ISSN: 0974-5823 Vol. 7 No. 6 June, 2022

International Journal of Mechanical Engineering

Optical features of CaF_2-PbF_2-Bi_2O_3-B_2O_3-Cr_2O_3 glass system

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Abstract

CPBBCR glasses with chemical formula $xCaF_2$-(25-x)PbF_2-25Bi_2O_3-49.8B_2O_3-0.2Cr_2O_3 where x changes from 0-25 mol% with an interval of 5 mol% have been synthesized by conventional melt quenching technique. The concentration of CaF_2 is increased in 5 mol% at the expense of PbF_2. Thus, prepared glass batch were investigated for structural and optical properties with the help of XRD and UV-Visible absorption spectra. With the increase of CaF_2 content, in the glass system it was noticed that the prepared CPBBCR glasses shows wide transmission window from UV to IR region. Calculated linear refractive index of the samples show opposite trend with transmittance. Lower values of extinction coefficient made the prepared glass system to be available for optical applications. The variation of real and imaginary part of dielectric constant are studied as a function of wavelength.

Keywords: UV-Visible, Refractive index, Transmittance, Extinction coefficient, Dielectric constant

1. Introduction

Glasses have considerable interest as they exhibit variety of properties and applications. The applications of glasses are in the fields of non-linear optics, solar conductors, solid-state laser, actuators, optoelectronic devices and radiation shielding [1-3]. From the literature, different types of glasses are studied and reported such as phosphate, tellurite, borate, germanite, silicate, fluoride and borosilicate etc. The high refractive index, high density, wide transmission ranges from UV to IR, high dielectric constant etc. made bismuth borate system to be chosen as host. These bismuth oxide glasses fall under the category of heavy metal oxide glasses (HMO) as bismuth is heavy metal. Moreover, bismuth oxide glasses have high polarizability which also finds applications in NLO (non-linear optics) and ultrafast optical switches, photonic devices etc [4-7]. However still attempts are made to improve the optical, thermal, mechanical and electrical properties of these bismuth borate glasses. Therefore, doping is the best choice and many reports is available on the variety of dopants and their properties.

Here, in our present work, it is proposed to add CaF_2 and PbF_2 to the bismuth borate system. Addition of CaF_2 leads to the improvement in the transmission window, viscosity and liquidous temperature are lowered [8-10]. The advantage of PbF_2 to the bismuth borate system improves the optical properties such that the fabricated glasses can be used in optical fibres and laser engineering [11, 12]. In addition to these metal fluorides (CaF_2 and PbF_2), Cr_2O_3 a transition metal oxide is added. Now this compositional glass can be used in lasers and high temperature sensors etc [13-16]. Thus, the glasses with compositional formula $xCaF_2$-(25-x)PbF_2-25Bi_2O_3-49.8B_2O_3-0.2Cr_2O_3 are synthesized. The procedure of synthesis, optical and spectroscopic properties are studied and reported [4]. Now in the present paper, it is proposed to evaluate the optical constants from the absorption spectra and is intended to study their variation.

2. Experimental

2.1 Sample preparation

The CPBBCR glasses were synthesized based on the chemical structure $xCaF_2$-(25-x)PbF_2-25Bi_2O_3-49.8B_2O_3-0.2Cr_2O_3 where x changes from 0, 5, 10, 15, 20, 25 mol % using melt quenching method. The required AR grade Sigma-Aldrich make chemicals were taken in an appropriate ratio (listed in Table 1) to prepare the glass system. Thus, chemicals of suitable weight were finely grinded and transferred into crucibles. These crucibles which contains of chemical mixtures placed in a electrically maintained furnace at 1127K for 45minutes. Thus, obtained melt was pressed on a stainless-steel plate which is maintained at 200^{o}C. Further the prepared glass samples were kept in a furnace at 200^{o}C for 5 hours to remove the stress in the glass samples.

2.2 Characterization

To investigate the structural information of prepared glass system, Philips X-pert PRO is employed to scan the XRD spectra. The optical absorption spectra of the synthesized CPBBCR glass batch were measured using spectrophotometer of JASCO V-760 make. The UV-Visible absorption spectra of well-polished samples were recorded over 400nm to 900nm range.

Table 1: Chemical composition of CPPBBCR glass batch in mol% [4]

Glass composition	Glass Code					
	CPBBCR1	CPBBCR2	CPBBCR3	CPBBCR4	CPBBCR5	CPBBCR6
CaF_2	0	5	10	15	20	25
PbF_2	25	20	15	10	5	0
Bi_2O_3	25	25	25	25	25	25
B_2O_3	49.8	49.8	49.8	49.8	49.8	49.8
Cr_2O_3	0.2	0.2	0.2	0.2	0.2	0.2

3. Results and discussion

3.1 XRD

Structural information of the prepared samples reveals the crystalline or amorphous nature of obtained glass samples. X-ray diffractogram was taken for the CPBBCR glass system for 2θ ranges from 10^o to 80^o displayed in Fig.1. From the graph it was noticed that the resultant pattern doesn't contain any sharp peaks. This absence of sharp Bragg peaks further confirms the prepared glass system is amorphous.

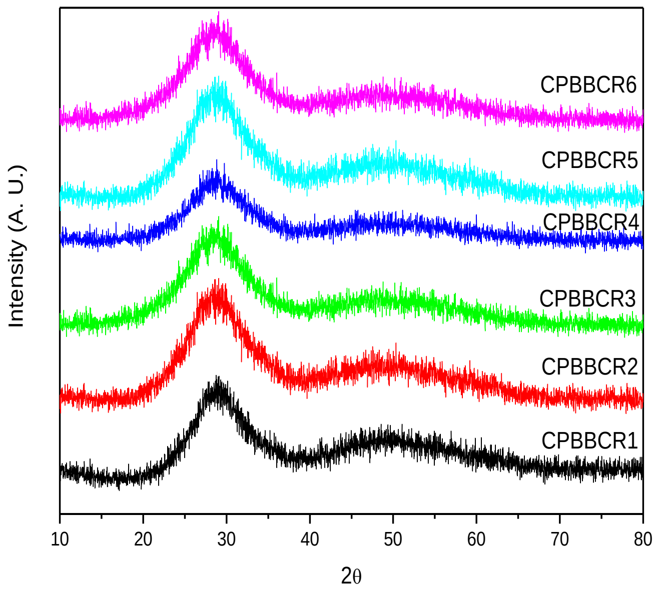

Figure 1: X-ray diffractogram of CPBBCR glass system [4]

3.2 Optical absorption spectra

The UV-Visible absorption spectra of CPBBCR glass batch shows a strong absorption band over UV to Visible region. Thus, obtained spectra contains absorption bands represented at 450nm, 620nm, and 710nm. The characteristic bands are ascribed to octahedral symmetry of Cr^{3+}ions. It was noticed from Fig.2 that, with increase in CaF_2 content in CPBBCR glass system the absorptions shift towards lower wavelength side [4]. It is evident that the optical constants like refractive index, extinction coefficient, dielectric constants (real and imaginary) were evaluated from absorption coefficient $\alpha(\upsilon)$. Hence $\alpha(\upsilon)$ is calculated from absorbance and thickness of the sample by using standard relation

$$\alpha(\upsilon) = 2.303\,\frac{A}{d} \qquad (1)$$

Where A $\rightarrow$ absorbance, d$\rightarrow$thickness of the sample.

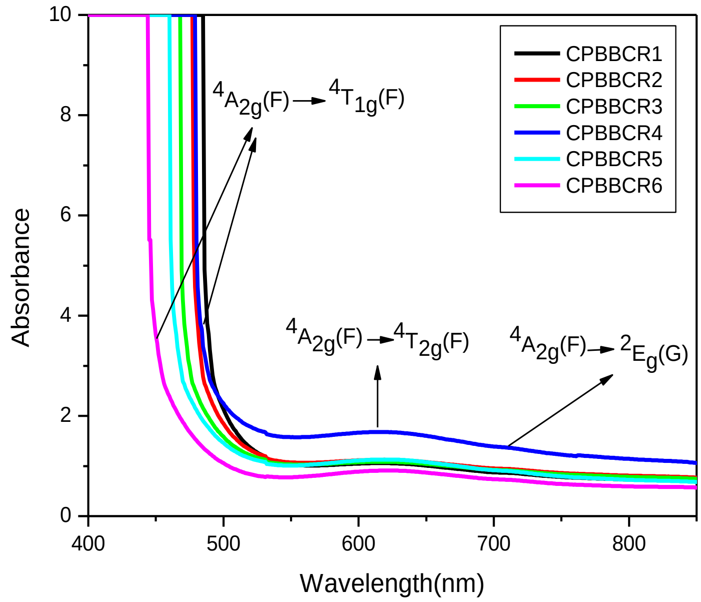

Figure 2: Absorbance vs Wavelength spectra of CPBBCR glasses [4]

From the transmittance graph, it has been noted that the prepared glasses show zero transmission around 400nm and sharp rise in transmission beyond cut-off wavelength in the IR region [17, 18].

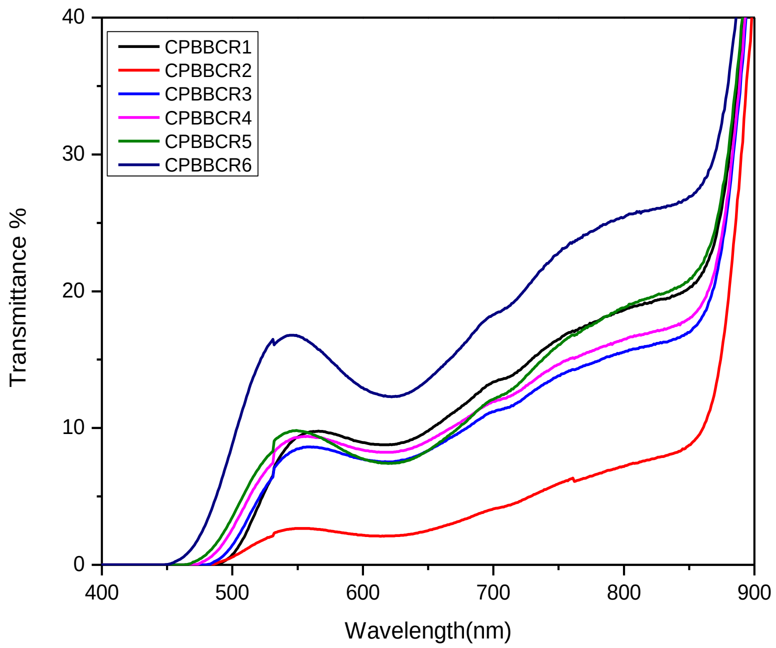

Figure 3: Optical transmittance spectra of CPBBCR glasses

All the glass samples in the present glass system having maximum central peak around 550nm confirms the CPBBCR glasses are green in colour. The high transmission is observed for the sample CPBBCR6 where the Pb content is absent. This is also because the calcium fluoride has wide optical window ranging from UV to IR and thus the CaF_2 rich sample possess high transmission.

The extinction index (k) and refractive index are the two significant factors for the glasses to study the optical properties. The information about the interaction of light during scattering and absorption are known from these factors. The extinction coefficient is evaluated from the values of absorption coefficient (α) and wavelength (λ) by the relation

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

The plot of extinction coefficient (damping coefficient) for the CPBBCR glass samples as a function of incident photon energy is shown in Fig. 4. The plot is similar to other glass samples reported in literature [19]. The values of damping coefficient lie in the range of 0.0001-0.0007 which are very less. These low values indicate the CPBBCR glass system have applications in optical devices.

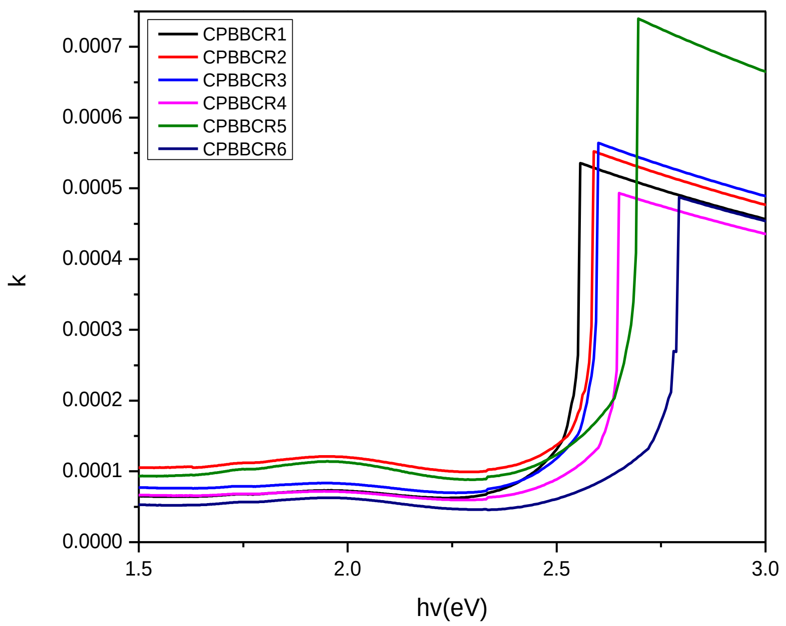

Figure 4: Extinction coefficient vs incident photon energy plot of CPBBCR glasses

The refractive index is plotted as a function of wavelength portrays in Fig. 5. There is a hump observed around 620nm and records a maximum value for the refractive index. Thereafter, these values decrease for higher wavelengths [20]. These glasses with high refractive index values open up applications in optoelectronic devices.

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

where T_s is the transmittance.

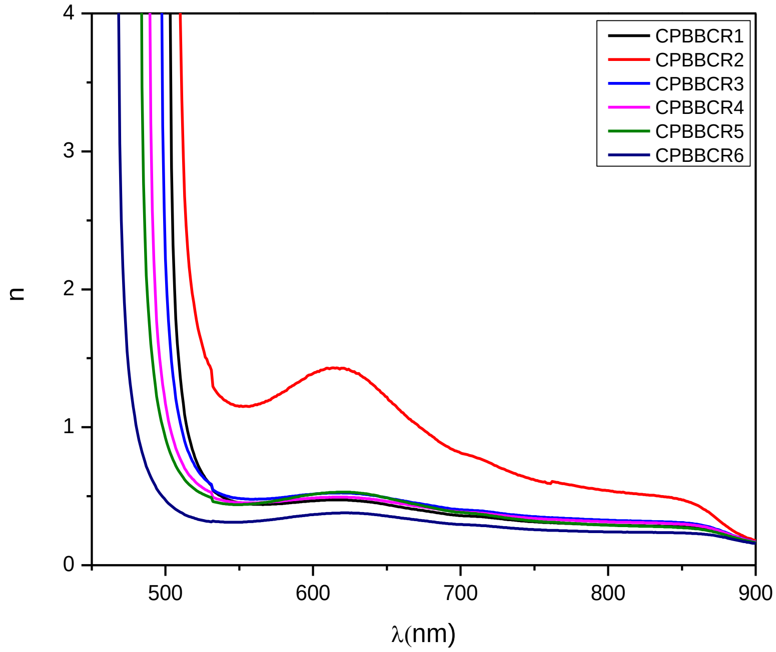

Figure 5: Refractive index vs wavelength plot of CPBBCR glasses

For the optical device makers, the properties like dielectric loss, dielectric constant provide information about the material. The dielectric constant of the material is given by the relation.

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \qquad (4)$$

where $\varepsilon \rightarrow$ dielectric constant

$\varepsilon_1 \rightarrow$ real part of dielectric constant and is given by $n^2 - k^2$

$\varepsilon_2 \rightarrow$ imaginary part of dielectric constant and is calculated from $\varepsilon_2 = 2nk$

The speed of the light in the material is given by the real part, the absorption energy of the light in the material is given by the imaginary part of the dielectric. These variations of real and imaginary part of the dielectric constant with wavelength have been portrayed in Fig. 6 and Fig. 7.

From the Fig. 6, it is evident that the ε_1 (real dielectric constant) for the sample CPBBCR2 shows a hump and attains a peak value at a wavelength 620nm. For all other samples, the ε_1 values are constant. In case of imaginary part of the dielectric constant (shown in Fig. 7.), for the sample CPBBCR2 the hump is observed at 620nm. All the other samples CPBBCR1, CPBBCR3, CPBBCR4, CPBBCR5, CPBBCR6 have almost same value at higher wavelengths. The lower values of dielectric constant shows the fabricated CPBBCR glasses will find applications in electro-optic modulators, microelectronics and field detectors etc.

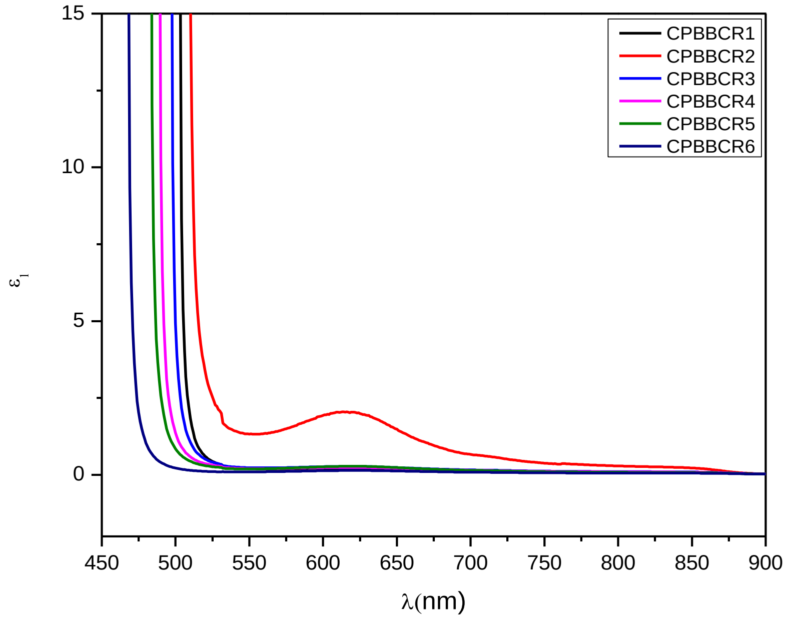

Figure 6: Real part of the dielectric constant as a function of wavelength in CPBBCR glass system.

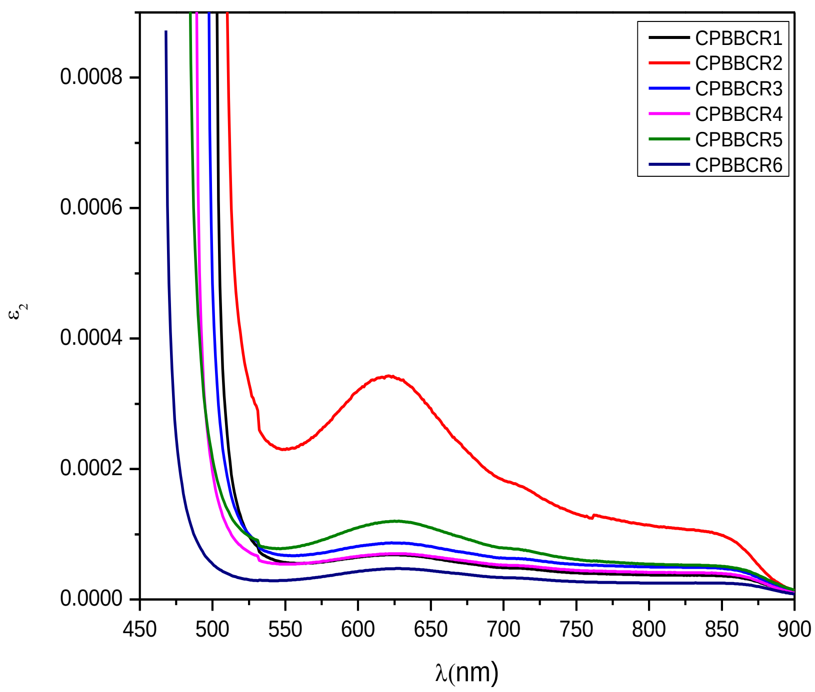

Figure 7: Imaginary part of the dielectric constant as a function of wavelength in CPBBCR glass system.

4. Conclusions

Glasses doped with CaF_2/ PbF_2 in bismuth borate system containing chromium ions have prepared by melt quenching method. Thus, obtained samples were taken for x-ray diffractogram to confirm their non-crystalline nature. As prepared samples were undergone for UV-visible absorption studies to study optical constants like refractive index, extinction coefficient, real dielectric constant and imaginary dielectric constant. From variation of transmittance and refractive index with wavelength it was confirmed that glasses with high concentration of CaF_2 possess high transmittance and low refractive index. Lower values of extinction coefficient reveal the possible applications of prepared CPBBCR glass system in making optical devices. The values of real and imaginary dielectric constants makes these glasses available for optical applications.

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