

# Dependence of thermo-mechanical and mechanical properties of novel fluorophosphate glass on various rare earth dopants

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**Abstract** The dependence of thermo-mechanical, and mechanical properties on various rare earth dopants (RE) including  $\text{Nd}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$  in  $0.4\text{MgF}_2$ - $0.4\text{BaF}_2$ - $0.1\text{Ba}(\text{PO}_3)_2$ - $0.1\text{Al}(\text{PO}_3)_3$  glasses (MBBA system) is systematically investigated. MBBA system doped with RE dopants presented the potential application in the field of communication and high power layer system in the previous reports. In this work, it is found that the density of the doped glass increases with an increasing of RE concentration, which could be understood in terms of cationic field strength (CFS) effect. The Knoop hardness is found to decrease with the loading time and dopant concentration due to the indentation size effect (ISE) effect. The observed decrease of thermal expansion coefficient and the increase of glass transition temperature  $T_g$  with increasing dopant concentration are elucidated in terms of the increasing number of strong covalent bonds with increasing RE dopant concentration. Those results will be of paramount importance before designing optical devices.

## Introduction

Photonic active glasses with or without rare earth dopants have been actively used for potential passive and active fiber optic device applications [1–9]. Among those glasses, fluorophosphate glasses exhibit unique properties including low

phonon energy, broadband transparency covering UV to IR spectral range, and low nonlinear refractive index [10–12]. In general, however, glasses with or without dopant suffer from brittleness and chemical degradation because of low fracture toughness and low durability against moisture. This causes decrease of life duration in service. Thus, it is very important for glasses to be technologically useful to exhibit both outstanding thermo-mechanical/mechanical properties as well as spectroscopic properties [13–15]. It has been already reported that the newly developed fluorophosphate glasses can be doped with various dopants, and they represent promising candidates for compact waveguides and fiber lasers in previous works [4–9].

The objective of the present study is to understand the dependence of thermo-mechanical and mechanical properties in the newly introduced fluorophosphate glasses on the dopant concentration of technologically significant RE dopants, i.e.,  $\text{Nd}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$ . More specifically, Knoop hardness tester, which was an alternative to a Vickers hardness tester with a square indenter, was used to determine the hardness of the relatively brittle glass materials. The Knoop hardness was investigated as a function of dopant concentration, dopant types, and loading time. The deformation of the indentation was also characterized by a confocal microscopy. In addition to mechanical properties, thermo-mechanical properties including the thermal expansion coefficient and the glass transition temperature  $T_g$  were as a function of dopant concentration by using thermal mechanical analysis (TMA).

## Experiment

The glasses were prepared from reagent-grade  $\text{MgF}_2$ ,  $\text{BaF}_2$ ,  $\text{Al}(\text{PO}_3)_3$ , and  $\text{Ba}(\text{PO}_3)_2$  as starting materials (City

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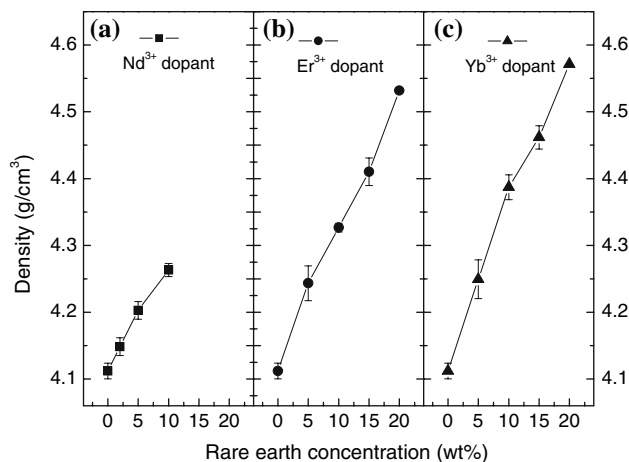
Chemicals). Neodymium oxide ( $\text{Nd}_2\text{O}_3$ , 99.99%), erbium oxide ( $\text{Er}_2\text{O}_3$ , 99.99%), and ytterbium oxide ( $\text{Yb}_2\text{O}_3$ , 99.99%) were used as rare earth dopants (Spectrum Materials). A series of 20 g batches were weighed with 0.1% accuracy and mixed thoroughly. The raw mixed materials according to  $0.4\text{MgF}_2\text{-}0.4\text{BaF}_2\text{-}0.1\text{Ba}(\text{PO}_3)_2\text{-}0.1\text{Al}(\text{PO}_3)_3$  (Hereafter, MBBA system) doped with RE dopants were melted in a vitreous carbon crucible in Ar-atmosphere at  $1,200^\circ\text{C}$ . The quenched samples were annealed at  $380^\circ\text{C}$  for 48 h to remove an internal stress and then examined using a polariscope (Rudolph Instruments).

The annealed glasses for Knoop hardness and density measurement were cut and optically polished into bars  $15 \times 10 \times 2$  mm in size. The density of sample was measured using the Archimedes method at  $20^\circ\text{C}$ . High-purity kerosene was used as immersion liquid. Five samples were measured for the average density. The relative error in density measurement is about  $\pm 1\%$ . The Knoop hardness measurement was performed using a diamond Knoop indenter (Micromet 1500). The loading time and applied load of Knoop indenter were in the range of 15–120 s and 0.3–0.7 N, respectively. All the measurements were averaged over at least 3 different samples and 15 indentations on each sample. The topography of the indented surfaces and the dimension of Knoop indentation were analyzed using confocal optical microscopy (EH system).

The glass transition temperature, softening temperature, and thermal expansion coefficient were measured by thermal mechanical analysis (TMA). A glass sample for TMA was prepared by cutting the glass into a disk with  $2 \times 5 \times 5$  mm in size and by polishing it to make the upper and lower faces parallel to each other. The thermal expansion coefficient measured for three samples was averaged from room temperature to  $600^\circ\text{C}$ .

## Results and discussion

Figure 1 shows the variation of density as a function of RE dopant concentration in fluorophosphate glasses for three different types of dopants. The density linearly increases, regardless of dopant type, with increasing dopant concentration in the range of 2–20 wt%. For the undoped fluorophosphate glass, the density is found to be  $4.116\text{ g/cm}^3$ , from which the density linearly increases to 4.263 at 10 wt% of  $\text{Nd}_2\text{O}_3$ , 4.531 and 4.571 at 20 wt%  $\text{Er}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$ , respectively [9]. The observation on the concentration dependence of density can be understood by considering the fact that an incorporation of RE dopants increases the average cationic weight unit volume, which then leads to a linear increase in density. The effects of



**Fig. 1** The variation of density as a function of RE dopant concentration

dopant types can be understood by considering the cationic field strength (CFS). The CFS ( $=Z/r^2$ ) is calculated using Shannon's values for the cationic radius [16] where  $Z$  is the valence of the respective RE ion and  $r$  the ionic radius of RE ions. CFS of three RE ions are obtained by ion radius, atomic weight [17] and listed in Table 1. In case of the MBBA system doped with 10 wt%  $\text{Nd}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$ , the values of density are found to be 4.2632, 4.3267, and 4.3871 as listed in Table 2. The ion radius decreases while atomic weight increases ( $\text{Nd}^{3+} \rightarrow \text{Er}^{3+} \rightarrow \text{Yb}^{3+}$ ) which results in the increase of CFS in the MBBA system. The values of CFS for  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Yb}^{3+}$  are determined to be 2.74, 2.83, and  $2.95\text{ \AA}^{-2}$ , respectively. Variation of density with respect to 10 wt% of  $\text{Nd}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$  are consistent with the increase of CFS in the order of  $\text{Nd}^{3+} \rightarrow \text{Er}^{3+} \rightarrow \text{Yb}^{3+}$ . Its relationship between density and CFS is also supported by Ohashi's et al. [18] that the glass network becomes more compact resulting in the increased density because of the increase of CFS.

Figure 2 shows the optical micrograph of Knoop indentations in the MBBA system doped with 10 wt%  $\text{Nd}_2\text{O}_3$  after 0.5 N loads for 30 s showing 3D micrograph. A diamond Knoop indenter was employed because of its less tendency of producing cracks than a diamond Vickers indenter. The uncracked indentation for 10 wt%  $\text{Nd}_2\text{O}_3$  doped MBBA system was shown in 3D image taken by the

**Table 1** Atomic weight, cationic field strength, and ionic radius of RE ions

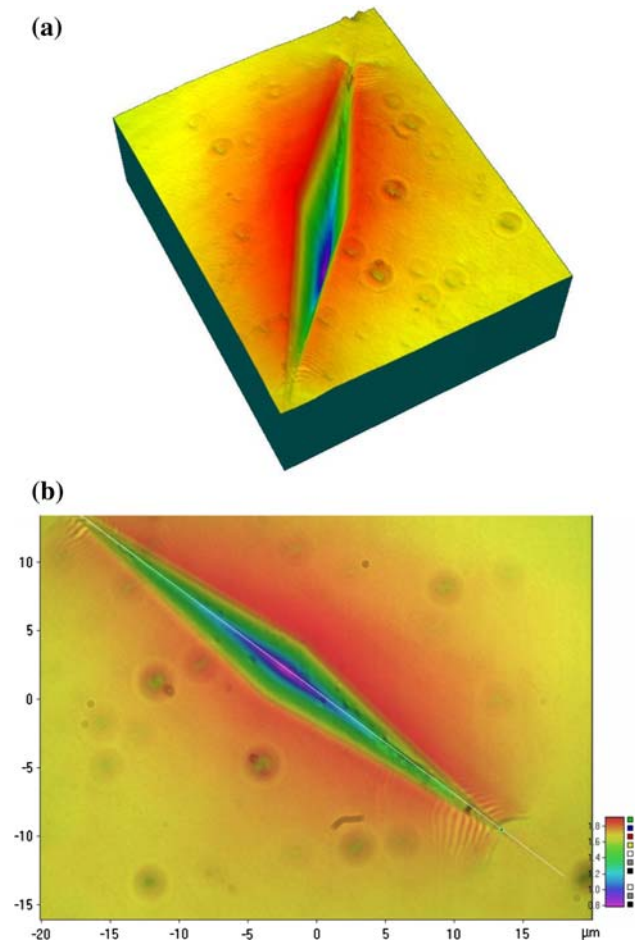
	$\text{Nd}^{3+}$	$\text{Er}^{3+}$	$\text{Yb}^{3+}$
Atomic weight	144.24	167.26	173.04
CFS	$2.74\text{ \AA}^{-2}$	$2.83\text{ \AA}^{-2}$	$2.95\text{ \AA}^{-2}$
Ionic radius	112 pm	103 pm	100.8 pm

**Table 2** Comparison of density, Transition temperature ( $T_g$ ), thermal expansion and Knoop hardness in the MBBA system doped with 10 wt% RE dopant concentration

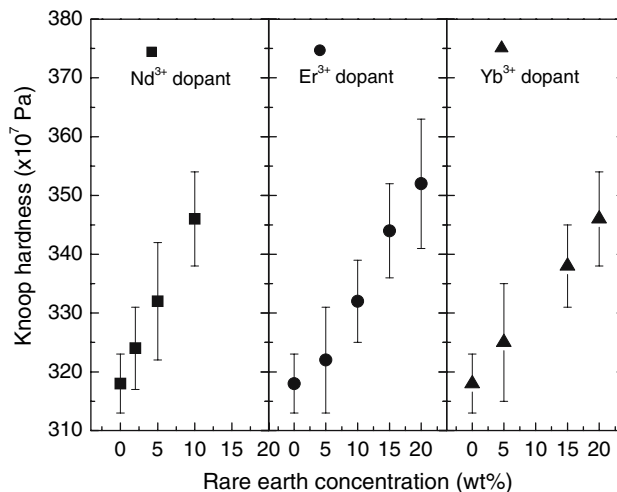
	Density (g/cm <sup>3</sup> )	T <sub>g</sub> (°C)	Thermal expansion (μm/°C)	Knoop hardness (GPa)
10 wt% Nd <sub>2</sub> O <sub>3</sub>	4.2632	505.6	0.02534	3.46
10 wt% Er <sub>2</sub> O <sub>3</sub>	4.3267	502.2	0.02434	3.32
10 wt% Yb <sub>2</sub> O <sub>3</sub>	4.3871	501.0	0.02309	3.29

conforcal optical microscopy. The length between short apexes and long apexes was found to be 4.7 and 45 μm, respectively and the depth of the indentation was also found to be about 1 μm.

Figure 3 shows the variation of Knoop hardness as a function of RE concentration. It is evident from Fig. 3 that the Knoop hardness linearly increases as the concentration of RE dopants increase. The observed increase of hardness is due to the increasing number of strong covalent bonds as



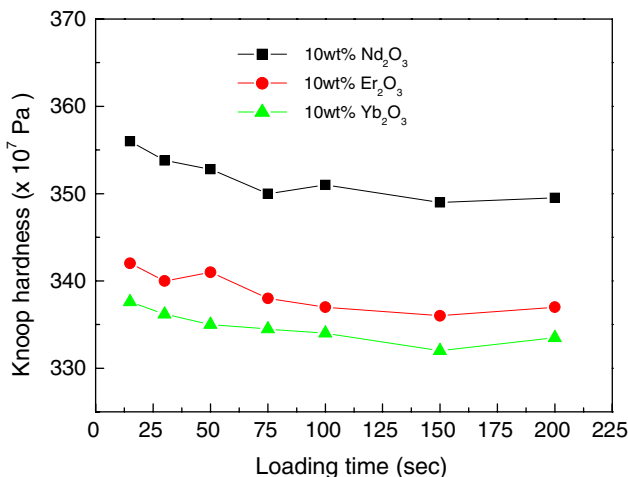
**Fig. 2** The optical micrograph of Knoop indentations in the fluorophosphate glass doped with 10 wt% Nd<sub>2</sub>O<sub>3</sub> after 0.5 N load for 30 s showing 3D micrograph



**Fig. 3** The variation of Knoop hardness as a function of RE dopant type and respective concentration

RE dopants leads to increase of network cross linking in glasses. Previous study on spectroscopic properties on MBBA system doped with Nd<sup>3+</sup> represents that the increase of hardness with an increase in Nd<sub>2</sub>O<sub>3</sub> concentration, since the increase of  $\Omega_2$  indicates the increase of covalency with an increase in Nd<sub>2</sub>O<sub>3</sub> concentration [7].

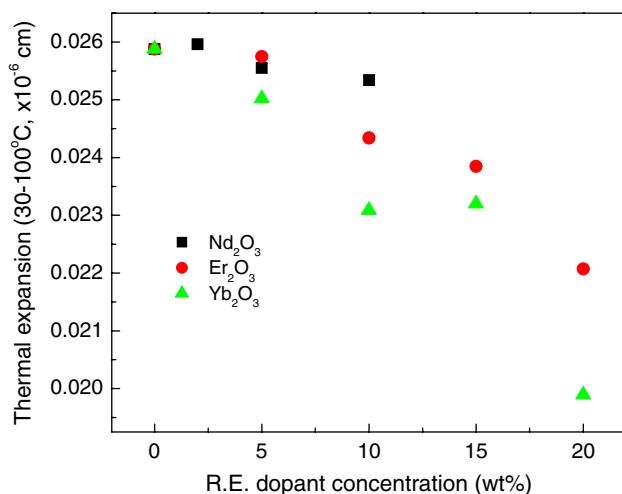
Figure 4 shows the variation of Knoop hardness for 10 wt% of RE doped MBBA system as a function of loading time. It is observed that Knoop hardness gradually decreases as the indentation loading time increases from 15 to 200 s. The indentation size effect (ISE) is a general trend wherein hardness decreases with increasing indentation size or indentation load. As the loading time increases, the indentation size is also increased. Therefore, the gradual decrease of the hardness is due to the indentation size effect (ISE). The similar trend was also observed by Guin’s et al. [19].



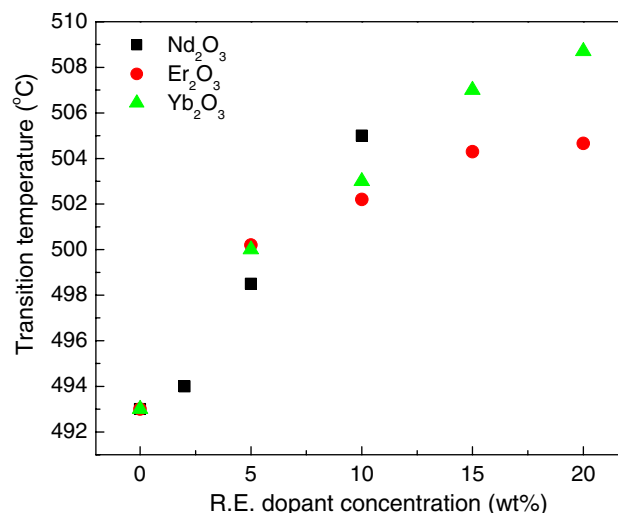
**Fig. 4** The variation of Knoop hardness for the 10 wt% RE doped fluorophosphate glasses as a function of loading time

In order to investigate the effect of RE dopant concentration on thermal expansion, the variation of thermal expansion in the range of 30–100 °C is shown in Fig. 5 as a function of dopant concentration. The dependence of dopant concentration less than 10 wt% is not significant but for the dopant level above 10 wt% in both Er<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> doped systems, a linear decrease of thermal expansion coefficient is evidently observed as shown in Fig. 5.

Figure 6 shows the variation of  $T_g$  for the MBBA system doped as a function of RE dopant concentration. The glass transition temperature,  $T_g$ , for undoped MBBA system is found to be 492.5 °C. It is clear that  $T_g$  increase as RE dopant concentration increases. The value of  $T_g$  for the 10 wt% Nd<sub>2</sub>O<sub>3</sub> doped MBBA system is found to be 505.3 °C. Those for 20 wt% Er<sub>2</sub>O<sub>3</sub> and 20 wt% Yb<sub>2</sub>O<sub>3</sub> doped MBBA systems are found to be around 504.6 and 506.3 °C, respectively. The MBBA system doped with three RE dopants show a roughly identical tendency, which might be due to the increasing number of strong covalent bonds, which is also responsible for the observed in Knoop hardness behavior as described above. A detailed study using Racha parameter has to be carried out in future to elucidate the variation of degree of covalent bonding. But the covalency between RE ions and ligands anions can be evaluated by using the intensity parameter ( $\Omega_i$ ) obtained from Judd-Ofelt theory indicated, since  $\Omega_2$  reflect the asymmetry of the local environment at the RE ion site. The weaker the value of  $\Omega_2$  the more centrosymmetrical the ion site is and the more ionic its chemical bond with the ligand is [20]. In the MBBA system, it is observed that the increase of  $\Omega_2$  with an increasing of Nd<sub>2</sub>O<sub>3</sub> concentration could indicate the increase of covalency [7].



**Fig. 5** Variation of thermal expansion in the range of 30 °C–100 °C as a function of RE dopant concentration: (■) Nd<sub>2</sub>O<sub>3</sub> doped (●) Er<sub>2</sub>O<sub>3</sub> doped (▲) Yb<sub>2</sub>O<sub>3</sub> doped system



**Fig. 6** Variation of  $T_g$  as a function of RE dopant concentration in the MBBA system

## Conclusions

The thermo-mechanical, and mechanical properties of a newly developed series of 0.4MgF<sub>2</sub>-0.4BaF<sub>2</sub>-0.1Ba(PO<sub>3</sub>)<sub>2</sub>-0.1Al(PO<sub>3</sub>)<sub>3</sub> glasses doped with various rare earth dopants including Nd<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, and Yb<sub>2</sub>O<sub>3</sub>, respectively, have been investigated as a function of dopant type and their concentration. The increase of density with dopant concentration is suggested to be caused by the increase of cationic field strength (CFS). The observed decrease of Knoop hardness with the loading time and dopant concentration is attributed to the indentation size effect (ISE) effect. The observed decrease of thermal expansion coefficient and the increase of  $T_g$  with increasing dopant concentration are elucidated in terms of the increasing number of strong covalent bonds with RE dopant concentration.

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