EuB_4O_7 were prepared from Eu_2O_3 and B_2O_3 at the temperature 1000 °C in the atmosphere of nitrogen (95% of the volume) and hydrogen (5% of the volume) during 6 h. During the process Eu^{3+} was reduced to Eu^{2+} .

FR and optical absorption measurements were made on polished glass samples of thickness ranging from 0.02 to 1.1 mm. For magnetic measurements bulk glass samples of $4 \times 4 \times 2 \text{ mm}^3$ were used. FR measurements were made by null-analyzer method (with modulation of light polarization plane) in the wavelength range 220–600 nm and in the temperature range 80–350 K using an original spectropolarimeter. The accuracy of FR measurements was 0.2 min. The magnetic field changed from -5 to $+5$ kOe, with an accuracy of 10 Oe. Measurements of magnetization were performed using a commercial SQUID magnetometer (Quantum Design MPMS-55) with the scan length of 4 cm in the temperature interval 5–300 K and in the magnetic field up to 50 kOe.

FR spectral dependencies for several samples at the room temperature are shown in Fig. 1. As is well known, FR in a material is given by the equation:

$$\alpha = VIH, \quad (1)$$

where α is the rotation angle, l is the length of the

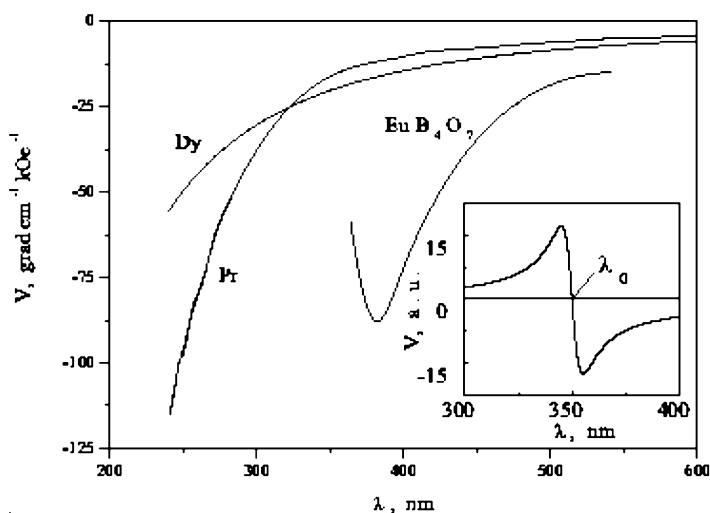


Fig. 1. Verdet constant for Pr, Eu and Dy glasses presented in Table 1 as a function of the wavelength at room temperature. In the inset, FR spectrum calculated according to the formula (Eq. (3)) where $\lambda_0 = 350 \text{ nm}$ and $\Delta\lambda_0 = 10 \text{ nm}$.

light path in a medium, H is the magnetic field applied along the light beam, and V is Verdet constant. In general, Verdet constant contains three terms [15,16]:

$$V = A(\lambda) + B(\lambda) + C(\lambda, T) \quad (2)$$

The diamagnetic term A is proportional to the splitting of electronic states in the magnetic field and does not depend on temperature T . The paramagnetic term C is proportional to the difference in thermal populations of the components of the ground state splitting in the magnetic field; therefore, it depends on temperature. The term B is called paramagnetic as well. It is due to the mixing of the states by the magnetic field, so it is independent of temperature (in a limited temperature range). This term exists only for the condensed matter, when crystal field splitting of the states takes place. Both paramagnetic terms have identical dispersions (λ is the light wavelength), different from the dispersion of the diamagnetic term.

Van Vleck and Hebb [9] derived the following relationship between the paramagnetic Verdet constant (C -term) and magnetic susceptibility χ for a free ion:

$$V = \chi K_0 g^{-1} \left[1 - \frac{\lambda^2}{\lambda_0^2} \right]^{-1} \equiv C_0 \left[1 - \frac{\lambda^2}{\lambda_0^2} \right]^{-1}, \quad (3)$$

where g is Lande factor of the ground state splitting, λ_0 is the wavelength of the effective electron transition equivalent in action to all transitions, producing FR far enough from the resonance absorption and K_0 is a coefficient of proportionality between magneto-optical activity of effective transition, C_0 , and magnetic susceptibility. Here the line width is not taken into account for the simplicity. The FR dependencies on the wavelength λ are shown in Fig. 1 for several samples representing each glass composition. The shortest wavelength values, where FR curves stop, correspond approximately to the fundamental absorption edge for each composition. The character of FR spectral dependence is the same for different RE ion concentrations of (a) and (b) compositions and does not change in the temperature interval 80–300 K. Spectral dependencies of FR shown in Fig. 1 follow the formula (3) quite well. The theoretical FR curve calculated according to the formula (3) with $\lambda_0 = 350$

nm and the half line width $\Delta\lambda_0 = 10$ nm is shown in the inset in Fig. 1. One can see that for Pr^{3+} and Dy^{3+} λ_0 is far in UV beyond the region of glass transparency, and for Eu^{2+} λ_0 is very close to this region. The effective wavelengths, λ_0 , determined from the experimental dispersions according to Eq. (3), are 180, 190 and 360 nm for Pr, Dy and Eu containing glasses, respectively. The FR linear dependence on RE ions concentration was observed for (a) and (b) compositions. Both of these compositions are transparent up to 240 nm and are characterized by large enough FR value in the shortwave length region. The highest FR value in UV has been obtained for Pr containing glasses. The (c) sample is transparent up to 350 nm only, but in the interval 350–450 nm there is a maximum of FR absolute value, which is observed in the vicinity of the wavelength λ_0 , according to the formula (3). The FR maximum value near 380 nm is very high. Basing on the FR and optical absorption measurements the magneto-optical figure of merit described by:

$$Q = 10^{-1} \left(\frac{V}{k} \right), \quad (4)$$

where k is the absorption coefficient, was obtained for all the samples. The highest Q values obtained are presented in Table 1.

Temperature dependencies of the magnetization and FR in the temperature interval 80–300 K are similar. Temperature dependencies of reciprocal magnetization of the glasses presented in Table 1 at $H = 2$ kOe are shown in Fig. 2. They display the Curie–Weiss type of magnetic behavior at high temperatures. However, some deviations of the magnetization temperature dependence from the Curie–Weiss law are observed at low temperatures. These deviations can be due to different causes one of which can be the formation of RE clusters. Due to indirect exchange interaction through oxygen, RE ions can be ordered antiferromagnetically at low temperatures producing the deviations observed. Though at high temperatures this order can not take place, RE clusters lead to the enhancement of optical absorption and, consequently, to the decrease of Q value. Additional investigations are needed to clear up this question. However, if RE cluster formation did take place, technological efforts should be undertaken to avoid this phenomenon and thus enhance the

Table 1
Optical absorption k , Verdet constant V and magneto-optical figure of merit Q for several samples at different wavelengths

λ (nm)	k (cm ⁻¹)	V (grad cm ⁻¹ kOe ⁻¹)	Q (grad kOe ⁻¹ dB ⁻¹)
15Pr ₂ O ₃ -85(SiO ₂ +P ₂ O ₅ +GeO ₂)			
240	3.0	115.0	3.80
250	1.5	97.9	6.53
270	1.1	64.6	5.80
25Dy ₂ O ₃ -75(Al ₂ O ₃ +B ₂ O ₃ +SiO ₂ +GeO ₂)			
240	39.3	55.7	0.14
250	34.3	49.8	0.15
270	28.5	40.3	0.14
EuB ₄ O ₇			
487.5	6.4	21.6	0.34
500.0	4.8	18.9	0.40
512.5	3.0	17.1	0.57

magneto-optical figure of merit of the material under discussion.

Summarizing the results we can state that some of the glasses investigated possessed good transparency and high value of Verdet constant in UV simultaneously. So, they can be considered as good candidates for the application in the UV spectral region. Pr containing glasses have shown the best

magneto-optical characteristics in the spectral region 250–300 nm.

Acknowledgements

This work has been partially supported by the Russian Foundation for Basic Research (Grant No.

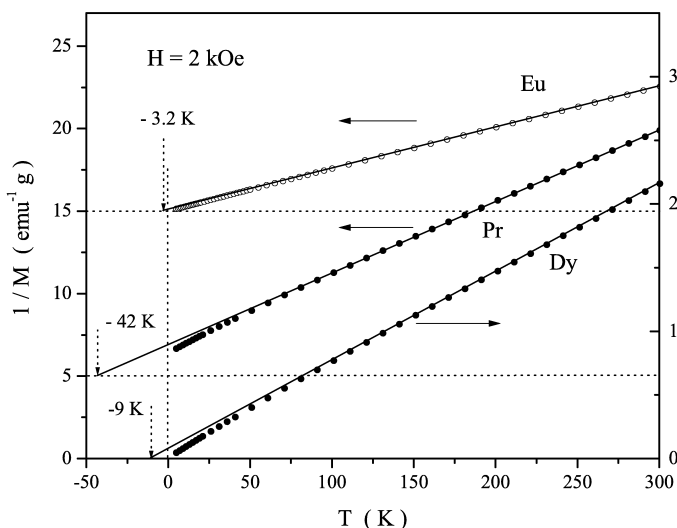


Fig. 2. Reciprocal magnetization vs. temperature for the same glasses.

02-02-16428 and 03-02-06729) and by the Program of the Russian Academy of Sciences, Project no. 9.

References

- [1] H. Li, L. Li, J.D. Vienna, M. Qian, Z. Wang, J.G. Darab, D.K. Peeler, *J. Non-Cryst. Solids* 278 (1–3) (2000) 35–57.
- [2] N.F. Borelli, *J. Chem. Phys.* 41 (1964) 3289–3293.
- [3] S.B. Berger, C.B. Rubinstain, C.R. Kurkjian, A.W. Treptow, *Phys. Rev. A* 133 (3) (1964) 723–727.
- [4] V. Lettelier, A. Seignac, A. LeFloch, M. Matecki, *J. Non-Cryst. Solids* 111 (1989) 55–62.
- [5] G.T. Petrovskii, I.S. Edelman, T.V. Zarubina, A.V. Malakhovskii, V.N. Zabluda, M.Y. Ivanov, *J. Non-Cryst. Solids* 130 (1991) 35–40.
- [6] J. Qiu, J.B. Qiu, H. Higuchi, Y. Kawamoto, K. Hirao, *J. Appl. Phys.* 80 (9) (1996) 5297–5300.
- [7] V. Zabluda, A. Pozeluyko, I. Edelman, A. Malakhovskii, T. Zarubina, G. Petrovskii, M. Ivanov, *J. Magn. Magn. Mater.* 185 (1998) 207–212.
- [8] A.M. Potseluyko, I.S. Edelman, V.N. Zabluda, O.A. Bol-sunovskaya, A.V. Zamkov, A.I. Zaitsev, *Physica B* 291 (2000) 89–96.
- [9] J.H. Van Vleck, M.H. Hebb, *Phys. Rev.* 46 (1934) 17–32.
- [10] M.A. Valente, S.K. Mendiratta, *Phys. Chem. Glasses* 33 (3) (1992) 149–153.
- [11] I. Ardelean, E. Burzo, D. Mitulescu-Ungur, S. Simon, *J. Non-Cryst. Solids* 146 (2–3) (1992) 256–260.
- [12] E. Culea, T. Ristoiu, I. Bratu, *Mater. Sci. Eng. B57* (3) (1999) 259–261.
- [13] E. Culea, I. Bratu, *J. Non-Cryst. Solids* 262 (1–3) (2000) 287–290.
- [14] T. Hayakawa, M. Nogami, *Solid State Commun.* 116 (2000) 77–82.
- [15] R. Serber, *Phys. Rev.* 41 (1932) 489–506.
- [16] P.J. Stephens, *J. Chem. Phys.* 52 (1970) 3489–3516.