



## Structural studies of $\text{PbF}_2\text{-CdO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses

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### ABSTRACT

The primary objective of the current publication is on the procedure of manufacturing lead fluoro cadmium bismuth borate glasses, as well as an investigation into the structural feature of the samples of glass that were made utilising FTIR and Raman spectra. The amorphous nature of the samples which were synthesised was revealed by the XRD spectra by its absence of strong peaks in the spectrum. Raman and infrared spectroscopy are both excellent tools for examining the local structure of prepared glasses. A deconvolution approach was applied to the Raman spectra in order to establish the precise locations of the bands in the spectra. In order to further enhance the reliability of the deconvolution of the Raman spectra, a residue plot was utilised. The Raman bands which were acquired from the spectra were allocated to the different vibrations of borate and bismuthate, in addition to the vibrations of the metal cations. There was a correlation between the amount of  $\text{PbF}_2$  found within these glasses and the shifting positions of the bands, which can be ascribed to the associated vibrations. Additionally, the samples have been examined using FTIR at frequencies ranging from 200 to  $1600\text{ cm}^{-1}$ . The FTIR analysis demonstrated the presence of the distinctive structural units of borate and bismuthate units. These units were found to be present. The distinctive connections that can be seen in the FTIR spectra point to the fact that bismuth oxide is functioning as a glass modifier.  $\text{BO}_3$  units are transformed to  $\text{BO}_4$  units when  $\text{PbF}_2$  is introduced to borate glasses, which are made of borate.

Key Words: Bismuth borate glasses; XRD; FTIR; Raman Spectra.

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### 1. Introduction

Recent studies on glassy materials has made significant strides in the development of transparent optical and shielding devices. Researchers have recently shown a great deal of interest in the development of innovative glassy materials containing heavy metal compounds as a result of the wide number of applications that may be found for these glasses in the various worlds.

Particularly, applications in the fields of ionisation radiation detection and shielding have found these particular sorts of glass materials to be beneficial [1-3]. These qualities have reportedly been enhanced as a result of several borate structural units, including  $BO_3$  and  $BO_4$  units, changing one another. Due to this reciprocal transformation of the borate units, the percentage of oxygen atoms which interconnect the two borate units gets higher, which is necessary for increasing the stiffness of these glasses [4-6]. Oxy-halide glasses are essential to the functioning of powerful laser systems due to the fact that these glasses are used in place of host substances in these systems. The formation of  $BO_3$  and  $BO_4$  units as the consequence of the incorporation of  $PbX_2$  into the borate formulation brought about yet a further substantial improvement in the material's transparent to IR radiation. Lead glasses with halides are used in optics owing to their distinctive optical properties. Both the development of technology for lasers and the drafting of optical fibres are examples of these kinds of uses. [7-9]. The structural characteristics of the materials, which may be determined using techniques like as XRD, FTIR, and Raman spectroscopy, amongst others, have a substantial impact on the strength of the materials. As a result of this, the authors looked into the properties of the  $PbF_2$ - $CdO$ - $Bi_2O_3$ - $B_2O_3$  spectrum using FTIR and Raman spectroscopy.

## 2. Experimental analysis

The glass samples were created using the melt-quenching process and had the necessary composition of  $xPbF_2$ - $10CdO$ - $20Bi_2O_3$ - $(70-x) B_2O_3$  in which  $x$  went up from 0 to 40 at the intervals of 10.  $PbF_2$ ,  $CdO$ ,  $Bi_2O_3$ , and  $H_3BO_3$  were purchased from the Sigma-Aldrich Company in order to make the glasses. Each of these substances had purity levels higher than 99.9%.

A mono pan balance was the instrument used for calculating the quantities of the chemicals that were employed in the composition. These chemical mixes were then deposited in crucibles and put into a furnace that continued to operate at a temperature of one thousand degrees centigrade. These combinations were swirled continuously throughout the melting process to ensure consistency throughout the mixture. After that, the mixture is cooled by placing it on a plate made of steel made of stainless, and the resulting glasses are annealed for twenty-four hours to remove the stress and strain from the samples and ensure that the created samples do not contain any bubbles. The glass compositions are given in Table 1.

**Table 1. Composition of  $x\text{PbF}_2\text{-10CdO-20Bi}_2\text{O}_3\text{-(70-x) B}_2\text{O}_3$  glass system in mole %**

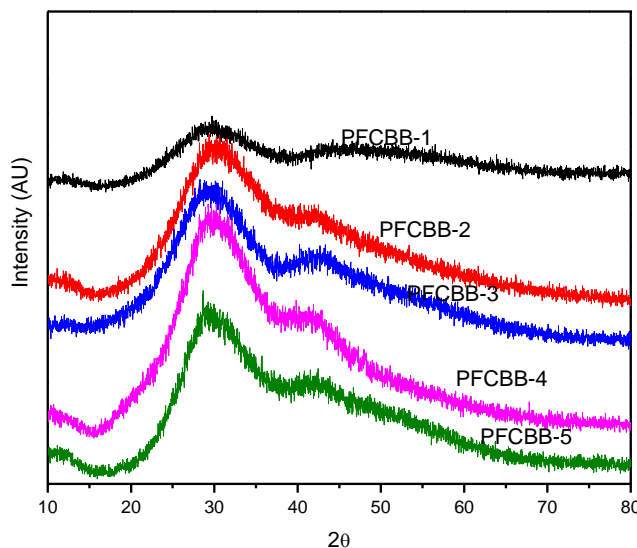
Sample code	Composition in mole %			
	$\text{PbF}_2$	$\text{CdO}$	$\text{Bi}_2\text{O}_3$	$\text{B}_2\text{O}_3$
PFCBB-1	0	10	20	70
PFCBB-2	10	10	20	60
PFCBB-3	20	10	20	50
PFCBB-4	30	10	20	40
PFCBB-5	40	10	20	30

X-ray diffraction patterns were taken for the present study on powdered samples using a Philips X-ray generator with Cu  $K\alpha$  radiation. In the present study, the structural investigation of glasses was performed using Perkin Emler Frontier FTIR spectrometer ranging from 400-4000  $\text{cm}^{-1}$  at an average of 32 scans with a resolution of  $1\text{cm}^{-1}$  and Raman spectra were recorded on J. Y. H. LABRAM- HR Raman spectrometer. In this experiment, every measurement was made at room temperature.

### 3. Results and discussions

#### 3.1 X-ray diffraction (XRD)

The samples' X-ray diffraction analyses support the existence of a crystalline structure with distinct Bragg characteristic peaks. The materials' long-range orderliness is what causes the strong peaks. The short-range order is indicated by the lack of such prominent peaks. Only short-range order, in particular in glassy materials, is dominant and exhibits no significant peaks. XRD patterns of the PFCBB glasses are displayed in Figure 1. This demonstrates that there in fact are no distinct peaks, which suggests the aforementioned PFCBB samples are of an amorphous texture.



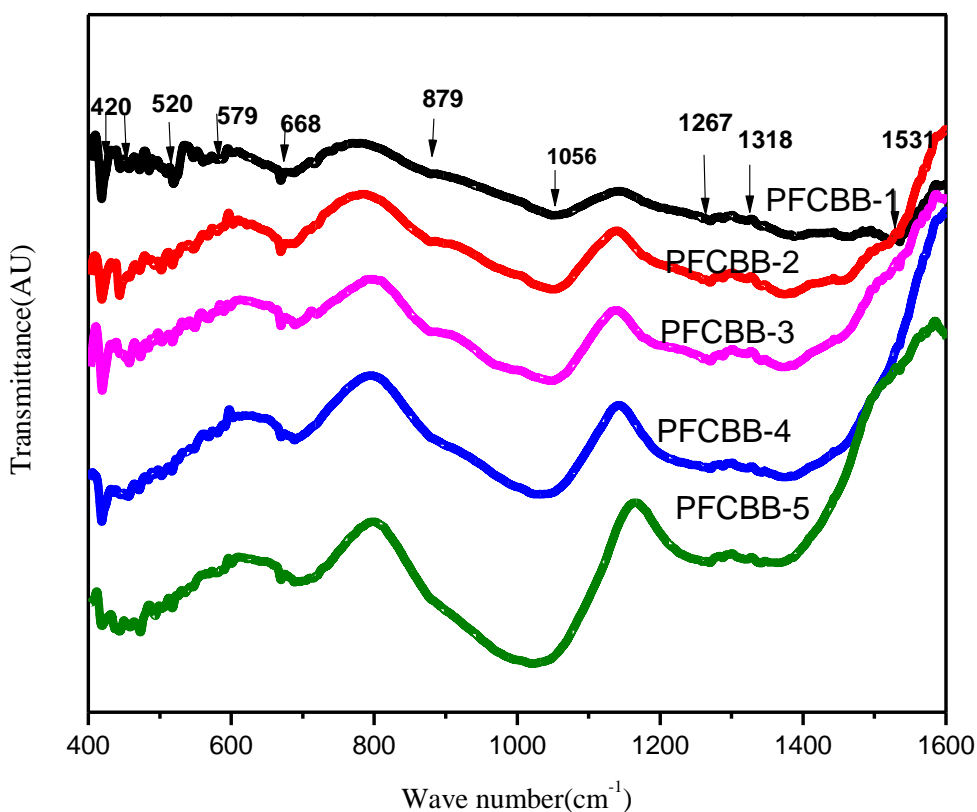
**Figure 1. XRD spectra of PFCBB glass system**

### 3.2 FTIR spectroscopy

The FT-infrared spectra in the wave number range between 400 and 1600  $cm^{-1}$  of PFCBB-1, PFCBB-2, PFCBB-3, PFCBB-4 and PFCBB-5 glasses are shown in **Figure 2**. There are three distinct regions that can be identified in the FTIR spectra of glasses that contain borate. The first region, which begins at 400  $cm^{-1}$  and continues all the way up to 780  $cm^{-1}$ , is where you'll find the bending modes of the various borate groups as well as the vibrations of the transition metal ions. The second zone is caused by the elongation of B-O bonds of tetrahedral borate groups ( $BO_4$ ), which is formed by vibrations of diborate to pentaborate groups. This zone ranges in frequency from 780 to 1100  $cm^{-1}$ . The third region, which begins at 1100  $cm^{-1}$  and continues all the way up to 1600  $cm^{-1}$ , is where the extended vibrations brought on by many trigonal  $BO_3$  units are addressed.

Deformed  $BiO_6$  units with Bi-O and metal cation ( $Pb^{+2}$ ,  $Cd^{+2}$ ) vibrations were the cause of the absorption band that was found between 420 and 520  $cm^{-1}$ . Both symmetrically extended Bi-O bonds on  $BiO_3$  pyramids and B-O-B vibrations on  $BO_3$  units have been accountable for the band that may be observed in the region approximately wave number 668  $cm^{-1}$ . The band at the wave number 879  $cm^{-1}$  was created by the symmetric growth of the Bi-O bonds that are present

in the  $BiO_3$  molecules. A broad infrared dip can be noticed when  $PbF_2$  is utilised, and it can be observed at  $1056\text{ cm}^{-1}$ [10]. The depth of the dip gets deeper when the amount of  $PbF_2$  that is included in PFCBB glasses gets steadily higher. The presence of this band has become increasingly evident inside the inner structure of the glass ever since the B-O-B elongations occurred in the  $BO_4$  tetrahedron. The observation of a vibration associated with stretching in tetragonal  $BO_3$  units provided support for the finding of an infrared band at a frequency of  $1267\text{ cm}^{-1}$ [11].

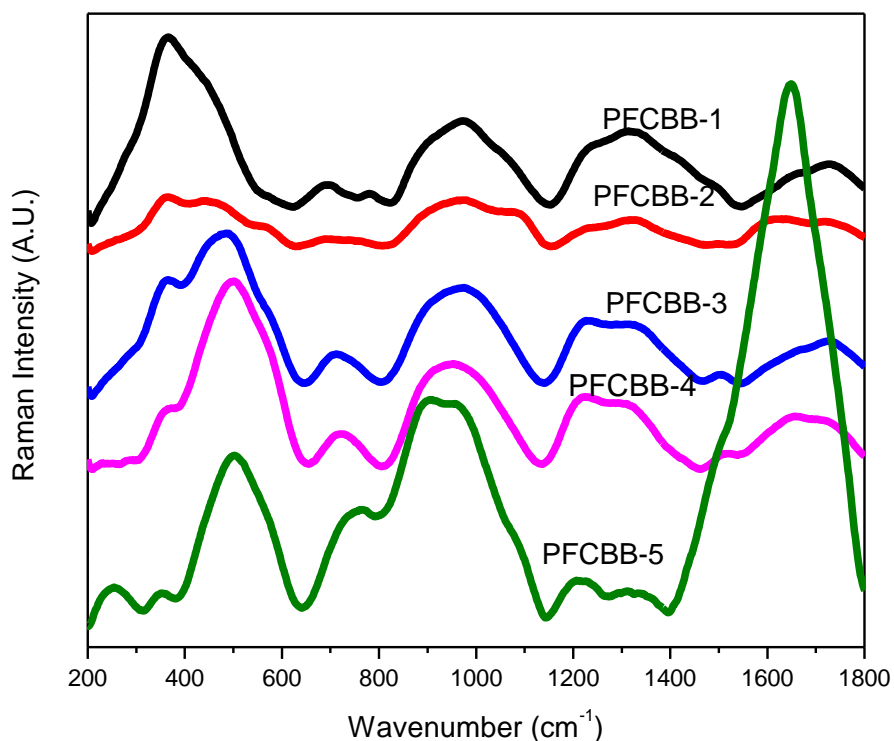


**Figure 2. FTIR spectra of PFCBB glasses**

### 3.3. Raman spectra

Vibrational spectroscopy is one of the numerous crucial techniques for figuring out the makeup of glasses. Glasses can be positioned throughout a 3D network and have structural elements that

are similar to crystalline samples despite having amorphous. Raman spectroscopy is one of the greatest useful vibrational spectroscopy methods for studying the interior structure of glass. The inelastic scattering chemical reaction can be thought of as a photon of light interacting with a substance to produce scattered radiation at various wavelengths. It is possible to think of this interaction as the cause of inelastic scattering. Nevertheless, not every one of vibration modes exhibit Raman activity uniformly. For this reason for an instance to be regarded as Raman active, the polarizability of the molecule must change and remain active regardless of whether the molecule communicates with the light well. Raman spectra of PFCBB glasses as shown in **Figure 3** and deconvoluted spectra as shown in **Figure 4**. Deconvoluted spectra are drawn for one sample to locate the exact positions of Raman bands. Residual graph shown in **Figure 5**.

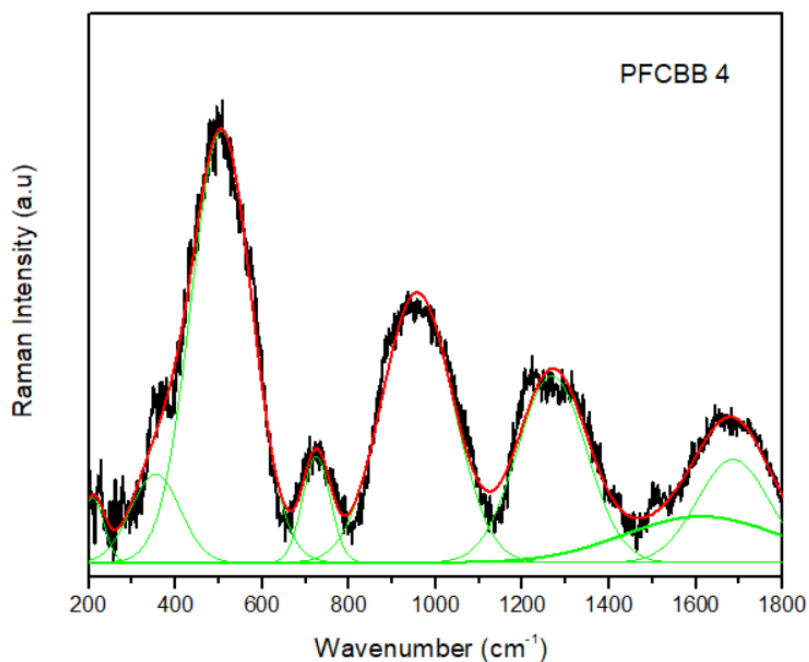


**Figure 3 Raman spectra of PFCBB glasses**

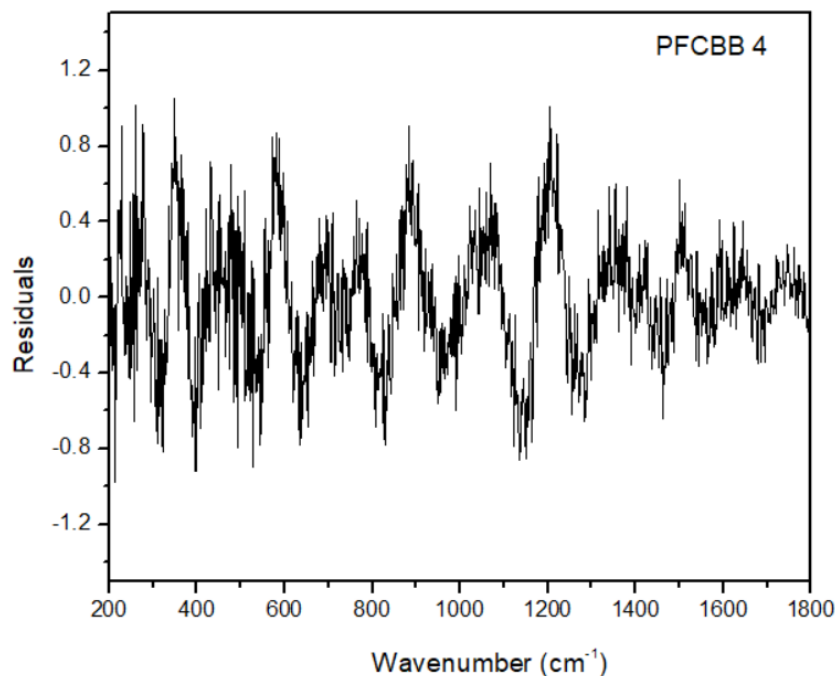
The bands observed at 366, 496, 694, 778, 972, 1212, 1318, 1503 and 1646  $cm^{-1}$ . The bands between wave numbers 366 and 496  $cm^{-1}$  were attributed to the symmetric stretching of Bi-O in  $[BiO_6]$  polyhedral, whereas 496  $cm^{-1}$  band was may be due to isolated diborates [12,13]. The

band at  $690\text{ cm}^{-1}$  proves the sample contains  $BO_2O_2^{3-}$  units. This peak resembles oxygen breathing vibrations in boroxol rings. Because of the likelihood of  $B\text{O}_4^-$  tetrahedra filling a new site abandoned by one or two  $B\text{O}_3$  triangles, the band at  $781\text{ cm}^{-1}$  has enlarged. The band at  $972\text{ cm}^{-1}$  represents Bi-O bond symmetrical extending vibrations in  $[BiO_3]$  units [12, 14].

The existence of diborate groups can be deduced from the Raman band that is observed at a wavelength of  $1212\text{ cm}^{-1}$  [12, 15]. The band that can be seen at  $1318\text{ cm}^{-1}$  has been categorised as belonging to extended B-O bands, which are linked to borate groups. Additionally, this band can be explained by  $B\text{O}_2O^-$  triangles that are linked to  $BO_4^-$  units [14, 15]. The bands with a frequency that is more than  $1503\text{ cm}^{-1}$  are the ones that have been attributed to being B-O expanding modes, and they entail one NBO of  $[BO_3]$  triangles [16].



**Figure 4** De Convoluted Raman spectra of PFCBB glasses



**Figure 5 Residual Raman spectra of PFCBB glasses**

#### 4. Conclusions

The melt quenching process was employed in the production of glass samples that had the formula  $x\text{PbF}_2\text{-}10\text{CdO-}20\text{Bi}_2\text{O}_3\text{-(}70\text{-}x\text{) B}_2\text{O}_3$ , in which  $x$  went up from 0 to 40 at the intervals of 10. These intervals were spaced by ten apart. In order to gain a deeper understanding of the glass structure, the samples that were collected were analysed using spectroscopic techniques such as XRD, FTIR, and Raman. In the beginning, the XRD spectra showed that the samples were in an amorphous state by observing the absence of distinctive sharp peaks in the spectra. The FTIR spectra made it clear that there were three distinct groups present, namely borate, bismuth, and metal cation. The rise in the intensity of the depth of the IR band near  $1056\text{ cm}^{-1}$  was observed in all of the samples, which provided evidence that  $\text{BO}_3$  units were converted into  $\text{BO}_4$  units. Raman spectra that had been deconvoluted were analysed in order to pinpoint the precise locations of the Raman bands, and a residue plot was created in order to check how accurately the deconvolution had been performed. The Raman bands locations were found to be the same in all of the glass samples; however, small differences were seen with increasing  $\text{PbF}_2$  level in the PFCBB glasses. It was determined that each of the band positions could be mapped to a corresponding borate or bismuth vibration.



## 5. References

- [1] H. Aboud, M.J.R. Aldhuaibata, Yasser Alajermi, Radiation shielding traits of bismuth–cadmium–barium-borate glasses: Role of lead activation, *J. Phys. Chem. Solids* 164 (2022), <https://doi.org/10.1016/j.jpcs.2022.110597>.
- [2] K. Chandra Sekhar, B. Kavitha, N. Narsimlu, Vasant Sathe, Miysoon A. Alothman, I.O. Olarinoye, M.S. Al-Buriahi, Md. Shareefuddin, Enhancement of shielding ability using  $PbF_2$  in Fe-reinforced bismuth borate glasses, *J. Mater. Sci.: Mater. Electronics* 32 (2021) 23047–23065, <https://doi.org/10.1007/s10854-021-06788-4>.
- [3] Y.B. Saddeek, A. El-Denglawey, H. Doweidar, Role of  $Al_2O_3$  in  $Al_2O_3$ – $Bi_2O_3$ – $P_2O_5$  glasses, *Appl. Phys. A* 127 (2021) 868, <https://doi.org/10.1007/s00339-021-05017-3>.
- [4]. Z.A. Alrowaili, H. Ali, S. Alomari, N. Al-Qaisi, C. Alwadai, I.O. Eke, C. Olarinoye, Mutuwong, M.S. Al-Buriahi, Silicate glass system and significant role of  $Bi_2O_3$  on radiation protection ability against gamma, neutron, and charged particle. *Radiat. Phys. Chem.* 203, 110609 (2023)
- [5]. M.M. Hivrekar, D.B. Sable, M.B. Solunke, K.M. Jadhav, Network structure analysis of modifier  $CdO$  doped sodium borate glass using FTIR and Raman spectroscopy. *J. NonCryst. Solids* 474, 58 (2017). <https://doi.org/10.1016/j.jnoncrysol.2017.08.028>
- [6]. K. Chandra Sekhar, N. Narsimlu, M.S. Al-Buriahi, H.A. Yakout, I.O. Olarinoye, S. Alomairy, Md. Shareefuddin, Synthesis, optical, and radiation attenuation properties of  $CaF_2$ – $TeO_2$ – $Na_2B_4O_7$ – $CuO$  glass system for advanced shielding applications. *Eur. Phys. J. Plus* 136, 903 (2021). <https://doi.org/10.1140/epjp/s13360-021-01906-x>
- [7]. J. Pisarska, L. Zur, W.A. Wojciech, Structural, Optical characterization of Dy-doped heavy-metal oxide and oxyhalide borate glasses. *Phys. Status Solidi A* 209, 1134 (2012). <https://doi.org/10.1002/pssa.201127555>
- [8]. K. Chandra Sekhar, A. Hameed, V.G. Sathe, M. Narasimha Chary, Md. Shareefuddin, Physical, optical and structural studies of copper-doped lead oxy chloro borate glasses. *Bull. Mater. Sci.* 41, 79 (2018). <https://doi.org/10.1007/s12034-018-1604-4>

- [9]. K. Katubi, A.A. Mohammedsaleh, Z.A. Ibraheem, Norah Alwadai, I.O. Alrowaili, C. Olarinoye, Sriwunkum, M.S. AlBuriahi, Enhancement on radiation shielding performance of  $B_2O_3+Li_2O+ ZnO+ Na_2O$  glass system. *Radiat. Phys. Chem.* 201, 110457 (2022)
- [10]. S. Rajesham, K. Chandra Sekhar, Md. Shareefuddin, J. Siva Kumar, Synthesis, physical, optical and structural studies of  $B_2O_3- CdO- Al_2O_3- PbF_2$  glasses modified with  $MoO_3$  ions *Optik* 272 (2023) 170241
- [11]. G. Chandrakiram, Y.A. Kumar, A.K. Singh, , A Review on Infrared Spectroscopy of Borate Glasses with Effects of Different Additives, *ISRN Ceram.* 428497 (2012)
- [12]. L. Haritha, S.K. Chandra, R. Nagaraju, G. Ramadevudu, V.G. Sathe, M.d. Shareefuddin, Effect of metal fluorides on chromium ions doped bismuth borate glasses for optical applications, *Chin. Phys. B* 28 (3) (2019), <https://doi.org/10.1088/1674-1056/28/3/038101>
- [13]. R. Nagaraju , B. Devaiah , L. Haritha , K. Chandra Sekhar , Md. Shareefuddin , M. A. Sayed , G. Lalitha , K. Vijaya Kumar, Influence of  $CaF_2$  on spectroscopic studies of lead fluoro bismuth borate glasses doped with  $Cr^{3+}$  ions, *Journal of Non-Crystalline Solids* 560 (2021) 120705.
- [14]. Y.B. Saddeek, H.M.H. Zakaly, K.C. Sekhar, S.A.M. Issa, T. Alharbi, A. Badawi, M Shareefuddin, Investigations of mechanical and radiation shielding properties of  $BaTiO_3$ -modified cadmium alkali borate glass, *Appl. Phys. A* 128 (2022) 1–10, <https://doi.org/10.1007/s00339-022-05413-3>.
- [15]. R. Ciceo-Lucacel, I. Ardelean, FT-IR and Raman study of silver lead boratebased glasses, *J. Non-Cryst. Solids* 2007 (2020) 353, <https://doi.org/10.1016/j.jnoncrysol.2007.01.066>
- [16]. A.K. Yadav, P. Singh, A review of the structures of oxide glasses by Raman spectroscopy, *RSC Adv.* 5 (2015) 67583–67609, <https://doi.org/10.1039/C5RA13043C>.