Functionalities in unconventional oxide glasses prepared using a levitation technique

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Over the last 20 years, many unconventional oxide glasses have been fabricated in bulk using a levitation technique. These glasses contain no or less network-former oxides; thus, they have been supposed not to vitrify so far. The levitation technique could vitrify them because the levitated melt was maintained without touching anything; thus, crystal nucleation was extremely suppressed. This review presents a brief introduction to the levitation technique. It also summarizes some functionalities that emerged in the glasses prepared using this technique, such as high refractive index, infrared transparency, strong luminescence, large magneto-optical effect, high elastic moduli, and crack resistance.

Key-words: Refractive index, Transparency, Luminescence, Verdet constant, Hardness, Glass structure

1. Introduction

The well-known glass-forming rules are constructed on short- and medium-range glass structures. The main structural units in oxide glasses are $M\text{O}_4$ tetrahedra comprising the cation $M^{++}$ and oxide ion $O^{2-}$ connected by corner-sharing to form a three-dimensional random network. Tetrahedral corner-sharing networks can be realized using specific components such as $SiO_2$ and $P_2O_5$. These simple oxides are called network-former oxides. Alkali metal oxides, alkaline earth metal oxides, and rare-earth oxides typically break the network and generate non-bridging oxygens by introducing oxygens accompanied with the cations. Thus, they are classified as network modifier oxides. Other oxides such as $Al_2O_3$, $TiO_2$, and $Nb_2O_5$ act as either a network-former or a modifier depending on their glass content, classifying them as intermediate oxides.

The glass-forming rules inevitably require many network-former oxides for the glass formation to develop three-dimensional random networks. Glass researchers synthesize bulk glasses with desired characteristics by adjusting the composition, including network-former, modifier, and intermediate oxides. When the proportion of network-former oxides is small, they crystallize without vitrification. This means that there is a limit in the range of the chemical composition of interest in glass science. Some synthesis methods can exceed the limitations in chemical composition and vitrify substances with no or few network-former oxides. However, many cannot produce bulk glasses but produce amorphous thin films, flakes, or nanoparticles. Among these synthesis methods exceeding the limit, the levitation technique has an advantage in fabricating bulk glasses.

Recently, techniques that levitate a melt in the air have been widespread in glass science because the method can produce many unconventional glasses in bulk form that have been supposed not to vitrify so far. The levitated melt does not have any contacts like a container wall where heterogeneous nucleation occurs frequently. Thus, it can be undercooled very deeply on cooling. Solidification without any crystallization from the deeply undercooled melt is often easily realized. This leads to a glass formation of a substance although it has a very low glass-forming ability. Various glasses with no or few network-former oxides have been successfully synthesized using a levitation technique. Some exhibit fascinating physical properties never observed in conventional oxide glasses, making the levitation technique valuable in glass science. In this review, the levitation technique for glass synthesis is briefly introduced, and some noticeable achievements, especially on optical and mechanical functionalities realized in the unconventional glasses, are summarized. Another review article that focuses on the characteristic atomic arrangements of densely packed oxide glasses prepared using a levitation technique can be found elsewhere.

2. Levitation technique for glass synthesis

A levitation furnace holds a melt in the air without a container like a crucible. It is a noncontact heating appa-
ratus that melts a substance levitated by an external force that opposes gravity. Levitation furnaces are often classified depending on the external force used for levitation. These are electromagnetic force,\(^ {19}\) electrostatic field,\(^ {20}\) magnetic field,\(^ {21}\) acoustic standing wave,\(^ {22, 23}\) microwave,\(^ {24}\) gas flow, and a combination of some of them.\(^ {25}\) Note that each levitation furnace has restrictions on substances, atmosphere, and temperature. They are selected according to their purposes, such as glass synthesis,\(^ {26}\) physical property measurements,\(^ {26}\) structural analyses,\(^ {27}\) observation of the solidification process,\(^ {28-30}\) and single crystal growth.\(^ {31}\)

A melt can be stably maintained even for several hours at temperatures higher than 2000 °C by careful heating without evaporation of components. Therefore, levitation furnaces are often used to perform structural analyses of the melt at high temperatures via synchrotron X-ray and neutron diffraction,\(^ {32-51}\) X-ray absorption fine structure,\(^ {52-54}\) Raman scattering,\(^ {55}\) or Nuclear Magnetic Resonance (NMR).\(^ {56}\) Furthermore, thermodynamic physical properties of melts, such as the temperature dependence of viscosity, density, and surface tension, can be measured using a levitation technique. Recently, space experiments using an electrostatic levitation furnace at the Japanese experiment module “KIBO” in the international space station have been performed to measure the thermodynamic physical properties of oxide melts.\(^ {47, 60-63}\) The results will provide a further understanding of glass formation from a melt.

**Figure 1** shows a schematic illustration of an aerodynamic levitation furnace using a gas flow as an external force. The gas flow levitates a target sample placed on the nozzle, and the sample is melted by irradiating a CO\(_2\) laser. The wavelength of the CO\(_2\) laser is 10.6 µm which is well absorbed by most of the oxides. This makes the CO\(_2\) laser suitable as a heating source for the levitation of oxides. Any gas type can be used, such as air, O\(_2\), N\(_2\), and He. The temperature of the sample was measured using a pyrometer. The laser power and gas flow rate are fine-tuned to maintain stable levitation while watching the magnified image of the sample with a charge coupled device (CCD) camera. After holding the melt for an appropriate period, typically several tens of seconds, for glass synthesis, the laser power is weakened to cool and solidify the melt. The time required to set, levitate, melt, solidify, and take out the sample is several minutes, much shorter than several hours for conventional melt-quench processes using a crucible and an electric furnace.

Furthermore, the nozzle will not become dirty or melt even if the temperature of the sample is raised above the melting point of the nozzle since the melt does not touch the nozzle. Therefore, there is no upper limit for increasing the temperature. Even high melting point oxides such as ZrO\(_2\),\(^ {40}\) Er\(_2\)O\(_3\),\(^ {50}\) TiO\(_2\),\(^ {52}\) Al\(_2\)O\(_3\),\(^ {37, 48}\) SiO\(_2\),\(^ {33, 38}\) and UO\(_2\)\(^ {41}\) can be easily melted in a levitation furnace. This indicates that the levitation technique can broaden the scope of materials search. Depending on the size and shape of the nozzle, a solidified sample with a diameter of 1–10 mm and a weight of 1–500 mg can be obtained using a levitation technique.

**3. High refractive index with low wavelength dispersion**

Glasses are transparent in a certain wavelength range, and they are used for windows, lenses, and optical fibers in that range. The refractive index is one of the essential properties of glasses that affect the performance of optical glass components. The refractive index of oxide glass, which is colorless and transparent in the visible range, is usually approximately 1.5–2.0 at 587.6 nm. TiO\(_2\), Nb\(_2\)O\(_5\), WO\(_3\), Ga\(_2\)O\(_3\), BaO, and La\(_2\)O\(_3\) are effective components that increase the refractive index with keeping colorless in the visible range. However, since TiO\(_2\), Nb\(_2\)O\(_5\), WO\(_3\), and Ga\(_2\)O\(_3\) are intermediate oxides and BaO and La\(_2\)O\(_3\) are modifier oxides, a bulk glass composed of a large amount of them is difficult to synthesize. It was thought that the material search for a higher refractive index in the visible range was almost exhausted, and a drastic increase in refractive index was no longer expected.

The glass formation at the composition of BaTi\(_2\)O\(_5\) using a levitation technique was firstly reported in 2006.\(^ {13}\) Initially, the giant dielectric response,\(^ {13, 64}\) nonlinear optical response,\(^ {65}\) metastable phase formation\(^ {66, 67}\) that occur at the crystallization temperature were the focus of attention. Afterward, superior optical properties such as colorless, transparent, and high refractive index exceeding 2.1 in the visible range were found as expected because BaO and TiO\(_2\) are typical components that increase the refractive index.\(^ {68}\) The glass-forming region is a narrow range of 62 ≤ x ≤ 69 near the eutectic point when the composition is expressed as (100 – x)BaO–xTiO\(_2\).\(^ {69}\)

Although bulk glass formation was not achieved in any binary system of TiO\(_2\) with other alkaline earth metal oxides, Ba of BaTi\(_2\)O\(_5\) can be substituted with other alkaline earth metals. In the composition of Ba\(_{1-x}\)A\(_x\)Ti\(_2\)O\(_5\) (A = Mg, Ca, or Sr), the glass formation was realized in the range x ≤ 0.05 for A = Mg, Sr, whereas it was in a wide range x ≤ 0.85 for A = Ca.\(^ {70}\) Generally, conventional oxide glasses containing alkaline earth metal oxides and certain network-former oxides have a glass-forming region depending on the ionic radius of the alkaline earth
metal or almost unchanged. The specific wide glass-forming region of $A = \text{Ca}$ compared with those of $A = \text{Mg}$ and $\text{Sr}$ in the $\text{Ba}1_x\text{Ca}_{(1-x)}\text{Ti}_2\text{O}_5$ system is interesting because it suggests a peculiar correlation between glass-forming ability and local structures around not only Ti but also Ca. Furthermore, Ca substitution for Ba increased the refractive index of $\text{Ba}_{1-x}\text{Ca_x}\text{Ti}_2\text{O}_5$ glasses. This contradicts the general trend that increasing the amount of heavier elements increases the refractive index. The Ca content dependence of the Raman scattering spectra suggested that the structural relaxation around TiO$_6$ polyhedra increased the refractive index by decreasing the bandgap energy.\(^7\)\(^0\)

Regarding the $\text{R}_2\text{O}_3$–$\text{TiO}_2$ system ($R$ is a rare-earth element), the first bulk glass was obtained by applying a levitation technique to $\text{La}_4\text{Ti}_9\text{O}_{24}$.\(^7\)\(^3\) $\text{La}_4\text{Ti}_9\text{O}_{24}$ also contains effective components that increase its refractive index, such as $\text{La}_2\text{O}_3$ and $\text{TiO}_2$, and it has a very high refractive index $n_d$ (at 587.6 nm) of 2.31. Subsequent studies have shown that the glass-forming region in the composition 66.7 $\leq x \leq$ 76.2 in the composition $(100 - x)\text{La}_2\text{O}_3$–$x\text{TiO}_2$.\(^7\)\(^2\) It is a narrow range near the eutectic point similar to that of the BaO–TiO$_2$ system.

The synthesis of colorless and transparent bulk glass consisting only of $\text{La}_2\text{O}_3$ and $\text{Nb}_2\text{O}_5$ ($30\text{La}_2\text{O}_3$–70$\text{Nb}_2\text{O}_5$ glass) was firstly reported in 2010.\(^\text{14}\) Subsequently, it was found that the glass-forming region was, interestingly, divided into two at compositions with a large amount of La ($38 \leq x \leq 41$) and a large amount of Nb ($60 \leq x \leq 75$) in the composition $(100 - x)\text{La}_2\text{O}_3$–$x\text{Nb}_2\text{O}_5$.\(^7\)\(^3\) Glass formation can be interpreted to not occur near $x = 50$ because the crystal phase of $\text{LaNbO}_4$ exists as a stable phase on the phase diagram. The refractive indices $n_d$ of Nb-rich glasses were 2.17–2.27, which is higher than 2.14 for La-rich glasses.

The colorless and transparent bulk glass formation in the $\text{La}_2\text{O}_3$–$\text{WO}_3$ binary system was firstly reported in 2012.\(^\text{15}\) The glass-forming region was limited to the vicinity of the eutectic point of 20 mol% $\text{La}_2\text{O}_3$. The refractive index $n_d$ of 20$\text{La}_2\text{O}_3$–80$\text{WO}_3$ glass was 2.01, which is higher enough but relatively lower than those of $\text{TiO}_2$-based and $\text{Nb}_2\text{O}_5$-based glasses. The most characteristic in the $\text{WO}_3$-based glass is the low glass transition temperature $T_g$. $T_g$ of unconventional glasses prepared using a levitation technique are usually higher than 700°C, and some reach 950°C, whereas that of 20$\text{La}_2\text{O}_3$–80$\text{WO}_3$ glass was 553°C. The low $T_g$ indicates the glass can be pressed into shapes easily.

In 2017, the wide glass-forming region in the $\text{La}_2\text{O}_3$–$\text{Ga}_2\text{O}_3$ binary system was found to be $20 \leq x \leq 57$ in the composition of $x\text{La}_2\text{O}_3$–$(100 - x)\text{Ga}_2\text{O}_3$.\(^7\)\(^5\) The refractive index $n_d$ increased from 1.920 to 1.962 with an increase in $\text{La}_2\text{O}_3$. The refractive indices are not as high as those of the high refractive index glasses prepared previously using a levitation technique. Furthermore, it was found that the maximum phonon energy of the $\text{Ga}_2\text{O}_3$-based glasses was much lower than those of most of oxide glasses, the related properties of which are described in a later section.

The $\text{La}_2\text{O}_3$–$\text{B}_2\text{O}_3$ binary system contains network-former oxides, $\text{B}_2\text{O}_3$. Therefore, B-rich $\text{La}_2\text{O}_3$–$\text{B}_2\text{O}_3$ bulk glasses can be available in the range of 0–28 mol% of $\text{La}_2\text{O}_3$ in the conventional melt-quenching method. The B-rich glasses were well-known glasses with a relatively high refractive index $n_d \approx 1.7$.\(^7\)\(^6\) except for the phase separation region (2–22 mol% of $\text{La}_2\text{O}_3$), where the glasses become milky white.\(^7\)\(^3\)–\(^8\)\(^0\) In 2019, vitrification was firstly achieved in the region with high $\text{La}_2\text{O}_3$ content (50–63 mol%) using a levitation technique.\(^7\) They are colorless and transparent without any phase separation. The refractive index $n_d$ increased with an increase in the La content from 1.75 to 1.92. The La-rich borate glasses exhibited high thermal stability, a high refractive index, and low wavelength dispersion.

Besides the binary systems described above, the glass forming regions in ternary or multicomponent systems were also explored.\(^\text{69}\)\(^\text{81}\)–\(^\text{82}\) Glass-forming ability was improved by increasing the number of components, and some glasses might vitrify without levitation. The problem that prevents fabricating bulk glass using a crucible is a melting point higher than 2000°C, which also melts a commercially available crucible in air.

It is crucial to investigate the origin of the very high refractive index of the glasses mentioned here. The refractive index of a substance follows the Lorentz–Lorenz equation:

$$\frac{n^2 - 1}{n^2 + 2} \rho = \frac{n^2 - 1}{n^2 + 2} V_m = \frac{4\pi\alpha_m N_A}{3},$$  \hspace{1cm} (1)

where $n$ is the average refractive index, $M$ is the molecular weight, $\rho$ is the density, $V_m$ is the molar volume, and $N_A$ is the Avogadro’s number.\(^\text{83}\) $\alpha_m$ is the electron polarizability of the whole molecule. $\alpha_m$ can be decomposed into the electron polarizability of oxide ion $\alpha_{O^2-}$ and that of cation $\alpha_i$ using the following equation:

$$\alpha_m = \sum \alpha_i + \alpha_{O^2-} N_{O^2-},$$  \hspace{1cm} (2)

where $N_{O^2-}$ denotes the number of oxide ions in the chemical formula. The respective values of $\alpha_i$ are available in the literature, i.e., $\alpha_{\text{Ba}^{2+}}$ and $\alpha_{\text{Zn}^{2+}}$ are 1.595 and 0.184 Å$^3$, respectively, while $\alpha_{O^2-}$ of general glasses containing network-former oxides as the main component is approximately 1.5, such as 1.43 (20$\text{B}_2\text{O}_3$–80SiO$_2$), 1.37 (20$\text{Na}_2\text{O}$–80$\text{B}_2\text{O}_3$), and 1.50 (25ZnO–75$\text{P}_2\text{O}_5$).\(^\text{86}\) The difference in electron polarizability between cations and oxide ions is small in those network glasses, indicating a strong covalent bonding nature between oxygen and network-former cations. Meanwhile, the $\alpha_{O^2-}$ of high refractive index glasses has a value greater than 2.0. For example, they are 2.57 for $\text{BaTiO}_3$, 2.44 for 60$\text{La}_2\text{O}_3$–40$\text{Nb}_2\text{O}_5$, and 2.28 for 20$\text{La}_2\text{O}_3$–80$\text{WO}_3$ glasses.\(^\text{15}\)\(^\text{68}\)\(^\text{74}\) This means that oxygen atoms exist in a highly ionic state in the glasses.

The Lorentz–Lorenz equation also indicates that the smaller $V_m$ yields the higher refractive index. Small $V_m$ comes from the large packing density of the constituent ions. The packing density of oxide ions is a more important factor for oxide glasses than those of other cations because the most abundant ion among constituent ions is the oxide ion. Here, the oxygen packing density (PD$_O$) is
used to estimate the ratio of the space occupied by oxide ions other than cations. PDO is calculated using the equation 

\[ V_{\text{O}} / (V_m - V_{\text{cat}}) \]

where \( V_{\text{O}} \) and \( V_{\text{cat}} \) are the partial molar volume of oxide ions and cations, respectively. Ions in glass are assumed to be a sphere. The volume of the \( i \)th ion is \( 4\pi r_i^3 / 3 \), where \( r_i \) is the ionic radius of the \( i \)th ion. Shannon’s ionic radii are used to calculate the volume.87) The PDO of La4Ti9O24, 30La2O3·70Nb2O5, 60La2O3·40Nb2O5, 20La2O3·80WO3, and 30La2O3·70Ga2O3 glasses are 0.579, 0.563, 0.523, 0.526, and 0.502, respectively, which is significantly larger than that of SiO2 glass, 0.455. Figure 2 shows the relationship between \( n_d \) and PDO. It can be clearly seen that \( n_d \) increases monotonically with increasing PDO. The large PDO values indicate that the high refractive indices of the glasses shown in this section are attributed to the large oxygen packing density and large electronic polarizability of oxide ions. The significant large oxygen packing density would not be realized in the tetrahedral corner-sharing network structure of conventional network glasses since the network structure generates a large number of voids. The structure of the high refractive index glasses prepared using a levitation technique should be different from the tetrahedral network structure, considering that the glasses contain no or less network-former oxides and have a large oxygen packing density. Thus far, much research on the structural analysis of the densely packed glasses prepared using a levitation technique has been performed by a combination of experiments and theoretical calculations. Brief summaries on structural analyses are described here. The atomic arrangements regarding the frame of the glasses comprise various structural units such as four-, five-, or six-coordinated polyhedra. The polyhedra connect each other with corner-sharing and edge- or face-sharing. Figure 3 shows the structural model of BaTi2O5 glass produced using MD simulation88) and the structural model of 30La2O3·70Nb2O5 glass obtained using RMC modeling.73) It is clearly shown that it is difficult to find tetrahedral corner-sharing networks in the glasses. Detailed quantitative analysis results are shown in the references.73,88)

The wavelength dispersion of the refractive index is as important as the value of the refractive index itself. Lower wavelength dispersion, indicating a smaller difference in the refractive index depending on the wavelength, is crucial for glasses used in optics such as lenses. The wavelength dispersion of the refractive index is quantitatively evaluated using the Abbe number 

\[ \overline{d} = (n_d - 1) / [(n_F - n_C)] \]

Here, \( n_d \), \( n_F \), and \( n_C \) are the refractive indices at 587.6, 486.1, and 656.3 nm, respectively. The greater the wavelength dependence, the smaller the value of \( \overline{d} \). An Abbe diagram with \( n_d \) on the vertical axis and \( \overline{d} \) on the horizontal axis is often used to compare and evaluate the characteristics of various optical glasses. Figure 4 is an Abbe diagram that summarizes the data of the high refractive index glasses prepared using a levitation technique and commercially available optical glasses.89)–92) Compared with the data of commercial optical glasses, those of the glasses prepared using a levitation technique are plotted at the upper left region, indicating higher \( n_d \) and lower wavelength dispersion. Some of these
high refractive index glasses with low wavelength dispersion are expected to be commercialized soon. The composition of the glasses is undergoing further optimization according to the purpose, such as increasing the size, increasing the refractive index, reducing the dispersion, improving the ultraviolet (or infrared) transparency, and lowering the softening temperature for molding.

4. Infrared transparency

Absorption in the infrared region is caused by vibration excitation between cation and oxygen. The vibration energy of the cation oxygen bond decreases with an increase in the atomic weight of the cation, which is formulated under the harmonic oscillator approximation. The absorption edge in the infrared region is determined via the multiphonon absorption of vibrations in multiple modes such as stretching, bending, and rocking modes. Generally, the lower the maximum phonon energy, the longer the absorption edge in the infrared region.

The high refractive index glasses mentioned in the previous section contain many relatively heavy components that form the frame of glasses, such as TiO₂, Nb₂O₅, WO₃, and Ga₂O₃, compared with conventional oxide glasses comprising SiO₂, B₂O₃, and P₂O₅. The Raman scattering spectra revealed that the maximum phonon energy of the high refractive index glasses is significantly smaller than that of conventional network glasses. The maximum phonon energy of borate, phosphate, and silicate glasses are approximately 1400, 1200, and 1100 cm⁻¹, respectively; whereas those of WO₃-based, TiO₂-based, and Ga₂O₃-based glasses are 950, 810, 790, and 650 cm⁻¹, respectively, as shown in Fig. 5. Note that a very low maximum phonon energy was realized in Ga₂O₃-based glasses.

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**Figure 6(a)** shows the infrared transmission of the glasses. The transmittance of Ga₂O₃-based glasses was over 50% up to 7 μm. The cutoff wavelength of the 55La₂O₃-45Ga₂O₃ glass reached over 10 μm, which was much longer than those of typical network glasses, such as silicate and borate, and slightly longer than those of heavy metal gallate glasses, and close to those of fluoride glasses. Those heavy metal gallate glasses are usually colored, whereas a characteristic of the Ga₂O₃-based glasses prepared using a levitation technique is colorlessness and transparency in the visible and infrared regions.

The infrared absorption edge of conventional borate glasses is as short as approximately 3–4 μm, which is caused by the large maximum phonon energy of B–O vibration and multiple vibrations of various types of BOₙ units. Therefore, borate glasses are not suitable for infrared optical applications. Indeed, the infrared transmittance spectra of xLa₂O₃-(100 – x)B₂O₃ glasses show that the main absorption edge was approximately 3.7 μm of the x = 25 and 30 glasses [Fig. 6(b)]. Meanwhile, two additional transmittance windows at approximately 4.3 and 5.6 μm were clearly observed in the spectra of x ≥ 50 glasses. Since these two transmittance windows had large transmittance, the main absorption edge of La-rich glasses was taken as 6.7 μm, much longer than that of B-rich glasses. The infrared transparency observed in La-rich La₂O₃–B₂O₃ glasses suggests new optical applications in the visible to near infrared region for borate glasses.

The origin of the additional infrared transparency of La-rich La₂O₃–B₂O₃ glasses was investigated based on local structure analysis. From the NMR and Raman scattering spectra results, it was concluded that La-rich glasses had only isolated BO₃ units, indicating a simple environment around B-atoms. The disappearance of diversity of BOₙ units diminishes the overlap of multiphonon absorption caused by various BOₙ units, leading to the formation of discrete absorption bands or the additional discrete transparency in a wide range. Thus, the remnant absorption was caused by B–O vibration only in isolated BO₃ triangles. The IR transmittance spectra of La-rich glasses are similar to those of crystalline LaBO₃. This means that the La-rich glasses optically get close to a single crystal. The additional infrared transparency was also confirmed in
R-rich $R_2O_3$–$B_2O_3$ glasses with the same origin as La-rich glasses. Although binary borate glass systems are regarded as conventional in glass science, simplifying the local structure around B-atoms produced new functionality, such as the additional infrared transmittance in the IR region.

5. Strong luminescence

Rare-earth ion doped oxide glasses are used as luminescent materials. The most important product using the Er$^{3+}$-doped glass is the Erbium-doped fiber amplifier, which amplifies optical signals transmitted through optical fibers and supports the worldwide optical telecommunication network. A problem in developing oxide glasses with strong luminescence is the deactivation of excited rare-earth ions. The maximum phonon energy of the base glass is a crucial parameter in affecting the luminescent performance because excitation energy is spent more via multiphonon relaxation with increasing phonon energy. The glasses with lower maximum phonon energy are expected to exhibit strong luminescence.

The 2.7 $\mu$m mid-infrared emission associated with the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er$^{3+}$ ions has been desired because its spectrum overlaps with the absorption region due to water. Thus, it is potentially used for applications in biomedical fields. However, the 2.7 $\mu$m emission is rarely observed in Er$^{3+}$-doped oxide glasses. This is because oxide glasses generally have large phonon energy and strong absorptions of OH$^-$ groups generated in the glasses. Multiphonon relaxation spends a small amount of energy between the $^4I_{13/2}$ and the $^4I_{15/2}$ levels. Fluoride glasses are alternative host materials for Er$^{3+}$ emission because of their low phonon energy, good solubility of rare-earth ions, and low OH$^-$ absorption. However, they generally have the disadvantages of the difficult fabrication process, poor chemical durability, and low mechanical and thermal resistivity for practical applications.

Among the high refractive index glasses shown here, La$_2$O$_3$–Ga$_2$O$_3$ glasses have a specifically low maximum phonon energy of 650 cm$^{-1}$, which is comparable with fluoride glasses. The glasses also contain less OH$^-$ groups and are highly transparent from the visible to near-infrared region. These features led to the findings that Er$^{3+}$-doped La$_2$O$_3$–Ga$_2$O$_3$ glasses exhibited strong luminescence at 2.7 $\mu$m. Figure 7(a) shows the emission spectra at 2.7 $\mu$m in $x$Er$_2O_3$–(50 $-$ x)La$_2O_3$–50Ga$_2O_3$ glasses under excitation by a 976 nm laser diode. Although no emission occurred at 2.7 $\mu$m from x $=$ 0.5 glass, the emission intensity increased from x $=$ 1 to 10 and then decreased at x $=$ 20. From the detailed analyses regarding the 2.7 $\mu$m emission, it was found that the quenching concentration of the $^4I_{15/2}$ level is much higher than that of the $^4I_{13/2}$ level. The emission cross-section and the gain bandwidth at 2.7 $\mu$m of x $=$ 10 glass were as large as 9.05 $\times$ 10$^{-21}$ cm$^2$ and 9.19 $\times$ 10$^{-20}$ cm$^2$, which are substantially larger than those of the ZBLAN glass and fluorophosphate glasses and are comparable to those of oxyfluorotellurite glasses. These results suggest that Er$^{3+}$-doped La$_2$O$_3$–Ga$_2$O$_3$ glasses are promising candidates for compact and high-power solid-state MIR laser materials.

The deactivation of excited rare-earth ions occurs when their concentration is high, called concentration quenching. The concentration quenching is caused by energy transfer between rare-earth ions nearby via ion–ion interaction mechanisms. Conventional network oxide glasses cannot contain so many R$^{3+}$ ions compared with other modifier cations such as Na$^+$, K$^+$, and Ca$^{2+}$. This might be because rare-earth ions have large valence states and a strong effect on breaking the tetrahedral network. When rare-earth ions are doped into network glasses, they easily aggregate and do not break the network more than necessary to maintain the glass structure. The aggregation makes energy transfer between rare-earth ions easy. Unlike conventional network glasses, La$_2$O$_3$–Ga$_2$O$_3$ glasses contain many rare-earth (La$^{3+}$) ions. This suggests a frame of LaO$_6$ polyhedra in the glasses, and substitution of R$^{3+}$ for La$^{3+}$ in LaO$_6$ polyhedra does not affect the glass structure drastically, leading to a higher concentration of R$^{3+}$ without their aggregation. Indeed, it was reported that Er$^{3+}$- and Eu$^{3+}$-doped glasses, concentration quenching did not occur until the concentration of Er$^{3+}$ exceeded approximately 10 mol % as described above.

Figure 7(b) shows the luminescence properties of Eu$_2$O$_3$–La$_2$O$_3$–Ga$_2$O$_3$ glasses under 375 nm UV light irradiation. Eu$_2$O$_3$ was successfully introduced into the glass at up to 30 mol %. The emission spectra exhibited five characteristic bands at 580, 593, 616, 658, and 710 nm, which are assigned to the $^4F_0$–$^4F_0$ transitions of Eu$^{3+}$ from the excited $^2D_0$ level to the ground state multiplet of $^2F_J$ (J $=$ 0, 1, 2, 3, and 4).
creased at $x = 30$. Furthermore, the measured lifetimes of the $^7D_0 \rightarrow ^7F_2$ emission showed slight degeneration with Eu$_2$O$_3$ over the 5–25 mol % range and a rapid drop at 30 mol % [Fig. 7(c)]. Compared with conventional oxide glasses where concentration quenching usually occurs at only a few mol % Eu$_2$O$_3$, the very high concentration at which concentration quenching occurred in Eu$_2$O$_3$–La$_2$O$_3$–Ga$_2$O$_3$ glasses is notable. Highly Eu$_2$O$_3$-doped La$_2$O$_3$–Ga$_2$O$_3$ glasses are suitable for intense luminescent solid-state materials. Besides La$_2$O$_3$–Ga$_2$O$_3$ glasses, many glasses can contain several tens of percentages of $R_2$O$_3$, such as La$_2$O$_3$–TiO$_2$, La$_2$O$_3$–Nb$_2$O$_5$, La$_2$O$_3$–WO$_3$, and La$_2$O$_3$–B$_2$O$_3$ glasses. These glasses are also possible candidates for substances with strong luminescence.

6. Large magneto-optical effect

The Faraday effect is a magneto-optical phenomenon. The polarization plane of linearly polarized light rotates when the light passes through a substance in magnetic fields or magnetic materials. Substances with a large Faraday effect have been used as optical isolators, optical circulators, and sensors of electrical current or magnetic fields. Crystalline Y$_3$Fe$_5$O$_{12}$, Gd$_3$Fe$_5$O$_{12}$, and Bi$_3$Fe$_5$O$_{12}$, with garnet structure exhibit a very large Faraday effect, and they are put to practical use. Since the garnet ferrite crystals have strong absorption in the visible range, they are used in the infrared range. However, the Tb$_3$Ga$_5$O$_{12}$ garnet crystal is highly transparent in the visible range and exhibits a large Faraday effect. Therefore, single-crystalline Tb$_3$Ga$_5$O$_{12}$ garnet is used for magneto-optical applications in the visible range. The Verdet constant, as well as optical properties. The Young’s modulus of glasses, are important properties that can be easily obtained at compositions near the eutectic point. Here, $E$ is the Young’s modulus, $V_p$ is the ion packing density, and $G_i$ and $x_i$ are the dissociation energy and mole fraction of component $i$, respectively. The dissociation energy is correlated with the bond strength of the cation oxygen pair in the component. It is known that Vickers hardness, which is a measure of glass hardness, is almost proportional to Young’s modulus. 

$$E = 2V_p(\sum G_i x_i).$$

(3)

Here, $E$ is Young’s modulus, $V_p$ is the ion packing density, and $G_i$ and $x_i$ are the dissociation energy and mole fraction of component $i$, respectively. The dissociation energy is correlated with the bond strength of the cation oxygen pair in the component. It is known that Vickers hardness, which is a measure of glass hardness, is almost proportional to Young’s modulus. Therefore, it is sufficient to increase the proportion of components with a large $G_i$ and the packing density to obtain glass with high hardness. An effective component is Al$_2$O$_3$, which has a large dissociation energy and small molar volume. Al$_2$O$_3$ is classified as an intermediate oxide. However, bulk glasses can be easily obtained at compositions near the eutectic point (64 mol % of CaO) using the conventional melt-quench method. Young’s modulus of 62CaO–38Al$_2$O$_3$ glass was reported to be 112.9 GPa, which is certainly larger than 80 GPa of window glass. In 2015, colorless and transparent Al$_2$O$_3$–Ta$_2$O$_5$ glass was successfully fabricated using a levitation technique. The glass-forming range is as narrow as 42–50.
x \leq 48 in the composition of \((100 - x)\text{Al}_2\text{O}_3-x\text{Ta}_2\text{O}_5\). The Young’s modulus of 54\text{Al}_2\text{O}_3-46\text{Ta}_2\text{O}_5 glass, estimated from the sound velocities that are measured by a pulsed echo overlap method and density, is 153 GPa, which is approximately twice that of typical oxide glass of approximately 60–80 GPa. The very large Young’s modulus has attracted significant attention since its discovery.

\(R_2O_3-Al_2O_3\) binary glasses can be synthesized not by conventional melting processes but by using a levitation technique. Bulk glass formation was always seen in the region where the \(R_2O_3\) content was greater than 25 mol%.\(^{112}\) Reportedly, \(R_2O_3-Al_2O_3\) binary glasses exhibit high elastic modulus. Young’s modulus of 32\text{Er}_2\text{O}_3-68\text{Al}_2\text{O}_3 glass is 162.9 GPa.\(^{113}\) The Vickers hardness of 32\text{Er}_2\text{O}_3 glass, estimated as introduced in the previous section. Figure 10 shows the packing density dependence of the fraction of \(\text{AlO}_4\) in binary aluminate glasses.

\(R_2O_3-Al_2O_3\) glasses might be due to the characteristic dense structure around Al atoms.

8. Crack resistance

Generally, an oxide glass is easily cracked and broken. Strengthening techniques to form a compression layer of a glass surface are often used to prevent crack propagation and breaking. Chemically strengthening techniques exchange alkali ions on the glass surface with larger alkali ions, e.g., Na\(^+\) to K\(^+\), by immersing the glass in molten salt such as KNO\(_3\). This is an essential technology to produce reliable cover glass for smartphones and tablet PCs. Strengthening techniques are being vigorously developed to improve glass surfaces to meet the consumers’ endless demands. Meanwhile, there is also a strong demand for glass that is inherently hard to break and does not require complicated strengthening processes. To prevent crack propagation on the glass surfaces, it is effective to release the applied force by moving the atom slightly. Therefore, a glass with a lower packing density and a lower elastic modulus is usually less brittle.\(^{118}\) High hard-
ness, which requires high packing density, and less brittle are contradictory functions in a glass.

$\text{Al}_2\text{O}_3$–$\text{SiO}_2$ binary vitrifies in bulk form by conventional method at $x < 25$ in the composition of $x\text{Al}_2\text{O}_3$–$(100 - x)\text{SiO}_2$. Transparent glass can be obtained with only a few mol% of $\text{Al}_2\text{O}_3$. The glass becomes cloudy at a higher concentration of $\text{Al}_2\text{O}_3$ because of phase separation. However, it has been reported that colorless and transparent glass can be made in the range of $50 < x < 67$ using a levitation technique. It was discovered that the elastic modulus increases as the $\text{Al}_2\text{O}_3$ component increases and Young’s modulus of $60\text{Al}_2\text{O}_3$–$40\text{SiO}_2$ glass (mullite glass) reached 134 GPa. The Makishima–Mackenzie equation makes this large value reasonable because the $\text{Al}_2\text{O}_3$ content, with its large dissociation energy and packing density, also increases.

Furthermore, $\text{Al}_2\text{O}_3$-rich glasses have shown characteristic mechanical properties, such as crack resistance. Figure 11(a) shows the Vickers imprints on $x\text{Al}_2\text{O}_3$–$(100 - x)\text{SiO}_2$ glasses for various loads. It is observed that with increasing $\text{Al}_2\text{O}_3$ content, the glasses become more resistant to radial cracking, although the atomic packing density increased. Normal (radial cracks) behavior is observed in all samples for $x = 30, 40, 45, 50$, and 55, whereas, for glasses with $x = 60$, no cracks were observed in more than 50% of the indentation imprints even using an indentation load of 49.03 N. The cracking probability curves are shown in Fig. 11(b) to quantify the resistance to fracturing. The cracking probability is the quotient of the number of cracks and the number of corners (four) in each indentation imprint. The quotients for different imprints at a certain load were averaged. The data were fitted using a sigmoid function. The loading force required to generate a 50% cracking probability or two radial cracks was estimated as a cracking resistance (CR) from the fitting curve. The inset shows that the CR increases drastically with an increase of the packing density PD. The CR value of 55.4 N for the $x = 60$ glass is considerably larger than those of the crack-resistant glasses.

Local structural analysis and theoretical calculations were conducted to investigate the origin of the crack-resistant properties accompanied by high hardness and high packing density. $^{27}\text{Al}$ MAS NMR spectra revealed $\text{AlO}_x$, $\text{AlO}_2$, and $\text{AlO}_4$ in the mullite glass, and the ratio of $\text{AlO}_4$ was significantly as high as approximately 46%. MD simulations suggested that the deformation mechanism shifts from densification to shear flow with increased alumina content. The intrinsic ductility is correlated with the observation that Al atoms can more actively engage in plastic deformation and reduce the creation of lower coordinated weak spots during deformation. Further research is still needed to elucidate the mullite glass’s crack resistant mechanism and produce intrinsically stronger glasses.

9. Summary

The levitation technique introduced here is powerful for developing new glass systems that have never been verified. Using the technique, many glasses with no or less network-former oxides have been prepared. They exhibited fascinating physical properties such as high refractive index with low wavelength dispersion, infrared transparency, strong luminescence, large magneto-optical phenomena, high hardness, and crack resistance that were never observed in conventional network glasses. Furthermore, the extension of the glass-forming region in the case of $R_2\text{O}_3$–$\text{B}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$–$\text{SiO}_2$ binary systems has led to the unexpected discovery of properties even in the classical glass systems. Structural analyses of the glasses prepared using a levitation technique revealed that there are not only MO$_2$ but also MO$_3$ and MO$_4$ and they are connected by not only corner-sharing but also edge or face sharing. The levitation technique successfully expanded glass science regarding the composition, physical properties, and characteristic glass structure, which strongly motivates the renewal of the concept of glass formation.

Based on the classic glass-forming rules, the intermediate oxides TiO$_2$ and Nb$_2$O$_5$ should form a network in the BaO–TiO$_2$ or the La$_2$O$_3$–Nb$_2$O$_5$ glasses. Structural analyses indicated that there are certainly connections of –Ti–O–Ti– and –Nb–O–Nb– in the glasses. Therefore, it is likely that the network structure consisting of not only MO$_2$ but also even MO$_3$ or MO$_4$ helps formation of a glassy state. Meanwhile, considering that Ba$^{2+}$, La$^{3+}$, and O$^{2-}$ have relatively large and similar ionic radii, it is possible to propose that the large ions occupy the space with a large packing density close to the closest packed structure, and small Ti$^{4+}$ and Nb$^{5+}$ are irregularly dispersed into tetrahedral or octahedral sites formed by oxide ions. This random packing model is an alternative concept of glass formation suitable for densely packed glasses. This concept is more applicable to R-rich $R_2\text{O}_3$–$\text{B}_2\text{O}_3$ glasses, because B-atoms are surrounded by three oxygens but there is no B–O–B connection in the glasses.

Finally, further new glass compositions with attractive properties and characteristic structures will be reported soon.

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