Supporting Information

High Verdet Constant Glass for Magnetic Field Sensor

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1 Experimental

1.1 Magneto-optical (MO) glass preparation

A series of Tb-Ge-B-Al glasses were prepared by the melt-quenching method. As listed in **Table S1**, the composition of the glasses was xTb_2O_3 -GeO₂-B₂O₃-Al₂O₃ (x=20, 30, 40, 45, in mol%). Raw materials include Tb₄O₇ (99.999%, Aladdin); GeO₂ (99.999%, Aladdin); H₃BO₃ (99.999%, Aladdin); Al₂O₃ (99.999%, Aladdin) were weighed proportionally. After being mixed in an agate mortar for 1 h, these powders with a total weight of 10 g are melted at 1500 °C for 90 minutes in corundum crucibles. After melting homogeneously, the melts were poured onto a preheated (400 °C) stainless plate to prevent fragmentation. The formed glasses were then annealed at 550 °C for 2 h and naturally cooled to room temperature. These prepared glasses were polished on both sides for optical characterization. The polished glasses were photographed and compared in **Figure S1**.

Abbreviation	GeO ₂	B_2O_3	Tb ₂ O ₃	Al ₂ O ₃
20T20A	15	45	20	20
20T25A	15	40	20	25
20T30A	15	35	20	30
30T10A	15	45	30	10
40T5A	15	40	40	5
45T5A	15	35	45	5

Table S1 Composition of glass studied



Figure S1 Pictures of the transparent MO glasses

1.2 Characterization

The glass structure was characterized by Fourier transformed infrared spectrometer (FTIR, INVENIO S). The glass was grinded into powder, and mixed with ultradry KBr powder at a ratio of 1:100, then pressed into thin sheets for testing. Raman spectra were recorded on Raman spectrometer (LABHRev-UV). The excitation wavelength is 532 nm. The valence state of Tb ions in the obtained samples was measured by X-ray photoelectron spectroscopy (XPS, JPC-9010MC, JEOL) with Mg-K α as the X-ray source. The binding energies from the XPS measurements were calibrated with reference to the C 1s. Differential scanning calorimetry (DSC, STA449F1) was used to determine the glass transition temperature T_g and onset of

crystallization temperature T_x . 40 mg of powder sample was placed in a platinum crucible for testing at the temperature range of 25 °C-1000 °C with a heating rate of 10 K/min. Based on Archimedes principle, the density of TGBA glass samples was determined with deionized water. The optical transmittance of prepared glass samples measured by the ultraviolet-visible-near infrared (UV-Vis-NIR) was spectrophotometer (UH4150, HITACHI, Japan). The photoluminescence (PL) was measured by an assembled optical system (QM/TM/NIR). The Faraday rotation angle was measured at room temperature by using a commercial measurement system (FD-FZ-C, Fudan Tianxin, Shanghai). The light source was a semiconductor laser, and the max external magnetic field was 1.35 T. Besides, the Verdet constant (V) can be calculated with the formula $V=\theta/Bd$, where θ is the rotation angle, B is the magnetic flux density, and *d* is the thickness of the sample.

2 Glass structure analysis

Wavenumber	Assignments				
(cm ⁻¹)					
499	Al-O-Al bending vibrations				
	Bending and stretching vibrations of [GeO ₄]	[1, 2]			
724	B-O-B bending vibrations				
/34	Asymmetric stretching vibrations of [AlO ₄]	[1-3]			
700	Vibrations of [GeO ₄]	[2, 5,			
790	Asymmetric stretching vibrations of [AlO ₄]	6]			
815	Al-O stretching vibrations of [AlO ₄] tetragonal units	[7]			
827	B-O stretching vibrations of [BO ₄] tetragonal units				
037	Boron oxygen ring respiratory vibration	[3]			
920	Al-O stretching vibrations of [AlO ₄]	[7]			
979	B-O stretching vibrations of [BO ₄]	[3, 4]			
1233	B-O stretching vibrations of $(BO_3)^{3-}$ units in metaborate,				
	pyroborate and orthoborates	8]			
1336	B-O asymmetric stretching vibrations of [BO ₃]	[4, 9]			
1425	B-O ⁻ vibrations attached to large segments of borate				
	network	[3]			
1507	B-O vibrations of [BO ₃]	[3]			

Table S2 FTIR spectral assignments.



Figure S2 FTIR absorption spectra of $[BO_4]$ tetrahedral units in the range of 950-1200 cm⁻¹ with the increase of (a) Al₂O₃ and (b) Tb₂O₃

Ge-B-Al	Assignments	Ref
350	O-Ge-O deformation mode	[10, 11]
597	Ge-O-Ge bending mode	[12-15]
	B-O-Al bending mode	
832	Stretching vibrations of B-O of BO ₄ units	[9, 16]
800	Vibrations of boroxol rings	[17, 18]
950	B-O ⁻ stretching mode in diborate structures	[13, 19]
990	B-O ⁻ stretching mode in metaborate structures	[20, 21]

Table S3 Raman spectral assignments

3 XPS spectrum and the peak assignment



Figure S3 XPS full spectrum of 20T20A sample

Assignments	20T20A	20T25A	20T30A	30T10A	40T5A	45T5A
$Tb^{3+} 3d_{5/2}$	1239.34	1239.42	1239.03	1239.43	1238.65	1239.43
$Tb^{4+} 3d_{5/2}$	1241.14	1241.22	1240.69	1241.01	1240.83	1241.15
Tb ⁴⁺ satellite	1243.6	1243.73	1243.2	1243.56	1243.51	1243.31
Tb ⁴⁺ satellite	1251.03	1251.26	1250.81	1250.95	1250.98	1250.69
Tb ³⁺ satellite	1265.16	1262.27	1264.59	1262.77	1262.81	-
$Tb^{3+} 3d_{3/2}$	1274.35	1274.57	1274.15	1274.2	1274.29	1274.07
$Tb^{4+} 3d_{3/2}$	1276.48	1276.29	1276.03	1276.66	1276.34	1276.09
Tb ⁴⁺ satellite	1277.98	1277.97	1277.42	1277.60	1277.81	1277.19

20T20A	20T25A	20T30A	Assignments
28.66	29.12	28.99	Ge^{0}
31.57	31.67	31.72	Ge ²⁺
32.52	32.53	32.57	Ge^{4+}

Table S5 XPS peak positions and their corresponding Ge ion valence

4 Optical properties

4.1 Calculation of band gap

The band gap (E_g) of MO glasses was calculated with the Tauc equation as follows:

$$\alpha hv = B \left(hv - E_g \right)^m \tag{1}$$

where α is the absorption coefficient, hv is the photon energy, B is the constant related to the band tail, and m is the parameter related to the type of electronic transition that causes light absorption, in amorphous glass material, m=2, representing the indirect optical transition. **Figure S4** gives the results of band gap $E_{\rm g}$.



Figure S4 Band gap of these MO glasses

4.2 Calculation of critical distance between Tb³⁺ ions

The critical distance (R_c) between Tb³⁺ ions was calculated with the following formula:

$$R_{\rm c} = \left(\frac{M}{N_{\rm A}\rho x}\right)^{1/3} \tag{2}$$

where *M* is the average molecular weight of the glass, N_A is the Avogadro constant, ρ is the density of the glass, and *x* is the concentration of Tb³⁺ ions. For magneto-optical glass with increasing Tb³⁺ ion doping concentration, the critical distance continues to decrease.



Figure S5 Critical distance R_c between Tb³⁺ ions

5 Density

By analyzing the density of the glass, it is helpful for us to better understand its structure and calculate the effective concentration of Tb ions. The ionic radius of Al^{3+} is 50 pm. As shown in **Figure S6**, when the Tb₂O₃ is 20 mol.%, the density of TGBA

increases with the addition of Al_2O_3 , because the atomic mass of Al_2O_3 (101.96 g/mol) is greater than that of B_2O_3 (69.62 g/mol). On the other hand, when Tb_2O_3 increases from 30% to 45%, the density increases as the molar mass of TGBA increases from 166.98 g/mol to 209.79 g/mol.



Figure S6 The density of the MO glasses

6 Optical basicity

As discussed by Duffy^[22, 23], an intrinsic relationship exists between electronic polarizability of the oxide ions (α_{O2-}) and optical basicity (Λ) of the oxide medium, as shown by the formula below,

$$\Lambda = 1.67 \left(1 - \frac{1}{\alpha_{0_{2^{-}}}} \right)$$
(3)

Since increased oxide ion polarizability means stronger electron donor ability of oxide ions, the physical background of the oxide ion polarizability and optical basicity is naturally the same. This means that the oxide with higher optical basicity has stronger ability to provide electrons. The theoretical optical basicity Λ_{th} for glass can be calculated using basicities assigned to the individual oxides:

$$\Lambda_{\rm th} = \sum x_i \cdot \Lambda_i \tag{4}$$

where Λ_{th} is the theoretical basicity of the glass, x_i is the molar percentage of the constituent oxide, Λ_i is the optical basicity of the oxide. ^[7, 24] According to the literature, the Λ_i of Tb₂O₃, GeO₂, B₂O₃ and Al₂O₃ are 0.954, 0.7, 0.425 and 0.6, respectively.^[25]

7 Thermal property

Based on the DSC test, the detailed thermal properties investigation has been given. According to Hruby theory^[26], ΔT (defined as $\Delta T = T_x - T_g$) is a parameter proportional to the trend of glass forming ability. The larger ΔT , the better the thermal stability of glass. As shown in **Figure S7**, the ΔT increased with the Al₂O₃ content and decreased with the Tb₂O₃ content in MO glasses.

According to the discussion in structural analysis, GeO₂, B₂O₃ and Al₂O₃ form the glass network, while glass network modifier (Tb₂O₃) will break the glass network and reduce its connectivity. Therefore, when Al₂O₃ replaces B₂O₃, stable [AlO₄] increases to replace [BO₄] and promote the transformation of [BO₄] to [BO₃]. Moreover, the radius of Al³⁺ is moderate (B³⁺ < Al³⁺ < Tb³⁺), which promotes the atomic connection as well. These two factors lead to the rise of ΔT along with the increase of Al₂O₃. Moreover, with the increase of Tb₂O₃, ΔT shows a downward trend, which is mainly due to the Tb₂O₃ breaking the glass network. Overall, 20T30A shows the best thermal stability (ΔT >180 °C) that can be applied to optical fiber preparation. 45T5A still has good thermal stability (ΔT >105 °C) and can prevent crystallization in the preparation process.



Figure S7 Thermal properties $(\Delta T = T_x - T_g)$ of MO glasses

8 Calculation of Tb³⁺ content in MO glasses

The effective concentration of Tb ions (N_{Tb}) of the MO glass is calculated as follows,

$$N_{\rm Tb} = 2\rho \cdot W_{\rm c} \cdot A_{\rm v} / M \tag{5}$$

where ρ is the glass density, W_c is the mass percentage of Tb₂O₃, *M* is the molar mass of Tb₂O₃, and A_v is the Avogadro constant. Taking the proportion of Tb³⁺ among Tb ions (P_{Tb}^{3+}) into consideration, the concentration of Tb³⁺ in MO glass (C_{Tb}^{3+}) is then calculated as follows,

9 Summarization of the experimental data

Table S6 Experimental data of density, band gap, Tb ions effective concentration, onset crystallization temperature T_x , glass-forming ability ΔT , theoretical optical basicity, Verdet constant (at 650 nm) of obtained glasses

Sample	Density (g/cm ³)	Band gap width (eV)	Tb ions effective concentration $(10^{21}/cm^3)$	<i>T</i> _x (°C)	Δ <i>T</i> (°C)	Optical basicity	Verdet constant (rad/(T·m))
20T20A	4.11	4.31	7.05	880	152	0.607	53.79
20T25A	4.23	4.26	7.17	899	164	0.616	60.65
20T30A	4.28	4.29	7.17	904	182	0.625	51.93
30T10A	4.43	4.07	9.59	830	159	0.642	53.22
40T5A	4.80	3.24	11.86	868	117	0.687	87.32
45T5A	5.49	2.32	14.19	907	106	0.713	113.62

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