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# Dispersion and Nonlinearity in Ultra-Optical Ga<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub>-PbO Glass Systems

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## ABSTRACT

ispersion, as the characteristic variation of refractive index with wavelength, is more pronounced, where the wavelength is approaching to the absorption band. In ultra-optical glasses, the nonlinear refractive index, concerning to the light intensity dependent phenomenon, becomes considerable. Here, two ultra-optical property glass systems;  $TiO_2-Bi_2O_3-PbO$ (TBP) and  $Ga_2O_3$ -Bi<sub>2</sub>O<sub>3</sub>-PbO (GBP), which exhibited the most refractive indices, were selected. Their refractive index and dispersion measurements were done by 'Minimum angle of deviation in a prism' method employing a spectrometer under different light spectra transmission. The corresponding nonlinear refractive indices of glasses were calculated by the Weber and Boling formulae and were analysed. The minimum refractive index in very long waves (infra-red),  $n_{\infty}$  and  $\lambda_s$  were estimated by Kordes semi-empirical formula and the dispersion curve fit method. Results suggested that the both glass systems could be good candidates for use in nonlinear optical applications, e.g. switches in all-optical telecommunications. Prog. Color Colorants Coat. 11 (2018), 179-191© Institute for Color Science and Technology.

## 1. Introduction

Optical glasses are industrially characterised by their refractive index and dispersion properties, particularly for their use in manufacturing lenses, photonic fibers and optical devices. In all-optical telecommunication applications, such as, optical switches, wafers and filters, the nonlinearity phenomena of ultra-high optical property glasses, under high intensity light (laser), comes into particular consideration, [1, 2].

Refractive index, n, as the ratio of the speed of light in vacuum on the speed of light in a material, is based on its constituents refractivity properties and molar volume,  $V_m$ . The refractivity is explained generally as the net polarisability of all oscillators in the material, and is expressed as molar refractivity, R<sub>M</sub>, [3]:

$$(n^{2}-1)/(n^{2}+2) = R_{M}/V_{M} = (4\pi/3) n_{0} \alpha_{0}$$
(1)

Where,  $n_0$  and  $\alpha_0$  are the number and polarisability of the independent oscillators per unit volume.  $R_M$  can be expressed as the sum of the refractivity's of constituting atoms in a material. For example; in a simple compound,  $X_i Y_i$ , [4]:

$$R_{\rm M} = \Sigma f_{\rm i} R_{\rm i} = {\rm i} R_{\rm X} + {\rm j} R_{\rm Y} \tag{2}$$

From the macroscopic point of view, the polarisability  $\alpha$  of an isotropic medium is related to the refractive index, n, by:

$$n^2 = \epsilon = 1 + 4\pi\alpha \tag{3}$$

 $\epsilon$ , is the dielectric constant of the medium [5].

The phenomenon of dispersion is described as the variation of refractive index with wavelength. It normally increases with refractive index, as the incident wavelength decrease towards the absorption peak in the uv/visible region, [6].

Augustin-Louis Cauchy (1830), [7, 8], proposed a general relationship between n and wavelength  $\lambda$  for some transparent materials:

$$\mathbf{n} = \mathbf{A} + \mathbf{B}/\lambda^2 + \mathbf{C}/\lambda^4 \tag{4}$$

Where, A, B and C are constants. The above equation was almost applicable for most glasses in the visible region. In long wavelength term  $C/\lambda^4$  is ignored.

Wilhelm Sellmeier, in 1871, [8] developed an empirical equation for refractive index dependence on wavelength, i.e., dispersion of light in the range of uv to 2.3 µm for transparent media:

$$n^{2} - 1 = B_{1}\lambda^{2}/(\lambda^{2} - C_{1}) + B_{2}\lambda^{2}/(\lambda^{2} - C_{2}) + B_{3}\lambda^{2}/(\lambda^{2} - C_{3})$$
(5)

Or

$$n^{2} - 1 = B_{1}/(1 - C_{1}/\lambda^{2}) + B_{2}/(1 - C_{2}/\lambda^{2}) + B_{3}/(1 - C_{3}/\lambda^{2})$$
(6)

Where,  $B_s$  and  $C_s$  are coefficients and have been curved fitted and calculated for some materials.

Rood [6] reported similar empirical formulae, which were believed to work for many glasses:

$$\log n = A + B \log \lambda + C (\log \lambda)^2 + \ldots + H(\log \lambda)^7$$
(7)

Where, A, B and H are constants. However, Vogel, in 1985 [9], introduced theoretical formulae as:

$$n^{2} = A_{0} + A_{1} \lambda^{2} + A_{2} \lambda^{-2} + A_{3} \lambda^{-4} + A_{4} \lambda^{-6} + \dots \quad (8)$$

Where,  $A_0$  to  $A_4$  are constants and related to the nature of the constituent ions and the density in the glass. The second term  $A_1 \lambda^2$  corresponds to the influence of the absorption from infra-red region.

For long wavelengths, Kordes [1956, 1965] proposed a semi-empirical formula, [2]:

$$\frac{(n_{\infty}^2 - 1)^2}{(n^2 - 1)^2} = 1 - \frac{\lambda_s^2}{\lambda^2}$$
(9)

Where  $n_{\infty}$  in the above is the effective refractive index for very long wavelength, and  $\lambda_s$  is the effective absorption.

Conventionally, in practice dispersion is presented by the differences between the refractive indices of particular spectra of light in a medium. For example;  $n_F$ - $n_C$  known as, Principal or Mean dispersion [10], where n is refractive index and subscripts F and C designate blue (486.1 nm) and red (656.3 nm) rays respectively.

Dispersive index referred as Abbe Number  $v_D$  is introduced to characterise dispersion [11]:

$$v_{\rm D} = \frac{(n_{\rm D} - 1)}{(n_{\rm F} - n_{\rm C})} \tag{10}$$

Where,  $v_D$  is also referred to partial dispersion. D designates the yellow (589.3 nm) spectrum or ray wavelength. There are other spectra of rays, which are considered, such as, F (480 nm), C (643.8 nm) and d (587.1 nm), corresponding to the blue, red and yellow spectra respectively. In fact, Abbe Number, in comparison with principal dispersion, characterises the dispersion property with respect to refractive index in a transparent material.

Morey [2], arbitrarily deduced an approximate relationship between refractive index,  $n_D$ , and dispersive index,  $v_D$  as:

$$n_{\rm D} = \frac{(1 - 0.11 \upsilon_{\rm D})}{(1 - 0.079 \upsilon_{\rm D})} \tag{11}$$

Rawson and Ahmadi Moghaddam [2, 4] referred to existence of an almost linear relationship between the mean dispersion and refractive index for series of optical glasses mainly based on the PbO content [4, 12].

Schott have represented a generalised ascending trend of refractive index with dispersion, i.e., Abbe Number, v for commercial glasses [12, 13] in which Lanthanum and Barium based glasses, due to their relatively ultra-low dispersion properties, do not lie in the curve trend.

In linear optics, when concerning an isotropic dielectric material, e.g., glass, the induced electronic polarisation,  $P_e$ , under the influence of single dimension monochromatic radiation with electric field intensity, E as a function of frequency,  $\omega$  (1/wavelength,  $\lambda$ ) is [4, 5]:

$$P_{e} = \alpha E(\omega) \tag{12}$$

In highly coherent polarisable materials under high intensity electromagnetic radiations, and in the absence of static dipole moment:

$$P_e = \alpha_1 E + \alpha_2 E^2 + \alpha_3 E^3$$
(13)

The second term in the above expression is zero in glass as a centrosymmetric medium, when the incident light has opposite direction electric vectors. This is generally referred to the third order nonlinear optic or Kerr Effect. The observed phenomenon has vast applications in the all-optical telecommunication industry [9].

Therefore, the intensity dependent nonlinear refractive index coefficient,  $\gamma$  may be simply expressed as:

$$n = n_0 + \gamma < I > \text{ or } n = n_0 + n_2 < E^2 >$$
 (14)

<I> and <E $^{2}>$  are the average intensity and mean square field amplitude respectively, and are related:

 $\gamma$  (m<sup>2</sup>/w) = (40 $\pi$ /cn) n<sub>2</sub> (esu-electrostatic unit) (15)

 $n_2$  is known as the nonlinear refractive index and c is the speed of light.

With the aim of investigating ultra-optical property glasses leading to considerable optical nonlinearity, the most stable glasses in the two systems; i.e.,: TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub>-PbO (TBP) and Ga<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>O<sub>3</sub>-PbO (GBP), have been selected. These systems are believed to constitute the most polarisable glass modifying oxides, such as; Bi<sub>2</sub>O<sub>3</sub> and PbO. Besides, Ga<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are relatively polarising conditional glass formers in relation to other glass formers. In order to study ultra-optical properties; refractive index and dispersion have been measured accurately by Minimum angle of deviation in a prism

method. A spectrometer equipped with white light Cd/Hg cord lamp transmitting discrete spectra, from red to violet. The corresponding nonlinear refractive indices have been estimated by the Weber and Boling formulae and are discussed. The minimum refractive index in very long waves (infra-red),  $n_{\infty}$  and  $\lambda_s$  are predicted by Kordes semi-empirical formula and the dispersion curve fit method. These glasses can be good candidates for use in nonlinear optical applications, e.g.: switches, filtering, and etc. in all-optical telecommunications.

## 2. Experiments

Homogeneous glass samples, free from any cracks, inclusions or any defects, were provided from the preceding studies [2]. Parallel-sided slabs of about  $1\pm0.05$  mm thickness were cut, ground with SiC powders starting from 200, 450 to 600 meshes consecutively, and then were polished with cerium oxide power (0.35 µm size) in liquid paraffin. Finally, appropriate specimens; with uniform, smooth and cleaned surfaces, were prepared. For refractive index and dispersion measurements, the "Minimum Angle of Deviation in a Prism" method was executed, [2, 14-16]. A spectrometer (goniometer, "Spectra-Master Vis") equipped with Cd/Hg white light source (cord) lamp, transmitting discrete light spectra from the red to violet, (7 colours), was employed (Table 1) [17, 18].

Spectrum Colour	Wavelength, $\lambda$ (nm)	Exited atom	Symbol	Intensity (relative scale)
Red	656.3	H <sub>2</sub>	**C	
Red	643.8	Cd	C	2000
Yellow	589.3	Na	*D	
Yellow	579.1	Hg		280
Green I	546.1	Hg	e	1100
Green II	508.5	Cd		1000
Blue	486.1	H <sub>2</sub>	**F	
Blue I	480.0	Cd	F	300
Blue II	467.8	Cd		200
Blue III	435.8	Hg	g	4000
Violet	404.7	Hg	h	1800

Table 1: Range of discrete colour bands in the Cd/Hg lamp used in Dmin measurements [17].

\*- D corresponds to a separate Sodium Na cord lamp with single spectrum.

\*\*- F and C were not transmitted from the Cd/Hg lamp.

In addition, separate sodium Na lamp with single spectrum D (589.3 nm) was also used. From each sample, thin accurate prisms were constructed employing large guiding reference prisms to ensure accurate flat side faces, [2]. The minimum angle of deviation Dmin was measured for every spectrum (colour) separately [19]. Figure 1 demonstrates constructed prisms and the deviations of colours in the prism [20].

## 3. Results and Discussions

The measured refractive indices of these fabricated glasses and their wavelength dependence are given in

Figure 2 and 3. The stability of TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub>-PbO (TBP) glass system, as reported by [21], is relatively similar to the Ga<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>O<sub>3</sub>-PbO (GBP) glass system [22-24], therefore, fast melt quenching operations is required to attain glass. Correspondingly, lower density or higher molar volume is demanded for the devitrified glass samples, which are in metastable state. Thus, the related measured refractive indices are slightly lower than expected, [2].

The refractive index measurements were not accurate beyond 3 digits, because of observing more absorption of light as tending to higher frequencies. In fact, blue and violet spectra (<500 nm) were hardly transmitted.



Figure 1: Dispersion of white light in a prism [20].



Figure 2: Variation and comparison of measured refractive index with wavelength for TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub>-PbO (TBP) system glasses.



Figure 3: Variation and comparison of measured refractive index with wavelength for TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub>-PbO (TBP) system glasses.

For ultra-refractive index samples, which have refractive index greater than 2, low angle prisms  $(A < 40^{\circ})$  ought to be designed and constructed, in order to prevent prism internal reflection and to obtain high range of measurements relating to high spectra rays (Figure 1). Consequently, the incident light rays travel less and exit from the opposite side of the prisms. However, for those samples, which cannot transmit high frequency spectra, e.g. F=480 nm, due to the high internal reflection, absorption or glass inhomogeneity, the principal dispersion  $n_F-n_C$  and the Abbe Numbers,  $v_D$ , were estimated from the above resultant curves fit (Figures 2, 3 and Table 2).

The non-linear refractive index,  $n_2$ , were calculated by Weber et al. and Boling et al. Semi-empirical Formulae, equations: (16) and (17), respectively, as following [25-28]:

$$n_2 = \frac{68(n_D - 1)(n_D^2 + 2)^2}{\nu_D [1.517 + \frac{(n_D + 1)(n_D^2 + 2)\nu_D}{6n_D}]^{\frac{1}{2}}}$$
(16)

$$n_2 = 391 \, \frac{(n_D - 1)}{v_D^{5/4}} \tag{17}$$

Referring to [29]  $n_2s$ , calculated from the Boling et al. formula equation (17) in comparison with the Weber et al. formula equation (16), they correlated better with the measured  $n_2s$  for glasses having  $n_D$ below 1.9. However, in this research, calculated  $n_2s$ from the equation (16) correlated well with the measured n<sub>2</sub>s for glasses with n<sub>D</sub>>2, i.e., n<sub>2</sub>=120-140 x10<sup>-13</sup> esu, and for the high refractive index crystals, such as; TiO<sub>2</sub>, which claim n<sub>D</sub>s greater than 1.9-2.5, i.e., n<sub>2</sub>=286x10<sup>-13</sup> esu. In fact, there were relatively large differences between results computed from the two above formulae, which could be resolved by a coefficient as it has been reported [29] (Table 2).

In attempts of achieving ultra-optical property glasses, the TBP samples possess refractive index and dispersion properties similar or, in some cases, slightly higher than those measured for the equivalent  $Ga_2O_3$ -Bi<sub>2</sub>O<sub>3</sub>-PbO (GBP) glass system [22]. It should bear in mind that from the computations (Table 2), TBP glasses comparatively constitute more number of heavy cations than GBP glasses. In addition, the concentrations of oxygen, as a strong polarisable anion in TBP, are higher than in comparable GBP glasses. This is also observed with other glass systems, for example;  $B_2O_3$ -Bi<sub>2</sub>O<sub>3</sub>-PbO (BBP) reported previously [2, 14], where the heavy cations are at their most concentration. These glasses are light absorptive, and appear brownish, particularly, when content high Bi<sub>2</sub>O<sub>3</sub>.

However, it can be seen that the characteristic of the curves, corresponding TBP and GBP glasses, obtained from the measured refractive indices against wavelength are almost similar for the both glass systems. The results suggest that generally, ultraoptical properties of the glass systems decrease with relative high contents  $Ga_2O_3$  in the glass. There is a discrepancy with 12.5  $Ga_2O_3$  mole% (12.5GBP50) sample, which might be genuine, and be ascribed to the glass structural stability and lower molar volume effects on the refractive index, for more details, refer to [22]. Similar analogy could imply to TBP glasses, where, addition of TiO<sub>2</sub> from 5 to 10 mole% improves ultra-optical properties.

From the previous works on the  $Ga_2O_3$ -Bi<sub>2</sub>O<sub>3</sub>-PbO (GBP) system, it is clear that while  $Ga_2O_3$  acts as an effective conditional glass former [14, 22-24], it reduces the refractive index and dispersion and consequently, the optical nonlinearity,  $n_2$ , decreases, particularly at  $Ga_2O_3$  high contents, [30-32]. See Figure 4 for the dependent of  $n_2$  on  $Ga_2O_3$ .

 Table 2: Comparing the ultra-optical properties measurements of the stable TBP and GBP glass systems and calculated nonlinear refractive index, n<sub>2</sub>, from Weber et al. Formulae.

Sample	Composition (mole %)				<b>n n</b>	11	Cal <sup>ed</sup> ., n <sub>2</sub> (x10 <sup>-13</sup> esu)	
	TiO <sub>2</sub>	Ga <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>	PbO	n <sub>D</sub>	n <sub>F</sub> -n <sub>C</sub>	υ <sub>D</sub>	
5TBP70	5	-	25	70	2.395	0.135	10.3	120
10TBP60	10	-	30	60	2.435	0.141	10.2	134
10TBP70	10	-	20	70	2.400			
10GBP50	-	10	40	50	2.427	0.143	9.99	135
12.5GBP50	-	12.5	37.5	50	2.447	0.141	10.26	135
15GBP50	-	15	35	50	2.401	0.148	9.57	140
17.5GBP50	-	17.5	32.5	50	2.376	0.137	10.05	123
20GBP50	-	20	30	50	2.355	0.136	10.00	119
22.5GBP50	-	22.5	27.5	50	2.335	0.129	10.38	109
25GBP50	_	25	25	50	2.296	0.106	12.19	80



Figure 4: Exhibits dependence of nonlinear refractive index, n<sub>2</sub> on conditional glasses formers; TiO<sub>2</sub> and Ga<sub>2</sub>O<sub>3</sub> content.

The observed maximum region in the nonlinearity curve may be attributed to the increase of oxygen concentration in the glass network by the addition of TiO<sub>2</sub>, though, heavy cation population decreases. Whereas, in the replacement of  $Ga_2O_3$  with  $Bi_2O_3$  in xGBP50 series glasses, heavy cation amount is reduced and oxygen anion concentration remains unchanged, so optical property declines.

TiO<sub>2</sub> is also a potential conditional glass former, due to its relatively high field strength (1.20), [31, 32], where it can participate in glass formation in its low concentrations. From the datas, concerning dependence of field strength of some cations upon the ionic radius [3, 30-32], both  $Ga^{3+}$  and  $Ti^{4+}$  cations claim relatively highest field strength and lowest ion radius in comparison with other intermediate glass former and so they can participate in glass formation in their low amounts [21]. Besides, Ti<sup>4+</sup> cation with respect to its atomic configuration, which possesses 2 electrons in the unsaturated d shell, is polarised under uv/visible electromagnetic spectra [21, 31-35]. However, while Ti increases in the glass composition and substitutes heavy atoms, such as; Pb or Bi, it is expected to reduce optical properties of TBP glasses. TiO<sub>2</sub>, in crystalline form, in comparison with Ga<sub>2</sub>O<sub>3</sub>, acquires considerably higher refractive index than  $Ga_2O_3$  (2.5 cf 1.91) [22-24], thus its addition to Bi2O3-PbO crystalline system will have less effect on reducing the molar refractivity in relation to G<sub>2</sub>O<sub>3</sub>. On the other hand, since TiO<sub>2</sub> introduces greater ratio of anion/cation or say higher proportion of oxygen into the system, it may raise the probability of nonbridging oxygen in the glass structure as an optical promoter. Therefore, in all, constituting small amount of TiO<sub>2</sub> favours glass formation and promotes ultra-optical properties [29]. In addition, likewise Ga<sup>3+</sup>, which facilitates vitrification process, Ti<sup>4+</sup>, in a vitrified state as a relatively high valence cation, can claim 4 to 6 coordination numbers. Thus, addition of the both above cations in the glass structure, pending upon their low amounts, is expected not to suppress the ultra-optical property of the glass system considerably. Observations in Figure 4 may endorse the above conclusion, [32, 36].

In the generalized refractive index versus dispersion increasing trend for commercial glasses presented by the Schott Company [12, 13], the corresponding ascending curve towards the absorption edge tends to perform nearly exponentially in the regions of ultraoptical property glasses. It indicates that dispersion and refractive index are less dependent in ultra-optical glasses and could behave conversely. This may refer to the PbO relative effect on reducing dispersion in comparison with  $Bi_2O_3$ , [23, 34]. In addition to the above phenomena concerning polarisability increase, the asymmetric situation of  $Pb^{2+}$  in the structure and its phonon vibration in the lattice would enhance ultraoptical properties [14, 24].

Generally, in the plot of mean or principal dispersion  $n_F-n_C$  versus refractive index  $n_D$ , referring [4], an almost linear curves are observed for different groups of glasses including commercial glasses, with exception to rare earth glasses [12, 13]. Whereas, results in this research suggest the reduction of mean dispersion as  $n_D$  approaches to high values, in particular in TBP glasses. Consequently, lower nonlinearity,  $n_2s$  are expected (Figure 5).



Figure 5: Depicts irregularity and deviation of dispersion from the linear relationship in ultra-refractive index glasses.

According to Morey's semi-empirical formulae for predicting glass optical properties, similar to the standard Schott and other companies curve trend for commercial glasses [12, 13], a non-linear curve is expected in the plot of refractive index,  $n_D$  against characteristic dispersion,  $v_D$ , in which for high refractive index property glasses, dispersion as Abbe Number  $v_D$  varies less, i.e., almost unaffected by refractive index. Results, in Figure 6, suggest that TBP and GBP glasses, in comparison with the Morey equation and above commercial curve trend, do not conform, and even tend towards lower dispersion properties. Figure 6 displays the irregularity in the generalised curve trend relating to TBP and GBP glass systems.

Results implies that in ultra-optical glasses, dispersion is less dependent on refractive index. Thus, beyond ultra-refractive indices of  $n_D=2$ , dispersion does not change appreciably. Therefore, according to the equations 16 and 17, it may be concluded that optical nonlinearity can be independent of dispersion. On the other hand, referring to [25, 29], the lowest B<sub>2</sub>O<sub>3</sub> content glasses in B<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>O<sub>3</sub>-PbO (BBP) system, i.e., <24 mole%, exhibit relatively higher dispersion with lower refractive index in comparison with TBP and GBP glasses. These glasses could deviate from the commercial glasses curve trend towards lower dispersions, [14], i.e.,  $v_D < 9$  and  $n_D > 2.2$ , and consequently, result high nonlinearity, i.e.,  $n_2 > 200 \times 10^{-13}$  esu. However, the low content  $B_2O_3$  are dark brown and highly absorptive as well as hygroscopic.

Moreover, from manipulating Morey equation (11), an equation can be derived, i.e.:

$$n_{\rm D} = \frac{0.496}{\upsilon_{\rm D} - 12.658} + 1.392 \tag{19}$$

It can be observed from data's in [4, 12, 13] that a smooth linear curve is expected, when n<sub>D</sub> is plotted against  $1/(v_d - 12.658)$ . It may be concluded that, Morey formula can be a good fit for glasses with refractive index below 1.9. Similar operation has been done for the sample glasses with refractive indices above 1.9 in which scattered results is observed (Figure 7). Thus, in the ultra-high refractive glasses concerning this research, the further increase of the both heavy oxide modifiers, PbO and Bi<sub>2</sub>O<sub>3</sub>, could increase refractive index, n<sub>D</sub> and suppress mean principal dispersion ( $n_F-n_C$ ), hence, the Abbe Number ( $v_D$ ) increases, i.e., dispersion property of glass lowers. Ultimately, it can be concluded that optical nonlinearity does not necessarily increase with ultraoptical properties in heavy oxide glasses.



Figure 6: Displaying scattering results for TBP and GBP glasses, which do not obey with the generalised curve trend.



Figure 7: Exhibits scattered results for TBP and GBP ultra-optical glasses, which do not comply with the suggested Morey equation for predicting optical properties.

In order to estimate the minimum or effective refractive index,  $n_{\infty}$  for very long wavelength, and effective absorption,  $\lambda_s$ , concerning to the above ultraoptical glasses in relation to refractive index dependent on wavelength, the semi-empirical Kordes formula, equation 9, has been employed and manipulated, equation 18 [10, 11].

$$\frac{1}{(n^2-1)^2} = -\frac{\lambda_s^2}{(n_{\infty}^2-1)^2} \frac{1}{\lambda^2} + \frac{1}{(n_{\infty}^2-1)^2}$$
(18)

The resultant linear dispersion curves, from plotting  $\frac{1}{(n^2-1)^2}$  versus  $\frac{1}{\lambda^2}$ , have been extrapolated and curve fitted (Figure 8 and 9).

The resultant linear curves with relatively root mean square R<sup>2</sup> near to 1 (Table 3), can quote good estimations for the minimum refractive index,  $n_{\infty}$  resulted from the extended curve tails to infra-red regions (i.e., >1µm).  $n_{\infty}$  is considered in all-optical telecommunication devices, such as switches, [36] where the pulses absorption and speed are important.

Sample	$\mathbf{R}^2$	$\frac{1}{(n_\infty^2-1)^2}$	$\frac{\lambda_s^2}{(n_\infty^2-1)^2}$	$\mathbf{n}_{\infty}$	λ <sub>s</sub> (nm)
5TBP70	0.9998	613.91	58.235	2.241	310
10TBP60	0.9974	568.65	53.881	2.275	312
10GBP50	0.9999	584.28	57.602	2.267	313
12.5GBP50	0.9949	553.54	53.024	2.289	311
15GBP50	0.9864	626.74	67.911	2.245	318
17.5GBP50	0.9982	644.75	62.857	2.221	312
20GBP50	0.9984	672.94	65.647	2.203	312
22.5GBP50	0.9989	694.58	66.2	2.190	308
25GBP50	0.9634	694.15	50.583	2.171	291.2

**Table 3:** Estimating corresponding values for minimum refractive index,  $n_{\infty}$  and effective absorption wavelength,  $\lambda_s$ .



Figure 8: Depicts the reliability of Morey semi empirical formulae for TBP glasses to estimate the absorption in very long wavelengths.



Figure 9: Depicts the reliability of Morey semi empirical formulae for TBP glasses to estimate the absorption, in very long wavelengths.

Figure 10 displays maximum values of  $n_{\infty}$  for lower  $Ga_2O_3$  contents, or say higher heavy cations population, in the glass structure. In the limited obtained results concerning TBP glasses, higher values of  $n_{\infty}$  with the addition of TiO<sub>2</sub> is believed to be due to the increase of  $O^{2+}$  population in the glass network. Generally, correlations are observed for TBP and GBP results. The increase of effective absorption,  $\lambda_s$  by addition of heavy cations to higher wavelength is normally expected [2] (Figure 11).

The unexpected maximum in the region  $10-15 \text{ TiO}_2$ 

and Ga<sub>2</sub>O<sub>3</sub> mole% may be ascribed to lower relaxation of heavy cation constitutes, e.g.,  $Pb^{2+}$  in the structure. Pb can be easily deformed and polarized by neighboring ions, such as, Ti<sup>4+</sup> and Ga<sup>3+</sup>. In this respect, oxygen anion, particularly non-bridging, can have great effects on Pb ion deformation, [4]. Later in the proceeding papers, analogies concerning results for absorption peaks predicted by variation of refractive index with wavelength, and those obtained by spectrophotometry; uv/visible and infra-red, are presented and discussed separately.



Figure 10: Displaying reduction of minimum or effective refractive index, n<sub>w</sub> with intermediate glass former content.



**Figure 11:** Representing effective absorption,  $\lambda_s$  dependent on intermediate glass former content.

## 4. Conclusions

Correlative dependence of refractive index on wavelength for both glass systems was observed.  $Ga_2O_3$  and  $TiO_2$  as glass former reduce dispersion in all. Both  $Bi_2O_3$  with PbO increase index of refraction and dispersion properties considerably. However, in their high contents, dispersion lags refractive index, and even tends relatively to lower values. It has been concluded that as a whole, molar substitution of  $Bi_2O_3$  with PbO will have reducing influences on dispersion. Consequently, high optical nonlinearity is expected,

since nonlinear refractive index,  $n_2$ , is inversely related to characteristic dispersion, i.e., Abbe Number. This makes these glasses suitable candidates for nonlinear optical application devices in all-optical telecommunication switches. Effective or minimum refractive  $n_{\infty}$  and effective absorption  $\lambda_s$  could be estimated by employing Kord Formula and the corresponding curve extrapolation. The correlation in the TBP and GBP glasses results, may have governing effects of heavy cations on ultra-optical property, however, oxygen anion in the non-bridging status plays the foremost role.

#### 5. References

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