Correlation among the oxide ion polarizability, optical basicity and interaction parameter in Gd$^{3+}$ ions doped oxyhalide borate glasses

G Chandrashekaraiah$^{1,2}$, V C Veeranna Gowda$^3$, A Jayasheelan$^3$, C Narayana Reddy$^4$ and K J Mallikarjunaiah$^5$,*

$^1$R&D Center, Bharatiar University, Coimbatore - 641046, India  
$^2$Department of Physics, Government First Grade College, Kunigal -572130, India  
$^3$Department of Physics, Maharani Science College for Women, Bengaluru -560001, India  
$^4$Department of Physics, PES Degree College, Bengaluru -560050, India  
$^5$Department of Physics, M. S. Ramaiah University of Applied Sciences, Bengaluru -560058, India

* kjmarjun@gmail.com

Abstract. A borate glasses doped with rare earth Gd$^{3+}$ ion in the system [60B$_2$O$_3$ + 30 Li$_2$O + x Gd$_2$O$_3$ + (10-x) BiCl$_3$] is prepared by the conventional melt quenching method and their optical properties have been studied. The oxide ion polarizability parameter is calculating by using refractive index of glass materials, which is obtained from UV-Vis spectra. The borate glasses are known to possess high oxide ion polarizability, high refractive index, high basicity and low interaction parameter values. In this present study, theoretical calculation of basicity and interaction parameter, using oxide ion polarization, of the glass network has been addressed. A good linear correlation between the interaction parameter and basicity is observed.

1. Introduction

The electronic polarizability property of glass materials play important role in the fields of optical devices like lenses, optical fibers and electronic gadgets. Hence, an estimation of the power of polarization of the ions in glass network is extremely important. Borate glasses possess high thermal stability, refractive index, basicity, oxide ion polarizability and low interaction parameter values. Among oxide glasses borate glasses are important in the fabrication industry associated with solid state lasers, waveguides and luminescent materials. The suitable rare-earth doped oxide glass materials show high luminescence and hence is mostly used in the optical devices and mechanical sensors.

In the field of optics and electronics industry, the materials which possess high electronic polarizability have high impact. When materials exposure to high dense beam of light which results in the nonlinear behavior caused due to electronic polarizability of the ions, which intern depend on the oxide ion polarizability. The oxide ion polarizability can be calculated on the basis of refractive index and band gap energy. By adopting Tauc method, these parameters are calculated for simple oxide of glasses.

The oxide ion polarizability of glass materials are closely related to basicity of oxide materials. The basicity property of glass materials is the ability of transfer of oxygen ion density around the...
cation, which further depends upon its degree of polarizability. When an electron donor concentration in the glass networks alters, the glass will change from the acidic to basic and is measured by another parameter called “nephelaustic”. The acid-base property of the glass material can be calculated by using oxygen ion density in the network. Dimitrov et al, have calculated the theoretical basicity values for simple individual oxide glasses. Rare-earth doped glass materials have enhanced the optoelectronics and laser technology, because dopant alters the background structure and bonding character in the glass materials. Many studies on rare-earth doped glass materials have been performed. Moreover, rare-earth doped glass materials are very useful to study the Judd-Ofelt parameter, which describes the electric dipole strengths and magnetic dipole strengths. The interaction parameter between an anion and cation in the oxyhalide glass system is identified as difference in polarization of oxide ion with respect to the free state due to the polarization of the cation. The polarizing power is measured by using other components like size, positive charge, coordination number and polarizability of the cation. To verify the correlation between the polarizability of oxide ion and cation polarizability in the network, here LBG glass system has been choosen as a test case.

2. Experimental
The glass framework with substance chemical composition 60 B_2O_3 + 30 Li_2O + x Gd_2O_3 + (10-x) BiCl_3 (LBG) where 0.1≤x≤0.5 was set up by melt quenching method. Analag-grade Bismuth chloride (BiCl_3), lithium carbonate (Li_2CO_3), boric acid (H_3BO_3) and Gd_2O_3 were weighed according to the stoichiometry of the glass system. The chemicals were mixed thoroughly and then mixture was poured into a silicon crucible. The crucible was then placed in an electric furnace set at 400 °C. To ensure homogeneity, the mixture was melted at 1000 °C for about 15 minutes and then poured on a brass plate and quenched. All glass samples were then heated for 3 h at 180 °C to remove thermal strains that occurred during annealing. In the current work, optical band gap energy values were calculated from the UV-Vis spectra. Perkin Emer Lambda 35spectrometer, which works in the wavelength range of 400 to 1100 nm with an accuracy of ±0.1 nm is used to obtain UV-Vis absorption spectra.

3. Results and discussion
3.1. Oxide ion polarizability
The interaction parameter between an anion and cation in the oxyhalide glass system is identified as difference in polarization of oxide ion with respect to the free state due to the polarization of the cation. The polarizing power is measured by using other component like size, positive charge, coordination number and polarizability of the cation. Binary oxide glasses are interesting to study for various reasons. The present investigation attempts to verify the correlation between the polarizability of oxide ion and cation polarizability in the network. The Dimitrov and Sakka proposed the equation for the calculation of oxide ion polarizability of oxide glasses on the basis of linear refractive index (n) and optical band gap energy using the relation.

\[ \alpha_{O^{2-}}(n) = \left[ \frac{V_m}{2.52} \left( \frac{n^2-1}{n^2+2} \right) - \sum \alpha_{cat} \right] \frac{1}{q} \]  (1)

Where \( V_m \) is molar volume, \( \alpha_{cat} \) is the cation polarizability, \( \sum \alpha_{cat} = x\alpha_A + (1-x)\alpha_B \). \( q \) denotes the number of oxide ions in the chemical formula unit, \( \alpha_A \) and \( \alpha_B \) be the cation polarizability of the cations A and B respectively and \( x \) is molar fraction of the chemical substance. In amorphous materials, since there is lack of the crystal data, assuming the cation polarizability taken to be free-ion polarizability. Hence, with such assumptions, in the case oxide glass materials, electron cloud forms on cation more than that of anion. Therefore, even though larger size possessed by cation, it is not likely to be
efficiently polarized because cation will tend to hold its electron cloud. It was well established that the increase in the oxide ion polarizability of glass materials leads to increase in their refractive indices. The cation polarizability parameters of the compound are $\alpha_{\text{Bi}^{3+}} = 1.508 \, \text{Å}^3$, $\alpha_{\text{Li}^{+}} = 0.024 \, \text{Å}^3$, $\alpha_{\text{Gd}^{3+}} = 0.002 \, \text{Å}^3$ and $\alpha_{\text{Gd}^{3+}} = 0.61 \, \text{Å}^3$. The estimated values of oxide ion polarizability of LBG glass network with the variation of the concentration of Gd$_2$O$_3$ are listed in the Table 1. It is observed that the values of oxide ion polarizability are increased with the content of Gd$_2$O$_3$ and same is shown in the Fig 1. These oxide ion polarizability values are in good agreement with that of the values reported by Fazans et al.

**Table 1.** Oxide ion polarizability, Basicity and interaction parameter calculated values.

| Samples | Basicity calculated values | Interaction calculated values | Oxide ion polarizability |
|---------|---------------------------|------------------------------|--------------------------|
|         | Theoretical | Experimental | Theoretical | Experimental |                  |
| LBG1    | 0.51997      | 1.19325       | 0.17924      | 0.17903      | 3.52234          |
| LBG2    | 0.52094      | 1.19457       | 0.17929      | 0.17908      | 3.52343          |
| LBG3    | 0.52191      | 1.19627       | 0.17933      | 0.17913      | 3.52552          |
| LBG4    | 0.52288      | 1.19911       | 0.17938      | 0.17918      | 3.52666          |
| LBG5    | 0.52384      | 1.20041       | 0.17941      | 0.17923      | 3.52673          |

Fig 1. Variation of Gd$_2$O$_3$ mol% with Oxide ion polarization is shown. The solid line is drawn guide to the high.

3.2. **Optical basicity and interaction parameter**

The quantity optical basicity has been introduced to determine the quantitatively acid-base property of the oxide glasses. According to this theory, the oxygen behaves as a base and the metal ion behaves as acid. Duffy and Ingram have significantly contributed to the development of Lewis acid-base
principle by introducing optical basicity concept. UV – Vis spectroscopy can be used to measure the optical basicity. Further, in the d^{10}S^2p^6-block metal ions, ^1S to ^3P electron transition is very sensitive to the electron donating ability of oxygen in the medium, i.e., donor ability of oxygen is increased in the glass materials and become more basic. This effect is known as the “nephelauxetic” effect which explains the spectra of transition metal ions. The optical basicity $\Lambda_{th}$ of the investigated LBG glasses is calculated theoretically by using basicity values of the individual oxides based on the equation proposed by Duffy and Ingram $^{10}$ and the obtained values are tabulated in the Table 1.

$$\Lambda_{th} = X_{B_2O_3} \Lambda_{B_2O_3} + X_{Li_2O} \Lambda_{Li_2O} + X_{Gd_2O_3} \Lambda_{Gd_2O_3} \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

Where $X_{B_2O_3}$, $X_{Li_2O}$ & $X_{Gd_2O_3}$ and $\Lambda_{B_2O_3}$, $\Lambda_{Li_2O}$ & $\Lambda_{Gd_2O_3}$ are molar fraction and basicity of $B_2O_3$, $Li_2O$ and $Gd_2O_3$ respectively. In our present work the basicity value of the $\Lambda_{B_2O_3}$, $\Lambda_{Li_2O}$ & $\Lambda_{Gd_2O_3}$ are 0.425, 0.87 and 0.969 respectively $^{13}$. Equation (2) expresses the average bulk basicity from all oxide species such as bridging and non-bridging. In the present investigation, the estimation of the coordination number is not performed. Hence, it is expected that, in some cases a difference in the trends in the theoretical and experimental values of the basicity could be observed. Using the refractive index values we have determined the optical basicity of oxides glasses in terms of the oxide ion polarization in the presently investigated glass network using method adopted by Duffy $^{10}$ and the obtained values are tabulated in the Table 1.

$$\Lambda_n = 1.67 \left[ 1 - \frac{1}{\alpha_{O^2-(n)}} \right] \ldots \ldots \ldots \ldots \ldots \ldots (3)$$

It should be noted that for presently investigated glass network, the high basicity values are observed and they tent to increase slightly with the increase of the rare earth content and is shown in the Fig 2. However, the theoretically estimated basicity values of glass materials are not in good agreement with experimentally determined values for all concentrations.

Fig 2. Variation of basicity with concentration of $Gd_2O_3$ mol% is shown. The solid line is drawn guide to the high.

The charge overlapping of the negative ion with its neighbour positive ions for a given cation-anion pair is given by interaction parameter $A$. The interaction parameter is a measurable quantity for the inter-ionic interaction of negative ions such as $O^{2-}$ with the adjacent neighbours (cations) and ability to form ionic covalent bond with the cations $^{19}$. The weak interaction parameter indicates that feeble
strength in the electron density exists leading to unbounded electrons. The interaction parameter \( A \) of simple oxides can be calculated using the following equation as proposed by Dimitrov and Komatsu

\[
A(n) = X_{B_2O_3} \frac{(\alpha_f - \alpha_{O^2-})}{2(\alpha_{B^{3+}} + \alpha_f - \alpha_{O^2-})} + X_{Li_2O} \frac{(\alpha_f - \alpha_{O^2-})}{2(\alpha_{Li^{+}} + \alpha_f - \alpha_{O^2-})} + X_{Gd_2O_3} \frac{(\alpha_f - \alpha_{O^2-})}{2(\alpha_{Gd^{3+}} + \alpha_f - \alpha_{O^2-})} \ldots \ldots (4)
\]

where \( X_{B_2O_3}, X_{Li_2O} \) and \( X_{Gd_2O_3} \) are the equivalent fractions based on glass stoichiometry. \( \alpha_{O^2-} \) is the oxide ion polarizability in the glass, while \( \alpha_{B^{3+}}, \alpha_{Li^{+}} \) and \( \alpha_{Gd^{3+}} \) are the cation polarizabilities. The Pauling’s value of 3.921 Å\(^3\) for the free oxide ion electronic polarizability \( (\alpha_f - \alpha_{O^2-}) \) is used.

The assumption cited above is reasonable since the cationic electrons hold the cation charge making it not to get polarized. The deformability of electron cloud of the oxide ion plays larger role in the cations. The interaction parameter increases and results in reduction of the polarizability of an oxide ion \( O^2- \) placed in oxide crystal lattice in respect to its free-ion polarizability. The variation of the interaction parameter and concentration of \( Gd_2O_3 \) mol% is shown in the Fig 3 and calculated values are tabulated in the Table 1.

![Fig 3. Variation of interaction parameter with concentration of Gd_2O_3 mol% is shown. The solid line is drawn guide to the high.](image)

The interaction parameter proposed by Yamashita and Kurosawato indicates the polarizability state of an oxide ion and has been investigated in numerous simple oxides. Here binary oxide glasses and their ability to form ionic-covalent bond is addressed. The inter-ionic interaction of negative ions such as \( O^2- \) with the nearest neighbours is a measure of the interaction parameter. It has been established that the interaction parameter is directly connected to the oxide-ion polarizability and the optical basicity of simple oxides glasses, and the almost directly connected to the optical basicity against the interaction parameter could be used as an optical basicity scale for oxide glasses. On increasing the optical basicity decreases the optical basicity. It is, therefore, significant to estimate the interaction parameter of \( Gd_2O_3 \) containing glass systems. Using the value of \( A_{Gd_2O_3} = 0.044 Å^{-3}, A_{B_2O_3} = 0.244 Å^{-3}, \) and \( A_{Li_2O} = 0.11 Å^{-3} \), one can calculate the interaction parameter of \( Gd_2O_3 \) glass matrix.
The theoretical interaction parameter $A_{th}$ for $\text{Gd}_2\text{O}_3$–$\text{B}_2\text{O}_3$–$\text{Li}_2\text{O}$ oxide glasses is estimated by using the following equation\(^9\).

$$A_{th} = X_{\text{B}_2\text{O}_3}A_{\text{B}_2\text{O}_3} + X_{\text{Li}_2\text{O}}A_{\text{Li}_2\text{O}} + X_{\text{Gd}_2\text{O}_3}A_{\text{Gd}_2\text{O}_3}.$$ (5)

The calculated and experimental values of interaction parameters are in excellent agreement and the calculated values of the interaction parameter are slightly higher compare to that of experimental values.

The oxide ion polarizability values calculated in the present study for the LBG glass network are found to be in good agreement with values reported by Dimitrov et al \(^4\)\(^-\)\(^6\). Further, high oxide ion polarizability and high refractive index values are observed for the presently investigated borate glasses system. The linear relation among the theoretically calculated values of basicity and interaction parameter is observed. A good correlation was also observed among theoretical and experimental values of the interaction parameter. However it is not the case for basicity values and hence it needs to be addressed.

### 4. Conclusion

The oxide ion polarizability values calculated in the present study for the LBG glass network are found to be in good agreement with values reported by Dimitrov et al \(^4\)\(^-\)\(^6\). Further, high oxide ion polarizability and high refractive index values are observed for the presently investigated borate glasses system. The linear relation among the theoretically calculated values of basicity and interaction parameter is observed. A good correlation was also observed among theoretical and experimental values of the interaction parameter. However it is not the case for basicity values and hence it needs to be addressed.

### 5. References

[1] Zhaoa X, Wangb X, Lina H and Wanga Z 2007 Physica B 390 293 - 300
[2] Levin E. McDaniel C L 1962 J. Am. Ceram. Soc. 45 355
[3] Chandrashekaraiah G, Shivashankara Reddy N, Sujatha B, Viswanatha R and Nararaya Reddy C 2018 J. Non-Cryst. Solids 498 252 - 61
[4] Dimitrov V and Komatsu T 1999 J. Non-Cryst. Solids 249 160 - 79
[5] Dimitrov V and Sakka S 1996 J. Appl. Phys. 79 1736
[6] Dimitrov V and Komatsu T 2002 J. Solid State Chem. 163 100 - 12
[7] Meera B N, Sood A K, Chandrabhas N and Ramakrishna J 1990 *J. Non-Cryst. Solids* **126** 224 - 230
[8] Dimitrov V and Komatsu T 2005 *J. Solid State Chem.* **178** 831 - 46
[9] Dimitrov V and Komatsu T *J. Univ. Chem. Technol. Metall* **445** 219 - 50
[10] Duffy J.A and Ingram M.D 1976 *J. Non-Cryst. Solids* **21** 373 - 410
[11] Chandrashekaraiah G, Jayasheelan A, Mangala Gowri, Sivasankara Reddy N and Narayana Reddy C 2020 *J. Non-Cryst. Solids* **531** 119843
[12] Walsh B M, In: Di Bartolo B and Forte O (eds) *Advances in Spectroscopy for Lasers and Sensing* (Springer, Netherlands, 2006) p403 - 433
[13] Mallur S B, Czarnecki T, Adhikari A and Babu P K 2015 *Mater. Res. Bull.* **68** 27 - 34
[14] Dimitrov V and Komatsu 2010 *J. Chem. Tech. Metallurgy* **45** 219 - 250
[15] Honma T, Benino Y, Komatsu T, Sato R and Dimitrov V 2002 *Phys. Chem. Glasses* **43** 32 - 40
[16] Fajans K and Joos G 1924 *Z. Physik* **23** 1 - 46
[17] Georgi A D, Ramesh K P and Mallikarjunaiah K J 2018 *AIP Conf. Proc.* **1942** 070021
[18] Chandrashekaraiah G, Mallikarjunaiah K J, Veeranna Gowda V C and Narayana Reddy C 2021 *Mater. Today: Proc.* (in press)
[19] Narayana Reddy C, Veeranna Gowda V C and Chakradhar R P S 2008 *J. Non-cryst. Solids* **354** 32 - 40