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"Synthesis, Characterization, And Optical Properties Of Gadolinium Doped Bismuth Borate Glasses"

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Abstract
This study presents the synthesis and characterization of gadolinium-doped bismuth borate glasses (80 B_2O_5 + 10 Bi_2O_3 + 5 CdO + (5−x) Li_2O + x Gd_2O_3) using the melt-quenching method. Optical properties were analysed using UV-Vis spectroscopy, determining the energy gap (Eg) and Urbach energy (Eu), providing insights into the electronic structure and disorder in the material. The amorphous nature of the glasses was confirmed through SEM and EDAX analysis. Density was measured using Archimedes' principle. FTIR spectra were recorded to investigate the vibrational modes, and photoluminescence properties were studied to explore potential optical applications. The results offer valuable information for the potential use of these glasses in optoelectronic and photonic applications.

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I. Introduction

Bismuth-based borate glasses have garnered attention in the last few decades due to their unique optical and structural properties, making them promising candidates for a variety of applications, including optical fibers, laser technologies, and radiation shielding [1][2]. The high refractive index and the presence of heavy metal oxides, such as Bi_2O_3, contribute to enhanced shielding properties, especially in gamma radiation [3]. Borate glasses, specifically those with compositions containing Bi_2O_3 and Li_2O, have been studied for their high thermal stability, low processing temperatures, and favorable radiation protection abilities [4][5].

The incorporation of rare-earth elements such as gadolinium (Gd) into borate glasses introduces fascinating possibilities for modifying their optical and luminescent properties. Gadolinium oxide (Gd_2O_3) is particularly notable for its high atomic number, which enhances the ability of these glasses to absorb radiation [6][7]. Moreover, Gd-doped borate glasses have shown promising results in luminescence applications, particularly in the field of scintillation [8][9].

The role of cadmium oxide (CdO) in such glass systems is also of interest, as CdO can act as a network modifier that influences both the structural and optical properties of the glass. CdO-doped glasses exhibit superior thermal stability and improved optical properties due to their ability to form stronger bonds within the glass network [10][11].

In this study, we focus on the investigation of the composition **80 B_2O_5 + 10 Bi_2O_3 + 5 CdO + (5−x) Li_2O + x Gd_2O_3**, where x = 0, 0.1, 0.5, 1.0, and 1.5. The variation of gadolinium content is expected to provide insights into how doping with rare-earth elements influences the thermal, structural, and optical characteristics of borate-based glasses. Specifically, we aim to understand the relationship between Gd_2O_3 concentration and the material properties, such as refractive index, density, and radiation shielding capability.

The combination of these materials Bi_2O_3, CdO, Li_2O, and Gd_2O_3 opens avenues for the development of glasses that can be fine-tuned for specific applications in fields ranging from photonics and optoelectronics to radiation protection [12][13]. Recent studies have explored the synthesis and characterization of similar glass systems, emphasizing their potential for high-performance optical and radiation shielding applications [14][15].

Lithium oxide (Li_2O) is another critical component in glass systems. As a network modifier, Li_2O enhances the ionic conductivity, lowers the melting temperature, and influences the glass transition temperature (Tg) [13]. The addition of Li_2O also aids in the solubility of rare earth ions, allowing higher doping concentrations without phase separation or crystallization

II. Experimental Sections

1.Glass preparation

In this study, the melt-quenching technique was employed to synthesize glass with the composition 80 B_2O_5 + 10 Bi_2O_3 + 5 CdO + (5−x) Li_2O + x Gd_2O_3, where x = 0, 0.1, 0.5, 1.0 and 1.5. The raw materials used for the process included boron oxide (B_2O_3), cadmium oxide (CdO), lithium oxide (Li_2O), and gadolinium oxide (Gd_2O_3). These materials were processed under consistent conditions. As the concentration of gadolinium in the

glass samples increased from 0 to 1.5 mol%, the color of the samples transitioned from colorless to a light brown shade while maintaining their transparency.

Once the glass samples were prepared, they underwent an annealing process for approximately 12 hours. The resulting glass samples are shown in Figure 1. High-purity chemicals (99.999%, Sigma Aldrich) were used to ensure the quality of the glass. The prescribed mixtures were placed in porcelain crucibles and preheated (calcined) at 450 °C for one hour. The melting process was carried out at temperatures ranging from 1100 to 1150 °C, depending on the glass composition. The molten mixture was stirred continuously for one hour to ensure uniformity and eliminate bubbles. The homogenized molten glass was rapidly poured into a stainless-steel mould maintained at 200 °C and pressed with a second steel disk to shape the samples.

2.Glass Characterization

The synthesized rare earth-doped bismuth borate glasses were characterized to evaluate their structural, thermal, optical, and physical properties. The following characterization techniques were employed:

X-Ray Diffraction (XRD) Analysis

X-ray diffraction studies were conducted using the Rigaku SmartLab XRD system at HCU to confirm the amorphous nature of the prepared glass samples. The absence of sharp peaks in the XRD patterns confirmed the non-crystalline nature of the glass.

Density and Molar Volume Measurements

The density of the glass samples was measured using the Mettler Toledo Density Kit based on the Archimedes principle with deionized water as the immersion liquid. The molar volume was calculated using the measured density values and the molecular weight of the glass composition to analyze structural modifications due to rare-earth doping.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectra were recorded using the Bruker Alpha II FTIR Spectrometer in the range of 400–4000 cm^{-1} to identify functional groups and bonding structures. The characteristic vibrational bands confirmed the presence of borate network structures, with changes indicating interaction between rare-earth ions and the glass matrix.

Optical Absorption and UV-Vis Spectroscopy

The optical absorption spectra of the glass samples were obtained using a Shimadzu UV-3600 Plus UV-Vis-NIR Spectrophotometer. Absorption edge, optical band gap energy (E_g), and Urbach energy were determined to understand the electronic transitions and structural disorder within the glass network.

Photoluminescence (PL) Studies

Photoluminescence measurements were performed using the Horiba Fluoromax-4 Spectrofluorometer to investigate the emission properties of the doped glass samples. The excitation and emission spectra provided insights into the luminescence efficiency and potential applications in photonic devices.

Microstructural Analysis (SEM/EDX)

Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDX) was performed using the FEI Quanta 200 SEM with Oxford EDX system to examine the surface morphology and elemental composition of the glass samples, ensuring uniform distribution of rare-earth dopants.

The combined results from these characterizations provide a comprehensive understanding of the structural, optical, and thermal properties of the synthesized rare earth-doped bismuth borate glasses, aiding in their potential applications in photonics and optoelectronics.

III. Results And Discussion

1.Physical Properties

The average molecular weight (MW) of a mixture can be calculated using the following formula:

$Mn=\sum N_i M_i / \sum N_i$

Where:

M_i is the molar mass of each constituent component, N_i is the number of moles of each constituent component.

The density (d_s) of the material was calculated using Archimedes' principle with the formula:

$$d_s = \left[\frac{(w_{SA})}{(w_{SA} - w_{SL})}\right] \times d_L$$

where W_{SA} and W_{SL} are the weights of the sample in air and xylene, respectively, and d_L is the density of xylene at room temperature. (d_L = *0.86*g/cc). The measurements were carried out with an accuracy of ± 0.001 g/cc.

Molar volume is calculated using

$$v_m = \sum \frac{n_i M_i}{d_s}$$

Table1

	Avg. Molecular Weight(g)	Density(Theoritical)(g/cc)	Molar Volume(cc/mol)
BBiCdLiGd0	110.21	3.37	32.6931
BBiCdLiGd0.1	110.55	3.37	32.8046
BBiCdLiGd0.5	111.93	3.39	32.9934
BBiCdLiGd1.0	113.65	3.42	33.2107
BBiCdLiGd1.5	115.37	3.45	33.3823

2.XRD

The XRD results confirm the amorphous nature of the synthesized glass samples.

The broad hump in the diffraction pattern supports the disordered atomic arrangement typical of glass materials.

The successful formation of a homogeneous glassy phase is ideal for optical and photonic applications, as amorphous materials tend to have better transparency and uniformity.

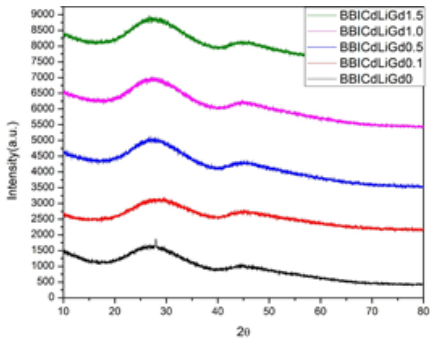

Figure 1

3.FESEM & EDAX

The scanning electron micrograph (SEM) of the analysed glass samples reveals a smooth surface devoid of any microstructures, confirming the presence of an amorphous phase, as illustrated in *Fig. 2.*

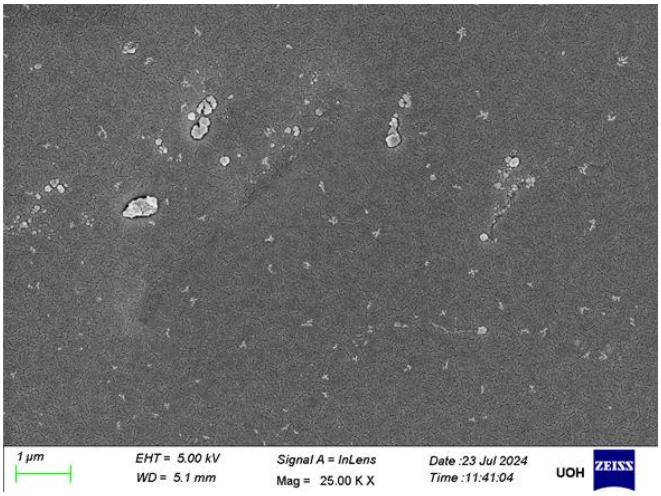

Fig. 2.

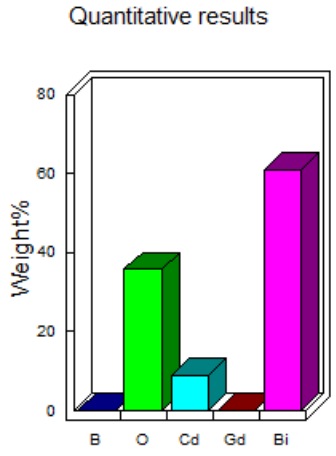

Figure 3

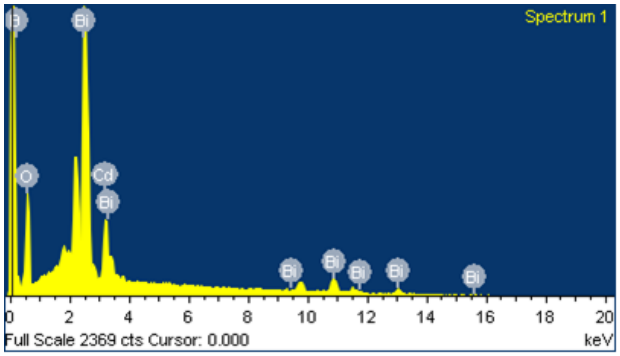

Figure 4

Figures 3 and 4 provide a detailed analysis of the elemental composition of my sample, highlighting the content of all ions present based on the EDX reports.

4.FTIR Spectroscopy

The FTIR spectrum of the prepared glass samples reveals key insights into the structural and bonding characteristics of the materials. The broad absorption peak observed at 2953 cm^{-1} is attributed to O-H stretching vibrations, which likely arise from residual moisture or hydroxyl groups adsorbed on the glass surface. This is a common feature in glass systems due to their hygroscopic nature. The peak at 1737 cm^{-1} corresponds to B-O vibrations in boroxol rings or Bi-O stretching vibrations, reflecting the structural contributions of both borate and bismuth oxide components within the amorphous matrix. These observations confirm the complex bonding network within the glass system, which is influenced by the presence of modifiers and dopants.

From Fig 5, The strong peaks at 1365 cm^{-1} and 1210 cm^{-1} are indicative of the presence of trigonal BO_3 and tetrahedral BO_4 structural units, respectively. These units form the backbone of the borate glass network, with BO_3 units contributing to non-linear optical properties and BO_4 units enhancing the glass's thermal and mechanical stability. The peak at 887 cm^{-1} signifies Bi-O vibrations or B-O-B bending, underscoring the role of Bi_2O_3 as a network modifier. This addition introduces non-bridging oxygen atoms (NBOs), which disrupt the continuous borate network and impact the glass's optical and structural properties. Collectively, the FTIR data validate the successful incorporation of rare earth oxides and modifiers into the glass matrix, highlighting the system's suitability for advanced optical and electronic applications.

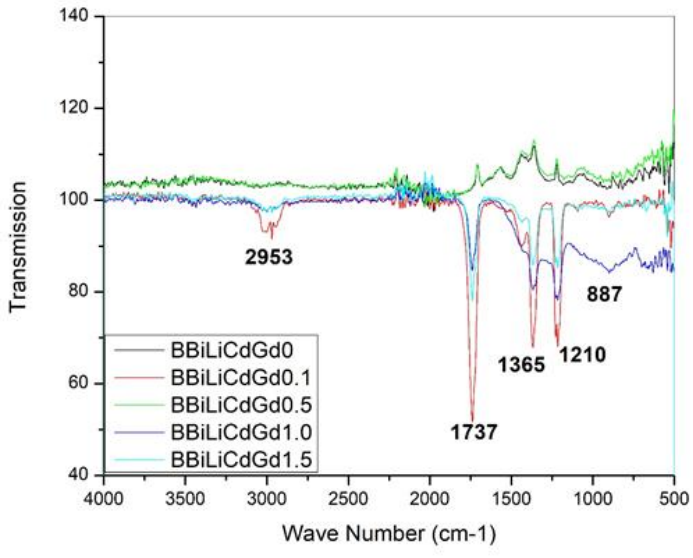

Figure 5

The peaks at 887, 1210, and 1365 cm^{-1} confirm the typical borate glass structure, with an increasing presence of BO_4 tetrahedra as a result of gadolinium doping.

The peaks at 1737 cm^{-1} and 2953 cm^{-1} are likely due to surface effects such as adsorbed water or organic compounds, and could be minimized with more careful sample handling.

Wavenumber (cm^{-1})	Assignment	Description/Analysis
2953	O-H stretching vibrations	Broad absorption attributed to hydroxyl groups or adsorbed water molecules present in the glass matrix.
1737	B-O vibrations in boroxol rings or Bi-O stretching	Likely associated with vibrations within boroxol rings or Bi-O bonds in the glass network.
1365	B-O stretching in BO_3 units	Characteristic of trigonal boron (BO_3) units, suggesting the dominance of triangular borate groups in the glass network.
1210	B-O stretching in BO_4 units	Associated with tetrahedral boron (BO_4) units, indicating the presence of a strong borate network in the glass matrix.
887	Bi-O bond vibrations or B-O-B bending vibrations in the borate network	Suggests the contribution of Bi_2O_3 as a network modifier and the connectivity within the borate network structure.

Table 2

The FTIR analysis of your gadolinium-doped bismuth borate glasses reveals characteristic borate network vibrations, confirming the structural integrity of the glasses despite the doping. The presence of BO_3 and BO_4 units highlights the influence of gadolinium on network modification, contributing to the glass's tunable optical properties. The peaks due to surface contamination suggest a need for further purification, but do not significantly affect the overall glass structure. These findings provide insights into the structural composition and suggest that these glasses are well-suited for optoelectronic applications.

5. Optical investigation

UV-Vis Spectroscopy

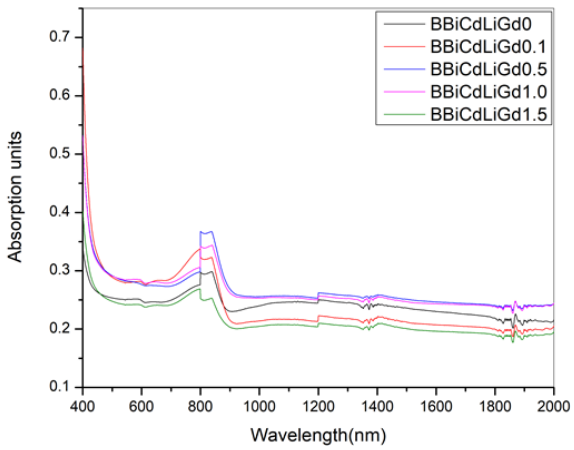

Figure 6

The energy gap (E_g) of the synthesized glass samples was calculated using UV-Vis spectroscopic data. Optical absorption spectra were recorded for finely polished samples at room temperature across the wavelength range of 200–800 nm. The absorption edge, corresponding to the photon energy at which significant absorption begins, was determined from the spectra.

To evaluate, Tauc's method was employed. The relation between the absorption coefficient (α) and photon energy (hν) is given by:

$(\alpha h\nu)^n = A(h\nu - E_g)$

Where A is a proportionality constant, hν is the photon energy, E_g is the optical band gap, and n depends on the nature of the electronic transition. For allowed direct transitions n=2, while for indirect transitions n=1/2.

The absorption coefficient (α) was calculated using the equation:

$$\alpha = \left(\frac{2.303 \text{ x Absorbance}}{Thickness}\right)$$

where the sample thickness was approximately 1 mm.

A Tauc plot, $(\alpha h\nu)^n$ versus hν, was generated, and the linear region of the curve was extrapolated to intercept the photon energy axis. The intercept corresponds to Eg.

The obtained energy gap values provide insights into the electronic structure and optical properties of the glasses. Variations in with composition changes were analyzed to understand the role of gadolinium ions and their interaction with the host matrix. This analysis is critical for tailoring the optical properties of glass for specific applications in optoelectronics and photonics.

Indirect Bandgap:

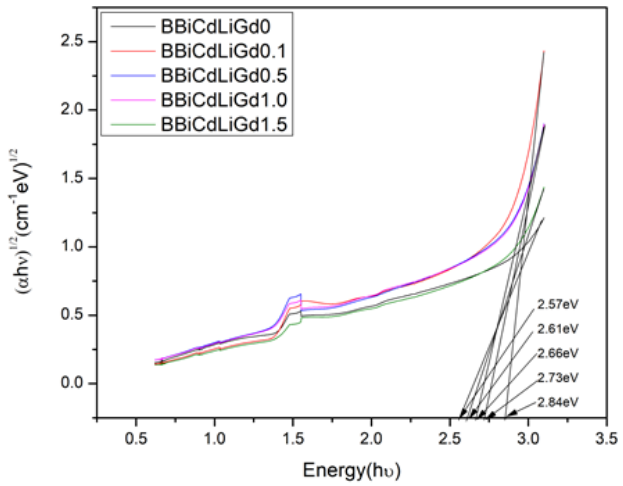

Figure 7

Direct Bandgap:

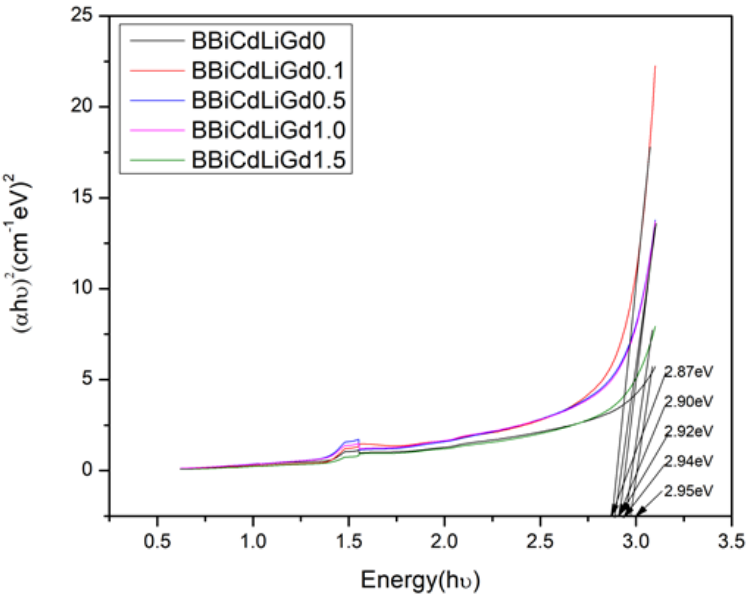

Figure 8

	Indirect Bandgap	Direct Bandgap
BBiCdLiGd0	**2.84eV**	**2.95eV**
BBiCdLiGd0.1	**2.73eV**	**2.94eV**
BBiCdLiGd0.5	**2.66eV**	**2.92eV**
BBiCdLiGd1.0	**2.61eV**	**2.90eV**
BBiCdLiGd1.5	**2.57eV**	**2.87eV**

Table 3

The Tauc plot analysis reveals that gadolinium doping significantly affects the electronic band structure of the bismuth borate glasses. The increasing bandgap values at lower doping levels indicate improved optical transparency and reduced defect states. The slight decrease in the indirect bandgap at higher doping levels may result from increased structural disorder. These findings underscore the tunable optical properties of the glasses, making them suitable for optoelectronic applications, such as transparent conductors, optical filters, and photonic devices.

The data represents the variation of indirect and direct optical band gaps in Gd-doped bismuth borate glass. As the Gd_2O_3 concentration increases from 0 to 1.5 mol%, both indirect and direct band gaps decrease, indicating structural modifications. The indirect band gap decreases from 2.84 eV to 2.57 eV, while the direct band gap reduces from 2.95 eV to 2.87 eV. This decline suggests increased structural disorder, formation of non-bridging oxygens (NBOs), and introduction of localized defect states by Gd^{3+} ions. The narrowing of the band gap enhances optical absorption, making the material suitable for photonic applications.

6. Photoluminescence:

Excitation Spectra

$E_{gap} = hc / \lambda_{cutoff} = 1239 / \lambda_{cutoff}$

Cutoff wavelength is calculated from the above equation.

Cutoff wavelength values are increased with the concentration of Gd^{+3} ion concentration.

The figure shows various excitation wavelengths of Gadolonium doped Cadmium lithium bismuth borate glasses.

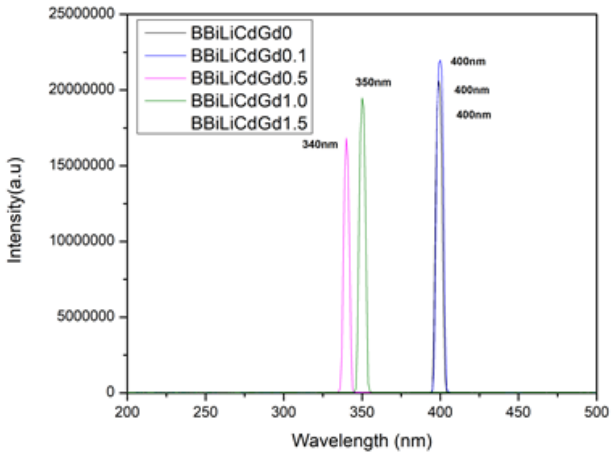

Figure 9

The excitation peak for undoped glass (0 mol% Gd) appears at 340 nm.With increasing Gd doping (0.1 to 1.5 mol%), the excitation peak shifts to ~350 nm and then stabilizes at 400 nm for higher doping concentrations.

This redshift indicates changes in the glass matrix, likely due to the incorporation of Gd^{3+} ions, structural modifications, and changes in the local field environment.

At low doping ($\leq$ 0.1 mol%), the glass retains a more ordered structure, leading to higher energy (shorter wavelength) excitation peaks.

At higher Gd^{3+} concentrations ($\geq$ 0.5 mol%), localized states increase, leading to band tailing and lower excitation energy (400 nm peak).

The shift to 400 nm at higher doping suggests an interaction between Gd^{3+} 4f states and the bismuth borate glass network, possibly due to energy transfer effects or defect state formation.

Increased non-bridging oxygen (NBO) sites at higher doping levels can also contribute to the spectral shift.

Emission

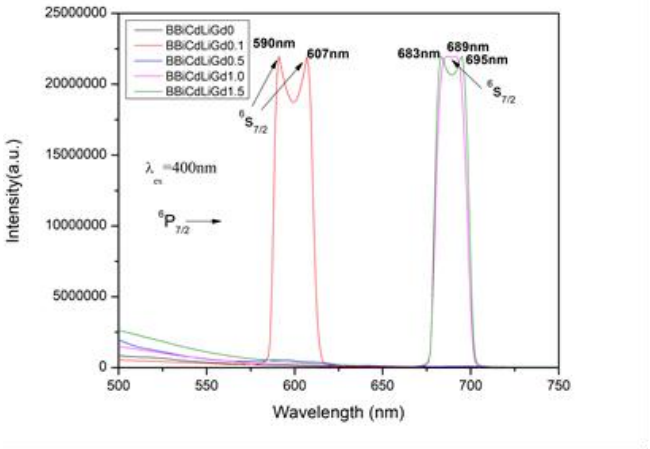

Figure 10

The emission spectra of Gd^{3+}-doped bismuth borate glass were recorded under appropriate excitation conditions, revealing characteristic luminescence peaks at 590 nm, 607 nm, 683 nm, 689 nm, and 695 nm. These emissions originate from the intraconfigurational 4f–4f transitions of the Gd^{3+} ions within the glass matrix.

The peaks at 590 nm and 607 nm correspond to the $^6P_{7/2} \rightarrow {}^6S_{7/2}$ and $^6P_{5/2} \rightarrow {}^6S_{7/2}$ transitions of Gd^{3+} ions, indicating strong intra-4f transitions characteristic of the Gd^{3+} luminescence. The emissions at 683 nm, 689 nm, and 695 nm are associated with the $^6P_{3/2} \rightarrow {}^6S_{7/2}$ and $^6P_{1/2} \rightarrow {}^6S_{7/2}$ transitions, leading to red-shifted emissions.

CIE Chromaticity

The analysis of CIE chromaticity coordinates for gadolinium-doped bismuth borate glasses demonstrates a clear influence of gadolinium concentration on the emission properties. The coordinates exhibit systematic shifts in the chromaticity diagram, transitioning from bluish-white (BBiCdLiGd0) to warm reddish tones (BBiCdLiGd0.1–BBiCdLiGd1.0) and then to neutral white (BBiCdLiGd1.5). The correlated colour temperature (CCT) values span a wide range, highlighting the tuneable nature of the emission characteristics. This tunability makes these glasses promising candidates for applications in lighting, display technologies, and photonic devices where colour customization is critical

This tunability in chromaticity coordinates highlights the potential application of these glasses in lighting and display technologies, especially for customizable light emission.

Table 3

Sample	X-Coordinate	Y-Coordinate	CCT(K)
BBiCdLiGd0	0.276	0.232	19927.04
BBiCdLiGd0.1	0.402	0.239	1728.69
BBiCdLiGd0.5	0.37	0.231	2011.99
BBiCdLiGd1.0	0.36	0.216	1909.79
BBiCdLiGd1.5	0.335	0.231	5085.28

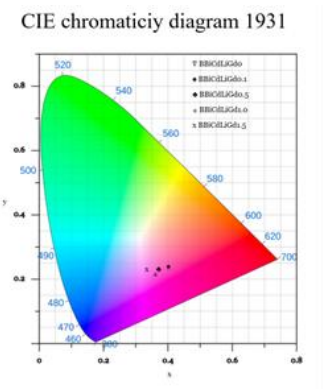

Figure 11

The X and Y coordinates systematically shift with increasing gadolinium content, showcasing the effect of doping on emission properties.

CCT values demonstrate a broad range, from warm (low CCT, red) to cool (high CCT, bluish-white) light emission.

IV. Conclusion

This study comprehensively analysed gadolinium-doped bismuth borate glasses synthesized via the melt-quenching method. The optical properties, including energy gaps and Urbach energies, revealed the impact of gadolinium doping on electronic structure and structural disorder. The CIE chromaticity coordinates demonstrated tunable emission properties, highlighting the potential for photonic and display applications. Tauc plots provided insights into direct and indirect band gaps, showing variations with doping levels and confirming the material's optical versatility. Photoluminescence studies under 396 nm excitation emphasized the glasses' suitability for light-emitting devices, while FTIR, SEM, EDAX analyses confirmed structural integrity and stability. These findings establish the doped glasses as promising candidates for advanced optoelectronic and photonic applications.

Acknowledgment

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