Spectroscopic Studies of Chromium Doped Boric Acid Glass (BAG)

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Abstract:- Chromium-doped boric acid glasses (BAG) were synthesized by rapid quenching techniquein appropriate proportions of a mixture of H_3BO_3, Pb_2O_3, and ZnO in the temperature range of 1050^0C-1150^0C. Cr_2O_3 has been used to dope chromium ions as Cr^{3+}. Optical spectra were recorded by UV-VIS and Raman spectroscopy. The glassy nature of the samples has been confirmed by X-ray diffraction (XRD). Laser Raman spectra have been recorded using 532nm and 750nm to study the vibrational nature of the glass structure. Chromium-doped boric acid glasses show BO_3 and BO_4 structural units in the FT-IR studies.Chromium-dopedboricacidglassesshowBO_3andBO_4structuralunitsintheFT-IRstudies.

Keywords*:Boric acid glasses (BAG), X-raydiffraction(XRD), Spectroscopy of UV-VIS ,absorption, FTIR.*

1. Introduction

Glasses form a versatile matrix in condensed matter studies that combines optics and material science. Glasses due to their reflectivity and transmittance properties find immense technological and industrial uses. In optics, glasses form the basic material for lenses, mirrors, beam splitters, etc. Modern optics have emerged with nonlinear properties, which makes glasses with immense importance, both technologically and scientifically. Due to a lack of perfect symmetry, possessing only short-range order, glasses form very good matrices for a nonlinear optical system. Doping of glasses finds technological and scientific uses like IR glasses used in IR technology [1]. The emergence of optical limiting glasses is a novel application. Glasses also find tremendous application in modern laser systems [2]. For example, Nd: Glass laser and Er: Glass laser. Glasses when synthesized as fibres have also revolutionized the optical fibre and communicationindustries. Chalcogenide glasses have been investigated to a large extent to synthesize novel glass matrices [3]. Fibre-based laser example: Erbium-doped in fibres and thulium-doped in fibres have made the integrated optical systems and photonics [4]. Laser technology and novel femtosecond laser systems have emerged as promising fields for doped and undoped glasses [5]. For example, prism pairs have been used in Titanium sapphire femtosecond laser cavities to compensate for dispersion losses in the ring cavity. Recently Dye doped glasses have shown significant optical limiting behaviour [6]. Phosphor glass is another system that in which glasses matrix is used with nanodopends. Rare-earth ions have shown significant transition in such phosphor systems [7].

1.1. *Chromium doped BAG (Boric Acid Glass)*

Chromium a transition metal ion is interesting from a spectroscopic point of view since it gives spectral lines at different wavelengths [8]. Boric acid glass provides a stable matrix for its confirmation ofits structure. It is well known that chromium gives the laser lines emitted from the ruby crystal matrix. Recently chromium doped lasers of varied structures with varied technology are being fabricated for scientific work. Chromium-doped lasers system has emerged as promising lasers both in a glass matrix and as a crystalline matrix [9]. The energy level scheme of chromium is shown below in Figure 1.

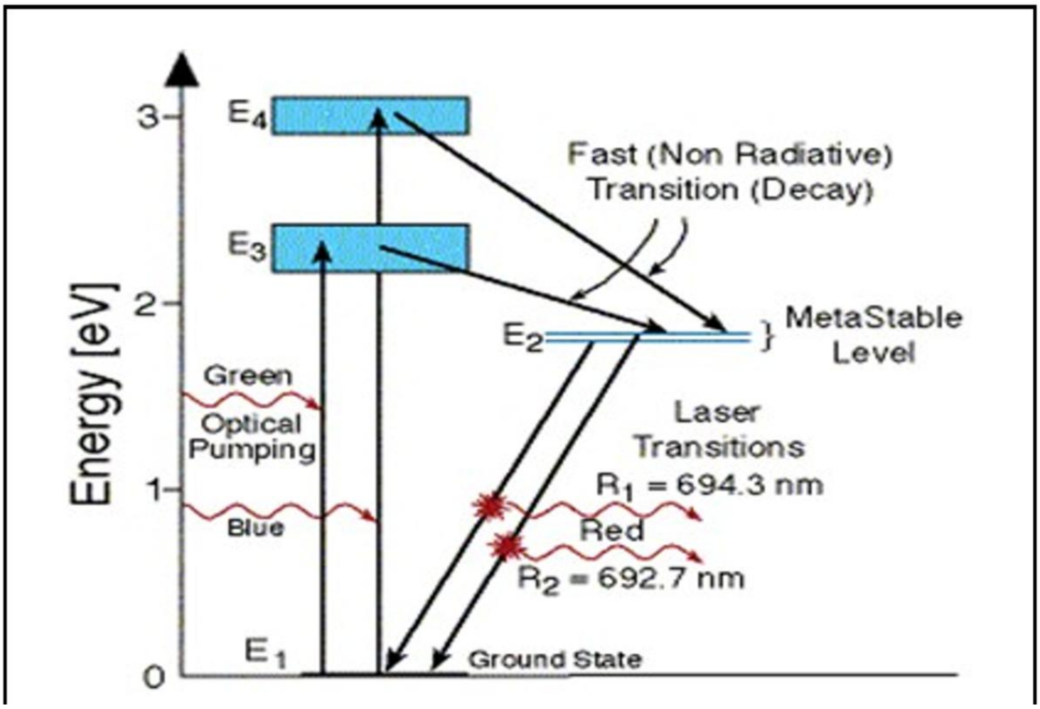

Figure1.EnergylevelschemeofChromiuminRubycrystal

In alkaline or heavy metal oxide environments, boric acid glasses form a stable matrix. Small concentrations of chromium ions, in particular, can alter the glass and change its linear and nonlinear optical properties. In BAG: Cr glasses, however, Cr^{3+} is the most abundant oxidation state. Because all glasses lack a long ranger order, the positions of Cr^{3+} vary depending on the locations of the ligands, the coordination number, and the average distance of central ion ligands [11].

2. Experimental

A series of four glass systems with the compositions of $50H_3BO_3$-$30PB_3O_4$-(20-X) ZnO-XCr_2O_3, Where X=0.7,0.8,0.9,1.0, and 1.1 were synthesized using the conventional rapid cooling technique. For the synthesis of glass samples, oxide powders of each reagent with purities not less than 99.99% were utilized.Using an agate mortar, all of the oxide particles were thoroughly blended with the correct molar ratios. The batches of 12g of powders were made and were then melted in a porcelain crucible in an electric muffle furnace under ambient conditions at temperatures ranging from 1015^0C to 1115^0C. For an hour, the powders were maintained at these temperatures. [13].The glass melts were then transferred rapidly over to a stainless-steel mold. The obtained glasses had meltedto form light greenish glasses

Table 1. Briefly, the glass composition is shown in Table 1. We have synthesized samples (A, B, C, and D) as below

GLASSSAMPLE	H_3BO_3 (mol%)	Pb_2O_4 (mol%)	ZnO (mol%)	Cr_2O_3 (mol%)
A	50	30	20	---------
B	50	30	19.30	0.7
C	50	30	19.20	0.8
D	50	30	19.10	0.9

2.1. X-Ray Diffraction

The broad peaks show the glassy nature of the sample. Typical powder XRD patterns for BAG glasses with and without chromium ion doping are shown in Figure 2.[10]

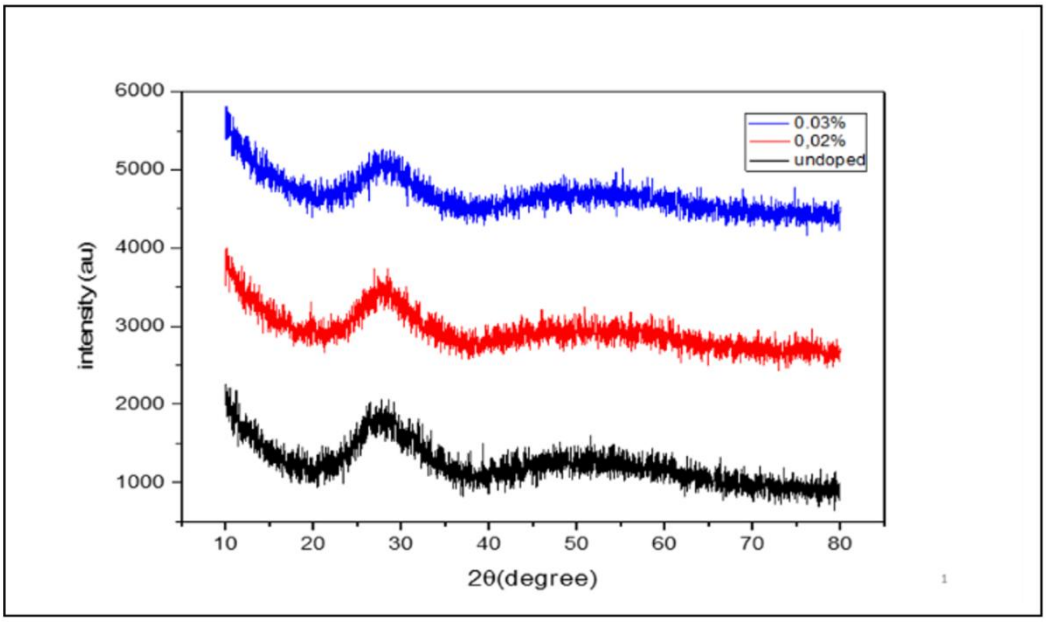

Figure2.XRDdataforChromiumiondopedandundopedBAGglass

2.2. ***Spectroscopy of UV-VIS absorption***

In the range of 200nm to 800nm, UV-VIS absorption spectra have been recorded.A typical Absorption plot for Cr_2O_3: BAG glass is given below in Figure 3.

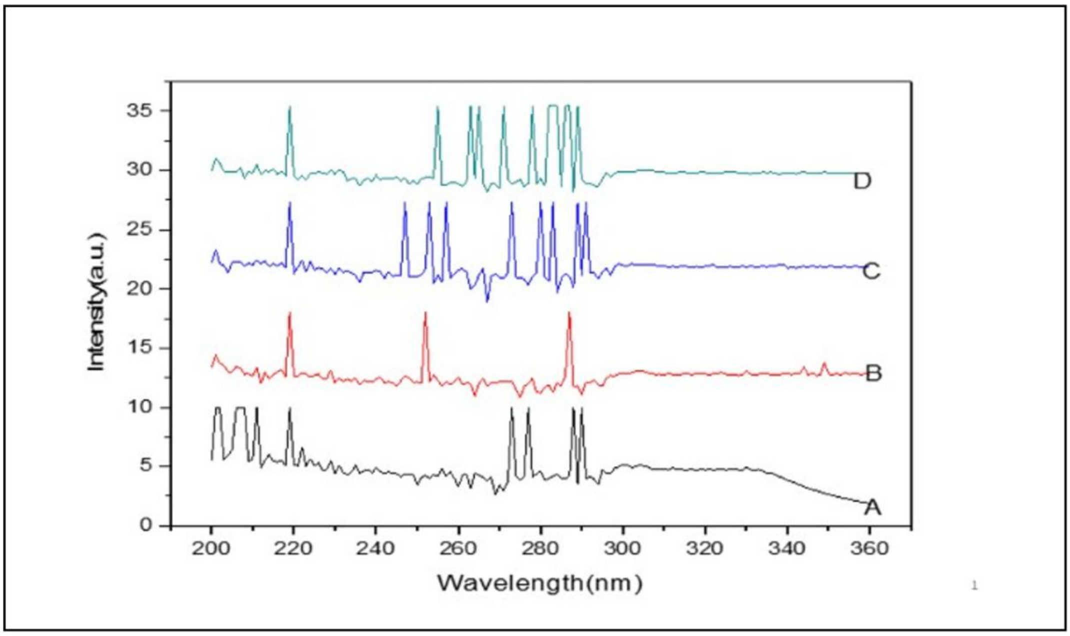

Figure 3.Absorption Data of Cr_2O_3 Doped BAG

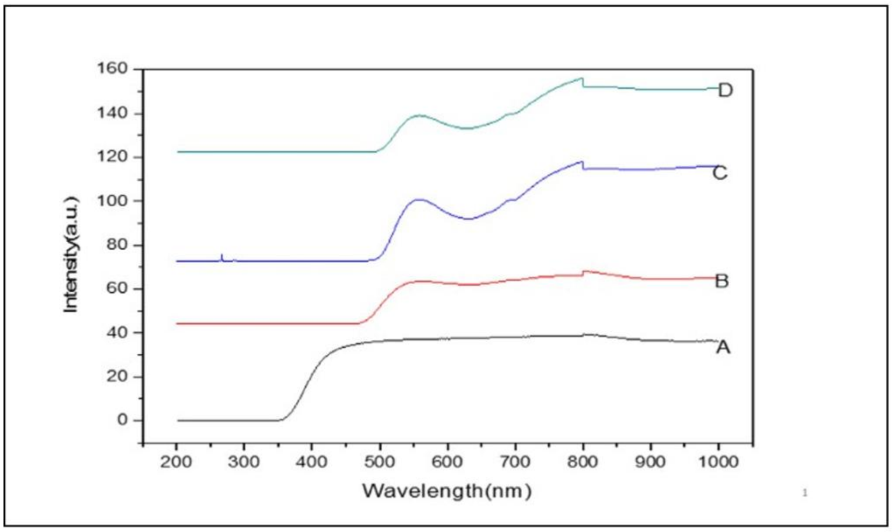

Figure 4. Transmittance Data of Cr_2O_3 Doped BAG

The two other peaks, at about 220 nm and 273 nm, are observed in all samples, but the peak at about 265 nm is notobserved in plots A and B of Figure 3.With rising concentration, the peak at 273 nm shifts to longer wavelengths and gains intensity. It is also clearly shown in Figure 3 that the peak at around 292nm is composed of several smaller peaks of different intensities.This absorption band undergoes broadening slightly as concentrationincreases, and the maximum absorptivity declines and shifts to longer wavelengths.[14]

2.3. FTIR Spectra

FTIR spectra of Cr^{3+} doped borate glasses are shown in Figure 5.Bands are identified in the range 400–500 cm^{-1} due to the bending vibrations of B–O–B linkages. In the range 500–800 cm^{-1} due to ZnO vibrations resulting from ZnO units, and in the range 800-1140 cm^{-1} due to the B–O symmetric stretching vibrations of BO_4 units are observed.Due to the vibrational modes of the hydroxyl or water group present in the glass system,[23] the vibrations bands appear at about 1638 cm^{-1}. In the region around 1660 cm^{-1}, O-H bending vibrations are present due to low concentration in the glasses.Table 2 shows the FTIR spectrum for Chromium doped andundoped BAG glass for various concentrations, compared with the work of Jayasankar et. al. [19]

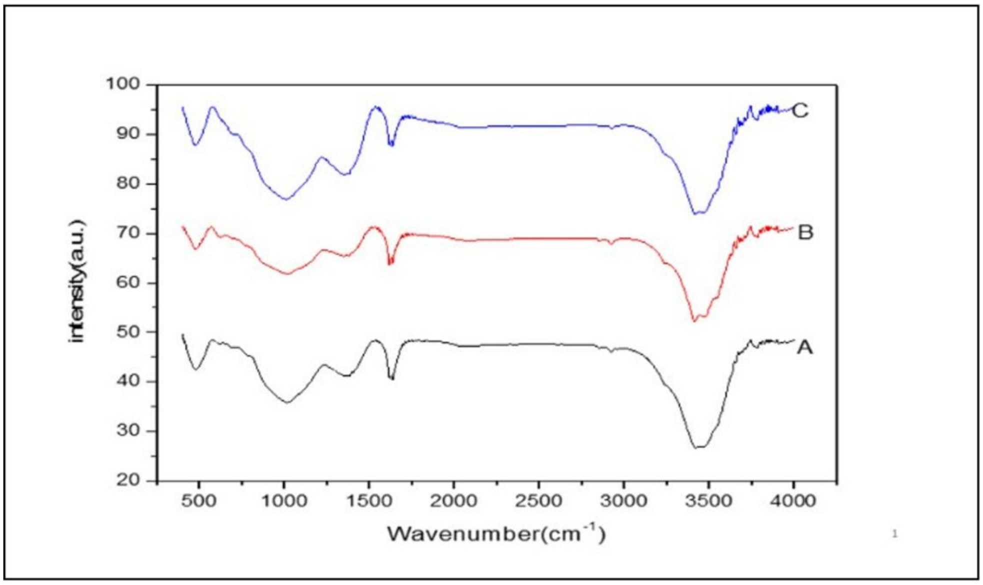

Figure 5. FTIR Spectra of Cr_2O_3 Doped BAG

Table 2.
The FTIR band positions (cm^{-1}) and their assignments ofCr-doped glass samples.
(Concentration in grams)

Cr(undoped)	Cr (0.02)	Cr (0.03)	band assignments
480.82	476.65	476.94	angle modification of B-O-B linkage
---------	526.09	---------	Zn-O vibrations of ZnO units
1019.94	1010.21	1019.94	B-O stretching vibrations in BO_4 units from the tri, tetra, and penta borate group
1384.33	1352.91	1354.02	Trigonal (BO_3) Units B-O stretching vibrations in different borate group
1638.02	1638.21	1638.33	O-H bending vibrations of water molecules
3419.45	3419.45	3415.88	C-H bending vibrations
3660.2	3659.85	3659.91	O-H stretching vibrations (low concentration)

2.4. Raman spectroscopy

Raman spectral studies using the 532nm as the exciting source have been done for undoped and Chromium doped boric acid glass using the WITEK model Alpha 300R Spectrometer. Experimental data for the sample are given in Figures 6 and 7 exposed using532nm laser and 785nm laser lines respectively.

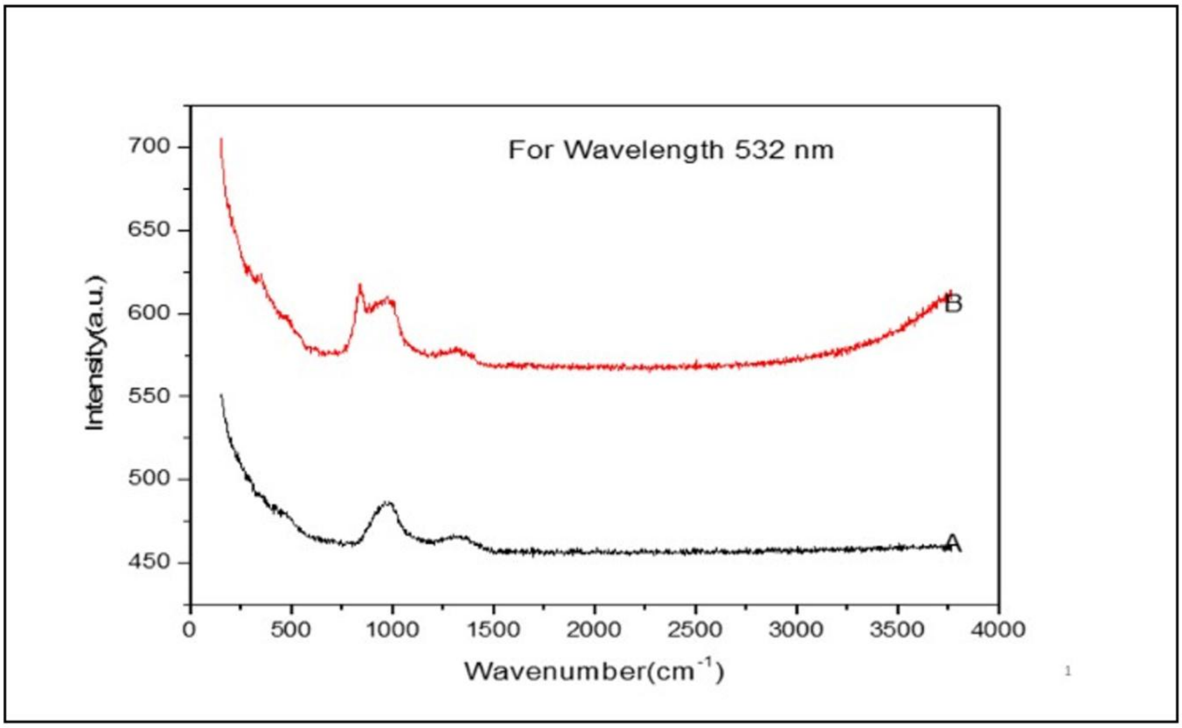

Figure 6. Raman spectra of Cr_2O_3 doped BAG glass at 532 nm

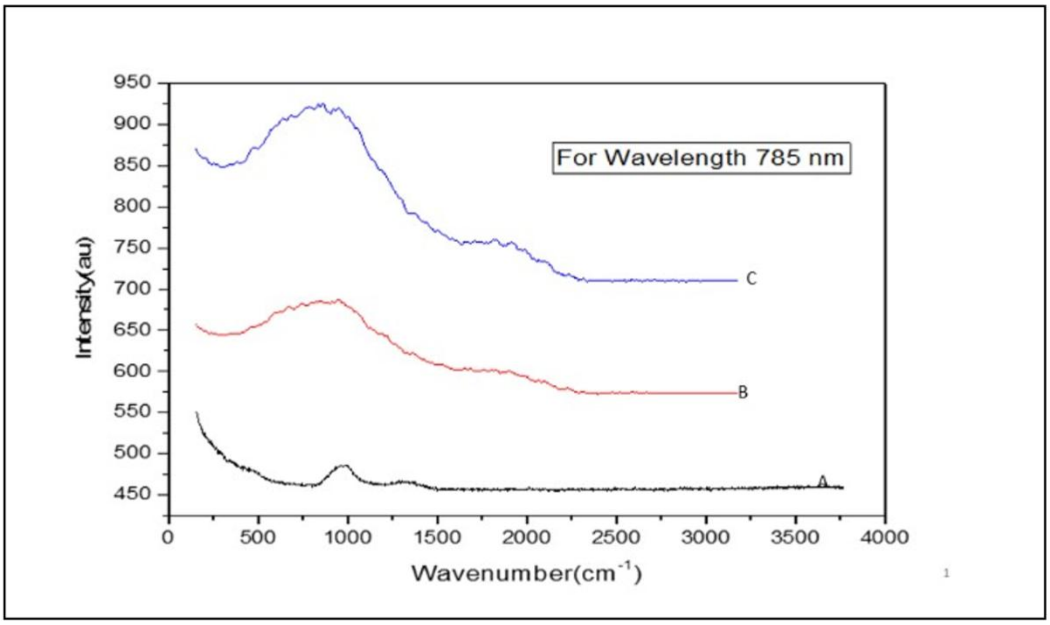

Figure 7. Raman spectra of Cr_2O_3 doped BAG glass at 785 nm

Raman spectra show differences in the lines but show five peaks as in Figure 6. Raman spectra for undoped glass show 2 to 3 well-shaped peaks for plot A as in Figure 6. Also, the plot of doped glass shows more peaks than undoped glass and has shifted to a higher wavelength in this case for plot B [21]. Figure 7 shows the Raman spectra observed for 785nm laser excitations. Broad peaks are seen for (B and C) which are doped whereas undoped sample A shows a relatively narrower peak.[22],[30]. These peak positions have been analyzed in Table: 3.

Table3. Raman Peak positions (cm^{-1}) for Cr_2O_3: BAG glass samples at different wavelength are tabulated below:

S.no.	For wavelength 532nm		For wavelength 785nm		
	A	B	A	B	C
1.	200	200	200	-----	-----
2.	400	------	----	800	800
3.	800	----	1000	------	----
4.	1000	1000	1300	-----	----
5.	1300	1300	-----	1900	1900

3. Conclusions

Present work was focused on studies of spectroscopic properties of chromium-doped BAG (Boric Acid Glass). Using Absorption, Raman, and FTIR spectrawe have characterized the (Cr_2O_3: BAG) synthesized glasses. The Raman spectra have been recorded for two wavelengths. For the 785nm excitation, the identical peak of 1000 cm^{-1} had been broadened after being doped by chromium for the Cr_2O_3: BAG system. This isinhomogeneous broadening occuring in glasses. FTIR studies show a broadening of peaks at 3400cm^{-1} as dopend concentration is increased. The broad peak in XRD patterns shows the glassy nature of the sample. The FTIR spectra of the present glass reveal the presence of Cr^{3+} ions in the glass matrix. Doping gives broadening of different peaks. Further nonlinear optical studies are being planned for these glasses.

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References

[1] G. Susoy"The impact of Cr_2O_3 additive on nuclear radiation shielding properties of LiF–SrO–B_2O_3 glass system," *Materials Chemistry and Physics*, **242,** 1527-1541,**2020**

[2] Mikhail A. Eronyan"Cr_2O_3 Doping Efect on Silica Glass Cooling Rate,"*Springer Nature B*, **15,**3479–3483,**2023**

[3] M S Sadeq"Influence of ZnO on the structural, optical, ligand field and antibacterial characteristics of sodium borosilicate glasses containing minor Cr_2O_3 additions,"*Phys. Scr.*,**98,**055933,**2023**

[4] Lokeswararao K "Physical, spectroscopicproperties of PBO – GEO_2glasses doped with CR_2O_3,"

[5] UGC Care Group I Listed Journal, **13**,136-142,**2023**

[6] Shamima Hussain"Effect of ZnO nanoparticles on physical, optical and radiation shielding properties of Bi_2O_3-B_2O_3-Cr_2O_3 glasses,"*Journalof Elsevier*,**12**,14–17, **2023**

[7] K. M. Jadhav "Nonlinear Optical Limiting and Radiation Shielding Characteristics of Sm_2O_3DopedCadmium Sodium Lithium Borate Glasses,"*Materials*,**15**, 1-14, **2022**

[8] A.H. Oravy"Structural and optical absorption studies on Cr_2O_3 doped SrO-P_2O_5 glasses,"*SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy*,**228,**163-166, **2020**

[9] Shuai-Jie Qu"Chromium arc plasma characterization, structure and properties of CrN coatings prepared by vacuum arc evaporation,"*Vacuum*,**209**,1165**, 2023**

[10] Ekaterina Kulpina "Lithium concentration effect on crystallization kinetics and spectral properties of Cr-doped Li_2O–K_2O–Al_2O_3–B_2O_3 glass-ceramics,"*Ceramics International*,**49**,20061–20070, **2023**

[11] LinganaboinaSrinivasaRao"Effect of ZnO nanoparticles on structure and magnetic properties of Bi_2O_3-B_2O_3: Cr_2O_3 glasses,"*Materialstoday proceedings,**56***,2483-2487, **2023**

[12] Afaf M. Babeer"Ligand field parameters, optical, thermal, magnetic, and structural features of ZnO containing cobalt-borate glasses"*Materials Chemistry and Physics***., *302*,** 281-288, **2023**

[13] F Rasheed "Disorder and the optical spectroscopy of Cr3+-doped glasses,"*J. Phys.: Condense.Matter*,**3**,3825-3840**(1991**).

[14] Marina Kanon "Crystallization of Cristobalite in Sodium Borosilicate Glass in the Presence of Cr_2O_3,"*Materials*,**16(14)**,19–27, **2023**.

[15] Lulu Song "Structural investigation of lithium borate glasses by Raman spectroscopy: Quantitative evaluation of structural units and its correlation with density,"*Journal of Non-Crystalline Solids*,**616**,99–104, **2023**

[16] R. Raja Ramakrishna"Structure and nonlinear optical studies of Au nanoparticles embedded in lead lanthanum borate glass,"*Elsevier* user license, 1-7, **2014**

[17] B R Venkateswara Rao"Spectroscopic studies of chromium doped alkali earth lead zinc phosphateglasses,"*Indian J Phys*,**89(1),**73–80, **2015**

[18] Silvia Barvbi"Structural and optical properties of rare-earth-doped barium bismuth borate glasses,"*Journal of non-crystalline solids*,**481**, 239-47**, 2018**

[19] Tiantian Yin "Characterization of the anomaly in immediate aqueous interactions of sodium borate glasses by dynamic vapour sorption with in-situ Raman,"*Ceramics International*,**49,** 28934-42, **2023**

[20] C.K. Jayasankar"A critical review and future prospects of Dy^{3+}-doped glasses for white light emission applications," *Optik*,**266**, 65-79,**2022**

[21] Artur G. Santos"Discoveries about the structure of alkaline earth-bearing borosilicate glasses doped with TiO_2 revealed by Raman spectroscopy,"*J.Am. Ceram. Soc*.,**80**,2903-909,**1997**

[22] Y.D. Yiannopoulos"Structure and Properties of alkaline earth borate glasses,"*Journals of Non-Crystalline solids*,**578,** 164-72**, 2022**

[23] R. Nagaraju, L. Haritha, K. Chandra Sekhar, Md. Shareefuddin, G. Lalitha,"Study of mixed heavymetal fluoride bismuth borate glasses for optical application*," journal of material science:materials in electronics***33**, 14397–14408, **2022**

[24] G. Nagarajn, K. Chandra Sekhar, Md. Shareefuddin, D. Karuna Saga, "FTIR and Raman analysisof $PbBr_2$-CdO-Bi_2O_3-B_2O_3 glasses," *materialstoday proceedings***2023**

[25] Djamilaaboutaleband brahimsafi, "annealing effect on copper-doped sodo-borateglasses ($Na_2O_4B_2O_3$)," *hungarianjournalof industry andchemistry* **51(1),**15–22,**2023**

[26] A.M. Othman, Z.M. Abd El-Fattah, M. Farouk, A.M. Moneep, Moukhtar A. Hassan,"Opticalspectroscopy of chromium doped bismuth-lithium borate glasses,"*Journal of non-crystallinesolids*,**558,2021**

[27] R. Nagaraju,L. Haritha, K. Chandra Sekhar, "Study of mixed heavy metal fluoride bismuthborateglasses for optical applications,"*Journal of Materials Science: Materials in Electronics,* **33,**14397-14408**,2022**

[28] S. Y. Marzouk, M. A. Azooz, H. M. Elsaghier, Nehad A. Zidan & W. Abbas,"Structural and optical properties of barium titanium borate glasses doped with ytterbium," *Journal of MaterialsScience: Materials in Electronics,***33**,18054–18071, **2022**

[29] Bejjipurapu Chandrasekhar, "Optical Absorption and Emission Spectral Properties of ZnO-$Bi_2O_3B_2O_3$:TiO_2 Glasses,"*Bulgarian Journal of Physics,* **33,**1-7,**2022**

[30] D. Manara, "Advances in understanding the structure of borosilicate glasses: A Ramanspectroscopy study," *American Mineralogist*, **94**, 777–784, **2009**

[31] Samia E. Ibrahim, R. El-Mallawany& A. S. Abouhaswa, "Structural, Optical and DielectricProperties of Tellurite Borate Glasses Doped with Cerium Oxide," *Journal of Inorganic andOrganometallic Polymers and Materials*,**2023**