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# UV-Vis and FTIR spectroscopic studies of CaO-$Na_2B_4O_7$-$PbF_2$- CuO glasses

*Aparna Dode*[*], *G. Sandya Rani*

Department of Physics, University College of Science, Osmania University, Hyderabad, Telangana, 500007

**Abstract.** The present work deals with the preparation of CaO-$Na_2B_4O_7$-$PbF_2$-CuO glasses and investigating the prepared samples with various spectroscopic methods. Melt quenching method is used for the preparation of the glass samples with the composition (89-x)$Na_2B_4O_7$-xCaO-10$PbF_2$-1CuO where x = 0, 5, 10. 15 & 20 mol%. Amorphous nature of the samples was confirmed with the absence of sharp peaks in the XRD spectra. Density measurements were done and are observed to be increasing with CaO in the glass composition. Various optical parameters were evaluated from absorption spectra and characteristic absorption is noticed in it as the glass samples contain $Cu^{2+}$ ions. Band gap values were found to decrease while the refractive index values increased. FTIR spectra was also recorded and analyzed for each sample as it is more important in exploring the structural features of borate glasses. The spectra revealed the existence of the metal ions and various borate groups in the glass structure.

## 1 Introduction

Glasses are a type of non-crystalline or amorphous substance that can be formed using a variety of methods, including liquid quenching and gas implantation, the general definition of which can be found in the following sentence. Glass is one of the earliest artificial materials, with a track record of being utilized that spans over five thousand years. It is actually considered the fourth state of traditional matter, following gas, liquid, and solid [1, 2]. Borate glasses are extremely important in the field of research due to their adjustable characteristics, which make them suitable for applications in the fields of biological medicine, optical technology, and the storage of energy. This is because of their flexible [BO3]/[BO4] framework, exceptionally stable temperature, and capability to integrate dopants such as rare earths. Borate glasses offer advantages over conventional silicate glasses in certain areas, such as biological activities and durability to corrosion [3,4]. In the field of investigations, alkali borate glasses play a crucial role in the customization of characteristics such as ion conduction, optical functioning, and protection from radiation. This is accomplished primarily through the modification of boron coordination ($BO3^-$/BO2 units) and the formation of non- bridging oxygens. This results in the formation of one-of-a- kind "borate anomalies" and enables applications in the fields of electronics, optics, and defense through

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[*] Corresponding author: aparna_dode@yahoo.com

the implementation of regulated structural alterations by means of the introduction or incorporation of alkali [5, 6]. Calcium oxide is an essential component in borate glasses because it allows for the modification of the network's makeup (by converting BO3 units into BO4 units), the enhancement of chemical strength, the improvement of thermal endurance (by increasing Tg ), the enhancement of biocompatibility for therapeutic uses, and the enhancement of optical properties (photoluminescence, radiation detection) through the provision of sites for dopants. These properties make borate glasses useful for dosimetry and luminescent materials [7, 8]. $PbF_2$(Lead Fluoride) is a crucial ingredient in borate glasses because it improves the protection against radiation (gamma and neutron), enhances optical attributes such as infrared (IR) transparency and luminescence, increases density, and modifies the structure of the glass. These properties make borate glasses suitable for use in optical fibers, lasers, radiation detectors, and advanced shielding materials. In essence, it adds the advantageous properties of heavy atoms (lead) and fluoride's network-altering consequences to the borate matrix [9, 10]. As a network modifier and an interior probe of the glass matrix, copper oxide (CuO) is a crucial ingredient for architectural study in borate glasses. This is due to the fact that it performs both of these functions simultaneously. The interaction of boron units and the general connectedness of the glass network are both considerably altered as a result of its existence [11, 12]. Keeping in mind with these importance's of $Na_2B_4O_7$, CaO, $PbF_2$ and CuO, the authors considered the composition (89-x)$Na_2B_4O_7$ −xCaO −10$PbF_2$-1CuO where x = 0, 5, 10, 15 and 20 and analysed the samples with the XRD, UV and FTIR spectra for structural analysis.

# 2.Experimental

## 2.1 Sample preparation

Glass samples with the composition : (89-x)$Na_2B_4O_7$ - xCaO -10PbF2-1CuO, where x = 0, 5, 10, 15, and 20, was synthesized via melt quenching. The requisite quantities of analar grade Na2B4O7, CaO , PbF2 and CuO were amalgamated and subsequently melted in a porcelain crucible within an electrically driven furnace for 45 minutes at approximately 1100°C under standard air circumstances. The glasses are produced by quenching the molten material on a prepared stainless steel plate and subsequently annealing at a temperature 200 degrees Celsius beneath the glass transition point. The glass compositions are enumerated in Table 1. Glasses were then fabricated by applying molten material onto a steel plate with the use of a secondary plate. To alleviate the stresses in the glasses, these specimens are further positioned in a secondary furnace maintained at 200°C.

## 2.2 Characterization

Upon preparation of the CNPC samples, they underwent XRD spectral analysis. The crystalline or non-crystalline nature of the manufactured materials can be ascertained by the XRD spectrum. The spectra must illustrate the materials' amorphous characteristics. X-ray diffraction spectra were acquired at room temperature in the range of 10° to 80° using the Philips Xpert Pro X-Ray Diffractometer. Archimedes' principle was employed to determine the density of CNPC glasses, with xylene as the immersion solvent. Three distinct pieces were selected from each glass sample for density measurements, and the average value was recorded as the final density for each sample. Furthermore, UV-Vis spectra were utilized on the polished samples. Absorption spectra are utilized to ascertain the band gap, Urbach energy, and refractive index, as well as to identify the absorption bands related with the TMI.

The optical absorption spectra of the glasses were acquired between 200 and 1000 nm using a JASCO V-670 UV-VIS spectrophotometer. FTIR spectra were acquired from these samples utilizing a Perkin Elmer Frontier FTIR across the wavelength range of 400–1600 cm$^{-1}$, with a resolution of 3 cm$^{-1}$.

## 3.Results and Discussion

### 3.1.X-Ray Diffraction

XRD is a helpful instrument for the growth of research in the glass industry since it can be used to understand the fundamental properties of glasses and develop new materials. XRD can be used to identify and characterize any crystalline states or particles that might be embedded in bulk glass and cause defects or alters the properties of the glass. XRD studies, especially high-energy XRD, can show the short- and medium-range atomic arrangements in glass- forming liquids and glasses that influence their properties like viscosity and crystal nucleation. Each glass system's X- ray diffraction spectra was analyzed , the lack of distinct, sharp peaks indicated that the glasses were amorphous. The current CNPC glasses' X-ray diffraction patterns are shown in Fig. 1. XRD did not show any sharp peaks in its spectra hence it is concluded that the CNPC glasses are amorphous in nature.

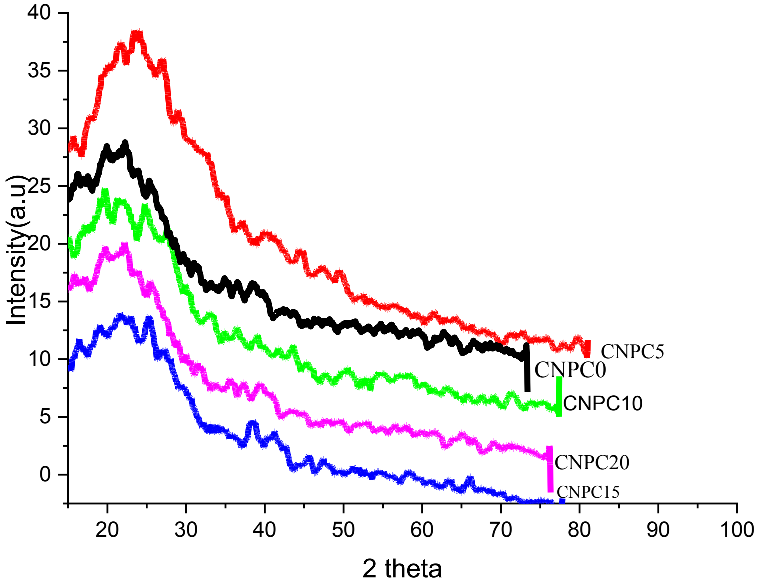


**Fig.1.** XRD spectra of CNPC glasses

### 3.2. Density and molar volume

The density of glass influences its capacity to endure pressure and adverse impacts, hence maintaining its structural integrity. Density is a vital factor in commercial and manufacturing contexts as it influences the efficacy and usefulness of glass for many applications. Glass samples are evaluated by density measurements, and it is improbable that two samples from the same source originated from the same location if their densities vary significantly[13, 14].

In samples containing many shards, density measurements can serve as a screening technique to identify various glass sources present. Table 1 presents the acquired density values for the CNPC glasses

**Table 1**: Acquired density values for the CNPC glasses

| Glass code | CNPC0 | CNPC5 | CNPC10 | CNPC15 | CNPC20 |
|---|---|---|---|---|---|
| ρ(gm/cm$^3$) | 2.9509 | 2.9730 | 3. 0461 | 3.2090 | 3.339 |
| Vm(cm$^3$/ mole) | 123.60 | 117.21 | 109.06 | 98.45 | 96.43 |
| OPD | 50.49 | 50.67 | 51.72 | 54.24 | 52.27 |

The density value clearly rises from CNPC-0 to CNPC-20 with the addition of CaO. The density data indicates that as CaO increases at the expense of $Na_2B_4O_7$, the glass sample densities elevate from 2.951 to 3.339 g/cc.

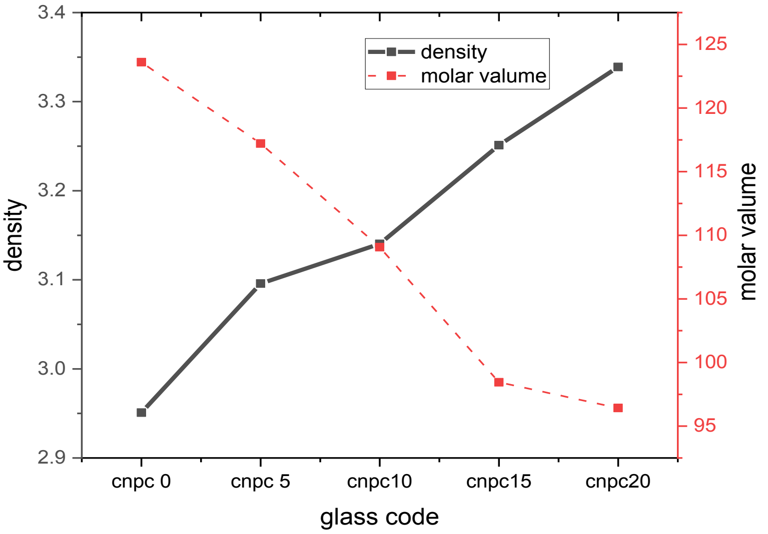
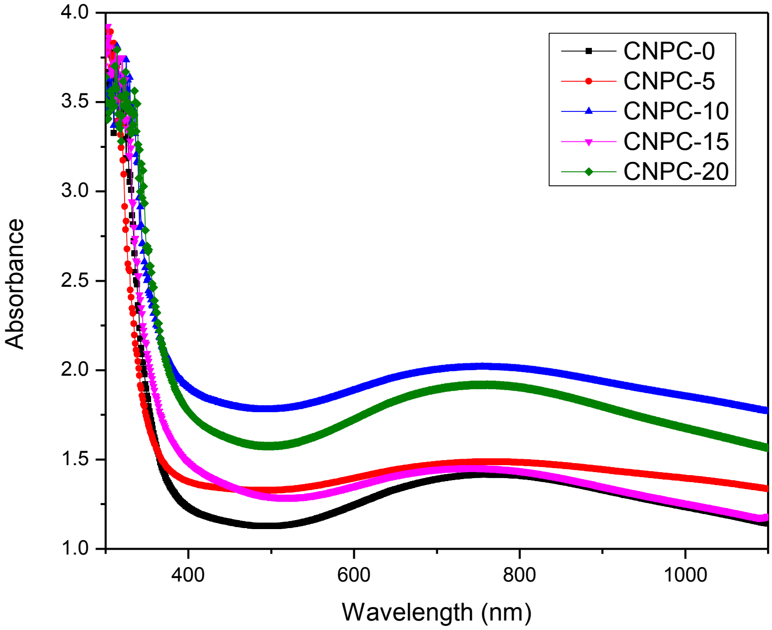


**Fig. 2.** Variation of density and molar volume with CaO in CNPC glasses

The density has increased due to the transformation of BO3 units into BO4 units. Figure 2 illustrates the fluctuation of density and molar volume in relation to CaO in CNPC glasses. The molar volume exhibits a markedly contrasting trend compared to the density values.

### 3.3. Optical properties

Information about the chemical composition of glass constituents, including the presence and concentration of dopants or impurities, can be acquired through UV-Vis spectroscopy. Furthermore, it can aid in identifying alterations to the glassy network structure induced by irradiation, doping, or other processes. Moreover, it can denote the coloration of glass, sometimes linked to the existence of particular impurities known as dopants. A multitude of glass varieties and compositions can be examined utilizing it. Figure3 illustrates the optical absorption spectra of each produced glass sample. The amorphous character of the manufactured glasses is evidenced by the absence of a clear optical absorption edge.



**Fig, 3.** Optical absorption spectra of CNPC glasses

For amorphous materials, Davis and Mott presented the following relation: for both direct and indirect transitions, the absorption coefficient α(v) is a function of photon energy (hν) [15].

$$\alpha(\upsilon) = B(h\upsilon - E_{opt})^2 / h\upsilon \qquad (1)$$

**Table 2:** Various energy values for CNPC

| Glass code | CNPC0 | CNPC5 | CNPC10 | CNPC15 | CNPC20 |
|---|---|---|---|---|---|
| $\Delta \boldsymbol{E}(\boldsymbol{eV})$ | 0.5025 | 0.6113 | 0.6975 | 0.6866 | 0.8818 |
| $\boldsymbol{E_{opt}}(\boldsymbol{eV})$ | 3.000 | 2.822 | 2.729 | 2.539 | 2.181 |
| n | 2.3971 | 2.5122 | 2.4742 | 2.5136 | 2.6617 |
| $\boldsymbol{R_m}(\boldsymbol{cc\ mol^{-1}})$ | 75.7299 | 73.1821 | 68.7741 | 63.3722 | 64.5861 |
| $\boldsymbol{\alpha_m}(\boldsymbol{10^{-24}})$ $(\boldsymbol{ccmol^{-1}})$ | 30.037 | 29.026 | 27.278 | 25.135 | 25.617 |

$E_{opt}$ denotes the optical band gap, [16]. Table 2 presents the values of $E_g$, obtained by extrapolating the linear segment of the curve to the (h$\upsilon$) axis, or $(\alpha h\upsilon)^{1/2}=0$ for indirect transitions. The measured band gap values for the CNPC glasses decreased from 3.000 to 2.181 eV as the mole percentage of CaO increased. This reduction indicates the structural alterations occurring in the glass. The fluctuation in band gap is mostly ascribed to the formation of bridging oxygens (BOs) and non-bridging oxygens (NBOs) [17, 18].

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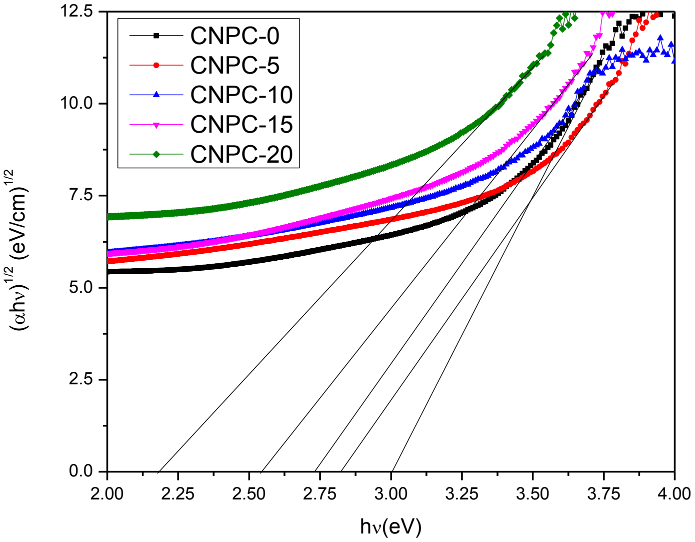

**Fig. 4**. Tauc plots of CNPC glasses

It became evident that when the mole percentage of CaO grew, the band gap values for CNPC glasses diminished from 3.000 to2.181 eV. This decrease signifies the structural changes occurring in the glass. The generation of bridging oxygens (BOs) and non- bridging oxygens (NBOs) accounts for the alteration in the band gap. The addition of CaO to sodium tetra borate glasses may enhance the formation of non-bridging oxygens (NBOs), perhaps leading to a reduction in the band gap values of CNPC glasses. The aforementioned rationale elucidates why the Eopt values for the samples in Fig. 3 exhibit a tendency to diminish as the CaO content increases. The composition significantly influences the Eopt value.

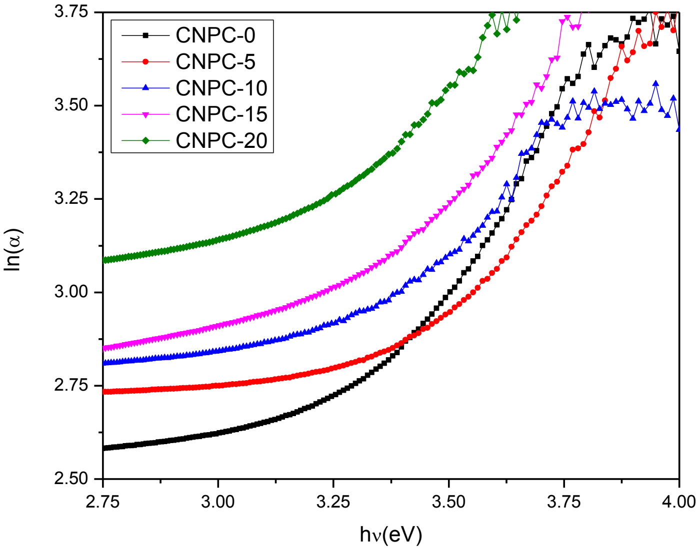

**Fig. 5.** Urbach plots of CNPC glasses

The Urbach energy values (ΔE) were derived from the plot of h$\upsilon$ versus ln(α), represented by the inverse slope of the linear segment of the Urbach curve ln(α) against (h$\upsilon$), as illustrated in Figure 5. Glasses with a higher ΔE are more likely to produce flaws in the glass matrix due to weak bonding. The Urbach energy values for the CNPC glasses span from 0.5025 to 0.8818 eV, suggesting a reduced presence of flaws in their glass structure[19].

## 3.4 FTIR spectra

FTIR spectroscopy can determine various vibrational patterns of chemical bonds in glass by measuring the absorption of infrared light by molecules. Investigators can ascertain the types and arrangements of chemical bonds, such as B-O-B bonds in borate glasses, by analysing the positions and intensities of these vibrational modes. Due to its remarkable sensitivity to the local structure of glasses, FTIR allows researchers to investigate variations in composition and bonding arrangements [20, 21]

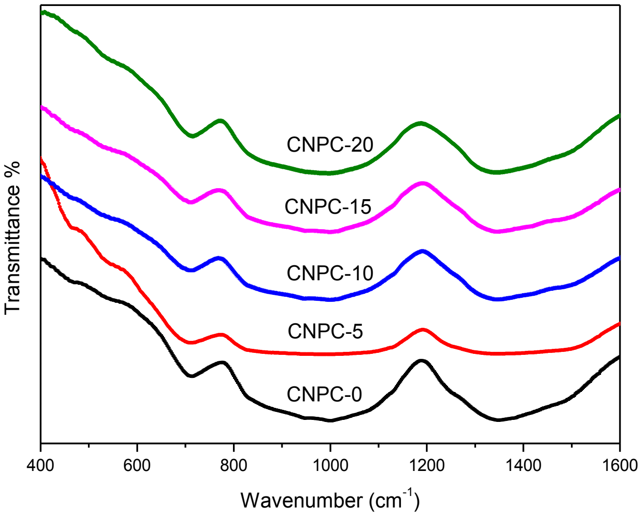

**Fig .6.** FTIR spectra of CNPC glasses

The wave numbers derived from FTIR are 458, 535, 618,705, 830, 883, 998, 1098, 1339, and 1481 cm$^{-1}$. The wave numbers were derived from the study of the substance CNPC. Typically, these wave numbers correlate to the vibrational frequencies of various chemical bonds inside the material. These wave numbers indicate the molecular structure and makeup. Region I: This region, spanning 400 to 700 cm$^{-1}$, is associated with the bending vibrations of metal ion bonds such as Ca-O, as well as the network vibrations of the borate glass matrix B-O. The peaks at 458, 535, and 618 cm$^{-1}$ originate from these vibrations. area II: The second area, spanning 700-1100 cm$^{-1}$, is indicative of stretching vibrations within the borate network, particularly B-O stretching in $BO_3$and $BO_4$ units. The peaks at 705, 830, 883, and 998 cm$^{-1}$ can be ascribed to these vibrations, exhibiting changes based on the unique bonding environment. The peak at 1098 cm$^{-1}$ may signify the existence of B-O stretching. Region III: The third region, spanning 1200-1500 cm$^{-1}$, pertains to the asymmetric stretching of B-O bonds inside $BO_3$ units. The peaks at 1339 and 1481 cm$^{-1}$ presumably correspond to these vibrations, with positional shifts indicating alterations in the borate network structure and the impact of the included oxides CaO and $PbF_2$[2, 11].

The current scenario indicates that the numbers ranging from 458 to 536 cm$^{-1}$ are attributed to the vibrations of metal cations ($Ca^{2+}$, $Pb^{2+}$) [2, 10, 11].The O-B-O vibrations occur at a wavenumber of 618 $cm^{-1}$, while the stretching B-O-B in $BO_3$ units ranges from 705 to 830 $cm^{-1}$. The range of 883 to 998$cm^{-1}$corresponds to B-O stretching in borate groups, whereas the peak at 1098 $cm^{-1}$ is attributed to B-O-B elongations in the [$BO_3$] tetrahedron. The stretching vibrations of tetragonal $BO_3$ units occur at wavenumbers of 1339 $cm^{-1}$, while wavenumbers beyond 1481 $cm^{-1}$ are attributed to the anti-symmetrical stretching vibrations of B–O–B groups [22, 23].

**Table 3.** Assignment of IR absorption bands present in the spectra.

| Wavenumber ($cm^{-1}$) | IR Assignment |
|---|---|
| 458 | Metal cation ($Ca^{2+}$, $Na^{+}$, $Pb^{2+}$) vibrational modes |
| 535 | B–O bending vibrations |
| 618, 705 | Stretching vibrations of B O–B linkages in $BO_3$ units |
| 830, 553 | B–O stretching vibrations associated with non bridging oxygen atoms |
| 998 | O–B–O bending vibrations and B–O stretching vibrations |
| 1098 | B–O–B stretching vibrations in [$BO_4$] tetrahedral units |
| 1339 | Anti-symmetric stretching vibrations of B–O–B groups |
| 1481 | Asymmetric stretching vibrations of B–O bonds in $BO_3$ units |

## Conclusion

Sodium tetra borate glasses doped with calcium ions containing PbF2 & CuO were prepared by the melt quenching method. The samples prepared were characterized using XRD, UV-visible & FTIR. The obtained band gap values for the CNPC glasses were found to decrease from 3.000 to 2.181 eV with increasing CaO mole%. This decrease reveals the structural changes which are happening in the glass. The Urbach energy values for the CNPC glasses range from 0.5025 to 0.8818 eV .indicating that the glasses contain less defects in its glass structure. The increase in the Urbach Energy, decrease in the optical bandgap and decrease in molar volume values [shown in table1]with increasing mole % of CaO indicates an increase in the NBOs and decrease in the BOs. As a result there are more number of trigonal planar BO3 units compared to the number of tetrahedral BO4 structural units. Larger the number of BO3 structural units larger is the number of NBOs and hence thus larger the structural disorder and density of defects. Further the decrease in the optical bandgap values with increasing mole % of CaO implies that electronic transitions can take place with low energy photons. This feature enables the suitability of the prepared glass samples in energy devices like solar cells, in various optoelectronic devices and in radiation shielding applications.

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