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Study of Stable Gallium Oxide Heavy Metal (Ga_2O_3-Bi_2O_3-PbO) System Glasses Proposed as a Base for Optically Noble Glazes and Enamels

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ABSTRACT

Ultra optical glasses are proposed for attaining noble glazes of high reflection and shine. In addition, these glasses can be used as semi-mirrors and optical instruments. In this research, attempts were devoted mainly to introduce a glass system with the highest possible refractive index in which the highest reflection is desirable. Thus, different amounts of heavy metal oxides modifiers, such as PbO and Bi_2O_3 were compounded with Ga_2O_3 as a glass former, and were melted to determine the stable glass regions in the corresponding three oxide glass systems. Results suggested that the most stable glasses were located in the eutectic region of the above oxides three phase diagram, where the melting point was as low as $900^{O}C$. DTA measurements presented glass stability values as the differences between the glass crystallinity and transition temperatures, T_c-T_g. The "Minimum angle of deviation of light in a prism" was employed to measure refractive indices greater than 1.8, in which the highest results were above the diamond refractive index, i.e. 2.417. Dispersion property, as Abbe Number, was as low as 10 for the lowest content Ga_2O_3. Noble glazes or coats can be tailored and fabricated based on these ultra optical glass systems, which possess high reflection and optical non-linearity. Prog. Color Colorants Coat. 7(2014), 201-212. © Institute for Color Science and Technology.

1. Introduction

Light refraction occurs at the interface of air/glass due to its relatively lower travelling speed in a condenser medium. Glass, as an isotropic medium, may reflect, transmit and absorb incident electromagnetic waves or here say light. The responses of glass as a transparent material to light, namely optical properties, are characterised by the structural compaction or molar volume, V_m, and polarisation of the glass, P, which is proportional to the induced field intensity, E of the light as:

$$P=\alpha E \qquad (1)$$

α is known as polarisability and is related to the refractive index (n) at a particular frequency [1-4]:

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$$n^2=1 + 4\pi\alpha \quad (2)$$

Where, n= (speed of light in vacuum)/(speed of light in a medium) for a particular spectrum.

Polarisability is generally the property of a medium, e.g. glass, and is dependent on the nature of the constituted atoms. Heavy and large atoms, which does not possess noble gases structures and have unsaturated d shell are polarized easily. Thus, glasses containing (Tl^{18+1}), (Pb^{18+2}) and (Bi^{18+3}) cations would claim high refractive indices. These atoms in comparison with other large atoms, such as (K^{8+1}), (Ba^{8+2}), (Sr^{8+2}) and (La^{8+3}) have more effects on the refractive index with respect to their higher ionic deformation under applying electromagnetic rays. In addition, the presence of high number of structural anions, e.g. oxygen ions (O^{2-}), especially in their non-bridging state, will increase refractive index greatly.

Other factors, which may enhance the refractive index of glasses, are the ionic coordination numbers and structural molar volume. The former virtually raises the polarisability, and it can be related to refractive index by Lorentz- Lorenz equation [2, 5, 6]:

$$V_m= R_m (n^2+2)/(n^2-1) \quad (3)$$

R_m is referred to as refractivity of the glass (medium) and is dependent on the nature of the constituting atoms and their network structure.

In highly polarisable glass structures or/and under ultra-high intensity electromagnetic radiations, such as laser, the linearity of equation (1) will differ and become a time dependent non-linear equation as below [7, 8]:

$$P(t) = P(0) + \alpha_1 E(t) + \alpha_2 E^2(t) + \alpha_3 E^3(t) + ... \quad (4)$$

P(t) and E(t) are time dependent structural polarisation and field intensity respectively, P(0) is static polarisation and α_1, α_2, α_3, are coherent polarisabilities.

Assuming that $\alpha_3 E^3(t)$ is negligible, a non-linear or intensity dependent equation of refractive index is deduced from equation (2), i.e.:

$$n = n_0 + n_2 I \quad (5)$$

where n_0 and n_2 are the linear and non-linear refractive indices respectively, I is the light with ultra-high intensity, e.g. laser. Hence, in the ultra-high optical glasses, refractive index varies with the intensity of laser beams, and the glass as a light guide may performs as an all-optical switch [9-13].

Inorganic glazes are generally based on glasses of different compositions tailored for desired optical properties, namely for attaining aesthetic appearances views. Correspondingly, the lustrous view or sheen property of a glass relates to its reflection properties, R that is dependent on the refractive index, n, as follows [2, 5]:

$$R = (n-1)^2/(n+1)^2 = [1-2/(n+1)]^2 \quad (6)$$

Other optical properties, which are considered in designing of glazes, are transparency, dispersion, absorption, scattering, luminosity, etc. These properties are in correspondence with the base glass tailoring in which the composition and relevant atomic structure are of the prime consideration.

Dispersion of integrated rays of lights occurs upon the phenomenon of the light speed change or in other words changes of refractive index with wavelength when passing from one medium to another [4-8]:

$$n = K+B/\lambda^2 +C/\lambda^4 + \ldots\ldots \text{(Cauchy Equation)} \quad (7).$$

Where, K is the refractive index for wavelength, $\lambda \rightarrow \infty$. B, C and … are attributed to the relative media characteristics and are considered constants. For relatively long wavelengths, $1/\lambda^4$ and proceeding terms are negligible. Later, Vogel [9, 10] theoretically proposed that K could be influenced by the infrared region absorption, i.e.:

$$K = A_0 + A_1 \lambda^2+\ldots\ldots \quad (8)$$

A_0 and A_1 are constant.

Dispersion in a transparent material, e.g. glass, is introduced by the partial dispersion [2, 11], i.e.:

$$\Delta n_{F\text{-}C} = n_F - n_C \qquad (9)$$

Where, F and C subscripts designate blue with spectrum of 486.13nm and red spectrum of 656.27nm, respectively.

Dispersive index or Abbe Number, υ_D characterizes dispersion in relation to refractive index at a particular wavelength normally; Yellow $_{(D= 589.3nm)}$:

$$\upsilon_D = (n_D-1)/(n_F - n_C) \qquad \text{Abbe No. or dispersive index (10)}$$

Figure 1 displays different characteristic modes of the refractive index in relation to the dispersion. In fact, υ_D states the dispersive power (dispersivity) of a medium, (say glass), at a particular n_D. Figure 1 (b) indicates the most dispersive glasses, when n_F-n_C is the highest and n_D is the lowest possible. Hence, the most reflective glazes according to equation (6) are those based on glasses depicted in Figure 1 c and d. In Figure 1d, light reflects with most differentiation, i.e. colours of a reflected white light are most distinguishable [10, 14].

In this research, the goal is to design and fabricate ultra-high optical glasses employed for the bases of special glazes, which could facilitate aesthetic look with high reflection or shine. In addition, these glasses could be utilized as transparent pigments embedded in low absorptive transparent glazes, in order to provide sparkling particles. Thus, gallium oxide, Ga_2O_3, with relatively large cation of high refractivity (0.6) was chosen [2]. It can behave as a semi-glass former and a host for large amounts of heavy metal cations [15-19]. Therefore, the glass-forming region in 3D glass diagram was firstly determined by melting and fabricating more than 20 glass samples of different compositions, some of which were fully and some partly devitrified, see Figure 2 and Table 1. Stable glasses were identified by the differential thermal analysis (DTA) experiments. Optical properties were characterised by the accurate measurements of high refractive index materials. The minimum angle of deviation of light passing through a prism experiment was performed by a spectrometer [20]. The test was able to measure high refractive indices (>1.8) and dispersion, and to some extent, the inhomogeneity in the samples.

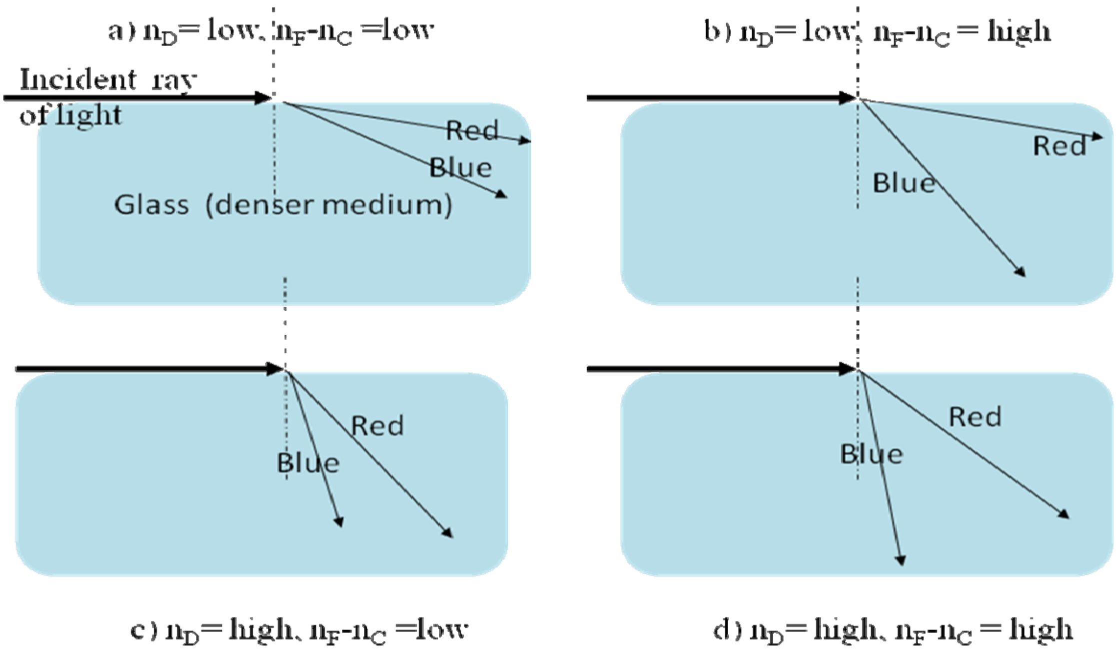

Figure 1: Different modes of refraction in a denser or polarisable medium, yellow $_{(D= 589.3nm)}$, blue $_{(F=486.13nm)}$, red $_{(C=656.27nm)}$.

Table 1: The samples prepared for optical tests.

No.	Compositions:[xGa_2O_3-(50-x)Bi_2O_3-50PbO] (mol%)			Codes (xGBP50)	Appearances
	Ga_2O_3	Bi_2O_3	PbO		
1	10	40	50	10GBP50	yellow
2	12.5	37.5	50	12.5GBP50	yellow
3	15	35	50	15GBP50	pale yellow
4	17.5	32.5	50	17.5GBP50	yellowish pale green
5	20	30	50	20GBP50	pale green
6	22.5	27.5	50	22.5GBP50	pale green
7	25	25	50	25GBP50	pale green
8	30	20	50	30GBP50	devitrified
9	40	10	50	40GBP50	devitrified
10	30	10	60	30GBP60	green
11	15	35	50(+5K)	20GBP50+5K*1	pale green
12	20	30	50	20GBP(1100^{o}C)*2	green
13	20	30	50	20GBP50(1.5)*3	green

*1- **5** K_2O moles were added to the composition, *2- the melt was heated at 1100^{o}C for 10 minutes and *3- the melt was stirred for 1.5 hours.

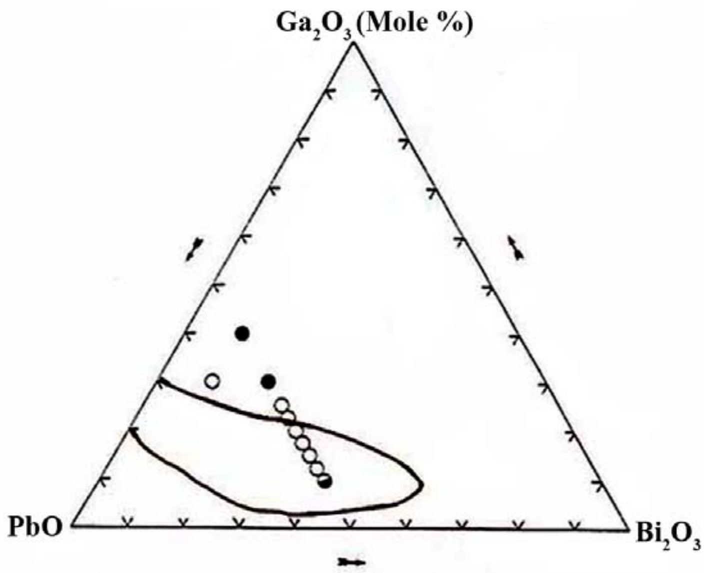

Figure 2: Depicts melted compositions in circles. ○ -white circles indicate stable glasses, ●- black circles indicate unstable or fully devitrified glasses and ⬬-half black circles indicate partly crystallized glasses.

2. Experimental

Attempts were to choose raw materials, which provided oxidative conditions in the melts. The major raw materials employed in the research were Ga_2O_3, Bi_2O_3, Pb_3O_4 and KNO_3 from Aldrich with 99.99% purity. Powders before mixing were ground and sieved to 150-mesh size.

They were dried in an oven at 120°C for 24 hours. Compounding was done by tumble mixing in a cylindrical jar filled with less than 50% of its volume for about 5 minutes. To prevent powder segregation, prolong mixing was avoided. More than 20 different formulated batches of 50-gram weights were prepared (see Table 1).

Batches were fed into hot crucibles at 800°C in three portions successively, in order to prevent overflowing of melting materials. Meltings were performed consistently in 90cc alumina crucibles at 800 to 1000°C for one hour under local ventilation. Due to the presence of health hazard raw materials in the batch formulas, (such as red lead, Pb_3O_4) in all sample preparation stages, mask, safety glasses and gloves were worn. Ultimately, all equipment's and experimental facilities were washed and cleaned thoroughly. The necessary precautions were practiced to observe the health and safety regulations, and environmental friendly cares too.

The crucible corrosion by heavy metal oxides was examined especially at the melt surface boundary regions, which were not appreciable. The volatilization of PbO at temperatures below 1000°C was minor [11].

The sample moulding was done quickly in a constructed steel mould with dimensions of about 5x20x50 mm^3. The annealing of preforms and prisms were done in a programmable treatment furnace at 450°C for 1 hour. It was preceded by cooling to 50°C at a rate of 30°C per hour. Cutting, shaping, grounding and polishing were executed to make samples into preforms of different shapes, e.g. prisms, rods, slides, etc.

Differential Thermal Analysis, DTA, measurements were carried out to maximum temperature of 800°C with heating rate of 10°C/min using platinum crucibles.

Density measurements were done using a 50cc pycnometer in a large stirred water bath at 25°C [21]. Optical properties such as refractive index and dispersion were measured according to the standard "Minimum Angle of Deviation in a Prism" method [20] using a spectrometer and Cd/Hg lamp which transmitted a range of discrete bands of white light of distinguished spectra [22].

3. Results and discussion

3.1. Melting results and observations

Melts in all Ga_2O_3 base glasses above 800°C were colourless and had water like viscosity ($\eta = 10^3$ Pose). On a controlled solidification, homogeneous and bubbleless large pieces (5mm thick) were moulded. As the heavy metal oxides content raised in the melt formulations, and the melting temperature exceeded 800°C, the volatilization of PbO and Bi_2O_3 increased and dominated B_2O_3 [11]. When samples compositions approached towards the eutectic region in the corresponding phase diagram [23-25], the sample melting temperature decreased and so volatilization reduced. Thus, attempts were made to avoid melting above 800°C, in order to weaken chemical attack to crucibles.

As the Ga_2O_3 in the melt composition decreased, glass colours changed from pale greenish to yellow, see Table 1. Away from the eutectic region, in low content gallium oxide compositions, white cloudy phases were developed as large scattered inclusions. Figure 3 shows different crystalline phases of dendrite and cubic shapes. The latter is believed to be reduced Pb atoms [14].

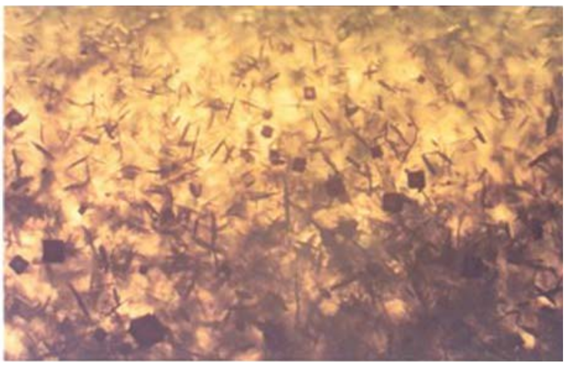

Figure 3: Devitrified crystals of unstable glasses scattered as inclusions.

Traces obtained from the Differential Thermal Analysis, DTA, test suggests the presence of two major crystal phases, see Figure 4, [16]. X-Ray Diffraction, XRD, from stable samples did not exhibit any crystal phases. The polarised optical microscopic views displayed undissolved gallium oxide powder in unsuccessful meltings, suggesting a delay in melting of Ga_2O_3, which is considered as a refractory oxide (melting point, T_m=1900°C), see Figure 5. Due to this and the highly dependent viscosity-temperature properties of the samples, high melt stress inhomogeneities were viewed for uncontrolled glass mouldings by a polarised optical microscope, see Figure 6. The above defects disappeared when the raw materials powders were ground to fine particles (<150 mesh) and the compounding was done thoroughly. In addition, in the sample preparation process, longer mixing and melt stirring were applied. However, volatilization of heavy metal oxides from the melts increased. In practice, the volatilization was reduced when refractory lids covered the crucibles. Lastly, for obtaining confidential results, the glass melting were performed consistently. Besides, annealing was performed carefully according to calculations presented in [2, 11].

3.2. Thermal properties

The traces from DTA experiment for high Ga_2O_3 content samples, i.e. 22.5 and 25 mol%, showed only one peak at about 460°C. As Ga_2O_3 was substituted for Bi_2O_3, the second peak appeared at lower temperatures, i.e. 430°C. With further reduction of Ga_2O_3 in the melt compositions, the second peak tended towards lower temperature regions, where the stability (i.e. T_x-T_g) of the samples below 10 mol% Ga_2O_3 weakened to a critical level. On the other hand, in the higher contents of Ga_2O_3, i.e. 30 and 40 mol%, devitrification almost started in the slow cooled region of the mouldings, i.e. top in the center.

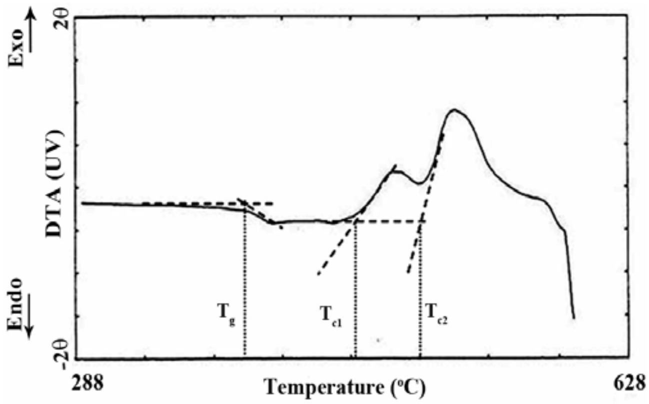

Figure 4: The DTA trace of glass 17.5GBP50 with two crystalline phases.

Figure 5: Undisolved Ga_2O_3 in an uncompleted melting of sample 20GBP50.

However, samples with high Ga_2O_3 content showed full crystallization. This results are in conformation with [26, 27] studies (See Figure 7).

Comparing the semi-stable 30GBP50 with the stable 30GBP60 glass, it can be observed that replacing 10 mol% of Bi_2O_3 by PbO has increased the stability and the sample with 30 mol% Ga_2O_3 can be achievable. Results in Figure 2 suggest that the stable compositions tend towards the eutectic regions in corresponding phase diagrams i.e. Ga_2O_3-PbO [23] which is about 20 mol% Ga_2O_3. Similarly for sample 20GBP50, when melting time was extended from 0.5 to 1.5 hours and stirring was applied for 10 minute, the stability of the sample (20GBP50(1.5)) increased to higher values, see Figure 7. This observation could suggest that prolong melting and stirring causes PbO and Bi_2O_3 in the melt to volatilize. In Bi_2O_3-PbO phase diagram [24] there are three eutectic regions, i.e.; 38, 62 and 75 mol% PbO. It may be concluded that the sample composition approaches to lower concentrations of PbO, because the results show a comparative rise for T_x, but not for T_g. This might support that the volatilization of PbO could dominate Bi_2O_3 [11].

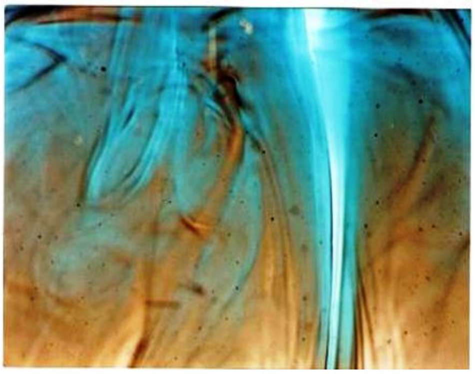

Figure 6: Example of a highly inhomogeneous melt stress of a glass sample (an optical microscope).

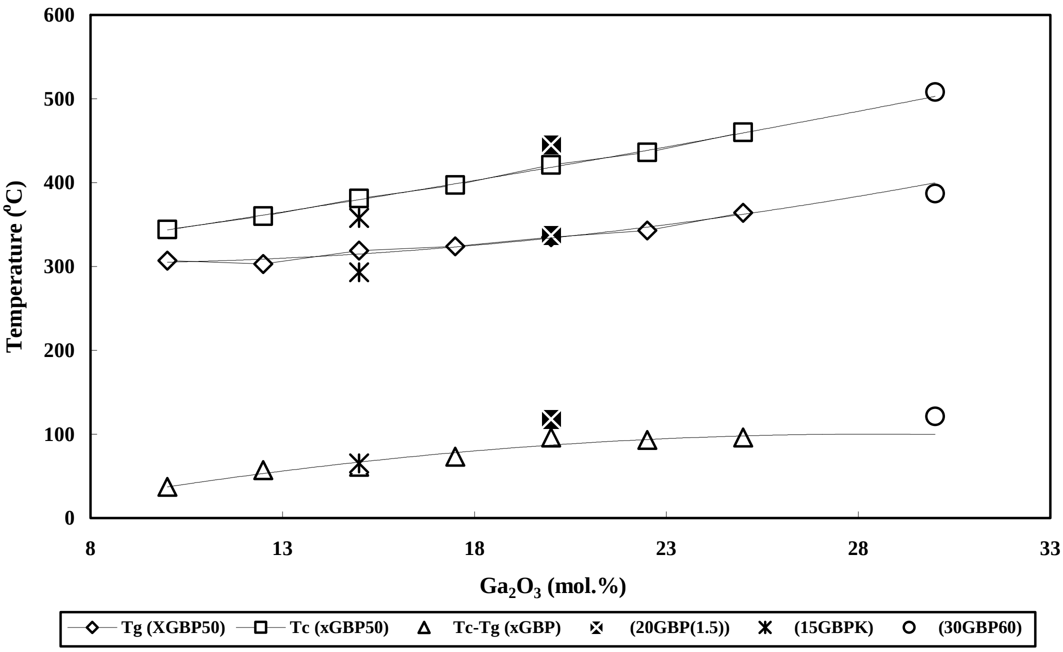

Figure 7: Dependence of thermal properties, T_m and T_g, and glass stability, ΔT_{c-g} =T_c-T_g, on Ga_2O_3 content in Ga_2O_3-Bi_2O_3-PbO glass system.

Addition of a strong alkali oxide, such as K_2O, helped decreasing both T_x and T_g. However, this might not be true for the stability which is expressed as T_x-T_g.

Introduction of the refractory phase, Ga_2O_3, might be expected to increase melting temperature, as a whole. There are evidences that Ga_2O_3 can play the role of a glass network former as well as being a stabilizer [2, 15, 27]. Figure 7 shows that the stability rises sharply as Ga_2O_3 is added to the formula. In fact, the relatively steep increase of T_g with Ga_2O_3 is ascribed to the strength of the Ga-O bond, [28, 29]. Nevertheless, its effects on T_x is greater than T_g, resulting in enhanced stability.

3.3. Density and molar volume

From results of density (d) measurements, molar volumes (V_m) of samples were calculated according to the following relation [11]:

$$V_m = M_w / d \quad (11)$$

In Figure 8, the measured density and calculated molar volume from equation (11) decrease with gallium oxide. The reason for this is believed to be due to the weakness of Ga_2O_3 acting as a partial network former in comparison with common strong network formers, such as B_2O_3, SiO_2, GeO and P_2O_5. In the other words, because of the relative weaker Ga-O bond and its larger distance, Ga_2O_3 network structure can host more heavy atoms up to 90 mol%. Thus, change in the structural compaction is expected to be low and linear, when Ga is replacing Pb and/or Bi. However, Ga can be regarded as a relatively heavy network former with coordination number of 4 to 6. Therefore, it would impart improving the optical properties of a glass system [5, 30, 31].

3.4. Refractive index

This study, in addition to determining the most stable glass regions in Ga_2O_3-Bi_2O_3-PbO (GBP) system, systematically investigates the effects of substituting Bi^{2+} by Ga^{2+} on the refractive index, while Pb^{+} and O^{2-} concentration are kept constant. Therefore, the efficacy of Bi^{3+} in the corresponding glass system is assessable. Correspondingly, the attempt has been devoted to incorporate the maximum possible heavy cation content in the above glass system in order to attain noble stable glazes with ultra-optical properties, where the refraction and reflection properties are of the prime objectives. These properties can be measured and evaluated by equation 5, see Figure 9.

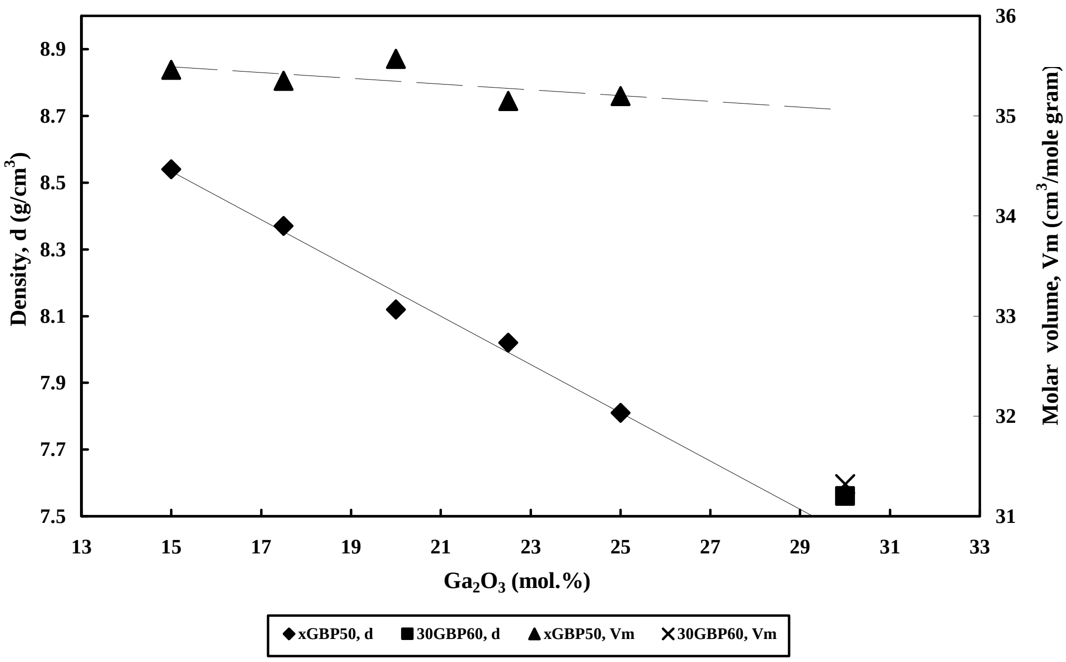

Figure 8: Dependence of density and molar volume on Ga_2O_3 in the GBP glass system.

It can be observed that the addition of PbO from 50 mol% in 30GBP50 sample to 60 mol% in 30GBP60 sample has not affected the trend of the descending refractive index as Ga^{3+} replaces Bi^{3+}. In fact, PbO has given the stability to the unstable or partly devitrified 30GBP50 by replacing 10 mol% of Bi_2O_3, see Table 1.

Subsequently, in the above heavy cation exchange, O^{2-} concentration becomes less in the glass structure and the 30GBP60 refractive index yet follows the trend in Figure 9, it may suggest the efficacy of Pb^{2+} over Bi^{3+}. The other factor that may support the above suggestion could be the higher overall coordination number and ionic refraction of Pb^{2+} than Bi^{3+} which has given considerable structural compaction, i.e. lower V_m of 30GBP60 sample, [30], see Figure 8. In this respect, from the Periodic Table and the atomic electronic structure, it could be concluded that Tl^{+} correspondingly is expected to dominate Pb^{2+}. Other researches [5, 32] has concluded that Thallium cation, Tl^{1+}, in comparison with Pb^{2+} may have more influences on enhancing the refractive index which is not of our concern here.

3.5. Dispersion

The dispersion in the above system is relatively high, see Figure 10. Results exhibit non-coherent differences between refractive index and the partial dispersion, which may suggest that in low Ga^{3+} (or high Bi^{3+}) contents, the dispersion is less dependent on the refractive index in these glasses.

Figure 11 depicts a maximum value for the dispersion property, as Abbe Number, in the region of 20 Ga^{3+} cation %.

In comparison with the trend of industrial glasses [33, 34,35], results from this research support the achievement of glasses with ultra-optical properties, i.e. the refractive index of 2.447 for yellow spectrum of 574 nm which is higher than diamond (n_D=2.417). These glasses have correlated with the trend of industrial glasses in Figure 12. In practice, they extended the tail of the curve in Figure 12 to higher values considerably [34, 35]. Moreover, these glasses in the ultra-high refractive index region claim lower dispersions, which are in the favour of higher reflection, i.e. the higher mirror effects, with lower rainbow view of white light.

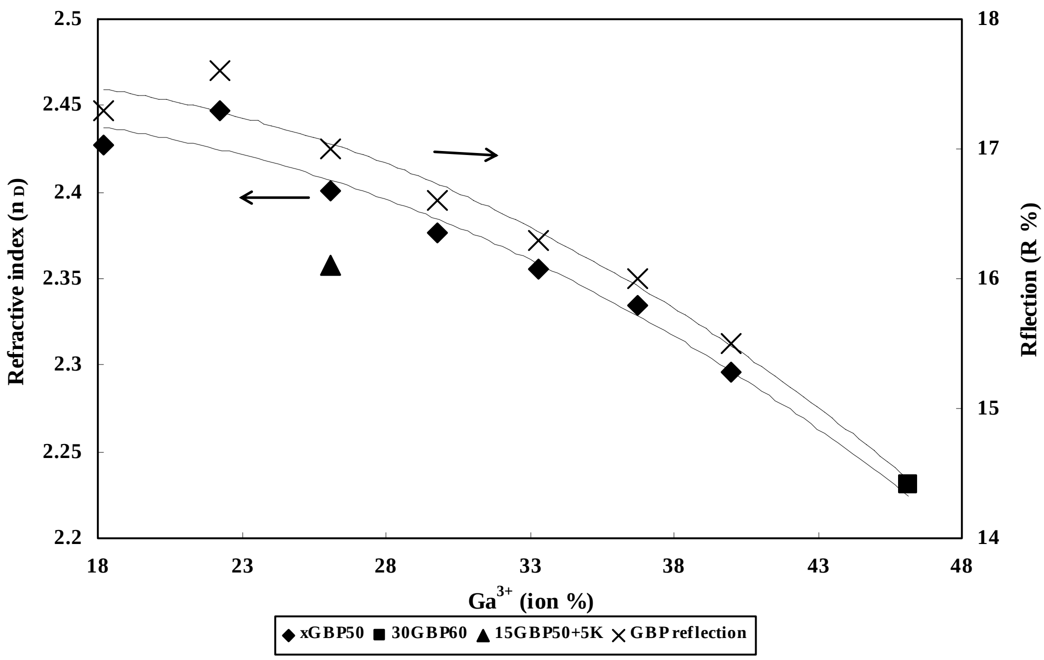

Figure 9: Descending values of refractive index and calculated reflection with gallium ion content in GBP glasses.

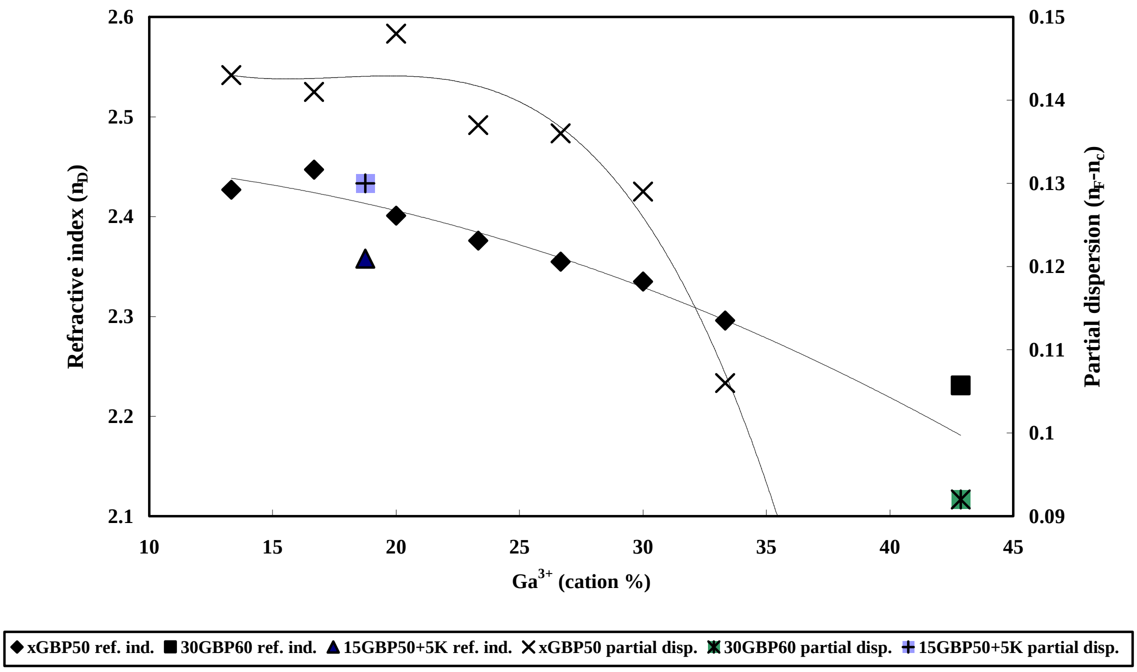

Figure 10: Representing characteristic variation of partial dispersion, $\Delta n_{F-C} = n_F - n_C$, with Ga^{3+} content in relation with refractive index.

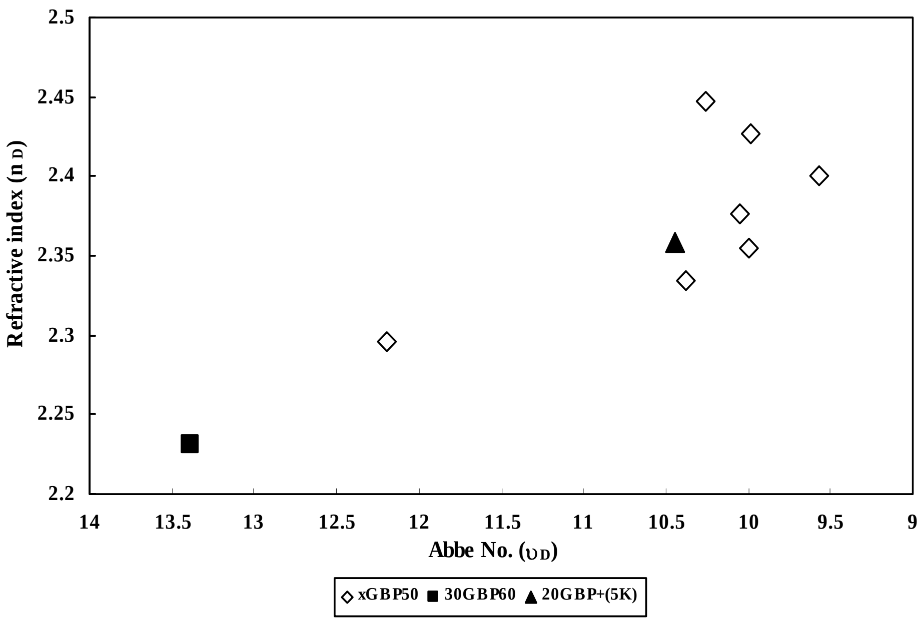

Figure 11: Representing optical properties of GBP glasses which tend to lower dispersions in high refractive indices, where they contain minimum Ga_2O_3.

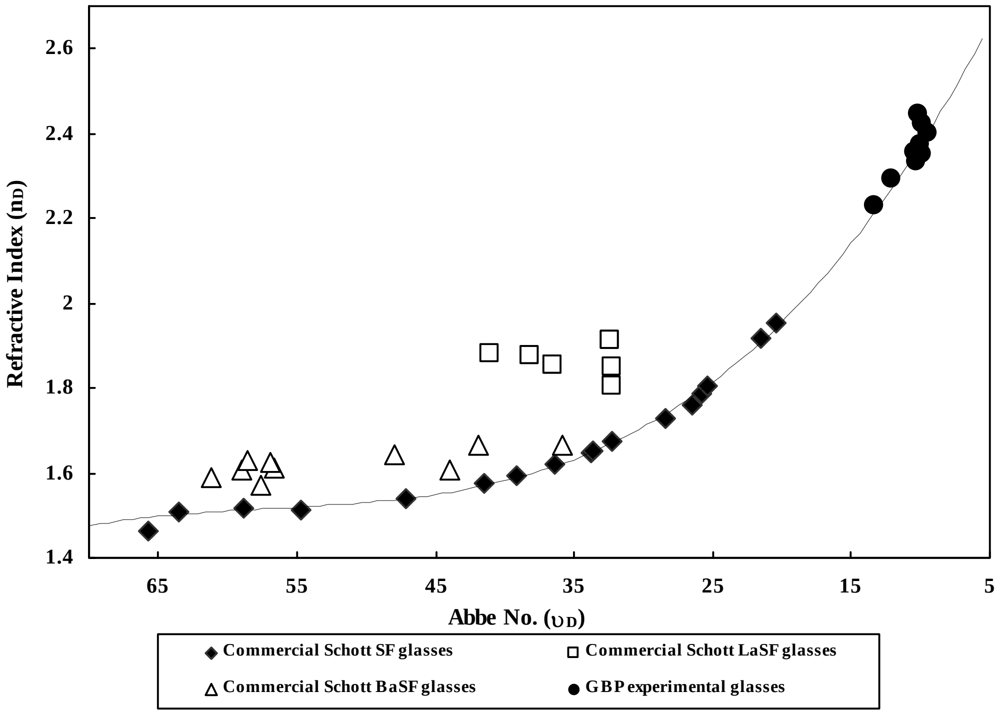

Figure 12: Extension of the trend of refractive index versus dispersion property, Abbe No., of the commercial Schott glasses by the experimental GBP glasses [34, 35].

Lastly, this glass system can be employed as the basis of especial glazes or coatings with relatively high non-linear optical properties, which have wide applications, e.g. laser switches, in electro or all optical fields [11, 31, 36].

4. Conclusions

Gallium oxide can act as a heavy glass former at concentrations as low as 10 mol% in heavy metal oxide containing glasses to maintain transparency and high optics.

In Ga_2O_3-Bi_2O_3-PbO glass base system, glass-forming region was determined and low melting stable glasses were obtained around eutectic and peritectic regions in the relevant phase diagrams.

In Ga_2O_3-Bi_2O_3-PbO glass base system, ultra refractive glasses of 2.447 (higher than diamond) were obtained.

Dispersion power as Abbe Number of 10 was achieved, which make these glasses unique in the optical glasses or their kind.

Pb^{2+} enhances optical properties more than Bi^{3+} due to its higher polarisability.

Although potassium oxide K_2O generally should have positive effects on optical properties, its introduction to the Ga_2O_3-Bi_2O_3-PbO system has impaired the optical properties.

The ultra-high refractive index of gallium and heavy oxide base glasses can be used in producing noble glazes, which claim high reflection in glazes of mirror effects with less rainbow effects.

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