



Gamma-rays interactions on the spectral properties of CuO-doped lithium

host barium borate glasses



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Abstract

Glass samples of undoped and CuO-doped barium borate host glasses were prepared. Combined optical properties together with structural FTIR spectral analysis were measured before and after gamma irradiation with a dose of 6 M rad. The optical spectral absorption of the base is characterized by prominent ultraviolet band which is correlated with trace ferric ions present as impurities. The CuO-doped glasses exhibit an extended broad visible –near IR band which is assumed to originate from octahedrally coordinated Cu²⁺ ions revealing obvious separation to two component peaks. The irradiation process is accompanied by an increase of the intensities of the absorption bands and can be attributed to proposed photochemical reactions between liberated electrons and formed positive holes with trace iron impurities. FTIR spectra reveal distinct two characteristic broad bands within the mid region 800-1200 cm⁻¹ and 1200-1600 cm⁻¹ indicating the presence of both tetrahedral borate groups and co-presence of triangular borate groups and the intensities of these two IR broad bands increase with the CuO content due to suggested polymerization of the borate network or changes in the ratio of BO₄ and BO₃ groups.

Keywords: Barium borate glass; gamma irradiation; UV/Vis.; FTIR; CuO

1. Introduction

Glasses which are constituted of borate groups are amongst the three widely interested and enormously investigated beside silicate and phosphate glasses. The basic B₂O₃ is highly soluble and chemically unstable when left to atmospheric condition, but when incorporated with varieties of divalent, trivalent or tetravalent oxides find extensive commercial applications [1, 2]. The network structure of borate glasses is exceptionally unique amongst the mentioned traditional three types of glasses being consisting of combined boron atoms in tri- and tetra-coordinations with oxygens with the possibility of the presence of different borate groups (such as diborate , triborate , tetraborate , metaborate , orthoborate). It is assumed that the reaction of modifier alkaline oxides , or any of many multivalent and trivalent

oxides (such as PbO , BaO, ZnO , CdO , Bi₂O₃) to B₂O₃ converts or modifies progressively some of the basic BO₃ units to tetrahedral BO₄ units until certain percent specific for each of the mentioned oxides. The excess introduced of any of the mentioned multivalent oxides is consumed to form nonbridging oxygens as produced in silicate and phosphate glasses with modifier oxides in all their entire compositional ranges [3, 4]. This variation in coordination number reflects new evidences and criteria in borate glasses. The introduction of BaO or SrO in glasses produces interesting candidates either in the vitreous or as crystalline glass-ceramics derivatives which are considered as gamma-ray shielding, second harmonic generation, biomaterials, dielectric materials and some optical applications [5-8]. Also, the addition of few percent of BaO improves the chemical durability

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and the optical properties of the glasses to be recommended as special optical materials [1, 2, 4].

Copper belongs to the 3d transition metals and was early used as colorants to glasses, enamels and to produce different and collectively colored aventurine and rubies where collective presence of Cu^{2+} , Cu^+ and metallic copper can be identified [4, 9-11]. When copper is introduced to glasses, bluish – greenish colors are developed when melted under ordinary condition due to the presence of octahedral Cu^{2+} ions exhibiting a broad visible – near IR band which is sometimes splitted into two or three component peaks [11]. The monovalent Cu^+ ions are not easily prepared except under distinct reducing condition. The increase of copper ions in glass introduces interesting electrical properties and also shows exhibit retardation upon gamma irradiation showing shielding stability [11, 12].

When glasses are impinging with ionizing gamma irradiation, most glasses are affected and the resultant effects are generally dependent on type of glass including all constituents and even impurities and on the dose of irradiation [13-16]. Glasses are generally affected because they possess nonperiodic arrangement including the presence of intrinsic defects (such as nonbridging oxygens, flaws, vacancies, voids) which trap sites for the generated released electrons and formed positive holes.

The present work aims to characterize by collective optical and infrared spectral investigation of prepared varying CuO-doped in host barium borate glasses before and after gamma irradiation. These mentioned spectral studies are supplemented by deriving the optical band gaps of the prepared samples.

2. Experimental work:

2.1. Preparation of the glasses

The glassy samples were prepared from laboratory chemicals. Orthoboric acid (H_3BO_3) was used as the source for B_2O_3 , barium carbonate (BaCO_3) for BaO while CuO was introduced as such. CuO was added as dopant up to 0.5%. The prepared batches were melted in platinum crucibles at $1150\text{ }^\circ\text{C} \pm 10\text{ }^\circ\text{C}$ in an electric SiC heated furnace type (Vecstar, UK). The melting was extended for 90 minutes which included rotating the crucibles at intervals of 20 minutes to promote complete mixing and homogeneity of the melts. The homogenized melts were poured into warmed stainless steel molds with the required dimensions. The prepared glasses were directly transferred to an annealing muffle

which was regulated at $400\text{ }^\circ\text{C}$. The annealing muffle was switched off after 1 hour.

2.2. Optical (UV-visible) absorption spectral measurements

Polished glasses with constant thickness ($2\text{ mm} \pm 0.1\text{mm}$) were measured for their optical absorption within the range of $200 - 2500\text{ nm}$ using a recording spectrophotometer (type SHIMADZU UV-3600, UV-VIS-NIR Spectrophotometer, Japan) at room temperature. The measurement was repeated for each sample to confirm the positions of the peaks.

2.3. Fourier transforms infrared absorption spectral measurements

FTIR spectra were collected at room temperature in the range $(400-4000)\text{ cm}^{-1}$ by a Fourier transform IR spectrophotometer type (NICOLET 6700 FT-IR, USA) using the KBr disc technique. 2 mg of the powdered glass was mixed with 200 mg of KBr and the mixture was subjected to a load of 5 tons/cm^2 to produce clear homogenous discs. The IR measurements were immediately carried out after the preparation of the discs to avoid moisture attack. Infrared spectra were corrected for the dark current noises and background using the two-point baseline corrections. The IR measurements were repeated after gamma irradiation of the glasses.

2.4. Gamma Irradiation facilities

An Indian ^{60}Co gamma cell (2000 Ci) was used as a gamma rays source with a dose of 1.5 Gy/s (150 rad/s) at a temperature of $30\text{ }^\circ\text{C}$.

2.5. Optical energy gap

The electronic band structure in crystalline and non-crystalline materials can be evaluated from the identified absorption edges. Optical band gaps were calculated using obtained absorption spectra for direct and indirect transitions for all prepared glass samples which can be determined through the relation given by Davis and Mott [17]:

$$\alpha h\nu = B (h\nu - E_{\text{opt}})^n \quad (1)$$

Where E_{opt} is the optical energy gap, B is a constant called the band tailing parameter and n is an index which can be assumed to have values of $1/2$, $3/2$, 2 and 3, depending on the nature of the electronic transition responsible for the absorption.

3. Results

3.1. Optical absorption spectral data

Figure (1) illustrates the optical absorption spectra of the prepared glasses before and after gamma irradiation. The spectrum of the base glass is characterized by strong distinct UV absorption extending from 200 to about 350 nm with a peak at 315 nm and with no observed bands up to 2500 nm. With gamma irradiation, the intensity of the overall spectral curve increases with irradiation and the UV peak shift to 307 nm.

The spectra of the CuO-doped glasses show the similar ultraviolet band as the undoped glass but slightly extended to higher wavelength and with a peak at 344 nm followed by a strong and very broad visible near IR band extending from about 500 to 1500 nm with two split peaks at 785 and 850 nm in all glasses. Upon irradiation the intensities of the absorption curves increase without the generation of any further UV or visible induced absorption bands.

3.2. FT infrared absorption spectra of the prepared glasses

Figure (2) shows FTIR spectra of the studied glasses. In general, the IR curves appear almost similar and repetitive except with increase of the intensities of the two mid broad bands. The intensity of the spectral curves increases with the increase of CuO content. The detailed infrared vibrational bands of the undoped glass are outlined in the following:

- The identification of two small far – IR peaks at about 440 and 485 cm^{-1}
- A further band is observed at about 704 cm^{-1} .
- A first broad band is identified to be centered at 950 cm^{-1} .
- The identification of a second broad band centered at 1373 cm^{-1} .
- The observation of a small band on the descending lobe of the second broad band at about 1640 cm^{-1}
- The appearance of a broad medium near IR band centered at 3456 cm^{-1}
- It is to mentioned that the two first and second broad mid bands increase in their intensities in the two glasses containing higher CuO contents.

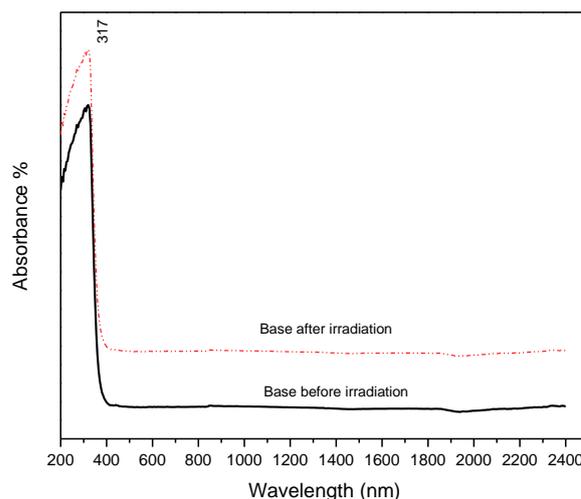


Figure (1) optical spectra of undoped binary barium borate glass before and after gamma irradiation.

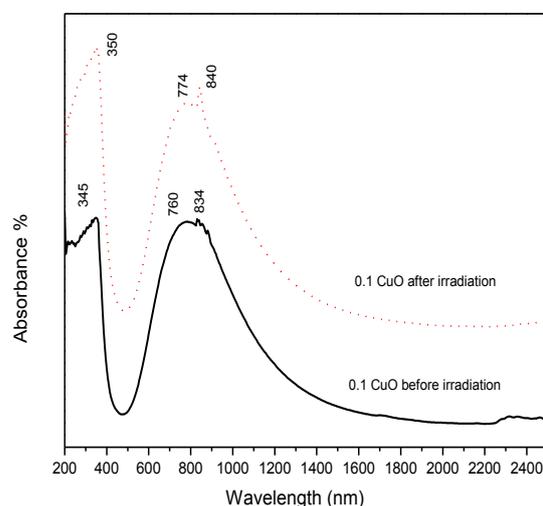


Figure (2) optical absorption spectra of 0.1% doped CuO in host barium borate glass before and after gamma irradiation.

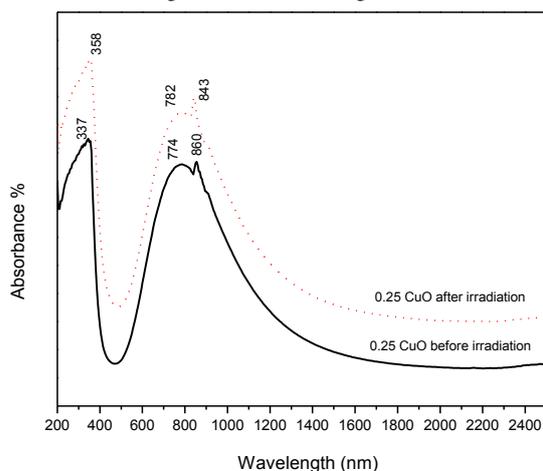


Figure (3) optical absorption spectra of 0.25 % doped CuO in host barium borate glass before and after gamma irradiation.

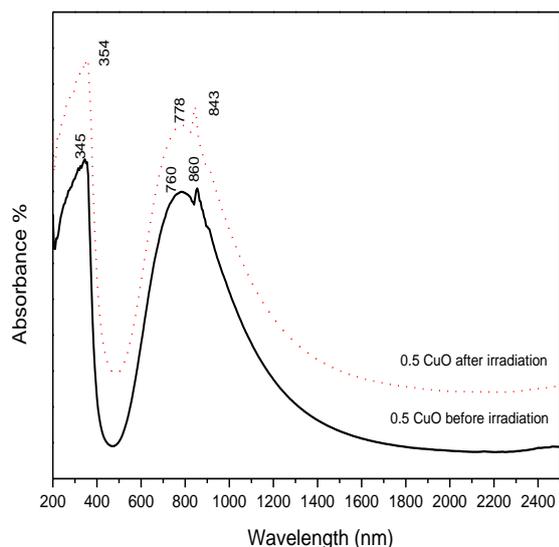


Figure (4) optical absorption spectra of 0.5 % doped CuO in host barium borate glass before and after gamma irradiation

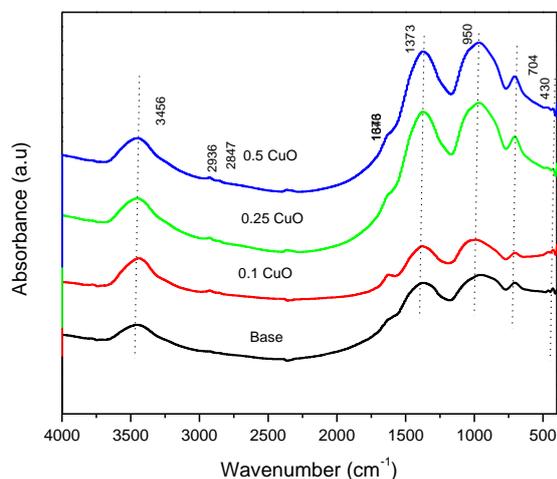


Figure (5) FTIR spectra of the prepared glasses before gamma irradiation.

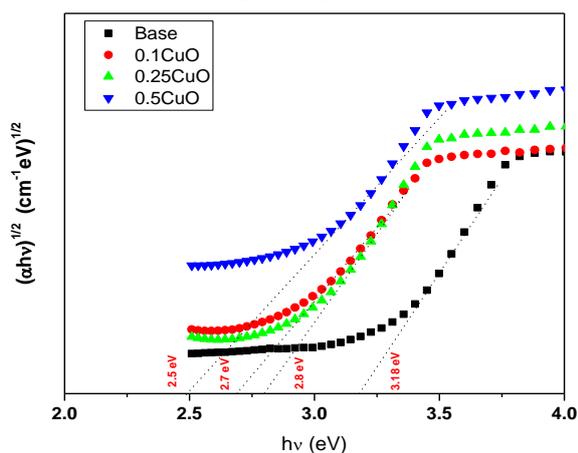


Figure (6) Optical band gap energy of the prepared glasses

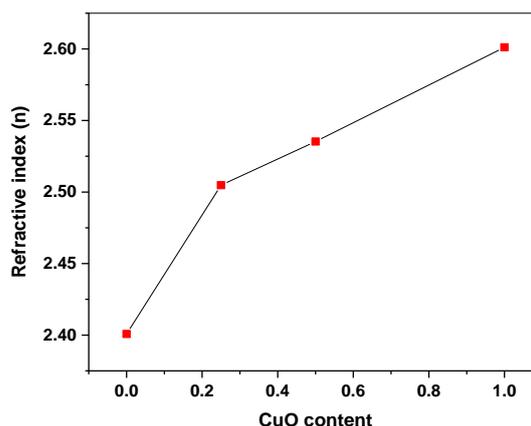


Figure (7) variation of the refractive index with CuO content

4. Discussion

4.1. Origin of ultraviolet absorption in the spectra of the studied glasses

Many authors had proposed that the observed ultraviolet bands within the optical spectra of many undoped commercial silicate glasses originated from contaminated and unavoidable trace ferric ions impurities in the raw materials used for the preparation of such glasses [18-20]. Further successive glass scientists [11, 14, 16, 21] have agreed to this postulation and have indicated that contaminated trace iron impurities (ferric Fe^{3+} ions) are the reason for the UV bands within the wavelength range (200-320 nm) and their strong appearance is due to its origin from charge electron transfer mechanism and such UV bands are commonly identified even if the impurities are within the ppm level.

4.2. Interpretation of the optical spectra of CuO-doped barium borate glasses

The bluish colored glasses of the CuO-doped samples are reflected by the appearance of a specific and characteristic very broad band with two distinct peaks at about 785 and 850 nm beside the strong UV absorption as the undoped sample. The broad visible-near IR band is attributed to be due to octahedrally coordinated Cu^{2+} ions. The broadness and asymmetry of the broad visible-near IR band is assumed to be correlated with splitting of the low-symmetry ligand field component of the Cu^{2+} ions [9-12]. Paul [23] assumed that the splitting of the broad band due to Cu^{2+} ions in glasses and its comparison with CuO-doped complexes indicates that this identified broad band is truly made up of at least two

and possibly three or four overlapping symmetrical bands. The values of the optical band gap was also observed to be decreases with increasing the CuO content within the glassy matrix as shown in Figure 6.

4.3. Interpretation of the FTIR spectra of the studied glasses

The realization and assignments of the identified IR bands can understood on the following basis [3, 5, 6, 24, 25]:

- a- The overall IR spectral features are due to main structural units are almost with distinct vibrational bands extending in the mid region of IR spectrum from 400-1650 cm^{-1} . The IR spectral curves reveal two distinct broad bands extending from 800-1200 cm^{-1} and from 1250-1650 cm^{-1} beside a broad near IR band. These vibrational bands are accepted to be familiar features for borate glasses indicating the presence of both triangular and tetrahedral borate (BO_3 , BO_4 groups).
- b- It is obvious that the increase of CuO content increases the intensities of the two broad mid peaks. The presence of such extended two broad vibrational bands confirms the assumption that when BaO is added to B_2O_3 , some of the basic BO_3 units are modified or changed to BO_4 units until certain percent which is characteristic for such added oxide.
- c- It is evident and reached by various glass scientists [3, 24, and 25] that the bands of BO_4 groups possess their characteristic vibrational wavenumbers within the range from 800-1200 cm^{-1} . Also, it is recognized that (BO_3) groups have their characteristic vibrational modes within the range 1250-1500 cm^{-1} .
- d- The suggested assignments of the resultant vibrational peaks are summarized as follows [3, 24, 25].
 - i. The two far-IR peaks (at 440 and 485 cm^{-1}) are related to vibrations of Ba^{2+} cations in their sites.
 - ii. The peaks within the range 580-800 cm^{-1} are due to the bending vibrations of borate groups.
 - iii. The vibrational peaks within the range 800-1200 cm^{-1} are correlated with stretching vibrations of tetrahedral borate (BO_4) groups as represented by the distinct peak at 950 cm^{-1} .
 - iv. The high frequency vibrational peaks within the range 1200-1550 cm^{-1} belong to modes of triangular borate (BO_3 and BO_2O) units as

illustrated by the appearance of the intense peak at 1373 cm^{-1} .

- v. The small peak at 1640 cm^{-1} is related to vibrations of OH and water.
- vi. The near-IR broad band centered at 3456 cm^{-1} is related to vibrational mode of OH, water and BOH.

It is to be added that the increase of the intensities of the broad mid bands upon the addition of increasing CuO content can be related to a process of depolymerization of the borate structures by the copper ions as suggested by previous researchers [10, 11].

4.4. Interpretation of the effect of gamma irradiation

When glasses are impinged or reacted with ionizing gamma irradiation, most glasses acquire deepening in color and some physical and chemical properties show obvious changes. These changes are generated through the liberation of electrons which travelled through the glass network with the consequent formation of positive holes. The induced defects or damages can be traced and compared through optical and ESR measurements [13, 26, 27].

Glasses are recognized to be materials with non-periodic arrangements and generally contain intrinsic defects before irradiation (such as nonbridging oxygens, vacancies, voids) which are trap sites for the pairs of electrons and positive holes generated during the irradiation process [13, 26, 27]. Also, the glasses may contain trace transition metal impurities which can react with electrons or positive holes leading to changes in their valences or coordination. Previous studies by various authors [5, 11, 27] reached the conclusion that some transition metals ions (e.g. Cu^{2+} , V^{5+}) are identified to shield continuous gamma irradiation and through photochemical reactions the net result is the almost maintenance of both the optical spectral and IR spectral curves as before irradiation or become parallel to them. The same retardation shielding effects of gamma irradiation have been identified in some glasses containing heavy metal oxides (such as PbO , Bi_2O_3 , BaO) due to their heavy masses which prohibit or retard the free passage of electrons during the process of gamma irradiation [29, 30].

The present experimental optical results gamma irradiation produces no extra induced defects either in the undoped and CuO-doped barium borate glasses but only the increase of intensities of the overall spectral curves from the irradiated undoped or CuO-

doped glasses. The previous peculiar result can be realized and explained on the following basis:

- i- Previous studies on the effect of gamma irradiation on glasses have reached the conclusion that the increase of the UV absorption bands in the vicinity of 200-300 nm is concerned with the absorption of trace ferric ions (Fe^{3+}) in the glasses and the increase of intensity is frequently ascribed to the increase of the percent of its presence through suggested photochemical reactions between some ferrous ions and positive holes and the formation of additional (Fe^{3+}) ions or (Fe^{2+})⁺.
- ii- Gamma irradiation is assumed to modify or causes some structural rearrangement of the existing species of borate glasses (such as metaborate, diborate,.....) and this behavior necessitates further studies by various techniques [2, 13, 25].

Conclusion

Varying CuO-doped barium borate glasses were synthesized and characterized through both optical and FTIR spectral measurements before and after gamma irradiation. Optical spectrum of the undoped glass shows distinct UV absorption bands which are collected with trace impurities ferric ions and the colored CuO-doped glasses show a pronounced very broad band with splitting peaks correlated with divalent copper (Cu^{2+} ions) in octahedral coordination. Gamma irradiation increases the intensities of the identified UV visible bands which are correlated with some proposed photochemical reactions. Infrared absorption spectra identify two characteristic distinct broad bands in the mid region at 800-1200 and 1200-1550 cm^{-1} due to both tetrahedral and triangular borate groups (BO_4 and BO_3) in their specific and characteristic vibrational sites.

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