# Dopant and concentration dependence of linear and nonlinear refractive index and dispersion for new (Mg, Ba)$F_2$ based fluorophosphates glass

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## ABSTRACT

Linear and nonlinear refractive index, Abbe number, electronic energy gap and oscillator strength are reported for a new series of (Mg, Ba)$F_2$-based fluorophosphates glasses (MBBA system) doped with rare earth dopants ($Er^{3+}$, $Nd^{3+}$) in the concentration range of $6.67 \times 10^{20}$ - $2.86 \times 10^{21}$ (ions/cm$^3$) and $2.5 \times 10^{20}$ - $1.25 \times 10^{21}$ (ions/cm$^3$), respectively. The linear refractive index is found to increase with increasing dopant concentration, while the Abbe number is found to be remarkably concentration invariant, i.e., around 66-68 for both dopants. The average electronic band gap is also found to be almost dopant concentration independent, i.e., about 4.1, while the electronic oscillator strength is found to slightly increase with increasing dopant concentration, i.e., from 6.2 to 6.4. The nonlinear refractive index is found to show a linear increase from 1.2866 to 1.4018 for the investigated dopant concentration range. Those results strongly suggest the present new series of glasses can be excellent laser hosts

**Keyword:** *Refractive index, Nonlinear refractive index, Optical dispersion, Flurophosphates glass*

## 1. INTRODUCTION

Because of a favorable combination of low nonlinear refractive index (due to fluoride as a glass-forming constituent) and high cross section (due to phosphate as a glass-forming constituent), fluorophosphates glass represents one of the

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best potential laser hosts [1]. It was found that with a fluorophosphate glass, a relatively higher degree of line broadening and smoother line shapers can be obtained [2]. It was also found that neodymium-doped fluorophosphate glasses can deliver relatively shorter pulses than pure phosphate glasses, which were attributed to the relatively higher degree of inhomogeneous line broadening in fluorophosphate glasses [3]. Other spectroscopic studies also indicated that the fluorophosphate glass is an excellent candidate for high power lasers and broadband amplifiers in the eye-safe region around 1.5 μm for applications in communication, medicine, and meteorology [4-8]. It was also found to be a good material for the generation of ultrashort pulses [9].

We have introduced a new family of fluorophosphates glasses which can be doped with an extremely high concentration of rare earth dopants. The doped glasses exhibit low optical dispersion and high refractive index. The objective of this paper is to report the dopant type ($Er^{3+}$, $Nd^{3+}$) and dopant concentration dependence of various optical properties including linear and nonlinear refractive index for the new series of (Mg, Ba)$F_2$ based fluorophosphates glasses.

## 2. EXPERIMENTAL ARRANGEMENT

### 2.1 Glass synthesis

The reagent-grade starting materials (City Chemicals) and rare earth materials such as $Er_2O_3$, and $Nd_2O_3$ (Spectrum Materials) have above 99.99% purity. A series of batches are weighed on 0.001% accuracy and mixed thoroughly. The raw mixed materials are melted in a vitreous carbon crucible in Ar-atmosphere at 1200-1250°C. The quenched samples are annealed at 50-100°C below the transition temperature to remove an internal stress examined by the polariscope (Rudolph Instruments). Samples for optical and spectroscopic measurements are cut and optically polished to the size of 15x10x2mm$^3$.

### 2.2 Optical properties

The refractive index ($n_D$, $n_F$ and $n_C$) is measured with a unit of Abbe refractometer (ATAGO) at 20°C at the wavelength of 486, 589, and 656nm, respectively. Three different measurements are carried out to get the average value for both types of rare earth dopants and at their concentration at least three samples. Abbe number is obtained for the following expression

$$\nu_d = \frac{(n_D - 1)}{(n_F - n_C)} \qquad (1)$$

where $n_D$, $n_F$ and $n_C$ are the refractive indices at the D-, C- and F-spectral lines. The refractive index values are used to calculate the partial dispersion ($n_F$-$n_C$) and reciprocal relative dispersion i.e. Abbe number ($\nu_d$). The refractive index variation with respect to photon energy can also be obtained from the following relationship, based on the single oscillator approximation suggested by Wemple [10]

$$n^2 - 1 = \frac{E_d E_o}{E_o^2 - E^2} \qquad (2)$$

where $n$ is the refractive index at a specific wavelength, $E$ is the photon energy ($=h\nu$), $E_o$ is the average electronic energy gap for transition and $E_d$ is the electronic oscillator strength. Eq.(2) can be written as,

$$\frac{1}{n^2 - 1} = \frac{E_o}{E_d} - \frac{E^2}{E_o E_d} \qquad (3)$$

which indicates that $E_o$ and $E_d$ can be determined from the linear fit of $1/(n^2-1)$ vs. $E^2$. Nonlinear refractive index related to minimize self-focusing and self modulation in high power laser application can be obtained from Eq. (4). $n_2$ values are deduced on the base of d-line refractive index ($n_d$) and Abbe number ($\nu_d$) [11].

$$n_2[esu] = \frac{k(n_d - 1)(n_d^2 - 2)^2}{\nu_d \sqrt{1.517 + (n_d^2 + 2)(n_d + 1)\frac{\nu_d}{6n_d}}} \qquad (4)$$

where the value of $K$ is an empirical factor that might be constant; 68x10$^{-13}$ [esu] for a variety of fluoride crystals and 70x10$^{-13}$[esu] for fluoride glasses. In this work, $K$ of 70x10$^{-13}$ [esu] was used to estimate the $n_2$ because major compositions in our MBBA system are mostly based on (Mg, Ba)$F_2$.

## 3. RESULTS AND DISCUSSION

### 3.1. Linear refractive index and Abbe number

The refractive index of a glass usually depends on individual ions present in the glass and their packing and polarizability, of cation. Furthermore, the refractive index generally increases with increasing size of cation [12]. In our systems, the host materials are fixed and composed of (Mg, Ba)$F_2$-based fluorophosphates glass (MBBA system). $Er^{3+}$ and $Nd^{3+}$ ions are doped in the form of $Er_2O_3$, and $Nd_2O_3$. Fig. 1 shows wavelength dependence of the refractive index of MBBA system with respect to (a) $Nd^{3+}$ (b)$Er^{3+}$ ion concentration. As shown in Fig. 1, the refractive index decreases regardless of types of rare earth dopants and their concentration as the wavelength increase. It is obvious that the refractive index measured at D-line spectra (486nm) should be relatively higher than those measured at F-line (589nm), C-line (656nm) spectra. The relationship between refractive index ($n$) and photon energy ($E$) in given by Eq. (2). Lower frequency ($\lambda_o$)

results in larger E (= $hc/\lambda_o$) and it means that photon energy $E$ is getting higher and total values of right-hand side in equation (2) will be finally increased. Therefore, refractive index ($n$) will increase with decreasing wavelength ($\lambda_o$).

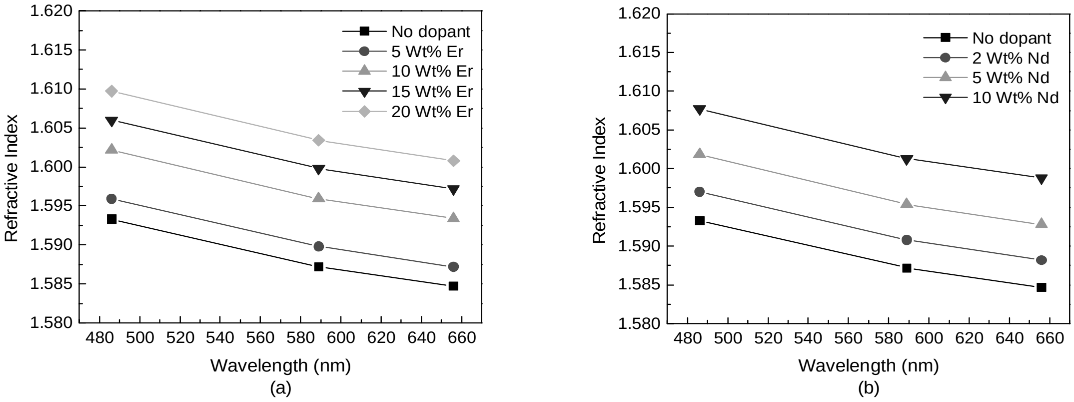


Fig. 1 Wavelength dependence of the refractive index of the MBBA system with respect to (a) $Er^{3+}$, (b) $Nd^{3+}$ ion concentration

Considering the concentration of rare earth dopants ($Er^{3+}$, $Nd^{3+}$), the refractive index of the MBBA system increases with the increase of the dopant concentration. This is due to the relatively dense packing of rare earth dopants into host materials: Incorporation of metaphosphate compounds into fluoride leads to an extra room for rare earth ions since an incorporation of $Ba(PO_3)_2$ and $Al(PO_3)_3$, could provide multiple sites for rare earth dopants. Moreover, an incorporation of metaphosphate compounds, which results in more dense packing of rare earth dopants, enhances the refractive index because of increasing dopant concentration. The expected improvement of thermal stability and chemical durability as a result of incorporating metaphosphate compound will be discussed in a separate paper.

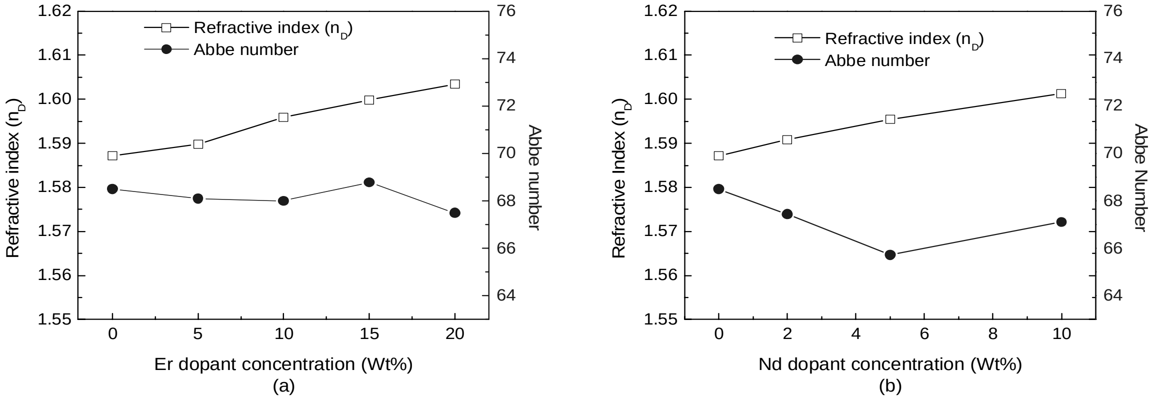


Fig. 2 Refractive index and Abbe number as a function of (a) $Er^{3+}$ dopant and (b) $Nd^{3+}$ dopant concentration

In general, there is an inverse relationship between the Abbe number and refractive index in optical glasses. In other word, the glass with a relatively high refractive index has a relatively low Abbe number i.e. high dispersion. In case of fluorophosphates glasses, Abbe number is in the range of 45-70 [1]. The reciprocal relative dispersion i.e. Abbe number ($\nu_d$) are calculated from refractive index and presented with respect to two types of dopants i.e. $Er^{3+}$, $Nd^{3+}$ ion and their concentrations. As shown in Fig. 2, the refractive index increases linearly with the concentration of rare earth dopants ($Er^{3+}$, $Nd^{3+}$), but Abbe numbers ($n_d$) do not noticeably decline and are found to be around 66-68. The Abbe number is fairly high compared with other fluorophosphates glasses. Thus, the new MBBA system exhibits a low dispersion even at an extremely high dopant concentration.

### 3.2 Average electronic energy gap ($E_o$) and the electronic oscillator strength ($E_d$)

The relationship between $1/(n^2-1)$ and $E^2$ based on Eq. (3) is presented in Fig. 3. The overall trend is a linear decrease with increasing rare earth dopant concentration and the increase in photon energy is independent of types of dopants. Refractive index dispersion $1/(n^2-1)$ is related to $E_o$ of the oscillator energy for electronic transition and $E_d$ of the dispersion energy. Fundamentally, the value of $E_d$, $E_o$ fitted to the linear lines in Fig. 3 depends on the neighbor cation coordination number and anion valence [13]. The MBBA system, the host materials are fixed and based on (Mg, Ba)$F_2$ and phosphate glasses. In order to investigate the dependence of different dopants ($Er^{3+}$, $Nd^{3+}$) and their concentration on the average electronic energy gap ($E_o$) and the electronic oscillator strength ($E_d$), the value of $E_o$ and $E_d$ are calculated from the linear fitting in Fig. 3.

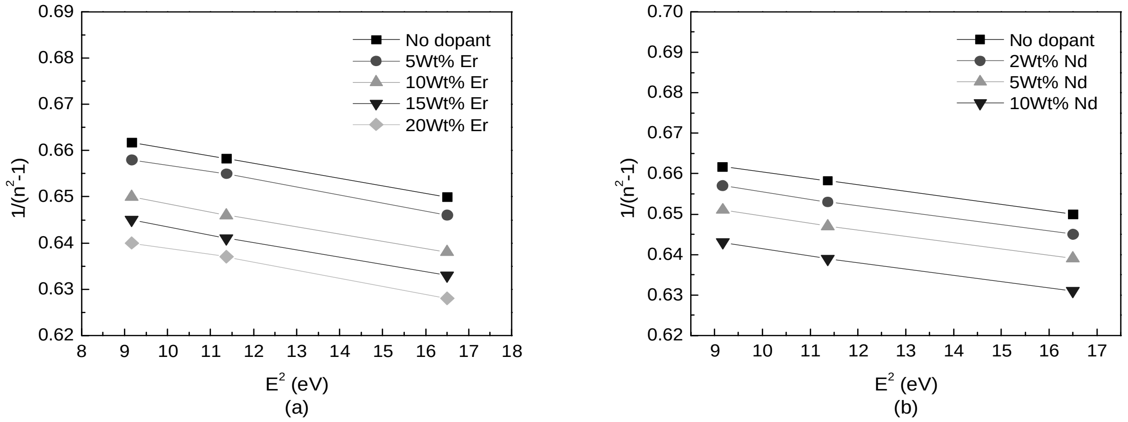
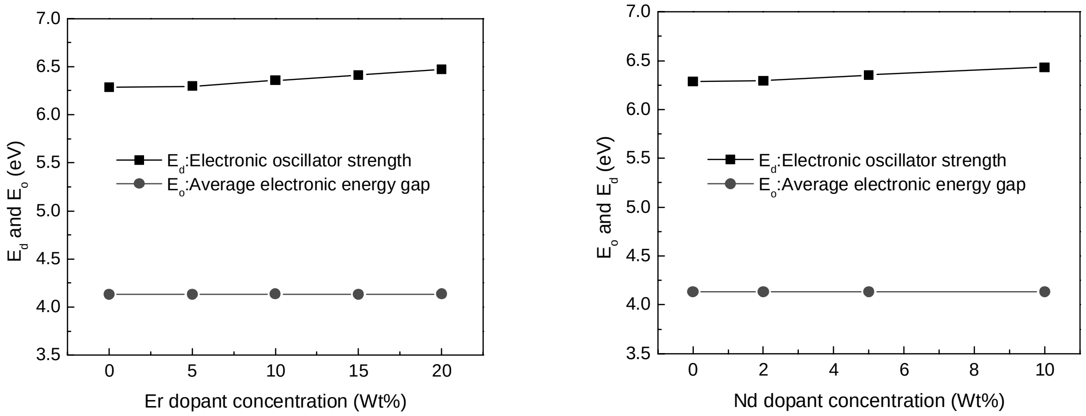


Fig. 3. Refractive index variation on photon energy in MBBA glasses according to (a) $Er^{3+}$ ion (b) $Nd^{3+}$ ion concentration

Figure 4 shows the dependence of different types of dopant ($Er^{3+}$, $Nd^{3+}$) and their concentration on the average electronic energy gap ($E_o$) and the electronic oscillator strength ($E_d$) in the MBBA glasses. A general tendency in all glasses systems, chalcogenide, oxide and fluoride glasses, is that a larger refractive index corresponds to a smaller $E_o$ [14]. But it is note that a larger refractive index is related to a smaller $E_o$ and it results in a larger dispersion for most glass systems. According to the Wemple's equation (2), refractive index increase as the electronic band gap ($E_o$) decreases and the electronic oscillator strength ($E_d$) increases.



(a) (b)

Fig. 4. The electronic oscillator strength ($E_d$) and average electronic energy gap ($E_o$) with respect to $Er^{3+}$ and $Nd^{3+}$ ion concentration

In the MBBA system, the average electronic band gap ($E_o$) is almost independent of i.e. dopant concentration. But the electronic oscillator strength ($E_d$) increases with dopant concentration. The electronic oscillator strength ($E_d$) and average electronic band gap ($E_o$) are not affected by dopants ($Er^{3+}$, $Nd^{3+}$) and their concentration.

### 3.3 Nonlinear refractive index

The refractive index ($n$) consists of linear refraction ($n_o$) and non-linear refraction ($n_2$) in electromagnetic intensity ($I$), i.e. $n=n_o+n_2I$. The nonlinear refractive index ($n_2$) can be estimated based on Eq. (4) from the data on refractive index and Abbe number. The knowledge of low nonlinear refractive index ($n_2$) is required for laser applications to prevent spatial intensity fluctuations in the wavefront and self-focusing [15].

Table 1. The dependence of expected non-linear index on $Er^{3+}$ and $Nd^{3+}$ ion concentrations

| Concentration (wt%) | | 0 | 2 | 5 | 10 | 15 |
|---|---|---|---|---|---|---|
| Non-linear index [esu] | MBBA /$Er^{3+}$ | 1.2866 | - | 1.3076 | 1.3336 | 1.3252 |
| | MBBA /$Nd^{3+}$ | 1.2866 | 1.3318 | 1.4018 | 1.3815 | - |

Table 1 summarizes the nonlinear refractive index ($n_2$) for $Er^{3+}$ and $Nd^{3+}$ ion as well as for different dopant concentrations. The nonlinear refractive index is found to be linearly dependent on the dopant concentration, although the increase is insignificant.

## 4 CONCLUSION

The dopant type and concentration dependence of linear and nonlinear refractive index and dispersion for a new (Mg, Ba)$F_2$ based fluorophosphates glass (MBBA system) have been investigated. The linear refractive index has been found to increase with increasing dopant concentration due to the dense packing of dopant materials into host materials, while the Abbe number is found to be remarkably concentration invariant, i.e., around 66-68 for a wide dopant concentration ranging in both dopants. The average electronic band gap has been also found to be 4.1 almost dopant concentration independent, i.e., about 4.1, while the electronic oscillator strength has been found to slightly increase with increasing dopant concentration, i.e., from 6.2 to 6.4. The non-linear refractive index has been found to exhibit a linear increase from 1.2866 to 1.4018 for the investigated dopant concentration range. New (Mg, Ba)$F_2$ based fluorophosphates glasses are promising materials based on results such as low nonlinear index and low dispersion for laser application. The systematic investigation on other optical properties is also useful for material designs.

## REFERENCES

1. W. Vogel, *Glass Chemistry*, Spring Verlag, chapter 7, 1992
2. D. Ehrt: Proc. *SPIE* **1761**, pp.213, 1992
3. D. Kopf, F.X. Kaertner, U. Keller, K.J.Weingarten: *Opt. Lett.* **20**, 1169, 1995
4. S. I. Todorroki, S. Sakaguchi, M. Peeters, *J. of American Ceram. Soc.* 80 [2] pp. 313-16, 1997
5. Ozturk, A., *Soc. Glass Technology*, vol.41, (no.3), June pp.106-8, 2000.
6. D. Warner, H. Rawson, *Journal of Non-Crystalline Solids*, vol.29, (no.2), Aug. pp.231-7, 1978
7. B. Kumar, R. Harris, *Physics and Chemistry of Glasses*, vol.25, (no.6), Dec. pp.155-8, 1984
8. S. Jiang, M. Myers, N. Peyghambarian*: Opt. Eng.* **37**, pp.3282, 1998
9. J.F. Philipps, T. T Opfer, H. Ebendorff-Heidepriem, D. Ehrt, R. Sauerbrey, *Appl. Phys. B* 72, pp.399–405, 2001
10. W. Rodney, H. Halitson, T.A. King, *J. Opt. Soc. Am.* 48, pp.633, 1958
11. N.L. Boling, A.J. Glass, A. Owyoung, *IEEE J. Quantum Electron*. QE-14, pp. 601, 1978
12. Yasi, J., Fusong, J, Gan F, *Chinese Physics*, 3, pp.162, 1983
13. G. Vijaya Prakash, D. Narayana Rao, A. K. Bhatnagar, *Solid state Communication* 119, pp. 39-44, 2001
14. H. Yayama, S. Fujino, K. Morinaga, H. Takebe, D.W. Hewak, D. N. Payne, *J. of Non-Cryst. Solids,* vol.239, (no.1-3), 187-191,
15. W. L. Smith, *The handbook of Laser Science and Technology*, (Chemical Rubber Co., Boca Raton), Vol. 3, Pt. 1, pp.259, 1989