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Optical properties of ZnF_2-PbF_2-Bi_2O_3-B_2O_3-Cr_2O_3 glass system

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ABSTRACT

Glass samples with compositional formula ZPBBCR: $xZnF_2$-(25-x)PbF_2-25Bi_2O_3- 49.8B_2O_3-0.2Cr_2O_3 (where x= 0, 5, 10, 15, 20, 25) have been prepared by adopting melt quenching technique. To study the structural information and optical features of the prepared glass system XRD, UV-visible absorption was performed on the synthesized glass batch. With the help of absorption spectra, optical parameters such as absorption coefficient, transmittance, refractive index, extinction coefficient, skin depth, optical density, optical conductivity and dielectric constants (real and imaginary) were evaluated. By analysing these optical characteristics of the prepared glass system, it is intended to extend their possible applications in the field of optical devices.

Keywords: XRD, absorption coefficient, transmittance, refractive index, skin depth, optical conductivity

1. Introduction

In the recent years there is a significant research contribution towards the optoelectronic devices, lasers, optical fibre communications, solar cells etc [1-4]. The properties and applications of various materials, crystalline, amorphous and thin films are widely studied to make them available for different purposes. Moreover, for the above said optical devices it is necessary to understand, study the optical properties and calculate various optical parameters mainly refractive index, energy gap, extinction coefficient, dielectric constant, optical conductivity etc. Therefore, glasses are well known for their wide transparency, density, peculiar physical and chemical properties, optical, magnetic and thermal properties.

Glasses have been in the centre of research and a variety of glasses were prepared (e.g. phosphate, silicate, borate, borosilicate etc) [5]. Among the variety of glasses, borate system is widely researched for its applications, the supremacy of borate system is only due to its availability, low cost, ease of formation, low melting temperature etc [6]. To this borate system heavy metal ion Bi is added, now referred as bismuth borate system which enriches the existing properties and opens up applications in wide areas. Hence bismuth borate system is readily available for ultrafast optical switches, optical fibre amplifiers, lasers etc. [7-8] and also in radiation shielding [9].

ZnF_2/PbF_2 are now added to the glass matrix to enhance the optical properties and opens applications in laser engineering, optical fibres etc [10-12]. Cr_2O_3 is also added, which is used to probe the spectroscopic properties and optical properties [12-13]. Thus ZPBBCR: ZnF_2-PbF_2-Bi_2O_3-B_2O_3-Cr_2O_3 glasses are prepared via melt quench process and optical properties are studied. The optical data is obtained from the optical absorption spectra, from which various optical parameters are evaluated. These optical parameters justify their applications in optical devices.

2. Sample preparation and characterization

Appropriate chemicals of suitable compositions have been taken to prepare the glass samples having glass code ZPBBCR1, ZPBBCR2, ZPBBCR3, ZPBBCR4, ZPBBCR5 and ZPBBCR6. Chemical formula associated with the glass samples is represented as $xZnF_2$-(25-x) PbF_2-25Bi_2O_3- 49.8B_2O_3-0.2Cr_2O_3, here x varies from 0 to 25 mol% with an interval of 5 mol% used to prepare the ZPBBCR glass system. These chemicals were grinded properly to make them fine. Thus, obtained chemical mixtures were taken in crucibles and heated in a electrical furnace at 1127K for about 45 minutes. Samples in the form of melt were poured on a pre-heated stainless-steel plate and pressed to obtain bubble free samples. Further, the samples were undergone for annealing at 373K around 5 hours in order to reduce the stress in the prepared samples.

To know the structural information of the prepared glass samples XRD of the glass batch were taken using Phillips x-pet PRO over a range of 10^o-80^o. Optical properties of the ZPBBCR glass samples investigated by UV-visible absorption spectra and it is recorded using JASCO V-760 spectrophotometer.

3. Results and discussion

3.1 XRD

Structural characterization of the prepared glass samples was recorded using x-ray diffractometer over 2θ ranges from 10^o-80^o and portrayed in Fig.1. The XRD pattern of prepared glass samples depicts the absence of sharp characteristic peaks. Therefore, the prepared ZPBBCR glass system is amorphous in nature.

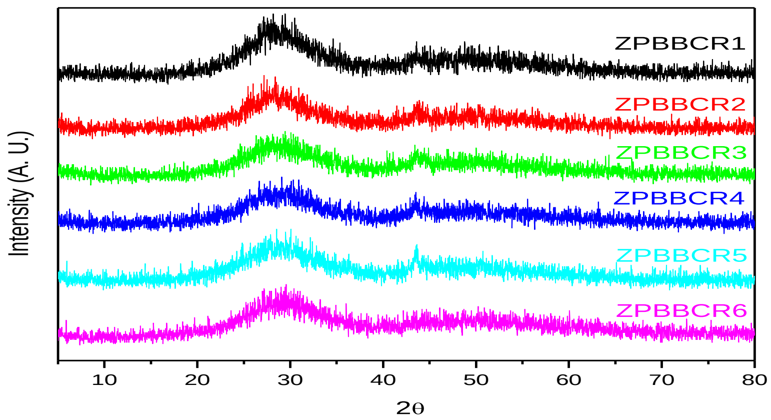

Figure 1: XRD of ZPBBCR glass system [14]

3.2 UV-visible absorption spectra

Measurements of optical absorption were made to comprehend the optical characteristics of the prepared glasses. Absorption coefficient of the synthesized glass batch was evaluated from the absorbance values obtained from UV-visible absorption spectra. In the present study the detailed information of optical features of prepared glass system such as transmittance, skin depth, refractive index, extinction coefficient, optical conductivity and dielectric constants (real and imaginary) of ZPBBCR glasses are evaluated. The UV-visible absorption spectra of the glasses were plotted over 400nm to 900nm range and is displayed in Fig. 2 [14].

The absorption coefficient of the prepared ZPBBCR glass batch were calculated by using standard relation $\alpha(\nu) = 2.303 * \frac{absorbance}{thickness\ of\ sample}$. For the present prepared glass samples the thickness is in the range of 0.112cm to 0.177cm [14].

Transmittance of the prepared ZPBBCR glass samples have been calculated using the relation [15]

$$T_s = \exp(-\alpha d) = 10^{-A} \quad (1)$$

Here $T_s \rightarrow$ transmittance, $\alpha \rightarrow$ absorption coefficient, d$\rightarrow$ thickness of the sample, A$\rightarrow$ absorbance.

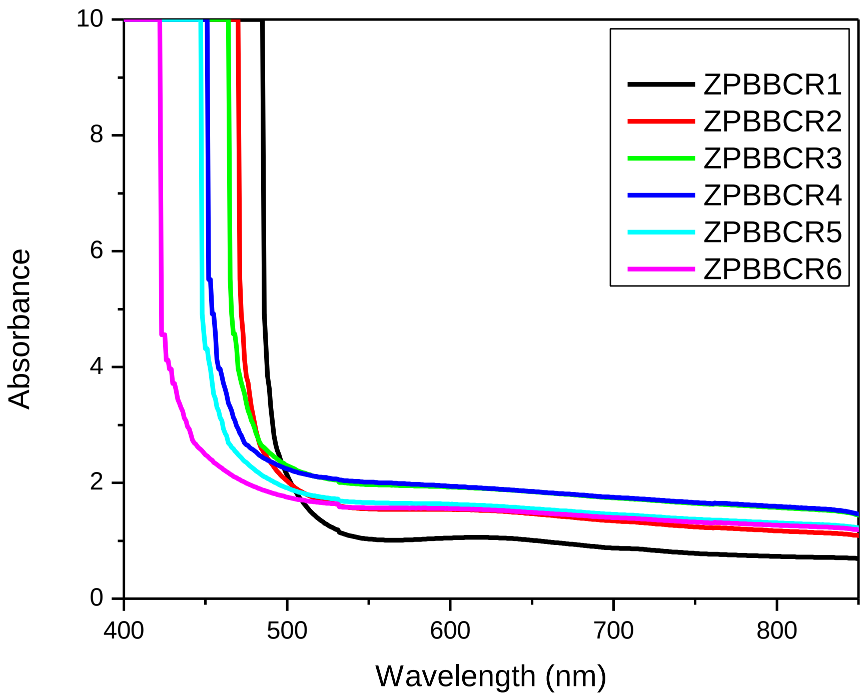

Figure 2: UV-visible absorption spectra of ZPBBCR glass system[14]

A graph is plotted between percentage of transmittance to the wavelength (nm) is displayed in Fig. 3. The decrease in the transmittance is observed around 470–670nm, indicating the presence of significant bands which resulted in the coloured glass specimens. The central peak around 550nm depicts the prepared glass samples to be green in colour.
Electromagnetic wave propagation in the material depends on optical constants of material, extinction coefficient (k) and refractive index (n) of material. The phase of electromagnetic waves is affected by refractive index where extinction coefficient impact on amplitude of wave. Extinction coefficient of the material is computed by relation [16]

$$k = \frac{\alpha\lambda}{4\pi} \qquad (2)$$

The variation of extinction coefficient with incident photon energy (eV) has been portrayed in Fig. 4. From the Fig. 4, it has been noted that the extinction coefficient is less at low photon energies. The plot of k vs hν also reveal that, with increase in content of ZnF_2 the peak shift towards the higher energy side.

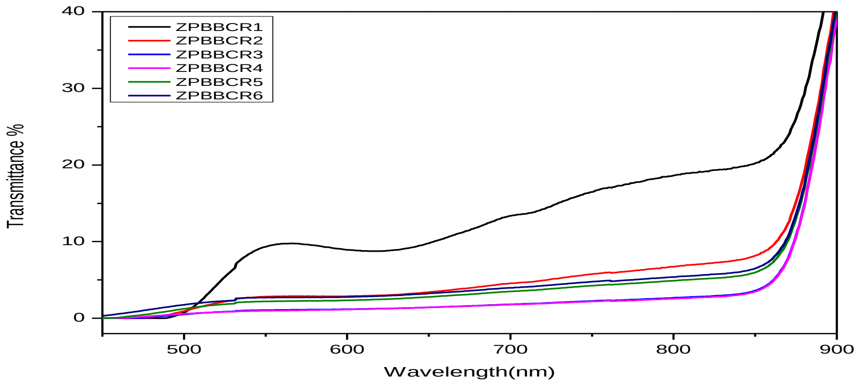

Figure 3: Transmittance spectra of ZPBBCR glass system

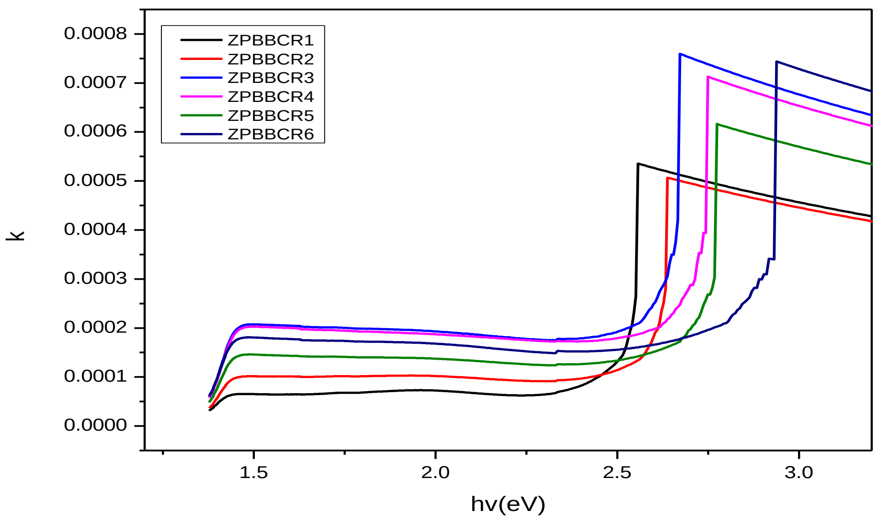

Figure 4: Variation of extinction coefficient with incident photon energy in ZPBBCR glasses
The refractive index is one of the significant factors in designing photonic devices. It is related to the polarizability of the ions and the local field. Evaluation of the refractive index of optical materials is essential for their application in integrated optical devices such as switches, filters, modulators, etc.[17].
The refractive index (n) values for different wavelength are calculated using the relation

$$n = \frac{1}{T_s} + \sqrt{\frac{1}{T_s - 1}} \qquad (3)$$

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Here $T_s \rightarrow$ transmittance percentage

Thus, obtained refractive index values were plotted against the wavelength as shown in Fig. 5. It is evident that the refractive index values decreased with increase in wavelength and attained a constant value at higher wavelengths. Similar type of behaviour was reported by K. H. Mahmoud for $xBi_2O_3(75\text{-}x)B_2O_325Li_2O_3$ glass system [18]. Thus, the decrease in refractive index may be attributed to the decrease in the density, which is due to the replacement of higher ionic radii of Pb^{2+} with lower ionic radii of Zn^{2+} [14]. From Fig.3 and Fig. 5 it is revealed that the refractive index and transmittance follows the opposite trend.

Generally, the amplitude of an electromagnetic wave drops by the factor $e^{-x/\delta}$, when it passes through the matter. The measurement of a material response to the incident radiation is called its skin depth (δ) or depth of penetration. It is referred as the distance inside the material where 63% of the initial beam intensity was absorbed. Skin depth value depends on frequency and conductivity of the material [19]. Fig. 6 shows the penetration depth which was evaluated from following relation

$$\delta = \frac{1}{\alpha} \qquad (4)$$

From the figure, it reveals that the depth of penetration is high at lower photon energies and decreases later and attains a constant value at higher photon energies.

Optical conductivity (σ_{opt}) is one of the significant metrics used to describe the material optical properties. It is used to identify the allowable inter band optical transitions in a material. The optical bandgap, refractive index, absorption coefficient, incident photon frequency and extinction coefficient are some of the factors that have an impact on material optical conductivity.

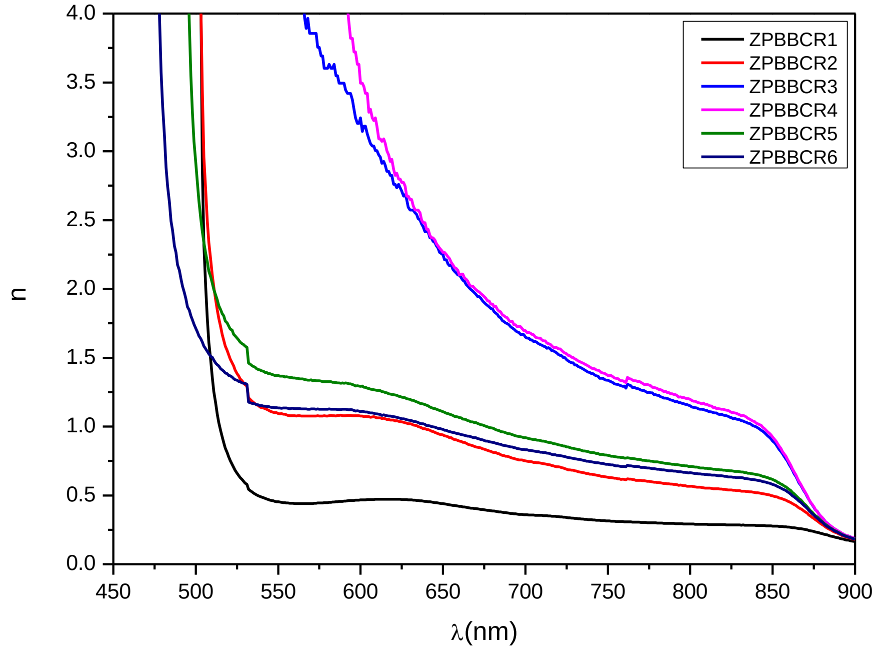

Figure 5: Refractive index as a function of wavelength of ZPBBCR glass system

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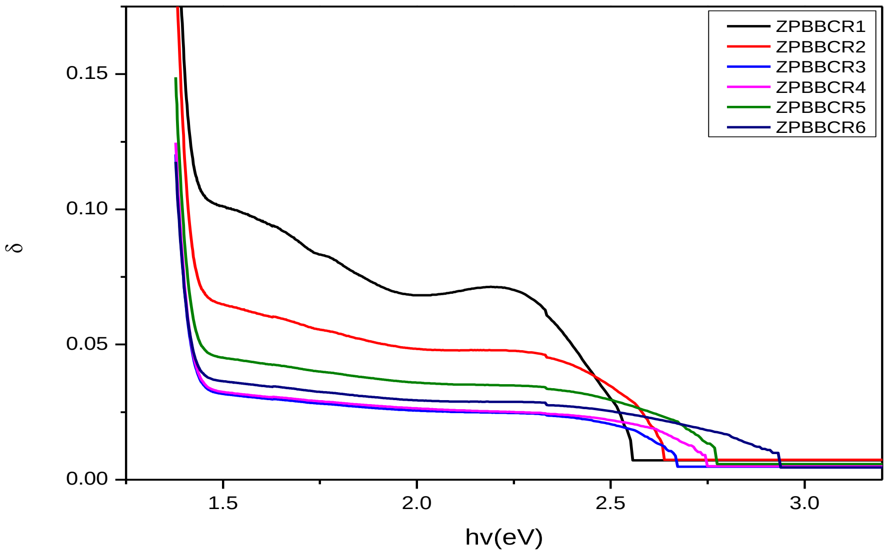

Figure 6: Variation of skin depth (δ) with incident photon energy in ZPBBCR glasses

The variation in optical response of the prepared glass system have been analyzed with incident photon energy is displayed in Fig. 7. The optical conductivity is evaluated from the relation

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \qquad (5)$$

where c is velocity of light in vacuum, α represents absorption coefficient and n is linear refractive index. The findings show that in ZPBBCR glass samples, computed optical conductivity rises with ZnF_2 weight percentage. High refractive index values and high absorbance of current glasses are responsible for higher values of optical conductivity [20].

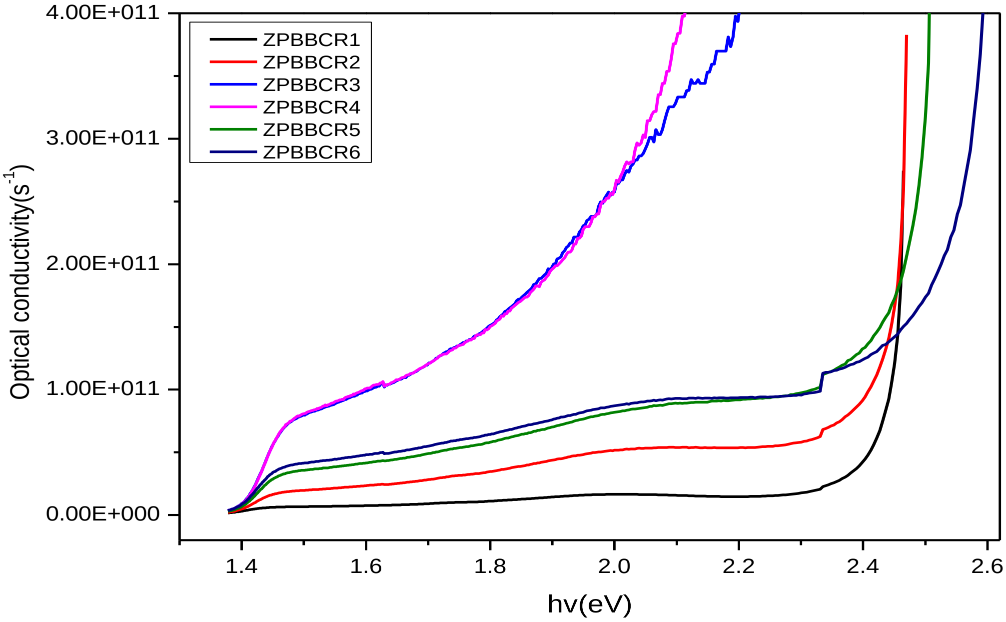

Figure 7: Optical conductivity with incident photon energy in ZPBBCR glasses

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The calculated dispersion parameters such as refractive index and extinction coefficient of ZPBBCR glasses were used to evaluate the real (ε_1) and imaginary (ε_2) dielectric constants of the prepared glass system. These dielectric parameters are calculated with the following relations [19].

$\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$ (6)

The variations in the real and imaginary part of dielectric constants with hν shown in Fig. 8(a) and Fig. 8(b). The interaction between the photons and electrons leads to the variation of dielectric constant with energy [21-23]. The real and imaginary components of the dielectric
function both exhibit the same pattern, but the real component has greater values. The range of real values of dielectric constant makes the prepared glass samples to be available for applications in optical devices.

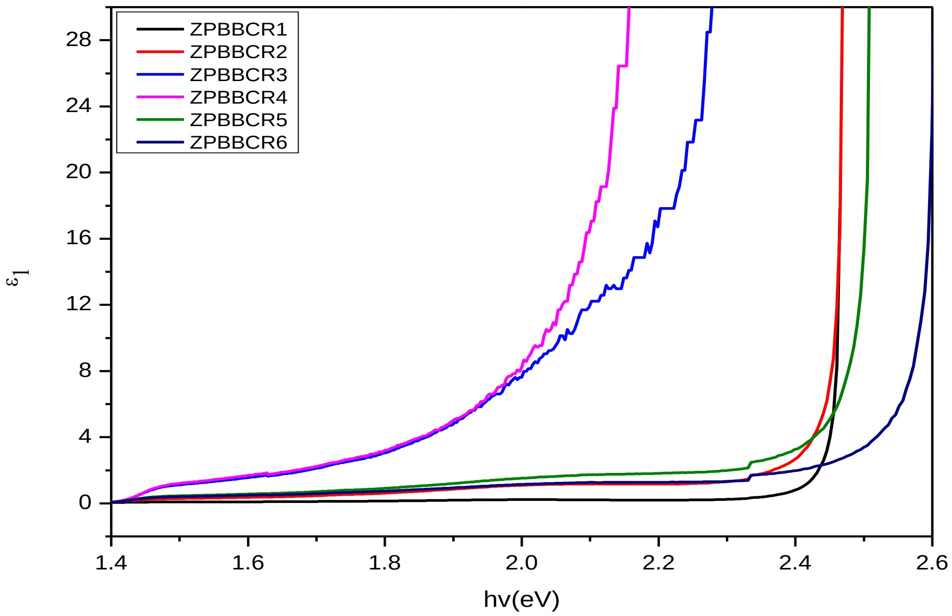

Figure 8 (a): Variation of real part of dielectric constant photon energy in ZPBBCR glasses

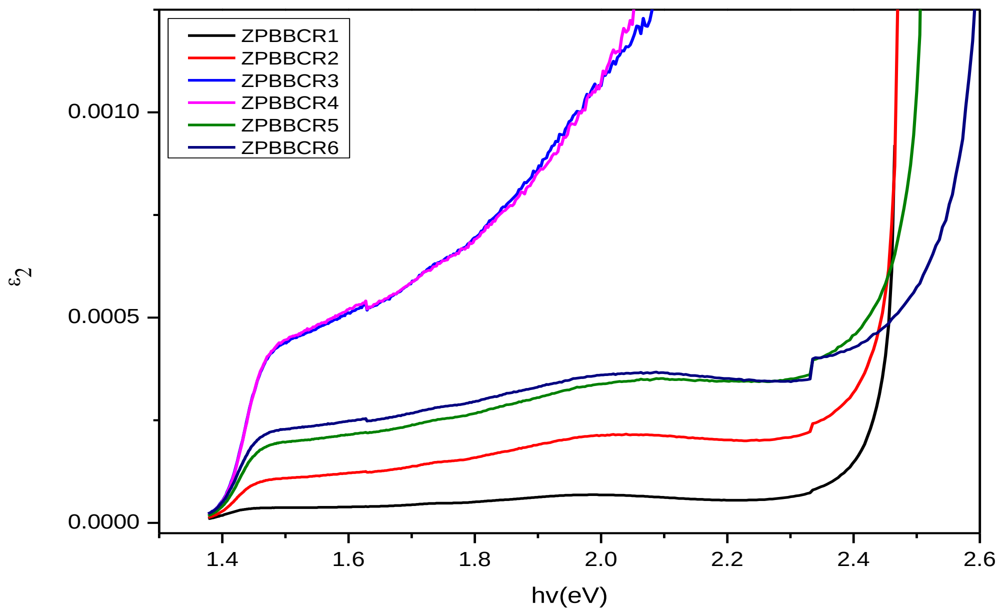

Figure 8(b): Imaginary part of dielectric constant vs photon energy in ZPBBCR glasses

4. Conclusions

In the present study ZnF_2/PbF_2 bismuth borate glasses with chromium ions with the compositional formula ZPBBCR: $xZnF_2$-(25-x)PbF_2-25Bi_2O_3-49.8B_2O_3-0.2Cr_2O_3 were synthesized using conventional melt quenching process. Amorphous nature of prepared glass system was confirmed from XRD spectra. From the absorbance spectra, transmittance have been plotted and analysed with wavelength variation. It is revealed that the prepared glass system possesses high transmittance at higher wavelengths which is the opposite trend of refractive index. Extinction coefficient is observed to shift towards higher energy side with increase in ZnF_2 content. Computed skin depth and optical conductivity were plotted against incident photon energy. The values of real and imaginary part of the dielectric constants are evaluated and the variation with photon energy is observed.

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