Faraday Rotation Effect of Highly Tb_2O_3/Dy_2O_3-Concentrated $B_2O_3-Ga_2O_3-SiO_2-P_2O_5$ Glasses

Tomokatsu Hayakawa,*,† Masayuki Nogami,† N. Nishi,‡ and N. Sawanobori‡

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan, and Materials Section, R&D Division, Sumita Optical, Inc., 4-7-25 Harigaya, Saitama 338-8565, Japan

Received December 27, 2001
Revised Manuscript Received June 24, 2002

Faraday rotation (FR) has been useful for an optical attenuater, circulator, and magnetic field (or current) sensor.[1−3] There is growing importance of such Faraday devices because an increasing number of optical and laser-based devices require either rapid switching or protection against a back-reflected beam. Especially, the feedback effect ultimately restricts the performance of laser systems, resulting in amplitude fluctuations, frequency shifts, limitation of modulation bandwidth, noise, and/or even damage.[4] Since the recent development of laser systems are mainly focused on a shorter wavelength region, as represented by GaN-based lasers,[5,6] it should be considered which kind of materials are prospective as Faraday devices working in the corresponding frequency region. FR glasses with a high concentration of rare-earth ions have the advantages in the wide optical window and relatively large Verdet constants in the visible region.[7,8]

The FR effect is generally evaluated by $\theta_F = VBL$, where θ_F (rad) is the angle by which the plane of a polarized light is rotated on a passage through a length L (m) of a glass in a density of magnetic fluxes B (T). The material constant V (rad/(T × m))[9] is the Verdet constant, which is a function of both the incident wavelength and the concentration of rare-earth ions in glass. The Faraday rotation of rare-earth-doped glasses except Gd^{3+}[7,10] is paramagnetic in origin (hence, θ_F is negative) and is characterized by the frequency dependence, $V = K(\lambda_t^2 - \lambda^2)^{-1}$,[11] where K is a combination of constants including the number-of-density and effective Bohr magneton ($p = g[J(J + 1)]^{1/2}$) of the magnetically active ion. λ_t is the effective transition wavelength, often close to a 4f−5d transition of the corresponding rare-earth ion. Thus, large Verdet constants were obtained for glasses containing Ce^{3+}, Pr^{3+}, Tb^{3+}, and Dy^{3+}.[12−15] This is due to the fact that the 4f−5d transitions of these ions are located to lower energies.[16]

In the previous works, the content of rare-earth oxides was restricted to 30 mol % because of the difficulty of the glass manufacture. However, there has been a great development of the glass manipulation of highly concentrated rare-earth oxide glasses so that the 40 mol % content of Tb_2O_3 or Dy_2O_3 was accomplished. Recently, further condensation, as much as 50 mol % in glass, has been achieved by the double incorporation of Tb_2O_3 and Dy_2O_3. In this paper, we present the Verdet constants and magnetic properties of these novel FR glasses.

Glass samples investigated were produced by a conventional melt-quenching method at Sumita Optical Glass, Inc. The glass compositions were based on $5B_2O_3-3Ga_2O_3-3SiO_2-P_2O_5$ (in mol %) with the addition of 0.5 wt % Sb_2O_3 as a reducing agent of tetravalent terbium ions. The mixtures of commercially available compounds of H_3BO_3, Ga_2O_3, SiO_2, H_3PO_4, Tb_4O_7, and Sb_2O_3 were melted at ≈1450 °C for 2 h in a platinum crucible, which were rapidly quenched on a carbon mould and then annealed at ≈650 °C (see Table 1). To study their glass structures, Raman spectra were measured using a Fourier transform Raman spectrometer (Perkin-Elmer, Spectrum 2000 system). The excitation source for the Raman observations was a 1064-nm line of a neodium:yttrium−aluminum garnet (Nd:YAG) pumped by a semiconductor solid-state laser. FR measurements were performed at a temperature over the range of 15−300 K in pulsed magnetic fields with a pulse width of 30 ms. The magnetic fluxes condensed up to 16 T at the top of the magnetic pulse were applied along with a z-direction of a rod-shaped sample of ϕ2 mm in diameter and 4−5 mm in height, which was placed between two linear-polarizer films (Koyo, HN-32).[17,18] A He−Ne laser (632.8 nm) with a random polarization was used for an incident source. The transmitted light was detected by a photomultiplier.

To best our knowledge, the largest Verdet constant previously reported in the literature was at most −102.7 rad/(T × m) (=−0.353 min/Oe/cm)at 632.8 nm at room temperature in binary $30Tb_2O_3-70B_2O_3$ glass.[19] As a

* To whom correspondence should be addressed. Tel.: +81-52-735-5110. Fax: +81-52-735-5294. E-mail: hayatomo@mse.nitech.ac.jp.
† Nagoya Institute of Technology.
‡ Sumita Optical, Inc.

(1) Asahara, Y. *J. Ceram. Soc. Jpn*. **1991**, *99*, 903.
(2) Ning, Y. N.; Wang, Z. P.; Palmer, A. W.; Grattan, K. T. V.; Jackson, D. A. *Rev. Sci. Instrum*. **1995**, *66*, 3097.
(3) Ballato, J.; Snitzer, E. *Appl. Opt*. **1995**, *34*, 6848.
(4) Wilson, D. K. *Laser Focus* **1988**, *24*, 103.
(5) Narukawa, Y.; Kawakani, Y.; Funato, M.; Fujita, Sz.; Fujita, Sg.; Nakamura, S. *Appl. Phys. Lett*. **1997**, *70*, 981.
(6) Zhao, G.; Ishikawa, J.; Egawa, T.; Jimbo, T.; Umeno, M. *Jpn. J. Appl. Phys.* **2000**, *39*, 1035.
(7) (a) Berger, S. B.; Rubinstein, C. B.; Kurkjian, C. R.; Treptow, A. W. *Phys. Rev*. **1964**, *133*, A723. (b) Rubinstein, C. B.; Berger, S. B.; Van Uitert, L. G.; Bonner, W. A. *J. Appl. Phys*. **1964**, *35*, 2338.
(8) Borrelli, N. F. *J. Chem. Phys.* **1964**, *41*, 3289.
(9) As a conventional usage, min/Oe/cm is also used for Verdet constants. The following equation is helpful for the unit conversion from cgs to MKS unit system: 1 min/Oe/cm = 290.74 rad/(T × m).
(10) Valiev, U. V.; Krinchik, G. S.; Levitin, R. Z.; Sokolov, B. Yu. *Sov. Phys. Solid State* **1985**, *27*, 140.
(11) Van Vleck, J. H.; Hebb, M. H. *Phys. Rev*. **1934**, *46*, 17.
(12) Petrovskii, G. T.; Edelman, I. S.; Zarubina, T. V.; Malakhovskii, A. V.; Zabluda, V. N.; Ivanov, M. Yu. *J. Non-Cryst. Solids* **1991**, *130*, 35.
(13) MacFarlane, D. R.; Bradbury, C. R.; Newman, P. J.; Javorniczky, J. *J. Non-Cryst. Solids* **1997**, *213&214*, 199.
(14) Leterllier, V.; Seignac, A.; Le Floch, A.; Matecki, M. *J. Non-Cryst. Solids* **1989**, *111*, 55.
(15) Qiu, J.; Tanaka, K.; Sugimoto, N.; Hirao, K. *J. Non-Cryst. Solids* **1997**, *213&214*, 193.
(16) Loh, E. *Phys. Rev*. **1966**, *147*, 332.
(17) Hayakawa, T.; Nogami, M. *Solid State Commun*. **2000**, *116*, 77.
(18) Imaizumi, D.; Hayakawa, T.; Nogami, M. *J. Lightwave Technol.* **2002**, *20*, 740.

10.1021/cm0117331 CCC: $22.00
Published on Web 08/02/2002

Table 1. Nominal Composition and Verdet Constant *V* (at 632.8 nm, 300 K) for Highly Tb_2O_3/Dy_2O_3-Concentrated Borate Glasses Synthesized in This Work

sample's name	Tb_2O_3	Dy_2O_3	B_2O_3	Ga_2O_3	SiO_2	P_2O_5	*V* (rad/(T × m))
Tb25B	25		75				−72.8
Tb30B	30		70				−82.9
Tb30BG	30		60	10			−89.2
Tb30BGS	30		50	10	10		−80.8
Tb40BGSP	40		25	15	15	5	−146.3
Dy40 BGSP		40	25	15	15	5	−129.7
Tb40Dy10BGSP	40	10	16.67	10	10	3.33	−185.3
Tb10Dy40BGSP	10	40	16.67	10	10	3.33	−168.6

structural model of a rare-earth metaborate $25R_2O_3-75B_2O_3$ glass, Chakraborty et al.[20] proposed a ladder-typed chain consisting of a four-coordinated boron (BO_4) and two three-coordinated borons (BO_3). A rare-earth ion R^{3+} is predominantly located near the negatively charged BO_4 unit and plays an important role as linkage between two ladder-type chains. It is supposed that with an increase in the R_2O_3 content up to 30 mol % a breakup of the infinite chains takes place so as to produce an amount of nonbridging oxygens and an aggregation of R_2O_3 between the BO_4-2BO_3 chains. In our course of the glass synthesis for increasing Tb_2O_3 content, the Ga_2O_3 component was introduced as the substitution for BO_4 units, resulting in the reinforcement of the ladder-type chains. Nevertheless, it was found that much incorporation of Ga_2O_3 tended to the precipitation of crystalline $GaBO_3$ and $TbBO_3$. Thus, the SiO_2 component was necessitated to prevent such crystallizations. The P_2O_5 component served for decreasing the viscosity of the glass melt. Eventually, we succeeded in the fabrication of a 40 mol % Tb_2O_3-containing borate glass with the $5B_2O_3-3Ga_2O_3-3SiO_2-P_2O_5$ matrix batch, which exhibits high Faraday rotation of −146.3 rad/(T × m), as seen in Figure 1 and Table 1. Raman spectroscopy was employed for the investigation of microscopic structural units in the glass. Figure 2 shows the Raman spectrum of the 40 mol % Tb_2O_3-containing glass, which exhibits a strong peak around 980 cm^{-1}. It appears that the peak is more prominent above the content of 30 mol % with respect to other peaks. The insertion of Figure 2 shows Raman data of $R_2O_3-B_2O_3-Ga_2O_3-SiO_2$ glasses, where R^{3+} was substituted with gadolinium ion (Gd) and a 514.5-nm beam of Ar^+ laser was used as a light source. On one hand, the addition of Ga_2O_3 to binary $R_2O_3-B_2O_3$ glass, denoted by "G" in sample names, increased the peak intensity at ≈980 cm^{-1}, and on the other hand, the incorporation of SiO_2 content, denoted by "S", decreased the 860-cm^{-1} peak assigned with pyroborate groups. It is also noticed that the condensation of the rare-earth oxide up to ≈40 mol % with incorporated SiO_2 component enhanced the 980-cm^{-1} peak. Since the SiO_2 component only gave a small contribution that appeared at ≈920 cm^{-1} ($Si-O^-$ stretching mode), we conclude at the present time that either silicate or a phosphate group is not responsible for the feature at 980 cm^{-1}, which is quite possibly attributed to isolated orthoborate groups, $(BO_3)^{3-}$.[21,22] The strong peak implies that a part of the B_2O_3 composition does not play the role of a network former anymore but exists as isolated ionic groups with three nonbridging oxygens which can compensate positive charges of the trivalent rare-earth ions. For such a highly Tb_2O_3-concentrated glass, curious behaviors in magnetic and optical properties were reported.[23,24]

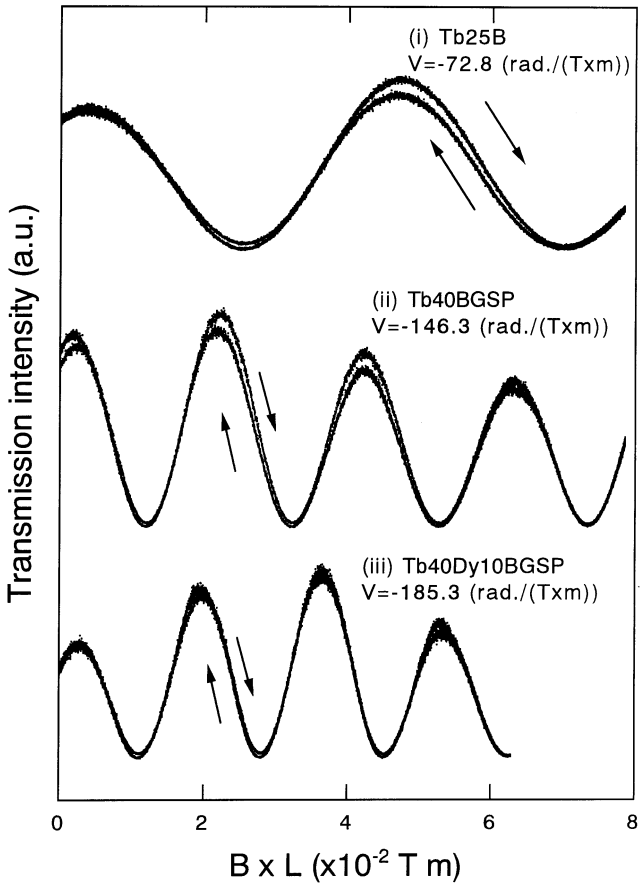

Figure 1. Dynamical Faraday rotation with a pulsed magnetic field of 16 T at 632.8 nm at 300 K for (i) Tb25B, (ii) Tb40BGSP, and (iii) Tb40Dy10BGSP glasses.

Dysprosium oxide was also used for the incorporation into the matrix glass because the paramagnetic rotation of rare-earth oxide glasses is dependent not only on the number of magnetic ions per volume but also on their magnetic moments.[7] Dy^{3+} has the largest total angular moment in the ground state ($J = 15/2$) in the lanthanide series and hence is also expected to contribute magneto-optical properties of the glasses. The temperature dependence of the Verdet constant of a 40 mol % Dy_2O_3 containing glass was estimated with 16T-pulsed magnetic fields. At 300 K the FR angle θ_F was a linear function of the applied magnetic field intensity B and the Verdet constant was −129.7 rad/(T × m). The Verdet constant increased with a decrease in the sample temperature and exhibited an inverse proportionality

(19) Tanaka, K.; Hirao, K.; Soga, N. *Jpn. J. Appl. Phys.* **1995**, *34*, 4825.
(20) Chakraborty, I. R.; Day, D. E.; Lapp, J. C.; Shelby, J. E. *J. Am. Ceram. Soc.* **1985**, *68*, 368.
(21) Konijnendijk, W. L.; Stevels, J. M. *J. Non-Cryst. Solids* **1975**, *18*, 307.
(22) Kamitsos, E. I.; Karakassides, M. A.; Chryssikos, G. D. *Phys. Chem. Glasses* **1987**, *28*, 203.
(23) Hayakawa, T.; Sato, K.; Yamada, K.; Kamata, N.; Nishi, N.; Maruyama, F. *Synth. Met.* **1997**, *91*, 355.
(24) Sato, K.; Yamaguchi, K.; Maruyama, F.; Nishi, N. *Phys. Rev. B* **2001**, *63*, 104416.

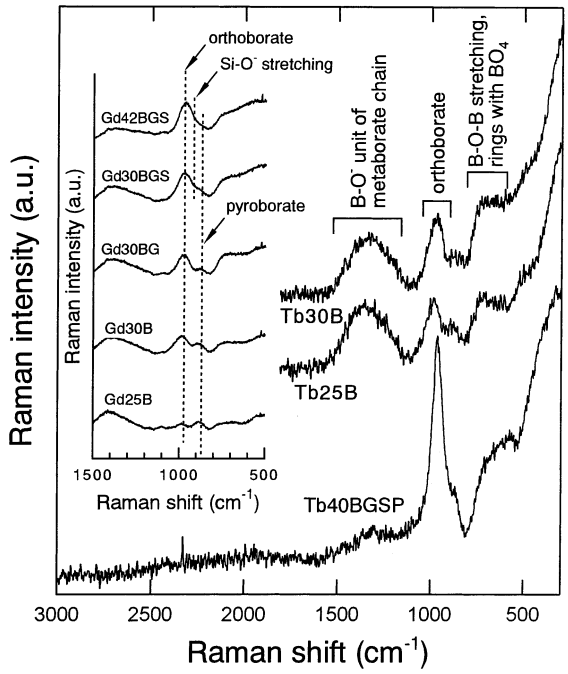

Figure 2. Raman spectra of Tb_2O_3-containing borate glasses of Tb25B, Tb30B, and Tb40BGSP. The insertion is a figure showing several Raman spectra of $25Gd_2O_3-75B_2O_3$ (Gd25B), $30Gd_2O_3-70B_2O_3$ (Gd30B), $30Gd_2O_3-60B_2O_3-10Ga_2O_3$ (Gd30BG), $30Gd_2O_3-50B_2O_3-10Ga_2O_3-10SiO_2$ (Gd30BGS), and $41.7Gd_2O_3-41.7B_2O_3-8.3Ga_2O_3-8.3SiO_2$ (Gd42BGS) are also given, which explains an increasing 980-cm^{-1} peak of orthoborate groups with an increase in rare-earth oxide in glasses.

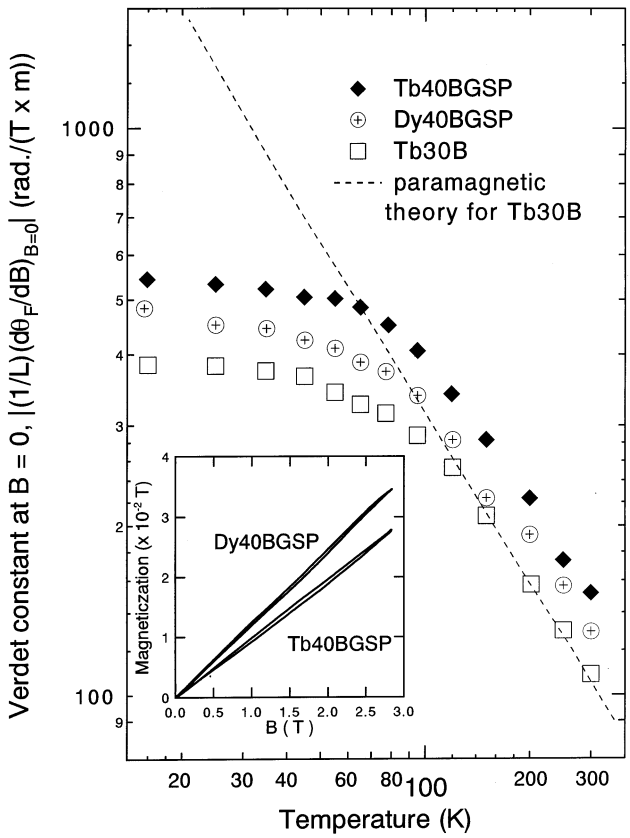

Figure 3. Temperature dependence of the Verdet constants of Tb_2O_3- or Dy_2O_3-containing borate glasses (Tb40BGSP, Tb30B, and Dy40BGSP). The insertion shows the $M-B$ curves for Tb40BGSP and Dy40BGSP at 300 K. The magnetic susceptibility of Tb40BGSP and Dy40BGSP is 0.952×10^{-2} and 1.18×10^{-2}, respectively.

against the temperature up to 100 K, as predicted in the paramagnetic theory.[11] Interestingly, the FR angle below 120 K was no longer a linear function of B; that is, the Verdet constant showed a B dependency. Thus, the temperature dependence of the Verdet constant was estimated as $L^{-1}(d\theta_F/dB)_{B=0}$. It is seen from Figure 3 that the temperature dependence had a tendency to be saturated to ca. −483.6 rad/(T × m). The saturation behavior stemmed from $Dy^{3+}(\downarrow)-O^{2-}-Dy^{3+}(\uparrow)$ superexchange interaction, which prevented the orientation of Dy^{3+} magnetic moments to the applied magnetic fields.[18]

Moreover, the simultaneous incorporation of Tb_2O_3 and Dy_2O_3 allowed us to increase the total concentration of rare-earth ions. On the basis of the $5B_2O_3-3Ga_2O_3-3SiO_2-P_2O_5$ composition, the total rare-earth content of 50 mol % has been successfully obtained. We prepared two borate glasses incorporated with Tb_2O_3 and Dy_2O_3 (see Table 1 and Figure 1(iii)). A comparison between the Verdet constants of Tb40Dy10BGSP and Tb10Dy40-BGSP reveals that Tb^{3+} ions have a quite high contribution to the Faraday rotation through the lower f−d transition energy (Tb^{3+}, ≈40 000 cm^{-1}; Dy^{3+}, ≈54 000 cm^{-1} [16]) and Dy^{3+} ions are also of importance due to the largest J value. The latter ions must increase the magnetic susceptibility of the total sample. To obtain direct evidence for the contribution of Dy^{3+} ions to the FR, we measured M(magnetization)−B curves of both Tb_2O_3 and Dy_2O_3 oxide glasses with 40 mol % content in the pulsed magnetic fields at 300 K (see the insertion of Figure 3). As expected, the magnetization of the Dy_2O_3 oxide glass was greater than that of the Tb_2O_3 oxide glass, where the magnetic susceptibility was 0.952×10^{-2} for Tb40BGSP and 1.18×10^{-2} for Dy40BGSP. The increase in the susceptibility resulted in the densification of the applied magnetic fluxes on the sample, and therefore the internal magnetic fields around Tb^{3+} ions were enhanced.

In conclusion, the higher Verdet constant was obtained when Tb_2O_3 and Dy_2O_3 were simultaneously incorporated to the $B_2O_3-Ga_2O_3-SiO_2-P_2O_5$ glass matrixes. Not only the small 4f−5d energy separation of Tb^{3+} ions but also the large total angular momentum of the ground state of Dy^{3+} ions contributed quite a bit to the FR properties. The Raman investigation clarified the existence of an amount of orthoborate $(BO_3)^{3-}$ groups. With aid of the negative charges of the isolated borate units, the high incorporation of Tb_2O_3 and Dy_2O_3 as much as 50 mol % could been achieved. The Verdet constant of −185.3 rad/(T × m) was obtained at 632.8 nm at 300 K, which was nearly 2 times greater than the estimations reported previously.

Acknowledgment. Financial supports from the Research Foundation for the Electrotechnology of Chubu (REFEC) and partially a Grand-in-Aid for Scientific Research (No. 13305048 and No. 13026214) for the Ministry of Education, Science, and Culture of Japan are greatly acknowledged.

CM0117331