Spectroscopic Analysis of Lead Borate Glass Systems

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Introduction and Motivation

Oxide glass systems are of general interest due to their complex network containing bridging and non-bridging oxygens[1]. Depending on the modifier (ex: PbO), the B_2O_3 glass system, undergoes network modifications by increasing the formations of penta and diborate groups[2]. In this study, we have studied *x* PbO : (1-*x*) B_2O_3 systems using optical studies, such as Ultraviolet(UV)-visible and Refractive Index (RI) measurements. The present experimental results are subjected to re-examine the theoretical models[3–6] proposed for such systems by comparing energy band gap with respect to their refractive indices.

Experimental details

Samples:

Borate glass systems with lead oxide as a moderator

x PbO : (1- x) B_2O_3 with 0.3 < x < 0.85

Energy gap measurements:

UV-Visible spectrometer (*Miostech UV-360S*)
Wavelength range: 190 –1100 nm (*Absorption mode*)

Refractive Index measurements:

Based on Brewster's Principle (Pasco)

$$2d\ sin\theta = n\ \lambda$$

with three Diode lasers: Red (632 nm), Green (530 nm), and Violet (405 nm)

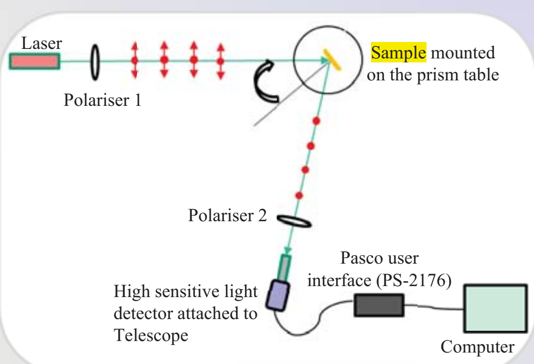

Figure 1. Schematic representation of the experimental set up used for Refractive Index measurements[7]. Here, the position of the high sensitive light detector is varied as a function angle (θ_B) as shown in the figure. The angle for which intensity is minimum, is accounted for RI calculations.

Results

UV vis and RI measurements

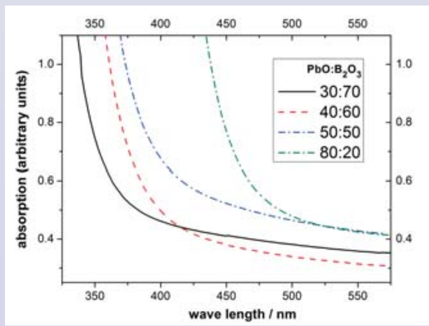

Figure 2. The representative graph of UV-visible data for some of *x* PbO: (1-*x*) B_2O_3 systems. It can be observed that, the absorption edge shifts towards higher wavelength with the increase of lead concentration.

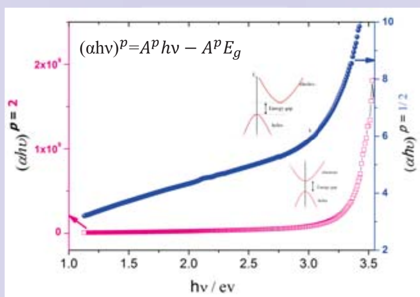

Figure 3. A representative graph is shown for identifying the type of semi conductor behaviour. Here open square (pink) symbols represent p=2 and circle (blue) represent p=1/2 in the general formula proposed by Tauc *et al*[8] $(\alpha h\nu)^p = A^p h\nu - A^p E_g$. This behaviour is observed for all of other compositions of Lead indicating that, Lead Borate systems are direct-band gap materials.

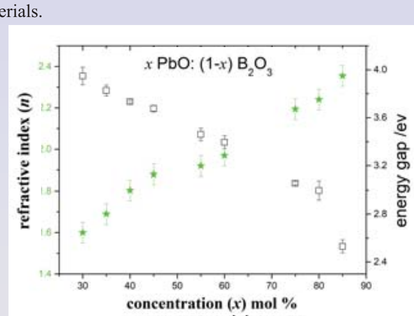

Figure 4. The plot of energy band gap (open square symbol:green) and refractive index (closed star symbol) with increase in lead concentration is presented. It is observed that, $\boldsymbol{E_g}$ decreases and n increases with increase in lead concentration in Borate systems.

Theoretical models proposed to relate refractive index (n) with energy gap (E_g)

$$n^4(E_g - 0.365) = 154 \quad (1)$$

$$E_g n^4 = 95 \quad (2)$$

$$n = KE_g^C \quad (3)$$

$$n^2 = 1 + \left(\frac{A}{E_g + B}\right)^2 \quad (4)$$

$$n = 4.084 - 0.62E_g \quad (5)$$

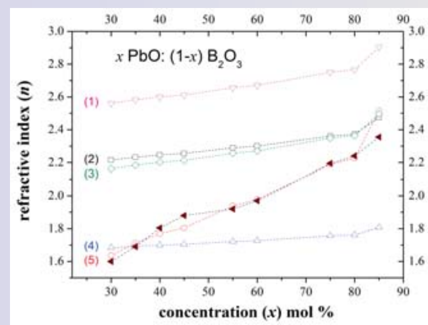

Figure 5. Present experimental data best fits with that of Ravindra relation (red). Hence Ravindra relation could be used to calculate refractive index from band gap for lead borate glass systems.

Conclusions

- Borate glass systems are found to be direct band gap material and addition of lead oxide into the system known to alter molecular structure in the systems which in turn lead to decrease in optical energy gap and increase in refractive index.
- Among the above proposed theories, theory proposed by Ravindra *et al*[3] (**Eq. 4**) is found to be in excellent agreement with our experimental data.

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Abstract. Oxide glass systems are interesting because of their bonding like bridging and non-bridging oxygens. Depending on the modifier, the B_2O_3 glass system can have various Boron-Oxygen network. It is found that, PbO modifies the borate network and increases the formation of penta and diborate groups. In this work, we investigated optical properties of Lead Borate glass systems (x PbO: (1-*x*) B_2O_3) with *x* varying from 30 − 85 mol % using UV-VIS Spectra and the corresponding band gap was estimated using Tauc relation and these systems behave like direct allowed band gap systems. These results show that, $E_g$decreases with the addition of lead content. Further the refractive index measurements also have been carried out at various wavelengths.Many correlation is found between the band gap and refractive index for different compositions. Using different theoretical models a best fit has been tried and Ravindra's relation is found to match with our experimental results.

INTRODUCTION

Generally glass systems are interesting to study for various reasons due to their applications in many fields and also of fundamental research in understanding their behaviour in variety of different environments [1]. In oxide glass systems, bridging and non-bridging mechanism are interesting to study. In Lead Borate glass systems (*x*PbO: (1-*x*) B_2O_3), it is found through Raman and IR studies [2,3] that, at very low PbO content boroxol rings exists in the structure. On increasing concentration of PbO,pentaborate and diborate groups are formed. With further increase of PbO, the presence of penta borate and diborate groups increase. This results in weakening of B-O bonds and helps in opening of ring and chain type meta borate groups. At 65 mol% PbOpyroborate groups begin to form, and about 70 mol % PbO di-borate groups disappear and orthoborate and pyroborate groups comes into existence [2]. Such changes produce variation in the band structure and also band gap of the material. Further, it is interesting to study these systems using other spectroscopic techniques, like correlation between refractive index and energy band gap [4].

UV-VIS spectra is characterised by two major parameters namely wavelength of maximum absorption (λ_{max}) and intensity for each band.Band gaps were found by using the absorption spectra. A correlation between band gap and refractive index is a subject of intensive research in recent times. Refractive index of a material is known to decrease with energy gap. There have been many attempts to find a suitable relationship both empirical and semi empirical between these two physical quantities. Here, we have summarised the results of different theoretical models proposed to explain the correlation.Moss [4] proposed a general relation for the variation of refractive index (*n*) with respect to energy band gap (*Eg*) as

$$E_g n^4 = 95 \quad (1)$$

Where E_g refers to energy gap and *n* stands for refractive index. Further, for the particular case of group IV elements, Moss proposed another relation

$$E_g n^4 = 173. \quad (2)$$

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Main concern with Moss formula is that there is uncertainty in the value of constant and it is based on an atomic model and not a band structure model.Srovastava and Ravindra[5] have shown that modern experimental data fit better if the Moss formula (Eqn 2) is modified to

$$E_g n^4 = 108 \ (3)$$

and have earlier proposed a linear relation governing the variation of refractive index with energy gap in semiconductors. The new relation is proposed by Ravindra and Ganapathy[6]given by

$$n = 4.084 - 0.62E_g \ (4)$$

The above relation is empirical but gives better values than that of Moss relation (Eqn1).The Ravindra relation was conceived to be an approximation of the Penn model[7]. These theoretical models were also revisited by Herve and Vandamme based on oscillation theory and assuming the UV resonance energy has a constant difference with energy gap, proposed a relation for group III-V and I-VII compounds given by[8]

$$n^2 = 1 + (\frac{A}{E_g+B})^2 \ (5)$$

where A is 13.6 and B is 3.47. Further, Reddy and his collaborators[9,10] gave an empirical relation considering band gap and refractive index of semiconductors

$$n^4(E_g - 0.365) = 154(6)$$

Similarly, Kumar and Singh [11]also attempted to give an empirical relation and is applicable to semiconductors, insulators, oxides and halides for entire range of energy gap.

$$n = KE_g^C \ (7)$$

Here we aim to find changes in optical properties such as band gap and refractive index values in the lead borate binary systems and to examine the different theoretical models proposed to establish the relation between refractive index and band gap.

EXPERIMENTAL

The glass systems used in the present study were prepared by Meera et al [2] and the method of the preparation and characterisation is reported elsewhere[2]. In the present work, energy gap measurements were performed on the glass samples using UV VIS spectroscopy. We used MiostechUV-Visible Spectometer (UV-360S), which works in the wavelength range of 190□1100 nm in the transmission mode. Ambient air was used as reference.

The refractive Index (RI) measurements were carried out on polished (using Grade II emery paper and singer oil as lubricant for getting smooth surface) samples usingBrewster's principle. To measure reflected light intensity for different angle of incidence we usedPasport high sensitivity light sensor PS-2176 attached to a telescope of a prism spectrometer [12]. Output of the light intensity was recorded on a computer interfaced to the spectrometer using Pasco Capstone software. Our samples were mounted on a prism table and incident angle was varied by rotating prism table. The data was collected and conducted experiment using red (632 nm), green (530 nm) and violet (405 nm)diode laser sources.The tangent of Brewster angle(angle of incident for which the reflected polarised light intensity is minimum) gives refractive index.

RESULTS AND DISCUSSIONS

The UV-Vis data was analysed using UVVIS analyst software and subsequent data processing was done with Origin 8.0 software, which uses Levenberg-Marquardt algorithm. We used the theory proposed by Tauc [13] to identify the nature of the behaviour and for energy gap measurements using the equation below.

$$\alpha = \frac{A(h\nu - E_g)^p}{h\nu} \quad (8)$$

where, $\alpha = \ln(1/T)/x$is the absorption coefficient, in which,T represents transmittance (10^{-A}),x is the thickness of the sample *and*$A$is the absorption, E_g is the energy band gap of the material(in eV).The Tauc relation (Eqn 8) can be rewritten as

$$(\alpha h\nu)^{1/p} = A^{1/p}\, h\nu - A^{1/p} E_g (9)$$

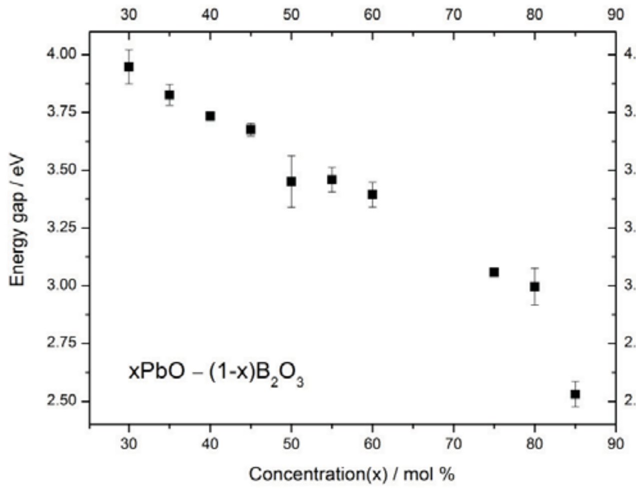
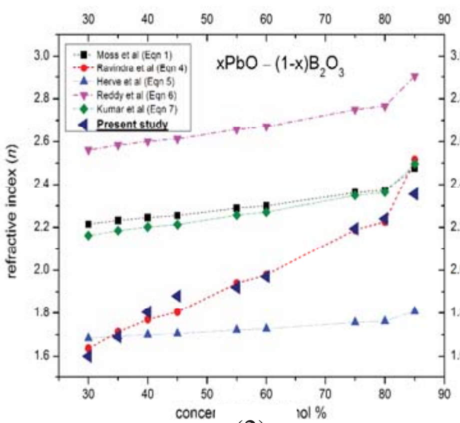


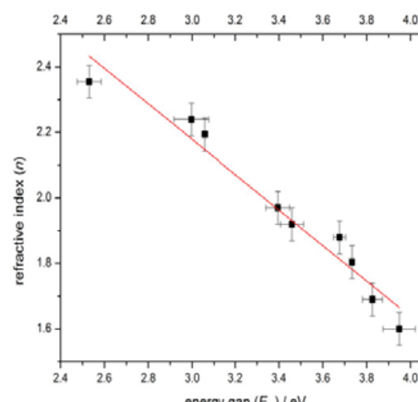
FIGURE 1. Variation of band gap with increasing concentration (x) of lead oxide into the borate system as xPbO- (100-x) B_2O_3. It is found that, as lead borate concentration varies, energy band gap decreases.

As it is evident that lead oxide system being a direct band gap material and hence the above equation can be expressed as a linear equation and estimate the energy gap E_g. The Energy band gap results thus obtained from UV-Visible spectra are presented in Fig 1.The band gap in borate glasses is found to decrease with addition of lead oxide into the glass. Oxygen ions are assumed to act as charge carriers in the case of glass containing lesser amount of PbO and Pb^{2+} ions act as charge carriers in higher lead oxide content system as described by A.Tawansi and his collaborates [14].

The refractive index measured for various samples for three wavelengths scale quite well with the equation proposed by Cauchy[15]. The theoretical values of refractive index for different concentration of lead oxide in borate glass are compared with that of present experimental results are given in figure 2.



(2)



(3)

FIGURE 2. The calculated refractive index values based on the different proposed relations for different concentrations of lead oxide in borate systems are presented along with present experimentally determined values.

FIGURE 3.A representative graph of variation of measured refractive index (n) with energy gap (Eg) values with green laser as a source of refractive index measurements. The theory proposed by Ravindra et al[6] fits well to the experimental results.

A representative graph of band gap(E_g) with refractive index (n), which was discussed earlier for various models has been presented in Fig.3 using n values obtained for green light. Further we found the variation in refractive index with band gap obtained using green laser light (532nm) is found to best fit with Ravindra relation given by (Eqn. 4) and it is supported by the works of S.K Sharma, B. Simos and F. Mammone [16].

CONCLUSIONS

The result obtained from UV-VIS absorption spectrum indicate the lead borate glasses fall under direct allowed band gap systems and we employed Tauc relation for Energy band gap(E_g) calculations. Oxygen ions are assumed to act as charge carriers in the case of glass containing lesser amount of PbO and Pb^{2+} ions act as charge carriers in higher lead oxide content system Further, Refractive index (RI) measurements were performed and these results were used to test the several theoretical models proposed to examine the relation between refractive index with E_g in these lead borate systems.

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