

Fabrication of La_2O_3 - TiO_2 - SiO_2 System Glass Derived from a Sol-Gel Process

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ABSTRACT

La_2O_3 - TiO_2 - SiO_2 glass, a type that could not be obtained so far by the conventional melting method, was prepared successfully using a sol-gel process. Glass derived with the sol-gel process has compositions of $5\text{La}_2\text{O}_3$ - 5TiO_2 - 90SiO_2 , $5\text{La}_2\text{O}_3$ - 10TiO_2 - 85SiO_2 , and $5\text{La}_2\text{O}_3$ - 20TiO_2 - 75SiO_2 . The UV-visible absorption edge of all glass compositions was below 400 nm. The measured density is in the range of 2.55-2.89, and was nearly identical to the calculated density and the refractive index of the glasses derived from the sol-gel ranges from 1.545 to 1.645. The molar additive coefficient of TiO_2 measured in this ternary system is lower than the calculated value, while the value of La_2O_3 is higher.

Key words : Sol-gel process, La_2O_3 - TiO_2 - SiO_2 glass, Low density, High refractive index

1. Introduction

Titanium oxide (TiO_2) has been known to be easily incorporated into glass and it greatly affects such properties as the refractive index, dispersion, density and elasticity of glass.¹⁾ In particular, it is an indispensable component in the fabrication of glass with a high refractive index and a low density. There are two factors in the improvement of the refractive index of glass; the glass packing density and its inherent absorption frequency. In order to obtain this purpose, it is very effective to incorporate the following components into glass.²⁾

- (1) Ba^{2+} , La^{3+} , and Th^{4+} ions with a high packing density.
- (2) Ti^{4+} , Pb^{2+} , and Bi^{3+} ions, of which the inherent absorption frequency is laid on the long wave side.

Accordingly, to materialize glass with a high refractive index and low density, it is necessary to incorporate a high packing density component such as BaO , La_2O_3 into glass and make the glass itself a multi-component system. But there have been a few optical glasses with a great quantity of TiO_2 and only a high dispersion glass has existed thus far. In addition, many problems exist with the fabrication of glass with a great quantity of the TiO_2 component by a conventional melting process.³⁾ First, the appearance of the melted glass is a yellow brownish color attributed to the electric charge transformation between TiO_2 and transition metal elements such as Fe or Cu originating from the raw material and crucible. Secondly, the glass can appear blackish in color

as Ti^{4+} may be reduced to Ti^{3+} when the glass melts. Moreover, free-alkali glass containing large quantities of La_2O_3 , Nb_2O_5 , and Ta_2O_5 is known to be difficult to fabricate as its liquid temperature is too high to melt at over 1500°C.

Meanwhile, sol-gel process is a new method used to fabricate a glass or ceramic material. And its main features are as follows.^{4,6)} Initially, it is a low-temperature synthesis process that obtains a high-density polycrystalline ceramic for a $5\text{La}_2\text{O}_3$ - 5TiO_2 - 90SiO_2 composition. Secondly, the high level of homogeneity could easily be fulfilled for the $5\text{La}_2\text{O}_3$ - 10TiO_2 - 85SiO_2 composition. Thirdly, it is possible to synthesize a new composition glass such as $5\text{La}_2\text{O}_3$ - 20TiO_2 - 75SiO_2 and a high purity glass such as $10\text{La}_2\text{O}_3$ - 10TiO_2 - 80SiO_2 without using the conventional melting process. Finally, its product yield is superior to sputtering or chemical vaporization deposition (CVD) process.

The objectives of this study are to prepare La_2O_3 - TiO_2 - SiO_2 glass with novel compositions by making full use of the aforementioned sol-gel features and to investigate the properties of these glass types.

2. Experimental Procedures

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Mitsuwa Chemical, Japan), $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ (TIP; Kando Chemical, Japan) and $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS; Kishida Chemical, Japan) were used as the La_2O_3 , TiO_2 , and SiO_2 as source material, respectively. And CH_3COOH (Kando Chemical, Japan) was used to control the hydrolysis rate.

The experimental procedure was as follows. First, tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$; TEOS) was added to ethanol dissolved with lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and the mixture was stirred for 1 h. Subsequently, acetic acid and tetraisopropoxide were added to the mixture in that order,

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and it was stirred for an additional hour. Following this, ammonia water adjusted to pH 10 was added dropwise for hydrolysis and condensation. This sol mixture was poured into a polypropylene tube (PP tube) sealed with aluminum foil and was kept at 50°C for gellation in a drying chamber (Shimatsu Model STAC-S45M). And then, the dried gels were heat-treated in a range between 20-950°C by using a muffle furnace (Yamato Science Co. Model FP-22). The composition of ternary gels were designated as the molar content of metal oxides (La_2O_3 , TiO_2 , and SiO_2) converted from each starting material, which was La_2O_3 - TiO_2 - $\text{SiO}_2 = 5$ -5-90, 5-10-85, 5-20-75, and 10-10-80 mole ratio, respectively.

Before and after the heat-treatment of the dried gels, the following measurements were made. TG-DTA for determining the decomposition and densification temperature of the dried gels was carried out, and FT-IR spectrometry was used to investigate the organic compound that remained in the dried gels after the heat-treatment. The specific surface area was determined by nitrogen adsorption at 77 K for the dried samples using a BET method. Powder X-ray diffraction (XRD; RIGAKU RINT 2500) for the dried gels was carried out after the heat-treatment using Ni-filtered Cu-K α radiation to identify the crystal formation. In order to confirm the potential as an optical glass, the absorption spectra of samples heat-treated at the optimum densification temperature were measured by using a Hitachi U-4000 spectrometer. The apparent density of each sample was measured by using a picnometer⁷⁾ and the immersion method was used to measure the refractive index of each sample,⁸⁾ of which the values were compared to those estimated from Appen's equation.⁹⁾

3. Results and Discussions

3.1. Properties of Gels

If ternary sol was kept at 50°C in a drying chamber, its gellation occurred after 95 h in the case of 5 La_2O_3 -5 TiO_2 -90 SiO_2 composition, after 30 h in the case of 5 La_2O_3 -10 TiO_2 -85 SiO_2 composition, after 3 h in the case of 5 La_2O_3 -20 TiO_2 -75 SiO_2 composition, and after 15 h in case of 10 La_2O_3 -10 TiO_2 -80 SiO_2 composition, respectively. After all, between 20 and 30 days was required to to obtain fully dried gels.

Increasing the TIP mole ratio in this ternary system shortened the gelling and drying time. This is attributed to the fact that the hydrolysis and condensation rate of TIP are faster compared to those of TEOS.¹⁰⁾ The color of the gel was opalescent just after gellation, but this became a yellowish transparent gel as the shrinkage progressed.

Fig. 1 shows the FT-IR spectra of La_2O_3 - TiO_2 - SiO_2 gels heat-treated for 2 h at 200, 400, and 600°C in an effort to determine the densification and decomposition temperature of inorganic ingredients. In this figure, the absorption peak around 1100 cm^{-1} observed in the dried gels is assigned to the stretching vibration of the Si-O-Si bond. The absorption peaks around 1720 cm^{-1} and 1300 cm^{-1} are attributed to acetic acid and nitric acid, respectively. However, after a heat-treatment at 200°C for 2 h, only the absorption peak attrib-

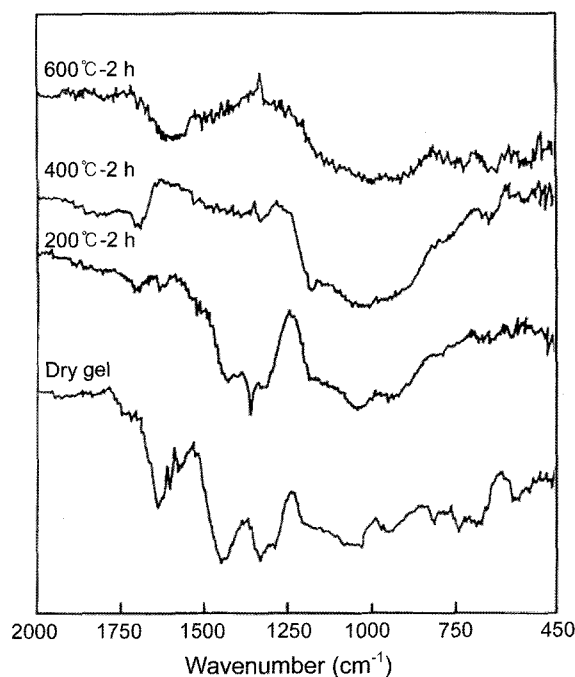


Fig. 1. FT-IR spectra of the La_2O_3 - TiO_2 - SiO_2 gels heated at various temperatures.

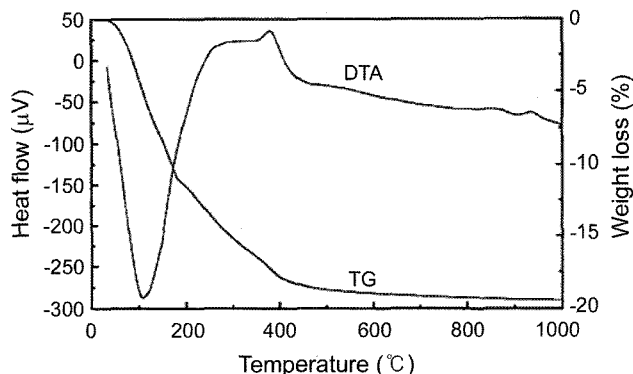


Fig. 2. TG-DTA curves of the 5 La_2O_3 -5 TiO_2 -90 SiO_2 gels.

uted to acetic acid was observed. Meanwhile, in the samples heat-treated for 2 h at 400°C and 600°C, respectively, this peak disappears, indicating that a 2 h heat-treatment over 400°C may effectively remove acetic and nitric acids that remained in the dried gels.

The results of the TG-DTA measurement in Fig. 2 show the decomposition temperature of the organic component and the crystallization temperature for the 5 La_2O_3 -5 TiO_2 -90 SiO_2 composition gels. An endothermic peak in the range between 100°C and 150°C in this figure is attributed to evaporation of absorbed alcohols or water in the dried gels, and the exothermic peak in the range between 300°C and 400°C results from the remaining organic component in the dried gels. Another exothermic peak in the range between 850°C and 950°C can be ascribed to the crystallization peak of dried gels.

Based on the above TG-DTA results, a two-step heat-treatment for the densification of dried gels was completed

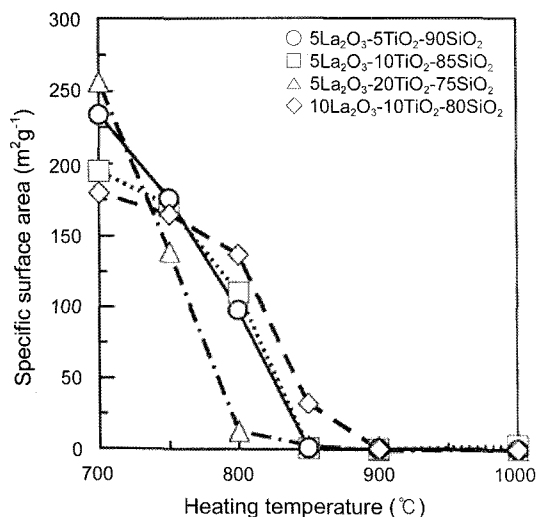


Fig. 3. Change in the specific surface area according to the heating temperature.

using the following procedure. After all samples were kept for 2 h at 400°C, the temperature was increased to the range between 700°C and 1000°C, and then it was kept at each temperature for 2 h.

3.2. Densification of the Dried Gels

The dried gels were heat-treated following the aforementioned heat-treatment schedule. BET results of the samples are shown in the Fig. 3. In the results, BET values abruptly decrease in the range between 750°C and 850°C for the $5\text{La}_2\text{O}_3\text{-5TiO}_2\text{-90SiO}_2$ and $5\text{La}_2\text{O}_3\text{-10TiO}_2\text{-85SiO}_2$ composition, in the range between 700°C and 800°C for the $5\text{La}_2\text{O}_3\text{-20TiO}_2\text{-75SiO}_2$ composition and in the range between 800°C and 900°C for the $10\text{La}_2\text{O}_3\text{-10TiO}_2\text{-80SiO}_2$ composition. It means that the viscous flow and pore collapse of these dried gels occurred around those temperature ranges.¹¹ The surface area nearly became to zero at 850°C for the $5\text{La}_2\text{O}_3\text{-5TiO}_2\text{-90SiO}_2$ and $5\text{La}_2\text{O}_3\text{-10TiO}_2\text{-85SiO}_2$ composition, at 800°C for the $5\text{La}_2\text{O}_3\text{-20TiO}_2\text{-75SiO}_2$ composition, and at 900°C for the $10\text{La}_2\text{O}_3\text{-10TiO}_2\text{-80SiO}_2$ composition, respectively. As the TiO_2 mole ratio for a constant La_2O_3 quantity in the composition became higher, the densification temperature became lower. This indicated that TiO_2 in place of SiO_2 caused the viscous flow in gels to occur easily.

Fig. 4 shows the results of X-ray diffraction patterns for the densified gels. A heat-treatment was completed at 850°C for 2 h for the $5\text{La}_2\text{O}_3\text{-5TiO}_2\text{-90SiO}_2$ and $5\text{La}_2\text{O}_3\text{-10TiO}_2\text{-85SiO}_2$ compositions. This was also done at 800°C for 2 h for the $5\text{La}_2\text{O}_3\text{-20TiO}_2\text{-75SiO}_2$ composition, and at 900°C for 2 h for the $10\text{La}_2\text{O}_3\text{-10TiO}_2\text{-80SiO}_2$ composition.

From Fig. 4, it is clear that $\text{La}_4\text{Ti}_9\text{O}_{24}$ and La_2O_3 diffraction peaks for the $5\text{La}_2\text{O}_3\text{-5TiO}_2\text{-90SiO}_2$ composition appear and it shows almost same tendency for the $5\text{La}_2\text{O}_3\text{-10TiO}_2\text{-85SiO}_2$ composition. For $10\text{La}_2\text{O}_3\text{-10TiO}_2\text{-80SiO}_2$ composition, $\text{La}_4\text{Ti}_9\text{O}_{24}$ and La_2SiO_5 , La_2O_3 , and SiO_2 crystalline peaks appears. However, clear peaks are not identified for the

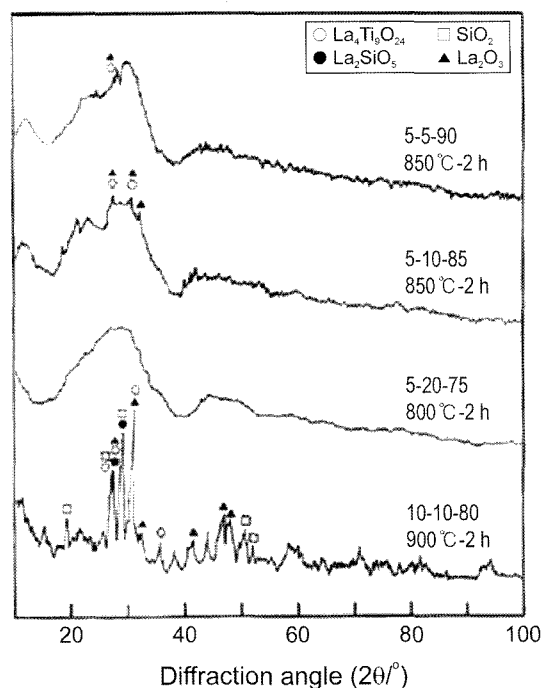


Fig. 4. X-ray diffraction patterns of $\text{La}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$.

$5\text{La}_2\text{O}_3\text{-20TiO}_2\text{-75SiO}_2$ composition heat-treated at 800°C for 2 h. As confirmed by the X-ray diffraction meter, it is amorphous and appears to be glass as its surface area becomes zero and its appearance is transparent. However, crystalline phases precipitate just after pore-free densification in case of the $5\text{La}_2\text{O}_3\text{-5TiO}_2\text{-90SiO}_2$, $5\text{La}_2\text{O}_3\text{-10TiO}_2\text{-85SiO}_2$, and $10\text{La}_2\text{O}_3\text{-10TiO}_2\text{-80SiO}_2$ composition. From these results, a heat-treatment in the range of 800°C and 900°C was conducted for different duration times.

The results of the surface area measurements for the $5\text{La}_2\text{O}_3\text{-5TiO}_2\text{-90SiO}_2$, $5\text{La}_2\text{O}_3\text{-10TiO}_2\text{-85SiO}_2$, and $10\text{La}_2\text{O}_3\text{-10TiO}_2\text{-80SiO}_2$ composition gels heat-treated at 750, 800, and 850°C are shown in Fig. 5(a), (b), and (c), respectively. Fig. 6(a), (b), and (c) show XRD patterns of these samples, respectively, before and after pore-free densification.

The surface area of the $5\text{La}_2\text{O}_3\text{-5TiO}_2\text{-90SiO}_2$ sample became lower as the heat-treatment time increased to 825°C and its value finally became zero after 8 h. Similarly, after a heat-treatment to 850°C over 2 h, its surface area became almost zero.

In Fig. 6(a), the results of XRD measurements for $5\text{La}_2\text{O}_3\text{-5TiO}_2\text{-90SiO}_2$ dry gels heat-treated at 825°C for 8 h, at 850°C for 2 h, and at 800°C for 8 h are shown in one graph. A small XRD peak halo between 28 and 31 degree in this figure is attributed to a $\text{La}_4\text{Ti}_9\text{O}_{24}$ crystal phase that precipitated in the dried gel heat-treated at 850°C for 2 h. However, no clear peak appears in samples heat-treated at 800°C for 2 h and at 825°C for 8 h. Accordingly, the optimum densification condition for the $5\text{La}_2\text{O}_3\text{-5TiO}_2\text{-90SiO}_2$ composition appears to be a heat-treatment at 825°C and for 2 h.

The $5\text{La}_2\text{O}_3\text{-10TiO}_2\text{-85SiO}_2$ composition gel, as shown in Fig. 5(b), became pore-free under a heat-treatment condition of 825°C for 6 h and at 850°C for 2 h. It was not pre-

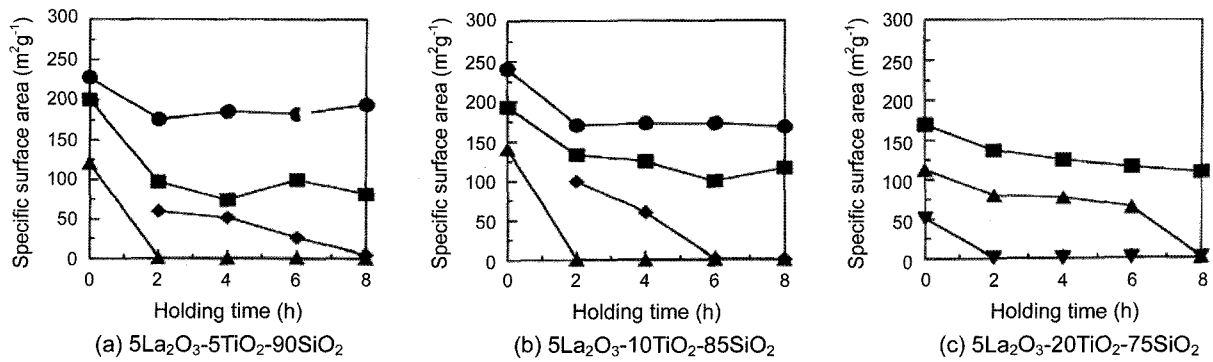


Fig. 5. Change in the specific surface area against the heat treatment conditions (●; 750°C, ■; 800°C, ◆; 825°C, ▲; 850°C, ▼; 900°C).

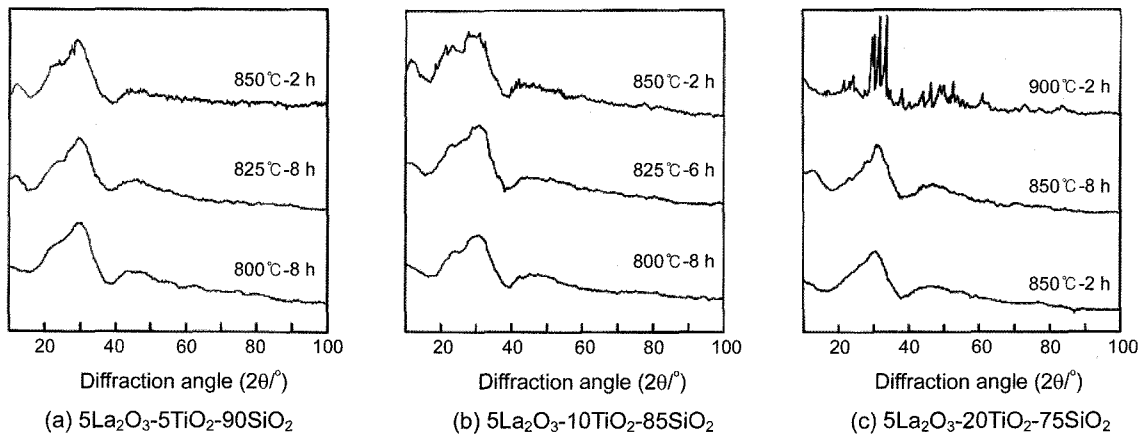


Fig. 6. X-ray diffraction patterns.

free, however, under a heat-treatment condition at 800°C for 8 h. Fig. 6(b) shows the results of the XRD measurement of the $5\text{La}_2\text{O}_3\text{-}10\text{TiO}_2\text{-}85\text{SiO}_2$ composition heat-treated under different heat-treatment conditions. In these results, $\text{La}_4\text{Ti}_9\text{O}_{24}$ and La_2O_3 crystalline peaks are confirmed in the samples heat-treated at 850°C for 2 h, but only a diffused halo peak was observed after heat-treatment at 825°C for 6 h. From these results, the optimum densification condition for the $5\text{La}_2\text{O}_3\text{-}10\text{TiO}_2\text{-}85\text{SiO}_2$ composition is likely a heat-treatment at 825°C and for 2 h.

By adopting the above same analysis to the $10\text{La}_2\text{O}_3\text{-}10\text{TiO}_2\text{-}80\text{SiO}_2$ composition (Fig. 5(c) and Fig. 6(c)), the optimum densification temperature and time was determined to be 850°C and 8 h, respectively.

3.3. Glass Properties

3.3.1. UV-Visible Spectra

Fig. 7 shows the results of the UV-visible spectra measurement for $\text{La}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ glass heat-treated under the optimum condition. The UV absorption edge of the $5\text{La}_2\text{O}_3\text{-}5\text{TiO}_2\text{-}90\text{SiO}_2$, $5\text{La}_2\text{O}_3\text{-}10\text{TiO}_2\text{-}85\text{SiO}_2$, $5\text{La}_2\text{O}_3\text{-}20\text{TiO}_2\text{-}75\text{SiO}_2$, and $10\text{La}_2\text{O}_3\text{-}10\text{TiO}_2\text{-}80\text{SiO}_2$ compositions was estimated as 355 nm, 380 nm, 390 nm, and 385 nm, respectively, from the spectrum plots. These absorption edges of translucent samples with a thickness of 1.0 mm shifted to a longer

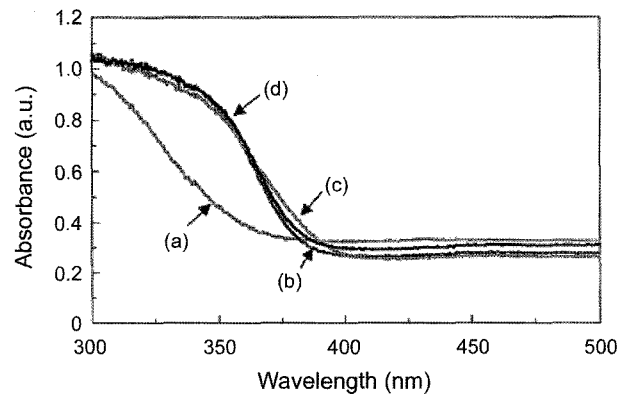


Fig. 7. Absorption spectra of $\text{La}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ glasses. (a) $5\text{La}_2\text{O}_3\text{-}5\text{TiO}_2\text{-}90\text{SiO}_2$, (b) $5\text{La}_2\text{O}_3\text{-}10\text{TiO}_2\text{-}85\text{SiO}_2$, (c) $5\text{La}_2\text{O}_3\text{-}20\text{TiO}_2\text{-}75\text{SiO}_2$, and (d) $10\text{La}_2\text{O}_3\text{-}10\text{TiO}_2\text{-}80\text{SiO}_2$.

wavelength with the incorporation TiO_2 and La_2O_3 and, especially, as the TiO_2 contents increased, which was due to the fact that UV absorption edge of TiO_2 is approximately 360 nm longer than the 200 nm absorption edge of SiO_2 .

3.3.2. Density

The calculated and measured density for various glasses heat-treated under the above optimum conditions are summarized in Table 1. The calculated density is represented by

Table 1. Calculated and Measured Densities for Various Glasses

Composition	Calculated	Measured
	Density	Density
5-5-90	2.57	2.55
5-10-85	2.64	2.65
5-20-75	2.80	2.81
10-10-80	2.86	2.89

Table 2. Calculated Index and Measured Refractive Index for Various Glasses

Composition	Calculated	Measured
	Refractive index	Refractive index
5-5-90	1.541	1.545
5-10-85	1.567	1.555
5-20-75	1.622	1.605
10-10-80	1.618	1.645

Table 3. Molar Additive Coefficient of the Refractive Index for Various Oxides

Component	La ₂ O ₃	TiO ₂	SiO ₂
Measurement	2.95	1.85	1.45
Appen ⁹⁾	2.57	2.00	1.46

the following equation using Appen's empirical law.^{9,12)}

$$G = \chi \text{La}_2\text{O}_3 \cdot a_{\text{La}_2\text{O}_3} + \chi \text{TiO}_2 \cdot a_{\text{TiO}_2} + \chi \text{SiO}_2 \cdot a_{\text{SiO}_2} \quad (1)$$

Here, χ is the mole ratio of MO (LaO_{3/2}, TiO₂, and SiO₂), and a is the molar density and/or molar refractive index of MO, respectively. Consequently, the calculated density value is nearly identical to the measured value.

3.3.3. Refractive Index

Table 2 shows the calculated and measured refractive indices for various glasses. The calculated value is estimated from the aforementioned Eq. (1). The measured refractive index of the 5La₂O₃-20TiO₂-75SiO₂ glass is lower than the calculated value. Meanwhile, for the 10La₂O₃-10TiO₂-80SiO₂ glass, the measured value is higher than the calculate one. The molar additive coefficients of the refractive index for various oxides derived from Appen's equation and estimated from refractive index of glass are given in Table 3. The results show that the molar additive coefficient of TiO₂ in the La₂O₃-TiO₂-SiO₂ glass system is lower than the Appen's value. In contrast to this, the value of La₂O₃ is higher. Generally, it is commonly known that Ti⁴⁺ in a SiO₂-TiO₂ glass system can easily be replaced into a Si⁴⁺ site as a 4-fold coordinate at lower TiO₂ contents: in reverse, this takes a 6-fold coordinate at higher TiO₂ contents. Similarly, the molar additive coefficient of TiO₂ appeared to become lower owing to the 4-fold coordinate Ti⁴⁺ in the La₂O₃-TiO₂-SiO₂ glass system. Meanwhile, for La₂O₃, its molecular additive coefficient becomes lower than Appen's value because La₂O₃ is assumed to be present as a segregate form in a

glass. From the results in which La₂O₃ crystallite is observed in the XRD patterns shown in Fig. 6 and from the finding in which Yamane *et al.* has reported that the PbO crystallite came into existence in a PbO-B₂O₃-SiO₂ gel in the case of using lead acetate as a PbO resource,¹¹⁾ lanthanum nitrate in this ternary system may be present in a precipitated form onto the internal pore surface.

Consequently, TiO₂ has a slight, unusual effect on the refractive index of the La₂O₃-TiO₂-SiO₂ glass and La₂O₃ has a reverse effect.

4. Conclusions

The fabrication of La₂O₃-TiO₂-SiO₂ glass, which had not been obtained thus far using the conventional melting methods, was been successfully accomplished using a sol-gel process with compositions of 5La₂O₃-5TiO₂-90SiO₂, 5La₂O₃-10TiO₂-85SiO₂, and 5La₂O₃-20TiO₂-75SiO₂. For the 10La₂O₃-10TiO₂-80SiO₂ glass composition, however, phase separation occurred and its appearance was opaque. The UV-visible absorption edge of all glass compositions was below 400 nm: thus these glasses are likely suitable for use as optical glass. The calculated density is nearly identical to the measured density. The molar additive coefficient of TiO₂ measured in this ternary system is lower than the calculated value, while, however, the value of La₂O₃ is higher.

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