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Preparation of high refractive index La_2O_3–TiO_2 glass by aerodynamic levitation technique and effects of Bi_2O_3 substitution on its thermal and optical properties

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Abstract

$La_4Ti_9O_{24}$ and Bi_2O_3-substituted La_2O_3–TiO_2 glasses were prepared by aerodynamic levitation technique. The effect of Bi_2O_3 substitution on the thermal stability, refractive index and transmittance spectrum of the as-prepared samples were investigated. After Bi_2O_3 substitution, the stability of La_2O_3–TiO_2–Bi_2O_3 glass decreased, but the Abbe number increased with glass refractive indices above 2.2 in visible region. The high refractive index can be attributed to the large oxygen packing densities and electronic polarizabilities of oxygen ions in the glasses.

Keywords: La_2O_3–TiO_2 glass; Bi_2O_3 substitution; Aerodynamic levitation; Thermal stability; Optical properties

1. Introduction

Oxide glass with high refractive index above 2.0 has great potential for application in small optical devices, such as micro-optical lenses. Traditionally, due to their high polarizability in glasses, heavy metals (such as Pb, Bi, Sb and Te) were added into the glasses to enhance the refractive abilities of the products [1,2], in which Bi_2O_3 is one of the most promising of these components. However, glasses containing Bi_2O_3 cannot be vitrified by conventional processing methods without network former oxides such as SiO_2, B_2O_3, P_2O_5 and GeO_2. On the other hand, as one of the most widely utilized containerless processing methods, aerodynamic levitation technique is ideal for preparing glass without network former oxides due to its ability in suppressing heterogeneous nucleation and precluding contamination from containers at high temperature.

In literature, $La_4Ti_9O_{24}$ glass was reported to possess high refractive index comparable to glasses containing heavy-metal oxides [3]. Therefore, in the present study, on the basis of $La_4Ti_9O_{24}$ glass, La_2O_3–TiO_2–Bi_2O_3 glasses were prepared by aerodynamic levitation technique for the first time, and the effect of highly polarizable Bi^{3+} ions on $La_4Ti_9O_{24}$ glass was investigated.

2. Materials and methods

Spherical glass samples with different nominal molar compositions ($30.8LaO_{3/2}\bullet 69.2TiO_2$, $25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$, and $30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$) were prepared with an aerodynamic levitation furnace. During processing, high-purity (99.99 wt%) powders of La_2O_3, TiO_2 and Bi_2O_3 were first stoichiometrically mixed and sintered at 1200 °C for 4 h in a Muffle oven. After grinding, the resultant fine composite powders were pressed into small columnar rods. The rods were sintered again at 1200 °C for 4 h. After

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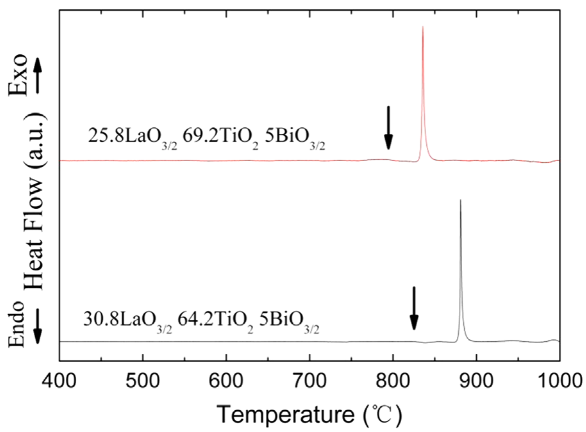

Fig. 1. DTA curves of $25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$ and $30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$ glasses. The arrows indicate the glass transition temperatures.

sintering, the rods were cut into pieces with a weight of approximately 40 mg and levitated by oxygen gas flow in an aerodynamic levitation furnace. Then, the samples were heated rapidly to the melting temperature by a laser and held there for few seconds. After that, the laser was turned off and the samples were cooled down naturally to room temperature. The volatility of Bi_2O_3 during heating was considered and the existence of Bi_2O_3 in the as-prepared glasses was confirmed by an x-ray fluorescence spectrometer (PANalytical, Axios^{mAX}).

The sample density was measured by a gas pycnometer (Micromeritics Accupyc II 1340). The glass transition temperature T_g and crystallization onset temperature T_x of the prepared glasses were measured by differential thermal analysis (DTA) at a heating rate of 10 K/min (Netzsch ATA 449). After polishing, the refractive index of the glasses was evaluated using a SPEC ellipsometer (Genuine Optronics Limited, V-VASE). And their transmittance spectra from 190 to 800 nm were recorded by an optical spectrum analyzer (PERSEE TU-1901).

3. Results and discussion

The as-prepared $25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$ glass was almost transparent and colorless, while $30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$ glass was transparent but yellow. Fig. 1 shows the DTA curves of $25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$ and $30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$ glasses. From this figure, it can be seen that the changes of their specific heats around the glass transition were small and the exothermic peaks were very sharp. Their T_g, T_x and $\Delta T = T_x - T_g$ values and those of $30.8LaO_{3/2}\bullet 69.2TiO_2$ sample [4] were compared in Table 1. The results indicate that the thermal stability and glass-forming ability of La_2O_3–TiO_2–Bi_2O_3 glasses were somewhat inferior to those of $30.8LaO_{3/2}\bullet 69.2TiO_2$ glass [5].

The transmittance spectra of all the samples in UV–vis region are displayed in Fig. 2. The apparent transmission presents maximum values of about 68%, 54% and 65% for $30.8LaO_{3/2}\bullet 69.2TiO_2$, $25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$ and $30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$ glasses, respectively, because of their high refractive indices. The UV absorption edges of La_2O_3–TiO_2–Bi_2O_3 glasses are longer than that of $30.8LaO_{3/2}\bullet 69.2TiO_2$ glass, implying decreased optical band gaps after Bi_2O_3 substitution.

Table 1
Glass transition temperature T_g, crystallization onset temperature T_x, and ΔT.

	T_g (°C)	T_x (°C)	$\Delta T = T_x - T_g$ (°C)
$30.8LaO_{3/2}\bullet 69.2TiO_2$	808	872	64
$25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$	793	834	41
$30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$	824	880	56

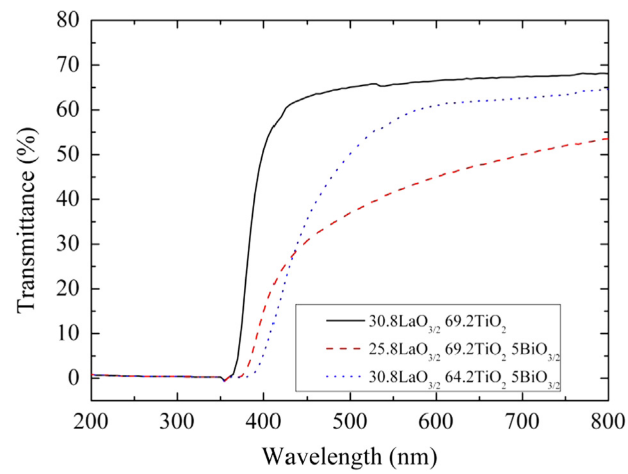

Fig. 2. Transmittance spectra of $30.8LaO_{3/2}\bullet 69.2TiO_2$, $25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$, and $30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$ glasses.

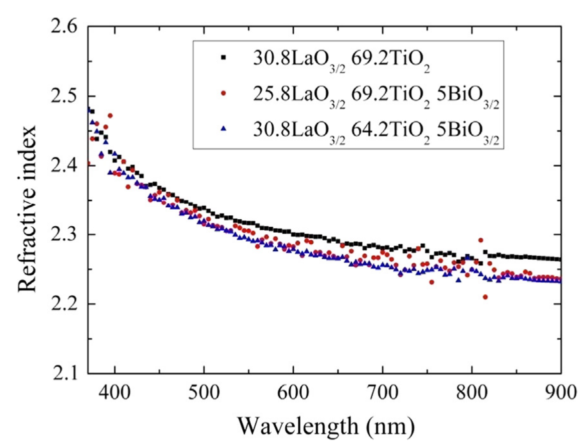

Fig. 3. Refractive index dispersions of $30.8LaO_{3/2}\bullet 69.2TiO_2$, $25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$ and $30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$ glasses as a function of wavelength.

Fig. 3 illustrates the refractive index dispersions of all the glass samples as a function of wavelength of the applied light for measuring. Although the refractive indices of both Bi_2O_3-substituted glasses were slightly lower than that of $30.8LaO_{3/2}\bullet 69.2TiO_2$ glass at the visible region, they were still keeping high values above 2.2, implying that the as-prepared Bi_2O_3-substituted glasses might be promising in the application of small optical devices.

According to the single oscillator model from the Drude–Voigt relationship, the refractive index n is expressed as a function of the wavelength λ by the following formula [2]:

$$\frac{1}{n^2-1}=\frac{\pi mc^2}{e^2Nf}\left(\frac{1}{\lambda_0^2}-\frac{1}{\lambda^2}\right) \quad (1)$$

where n is the refractive index, m and e are the mass and charge of an electron, respectively, c is the velocity of light, N is the number of molecules in unit volume, f is the average oscillator strength, and λ_0 is the inherent absorption wavelength. N is calculated from the formula $N=\rho N_A/M$, where N_A is Avogadro's number, ρ is the sample density, and M is the molecular weight determined from the glass composition. The values of f and λ_0 used in this model are their averages from oscillators such as bridging oxygen, non-bridging oxygen and cations. Based on this model, the plot of $1/(n^2-1)$ vs $1/\lambda^2$ is expected to be a straight line with a slope of $\pi mc^2/(e^2Nf)$ and a y-axis intercept of $\pi mc^2/(e^2Nf\lambda_0^2)$. The values of f and λ_0 are determined from this linear relationship. According to the refractive index dispersion, the Abbe number was estimated for each sample by the formula $\nu_d=(n_d-1)/(n_F-n_c)$, where n_d, n_F and n_c are the refractive indices of the glasses at 589, 486 and 656 nm, respectively. Part of the corresponding parameters applied in the calculation are listed in Table 2. Although the spectroscopic ellipsometer may be not accurate enough to estimate the Abbe number of glasses precisely, the substitution of Bi_2O_3 for both $LaO_{3/2}$ and TiO_2 does increase the Abbe number of the prepared glasses while keeping the refractive index high.

Table 2
Density ρ, refractive index n_d, Abbe number ν_d, and inherent absorption wavelength λ_0 of the as-prepared glasses with different compositions.

	ρ (g/cm^3)	n_d	ν_d	λ_0 (nm)
$30.8LaO_{3/2}\bullet 69.2TiO_2$	4.9748	2.3053	21.9	181
$25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$	5.0393	2.2842	22.5	190
$30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$	4.9669	2.2864	26.9	191

Table 3
The partial molar volume of oxygen and oxygen packing density of the as-prepared glasses.

	V_m (cm^3/mol)	V_O (cm^3/mol)	Packing density (%)
$30.8LaO_{3/2}\bullet 69.2TiO_2$	11.49	10.78	64.13
$25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$	11.72	11.02	62.74
$30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$	12.52	11.74	58.91

The dominant factors affecting the refractive index of oxide glasses are oxygen packing density and the electronic polarizability of ions [6–9]. Considering the number of oxygen ions in oxide glass, and relatively larger electronic polarizability of oxygen ions compared to that of cations, this study focuses on the oxygen packing density and electronic polarizability of oxygen ions α_O. The partial molar volumes of oxygen V_O and oxygen packing densities of all the prepared glasses in this study were calculated by the same method as proposed by Inoue et al. [9], where the ionic radii of six-coordinated La^{3+}, Ti^{4+} and Bi^{3+} were 1.06, 0.605, and 1.02 Å, respectively, according to Shannon's ionic radii [10]. The calculated results are presented in Table 3, revealing that when a part of $LaO_{3/2}$ or TiO_2 was substituted by $BiO_{3/2}$, the oxygen packing density decreased, which is supported by the correlation between the oxygen packing density and radius of the cations.

The electronic polarizabitiy of an ion can be estimated using refractive index and sample density by Lorentz–Lorenz equation:

$$\frac{n^2-1}{n^2+2}\frac{M}{\rho}=\frac{n^2-1}{n^2+2}V_m=R_m=\frac{4\pi}{3}\sum_i N_i\alpha_i \quad (2)$$

where ρ is the density of the glass, M is the molecular weight of the composition, V_m is the molar volume, N_i is the number of ion i, and α_i is the electronic polarizablity of ion i in the composition. The electronic polarizability of an oxygen ion α_O can be obtained from the molar refractivity R_m and electronic polarizabilities of the cations [6–8]. The calculated values of α_O and V_m for $30.8LaO_{3/2}\bullet 69.2TiO_2$, $25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$ and $30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$ glasses are all listed in Table 4.

The values of α_O and V_m increased when both $LaO_{3/2}$ and TiO_2 were substituted by $BiO_{3/2}$. This can be explained qualitatively using the values of V_m and α_O of single component crystals according to Dimitorv and Sakka [8]. The values of V_m and α_O for La_2O_3 [9], TiO_2 [9] and Bi_2O_3 are listed in Table 4, in which the values of Bi_2O_3 were calculated using density (8.55 g/cm^3 [8]), refractive index (2.572 at 589 nm [11]) and Eq. (5) proposed by Vesselin Dimitrov and Sumio Sakka in Ref. [8]. The increases in V_m and α_O of Bi_2O_3-substituted glasses were caused by the larger V_m and α_O values of Bi_2O_3 rather than that of the original La_2O_3 or TiO_2.

Glasses with higher refractive indices are accompanied by higher wavelength dispersion. Low wavelength dispersion glasses require small α_O and λ_0. However, refractive index tends to decrease with decreasing α_O. As shown in Eq. (2), the refractive index is determined by not only α_O but V_m as well.

Table 4
α_O and V_m values of the as-prepared glasses and the applied oxides in the study.

	$30.8LaO_{3/2}\bullet 69.2TiO_2$	$25.8LaO_{3/2}\bullet 69.2TiO_2\bullet 5BiO_{3/2}$	$30.8LaO_{3/2}\bullet 64.2TiO_2\bullet 5BiO_{3/2}$	La_2O_3	TiO_2	Bi_2O_3
α_O (Å^3)	2.45	2.50	2.66	2.52	2.58	3.69
V_m (cm^3/mol)	21.2	21.6	22.8	52.8	20.8	54.5

Therefore, by adding component with apposite values of V_m, α_O and λ_0, glasses with higher refractive index and larger Abbe number can be obtained using aerodynamic levitation technique.

4. Conclusions

aLaO$_{3/2}$–bTiO$_2$–cBiO$_{3/2}$ glasses were fabricated by aerodynamic levitation technique. Their thermal stabilities, densities and optical properties were investigated. The oxygen packing densities, electronic polarizabilities of the ions, and inherent absorption wavelengths were estimated from the sample densities and refractive indices. The high refractive index stems from high packing density and high electronic polarizability of oxygen ions in the glasses. The substitution of $BiO_{3/2}$ for $LaO_{3/2}$ or especially for TiO_2 was very effective in increasing the Abbe number by keeping the refractive index high. These results are helpful in glass composition design for optical applications in the visible region.

Acknowledgments

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