J Mater Sci (2008) 43:1109–1113
DOI 10.1007/s10853-007-2257-7

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

Ju H. Choi · Alfred Margaryan · Ashot Margaryan · Frank G. Shi

Received: 6 September 2007 / Accepted: 23 October 2007 / Published online: 4 December 2007

Abstract The dependence of thermo-mechanical, and mechanical properties on various rare earth dopants (RE) including Nd_2O_3, Er_2O_3, and Yb_2O_3 in $0.4MgF_2$-$0.4BaF_2$-$0.1Ba(PO_3)_2$-$0.1Al(PO_3)_3$ 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., Nd_2O_3, Er_2O_3, and Yb_2O_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).

J. H. Choi · F. G. Shi (✉)
OptoElectronic Integration and Packaging Lab., Department of Chemical Engineering and Materials Science, University of California, Irvine, CA 92697, USA
e-mail: fgshi@uci.edu

A. Margaryan · A. Margaryan
AFO Research Inc, P.O. Box 1934, Glendale, CA 91209, USA

Experiment

The glasses were prepared from reagent-grade MgF_2, BaF_2, $Al(PO_3)_3$, and $Ba(PO_3)_2$ as starting materials (City

Chemicals). Neodymium oxide (Nd_2O_3, 99.99%), erbium oxide (Er_2O_3, 99.99%), and ytterbium oxide (Yb_2O_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 $0.4MgF_2$-$0.4BaF_2$-$0.1Ba(PO_3)_2$-$0.1Al(PO_3)_3$ (Hereafter, MBBA system) doped with RE dopants were melted in a vitreous carbon crucible in Ar-atmosphere at 1,200 °C. The quenched samples were annealed at 380 °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 × 10 × 2 mm in size. The density of sample was measured using the Archimedes method at 20 °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 ±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 × 5 × 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 °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 g/cm^3, from which the density linearly increases to 4.263 at 10 wt% of Nd_2O_3, 4.531 and 4.571 at 20 wt% Er_2O_3 and Yb_2O_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 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% Nd_2O_3, Er_2O_3, and Yb_2O_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 ($Nd^{3+} \rightarrow Er^{3+} \rightarrow Yb^{3+}$) which results in the increase of CFS in the MBBA system. The values of CFS for Nd^{3+}, Er^{3+}, and Yb^{3+} are determined to be 2.74, 2.83, and 2.95 Å^{-2}, respectively. Variation of density with respect to 10 wt% of Nd_2O_3, Er_2O_3, and Yb_2O_3 are consistent with the increase of CFS in the order of $Nd^{3+} \rightarrow Er^{3+} \rightarrow Yb^{3+}$. 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.

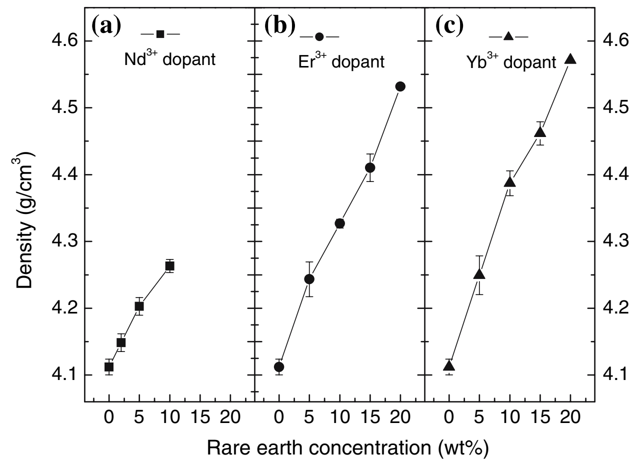

Fig. 1 The variation of density as a function of RE dopant concentration

Figure 2 shows the optical micrograph of Knoop indentations in the MBBA system doped with 10 wt% Nd_2O_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% Nd_2O_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

	Nd^{3+}	Er^{3+}	Yb^{3+}
Atomic weight	144.24	167.26	173.04
CFS	2.74 Å^{-2}	2.83 Å^{-2}	2.95 Å^{-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^3)	Tg (°C)	Thermal expansion (μm/°C)	Knoop hardness (GPa)
10 wt% Nd_2O_3	4.2632	505.6	0.02534	3.46
10 wt% Er_2O_3	4.3267	502.2	0.02434	3.32
10 wt% Yb_2O_3	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 RE dopants leads to increase of network cross linking in glasses. Previous study on spectroscopic properties on MBBA system doped with Nd^{3+} represents that the increase of hardness with an increase in Nd_2O_3 concentration, since the increase of Ω_2 indicates the increase of covalency with an increase in Nd_2O_3 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].

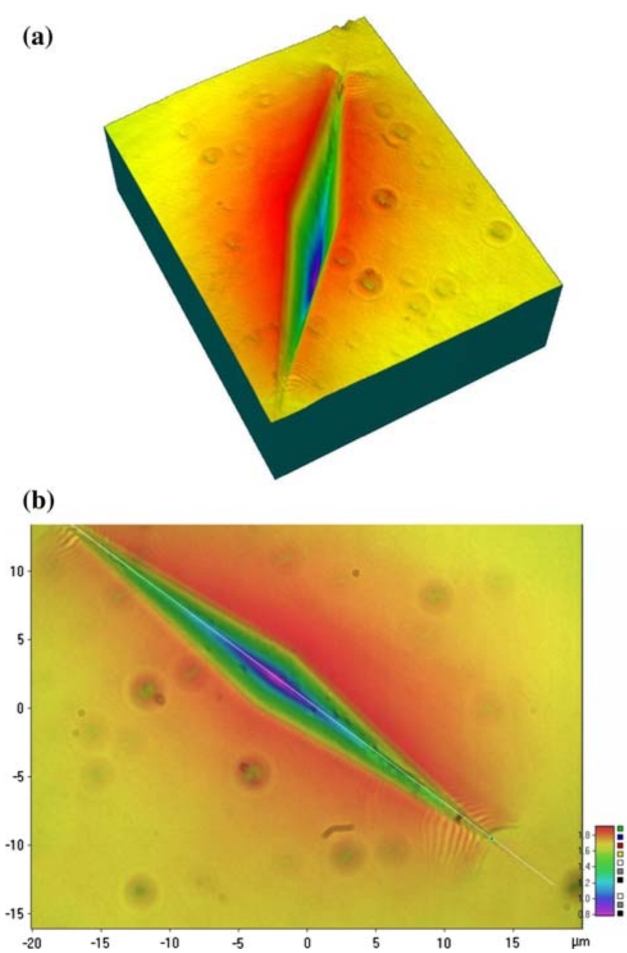

Fig. 2 The optical micrograph of Knoop indentations in the fluorophosphate glass doped with 10 wt% Nd_2O_3 after 0.5 N load for 30 s showing 3D micrograph

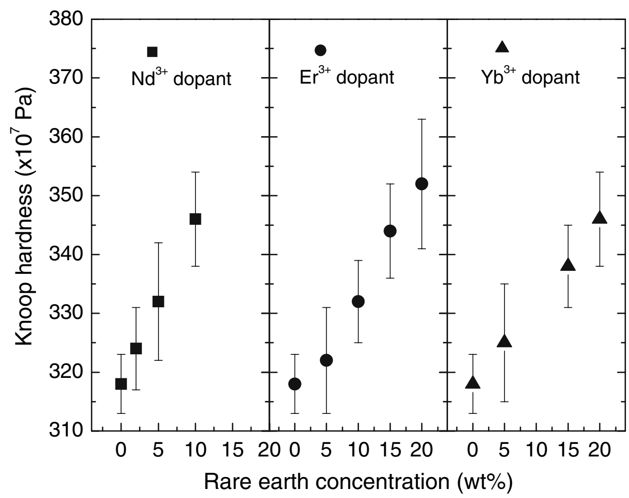

Fig. 3 The variation of Knoop hardness as a function of RE dopant type and respective concentration

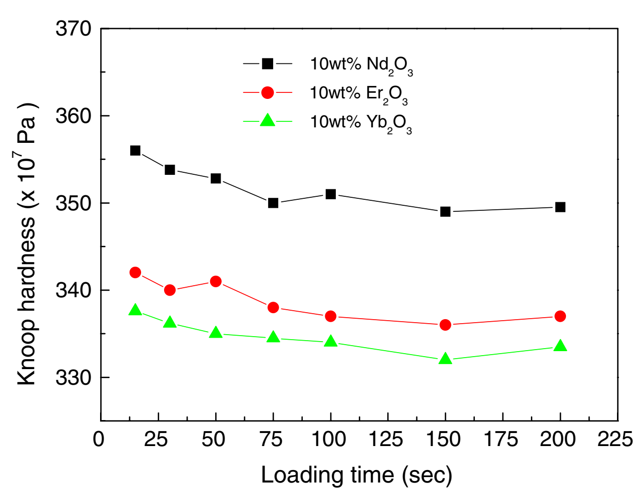

Fig. 4 The variation of Knoop hardness for the 10 wt% RE doped fluorophosphate glasses as a function of loading time

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_2O_3 and Yb_2O_3 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_2O_3 doped MBBA system is found to be 505.3 °C. Those for 20 wt% Er_2O_3 and 20 wt% Yb_2O_3 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 (Ω_t) obtained from Judd-Ofelt theory indicated, since Ω_2 reflect the asymmetry of the local environment at the RE ion site. The weaker the value of Ω_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 Ω_2 with an increasing of Nd_2O_3 concentration could indicate the increase of covalency [7].

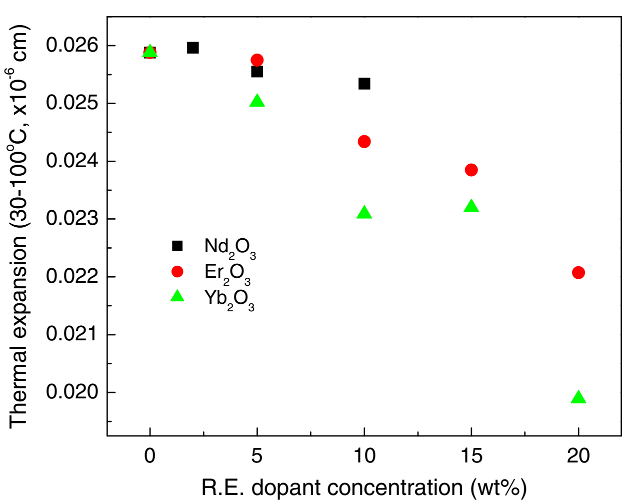

Fig. 5 Variation of thermal expansion in the range of 30 °C–100 °C as a function of RE dopant concentration: (■) Nd_2O_3 doped (●) Er_2O_3 doped (▲) Yb_2O_3 doped system

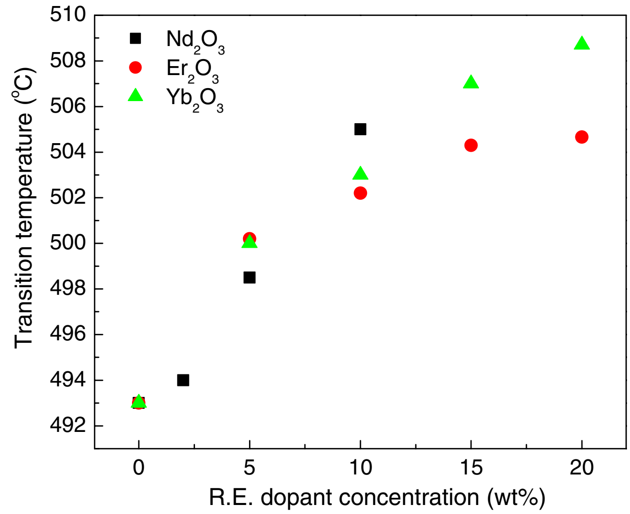

Fig. 6 Variation of T_g as a function of RE dopant concentration in the MBBA system

Conclusions

The thermo-mechanical, and mechanical properties of a newly developed series of 0.4MgF_2-0.4BaF_2-0.1$Ba(PO_3)_2$-0.1$Al(PO_3)_3$ glasses doped with various rare earth dopants including Nd_2O_3, Er_2O_3, and Yb_2O_3, 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.

References

1. Lira A, Camarillo I, Camarillo E, Ramos F, Flores M, Caldino U (2004) J Phys: Condnes Matter 16:5925
2. Ratnakaram YC, Chakradhar RPS, Ramesh KP, Rao JL, Ramakrishna J (2003) J Phys: Condnes Matter 15:6715
3. Hönninger C, Paschotta R, Graf M, Graf M, Morier-Genoud F, Zhang G, Moser M, Biswal S, Nees J, Braun A, Mourou GA, Johannsen I, Giesen A, Seeber W, Keller U (1999) Appl Phys B 69:3
4. Choi JH, Margaryan A, Margaryan A, Shi FG, Wytze Van Der Veer (2007) Adv OptoElectr 2007:8. doi:10.1155/2007/39892
5. Margaryan A, Choi JH, Margaryan A, Shi F (2004) Appl Phys B Laser Optics 78:409
6. Choi JH, Shi FG, Margaryan A, Margaryan A (2005) Mat Res Bull 40:2189
7. Choi JH, Shi FG, Margaryan A, Margaryan A (2005) J Lum 114:167

8. Choi JH, Shi FG, Margaryan A, Margaryan A (2005) J Alloys Comp 396:79
9. Choi JH, Shi FG, Margaryan A, Margaryan A. (2005) J Mat Res 20:264
10. Lakshman SVJ, Ratnakaran YC (1988) Phys Chem Glasses 29:26
11. Viana B, Palazzi M, LeFol O (1997) J Non-Cryst Solids 215:96
12. Jiang S, Luo T, Hwang BC, Smekatala F, Seneschal K, Lucas J, Peyghambarian N (2000) J Non-Cryst Solids 263–264:364
13. Duan RG, Roebben G, Van der Biest O, Liang KM, Gu SR (2001) J Non-Cryst Solids 281:213
14. Quinn GD, Green P, Xu K (2003) J Am Ceram Soc 86:441
15. Yoshida S, Aono S, Matsuoka J, Soga N (2001) J Ceram Soc Japan 109(9):753
16. Shannon RD, Prewitt CD (1969) Acta Crystallogr B 25:928
17. Weast RC, Astte MJ, Beyer WH (eds) (1987–1988) CRC Handbook of chemistry and physics, 87th edn. CRC Press, Boca Raton, pp 1–7, 4–127 to 132
18. Ohashi M, Nakamura K, Hirao K, Kanzaki S, Hampshire S (1995) J Am Ceram Soc 78(1):71
19. Guin JP, Rouxel T, Sangleboeuf JC, Melscoet I (2002) J Lucas J Am Ceram Soc 85(6):1545
20. Jorgensen CK, Reisfeld R (1983) J Less-Common Met 93:107