

Gamma Rays Interactions on Optical, FTIR and ESR Spectra of Alkaline Earth Binary Borate Glasses

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Received 29th Sept. 2019 Accepted 18th Oct. 2019 Alkaline earth binary borate glasses with the composition of $(100-x) B_2O_3 + X$ (BaO, CaO, SrO) where x=22, 32 or 42 wt. % were prepared by melting annealing technique. Some of their physical and spectroscopic properties have been studied before and after gamma irradiation such as Density, oxygen packing density, molar and specific volumes, as well as optical UV-visible absorption, optical energy gap (Eopt), FTIR and ESR spectroscopy. The UV-visible spectra show a shifting of the optical edge to higher wavelengths withincreasingthe polarizability of the introduced modifier ion and the dose of gamma radiation. FTIR spectra show the vibrational bands of the structural borate groups; the triangular BO₃ and tetrahedral BO₄ units at 1200-1600 cm⁻¹ and 800-1200 cm⁻¹ respectively. ESR spectra show a constant behavior of the glasses at the low doses of radiation up to 60 kGy but show high effect of radiation at the higher doses due to the formation of more paramagnetic defects and free radicals.

Keywords: Binary borate glasses/ UV/ EPR/ FTIR/ Gamma radiation.

Introduction

Because of the urgent requirements in the recent time for using nuclear energy in many applied fields, many nuclear plants are constructed. But they are associated with different harmful effects on humans and the surrounding environment. So many researchers have studied the preparation of cheap and flexible materials that may be used in radiation shielding processes [1]. From this interesting point of view, some types of glasses are selected to attain the desired goal of shielding radiation based on some compositions of borate glasses. The action of the ionizing radiation ontoborate glasses becomes widely under study because of their extensive applications in lenses, windows and many optical devices, they also have many applications in the radiative environment especially in the radiation dosimetry and shielding applications [2].

Borate glasses are the most distinguished among all types of glasses. They have the easiest way to prepare and they are suitable hosting candidates for many modifying ions like alkali and transition metal ions. They are most recently analyzed due to their premium optical, chemical and mechanical properties such as, good solubility of rare earth (RE) ions, low melting temperature and the well corrosion resistance [3].

Borate-based glasses consist of 3 or 4 coordination structures consistent with the concentration of bridging (BO) and non-bridging oxygen (NBO) in their networks. So they have high tendency to form many structural groups e.g. diborate, tetraborate, pentaborate or broxol ring...etc however, silicate and phosphate- based glasses form only the tetrahedral coordinated units with oxygens [4]. Accordingly, the glass properties depend essentially on the host glass matrix composition besides, the type and concentration of the introduced modifying ions. For instance; when alkali ions are introduced in the glass network, they incorporate into borate network ionically and cause the change in their coordination number

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between three and four depending upon their behavior with the adjacent oxygens [5]. This performance depends on the random manner of the borate glassy network which is formed from the triangular units BO3 associated together via bridging oxygens (B–O–B).However, introducing of modifying alkali ions such as; Ba²⁺, Sr²⁺or Ca²⁺ions would disrupt some of bridging oxygens into non-bridging oxygens NBO, consequently the transformation of the triangular BO₃into the tetrahedral BO_4 units is happened [6]. The properties of glasses are also directly associated to both the inter atomic forces of the glass lattice structure and their potentials. So any changes in the glassy network because of doping and/or irradiation, can be investigated by many techniques like; UV-visible, IR and ESR spectroscopies.

The ionizing radiation of gamma rays almost interacts with glasses by yielding secondary electrons that lose their excess of energy on collisions through the glass matrix, then the excited electrons travel within the glassy network and finally trappedin a form of defects like vacancies, NBOs, multivalent impurities or interstitial atoms [7]. Some of the resultant electronic configurations cause the absorption of preferential light creating "color centers". Studying the energy positions and characteristics of UVvisible optical absorption bands and electron spin resonance (ESR) spectra of irradiated glasses demonstrate many color centers types that induced in the studied glasses either by trapping holes or electrons at different sites into the glassy structure [8].

UV-visible and IR spectroscopy provide also information about bond lengths, average coordination number, nature of configuration and bonding between metal ion and first-shell neighbors. Also by studying FTIR we can examine the gamma radiation effect onto the glasses structures because it designates the structural features related to both the local units instituting the glassy network as well as the anionic positions hosting the modifying metal ions.

According to researchers[2] BaO, SrO and CaO are believed to occupy only the network modifying positions leading to the variation in the nonbridging oxygens number and then the shifting of bands on the UV-visible spectrum at higher wavelengths[2].Also, calculating optical energy gap (Eopt)is an important factor to provide information about the electronic transitions caused by irradiation and indicate the possibility of using the investigated glasses as radiation shielding candidates for gamma rays[9].

The aim of the current work is to study some physical characteristics of the prepared binary BaO-B₂O₃, CaO-B₂O₃ or SrO-B₂O₃ glasses like density, oxygen packing density OPD, molar and specific volumes and the changes in their spectroscopic properties after their exposing to some low and high gamma radiation doses like (UV–Vis.), FTIRas well as ESR spectra. It is then characterized the generated induced defects due to the alteration of the alkali ion concentration and the dose of gamma radiation in order to test to what extent the glasses may be used as gamma radiation shielding materials.

Experimental Procedure

Glass preparation

The glasses with compositions of $(100-x)B_2O_3-x$ MO, where M= Ba, Ca or Sr and x=22, 32 or 42 wt. % were prepared using melting annealing method. The chemically pure reagents; H₃BO₃, BaCO₃, CaCO₃, and SrCO₃from Sigma Aldrich Company were used in the preparation process. The batches were accurately weighed by using an electronic balance, mixed carefully and crushed into fine powders, after that they were melted by using alumina crucibles in an electric furnace at 1100-1200 °C for 2 hours and the melts were rotated for reaching homogeneity. After molding the melts, they were directly taken to a muffle furnace controlled at 350 °C for annealing. Then it was switched off after 1 h to reach to room temperature by a rate of 25°C/h.

Physical Parameters

By using Archimedes method of suspended weights, density of each glass sample was measured three times by a maximum error $\sim 0.0002 \text{ g/cm}^3$ using the following formula:

$$\rho = \{a/(a-b)\} \times 0.86$$
 g/cm³ (1)

Where ρ is the glass sample density, a and b are the glass sample weights in air and in xylene respectively, and 0.86 is xylene density at 20 °C.

Glasses molar volumes were calculated using the following formula:

$$Vm = (\sum Xi Mi)/\rho$$
 cm^3/mol (2)

Where Xi is the molar fraction, Mi is molecular weights of elements in each glass sample individually, and ρ is the glass density.

The oxygen packing density OPD was also calculated using the formula:

$$OPD = 1000 X C X \rho/M \qquad g atm/l \qquad (3)$$

M is the molecular weight of each glass sample and C is the number of oxygen atoms per unit formula.

Optical UV-Visible measurement

Well-polished glass specimens with dimensions of $1 \times 4 \times 0.2 \text{ cm}^3$ were measured optically at room temperature, before and after sequential gamma irradiation in the dose range from 10 to 280 kGy. The optical measuring was achieved in the area of 200–800 nm using the recording spectrophotometer model JASCO, Corp., V-570, Rel-00, Japan.

Estimation of the optical band gap

Mott and Davis [10] calculated the energy band gap (Eopt) values of amorphous solids using the relative formula:

$$\alpha h \upsilon = B (h \upsilon - E_{opt})^n$$
 (4)

Where; (E_{opt}) : optical energy gap, (α) : absorption coefficient, (h): Planck's constant, (v): the radiation frequency, (B): an energy independent constant and (n): an index with the values; 1/2, 3/2, 2 or 3 depending upon the electronic transition nature.

FTIR absorption measurements

By using the spectrometer model VERTEX 70, FT/IR-430, Japan, the FTIR absorption spectra of the prepared glasses were evaluated at different gamma irradiation doses in the wave number area $400-4000 \text{ cm}^{-1}$ at the room temperature.

Electron Spin Resonance ESR

ESR spectra of the examined glasses were evaluated using EMX spectrometer (X-band) with a standard Bruker rectangular cavity ER 4102, Germany. The conditions of the operating system were; a microwave power 0.796 mV, modulation amplitude 5 Gauss, time constant ~ 81.92 ms and sweep time~20.97s/scan. The glass specimens were placed into ESR tubes and recorded immediately after each radiation dose at the previous instrument parameters.

All of the last measurements are applied on the examined glasses before and after their subjecting to different doses of gamma radiation.

Gamma irradiation

The gamma ray source used in the irradiation process was Co 60 gamma cell (2000 Ci) with dose rate ~1.26 kGy/h at 25 ± 5 °C. The glass specimens were sited in the gamma cell in a way that each sample was subjected to the equivalent gamma dose.

Results and discussion

The Physical Parameters; density, molar volume, oxygen packing density and specific volume of the studied glasses

Measuring some glasses physical parameters like density, gives valuable information regarding the geometrical modification of the glass matrix, its compactness and changes that take place in the internal network dimensions holes. The glass density describes the relationship between masses and volumes of the structural groups in which the glass network consisted of. Therefore glass density is directly determined by the glass chemical composition and how compactly the atomic groups are connected with each other[4].So each metal oxide contributes in the glass network would have its specific effect on the glass density according to its properties and its behavior inside the glass matrix. For example, introducing of modifier ions such as Ba^{2+} , Ca^{2+} or Sr^{2+} ions tends to cause some disruptions in the glass network by varying the BO and NBO concentrations, then the conversion between triangular BO₃ and the tetrahedral BO₄structural groups would take place.

Results in Table 1 show the values of density, oxygen packing density, molar and specific volumes of the studied glasses before and after being irradiated with 60 and 280 kGy, where Ba^{2+} and Sr^{2+} containing glasses have density values higher than Ca^{2+} containing glasses. Early, density is well-defined as weight per unit volume, therefore it was estimated that the higher the atomic mass of the introduced ion, the higher density of the glass that introduced in [11]. According to this postulation, it was found that the order of the heavier introduced ions is relatively the same order of glass density increase; $Ba^{137.33}$ >

Sr ^{87.62}> Ca^{40.08}. So it may be interpreted that the Concentration leads to the increase in glass density values. This performance may be also due to enhancing the conversion process of triangular BO₃tothe tetrahedral BO₄units with the further increase in modifier ion concentration. So the availability of a high number of oxygens in borate network, and as a result more compactness would take place giving higher glass density values [12].

The oxygen packing density OPD represents the fraction of spaces occupied with the greatest possible oxygen density. So it is directly correlated to the forming of non-bridging oxygen bonding inside the glass matrix [13]. While molar volume VMis directly correlated to the spatial distributions of the oxygen into the glass matrix, so it is more significant in characterizing glass properties than density because it describes the entire free volume of glass including the volume of vacancies and interstices. Accordingly both molar and specific volumes give an indication for the compactness of the glassy network as it is obvious in Table 1,wherethe higher density values of glasses the lower their specific volumes and vice versa.

Effect or gamma irradiation on physical parameters of the studied glasses

Irradiating glasses with 60 kGy of gamma rays causes a slight variation in their density, OPD, specific volume in addition to the molar volume. This performance may be owing to the influence of radiation onto the glasses, where it produces increase in the introduced modifier ion displacements, electronic defects and /or breaks the network bonds. Hence creating more NBO and forming less compacted structures with lower density and OPD but higher specific and molar volumes. However by continuing the irradiation process to 280 kGy, more disruptions and displacements take place leading to the existence of more NBO. Thus the availability of high oxygen numbers in borate glass matrix. Consequently more compactness in the structure takes place then higher density values are obtained at the higher dose (280 kGy) than the lower one (60 kGy)[12].

This assumption is agreed with OPD values that have higher values at 280 kGy than those at 60 kGy, however molar and specific volume values are increased at the lower dose of radiation than the higher dose as shown in Table 1.

It is also observed from the table that upon irradiation, $Ca^{2+}and Sr^{2+}containing glasses give$ slightly more stable density values than glasses $containing <math>Ba^{2+}$ ions. This behavior may be argued according to their relatively lower ionic sizes comparing with $Ba^{2+}ions$, which enabled Ca^{2+} and Sr^{2+} ions to fit themselves easier inside the network interstices. So that some modifications in the network take place by decreasing the concentration of NBO, giving more blocked or more volume compacted network than the larger $Ba^{2+}ions$. Consequently, more strong structures are produced accompanying with the inhibition of gamma radiation effect.

Glass no.		Density ρ (g/cm ³)			Molar volume Vm (cm ³ /mol)			Specific Volume (cm ³ /g)			Oxygen Packing density OPD (g atm/l)			Optical band gap Eopt (e.V)		
Dose (kGy)	0	60	280	0	60	280	0	60	280	0	60	280	0	60	280	
22 Ba	3.00 13	2.61 35	2.8076	29.3 3	33.6 8	31.3 6	0.33 32	0.38 26	0.35 62	8727. 46	7599. 78	8164.2 0	2.6 6	2.1 1	1.7 5	
32Ba	3.38 48	2.96 66	3.0087	28.4 8	32.4 9	32.0 4	0.29 54	0.33 71	0.33 24	8285. 83	7262. 10	7365.1 6	2.7 6	2.2 4	1.7 6	
42Ba	3.62 60	3.23 05	3.3923	28.8 9	32.4 3	30.8 8	0.27 58	0.30 96	0.29 48	7475. 88	6660. 46	6994.0 5	3.0 2	2.4 3	2.0 9	
22 Ca	2.58 58	2.46 96	2.5376	25.7 7	26.9 8	26.2 6	0.38 67	0.40 49	0.39 41	9933. 26	9486. 88	9748.1 0	2.7 5	1.8 3	1.7 2	
32 Ca	2.74 04	2.49 28	2.5732	23.8 2	26.1 9	25.3 7	0.36 49	0.40 12	0.38 86	9905. 99	9010. 96	9301.5 9	2.7 7	2.1 4	2.0 3	
42 Ca	2.86 32	2.56 84	2.5916	22.3 3	24.8 9	24.6 7	0.34 93	0.38 93	0.38 59	9673. 39	8677. 40	8755.7 8	2.7 8	2.2 3	2.0 6	
22 Sr	2.84 47	2.55 61	2.7422	27.1 0	30.1 6	28.1 2	0.35 15	0.39 12	0.36 46	9445. 43	8487. 18	9105.0 9	2.7 4	2.0 4	1.5 1	
32 Sr	3.21 73	2.86 62	2.9076	25.0 2	28.0 8	27.6 8	0.31 08	0.34 89	0.34 39	9432. 08	8402. 77	8524.1 4	2.7 6	2.1 4	1.9 8	
42 Sr	3.44 31	3.05 50	3.3805	24.3 6	27.4 6	24.8 2	0.29 04	0.32 73	0.29 58	8864. 23	7865. 07	8703.0 7	2.7 7	2.3 2	2.0 3	

 Table 1 Characteristic physical parameters of the prepared binary borate glasses before and after gamma irradiation.

Uncertainties values of: density ± 0.04 g/cm³, Vm ± 0.5 cm³/mol, Specific Volume ± 0.03 cm³/g, OPD ± 2 g atm/l and Eopt ± 0.1 e.V.

Optical UV absorption spectra

Studying both the optical UV–visible spectra and infrared spectroscopy of glasses can give information around the average coordination number, local symmetry in addition to the covalent bonds of metal ion with the shell neighbors [14]. Figs. 1-3 illustrate the UV–visible absorption spectra of the studied borate glasses before gamma irradiation and after the effect of four radiation doses; 10,60, 140 and 280 kGy. The Figures show a relative optical similarity for the examined glasses accompanying with the formation of some induced bands as follows;

Before irradiation;

(a)An ultraviolet absorption peaks at 230 nm

(b) A peak at 280-320 nm

(c) No visible bands identified before irradiation. After irradiation:

(a) An ultraviolet absorption peak at 230 nm

(b) A high peak extends from 320-360 nm however its absorption intensity is decreased at the dose of 280 kGy in all the investigated samples.

(c) A shift of the cutoff to longer wavelengths with the increase radiation dose.

(d) A visible band identified broadly in the wave length area ~560-620 nm in most of the prepared glasses after irradiation.

Many glass scientists [15-16] have investigated that the intense UV absorption peaks detected at about 200-350 nm are obtained from the unavoidable traces of iron impurities specially Fe³⁺ ions. These impurities are founded in the final products of the commercial glass samples where they might be produced either from the raw chemicals used in preparing glasses or from the pollution of the molten glasses by the furnace refractories through the melting process. Moncke and Ehrt 2004, 2006 [17, 18] have recommended that even if the trace ferric iron impurities are present in very limited concentrations (p.p.m), they would cause a charge transfer absorption and the presence of the intense UV absorption bands. So that highly pure chemical materials must be utilized in the preparation of specific kinds of optical glasses. This hypothesis denotes the existence of UV band at~ 230 nm to the electron transfer mechanism of Fe³⁺ ions that were present as impurities in the raw materials consumed in preparing the glasses.

Effect of gamma radiation on the UV-visible absorption spectra

Irradiating the glass network with an ionizing radiation like gamma rays causes some variations controlled by some factors such as; the glass chemical composition, the internal defects that were already founded inside the glass matrix, in addition to the type and the dose of radiation [19].

It was approved that the disordered structure of glass contains essentially pre-existing intrinsic defects like; oxygen vacancies, NBO, and imperfections obtained from highly energetic electrons. By exposing glass to gamma radiation, it disrupts directly the glass structure through breaking the bonds and altering the BO and NBO concentrations. According to UV-visible absorption spectra shown in Figs 1-3, there are three observed changes after irradiating all the studied glasses and can be interpreted as follows;

(1)The increase in the intensity of the strong absorption UV bands (230-360 nm) which is associated according to Moncke and Ehrt, 2004[17]hypothesis to the formed extrinsic defects produced due to the effect of irradiation that in turn causes some photochemical reactions; either photo-reduction or photo-oxidation of the transition metal TM ions existing into the glass. In the examined glasses and based on the previous assumption, the conversion of Fe^{2+} ions into Fe^{3+} ions was often predicted by accepting the formed positive holes caused by irradiation through a photo chemical reaction; photo-oxidation, thus the intensity increase of UV bands [7]. In other word, the principle effects of gamma rays on glasses could be recognized because of many purely electronic processes [8]. These effects take place because the excited electrons leave their sites and travel through the glass matrix. Therefore the addition or removal of one electron or further electrons from the internal defects or impurity ions causes the creation of induced color centers that absorb light. Consequently, a darkening of the glasses and an increase in the UV absorbance intensity after irradiation [20].

(2) Irradiating borate glasses produces induced positive hole centers into the host borate network [8] which consists of mixed BO_3 and BO_4 groups. So determining the additional induced visible band at about 560-620 nm can be ascribed to the sharing of the host borate glass itself in the creation of non-bridging hole centers (NBOC) or boron hole centers (BHC) [21].

Bishay [8] investigated previously that upon the progressive gamma irradiation of glasses containing BaO and SrO, they revealed distinct spectral changes generated from the induced defects e.g. the creation of boron hole centers and non-bridging hole centers in the visible region besides electron defects in the UV region. This behavior interprets the presence of the broad additional visible band at about 580-620 nm which were detected inmost of the irradiated prepared glasses as shown in Figs1-3.

(3) A clear intensity decrease in theUV absorption at the dose of 280 kGy in all the investigated samples has been obviously observed in Fig.1-3. Previously, Bishay [8] also reported that; to examine the radiation-induced properties of glasses, they should be irradiated to their level of the saturation dose. So the further continuing of irradiation process and producing high excess of NBO may cause a recombination of defect color centers leading to a decrease in the UV absorbance intensity at such high dose (280 kGy) in all the investigated glasses [11].



Fig. (2): Optical UV-visible absorption spectra of binary calcium borate glasses before and after gamma irradiation



Fig. (3):Optical UV-visible absorption spectra of binary strontium borate glasses before and after gamma irradiation.

Optical energy gap Eopt

In the amorphous glassy systems, the lone–pair (LP) electron states producea valence band whereas antibonding states producea conduction band. The energy gap in betweenthe two bands; valence and conduction; is well-defined as the optical energy gap (Eopt). This performance based on the belief that the photon energy is higher than the energy absorbed for the band gap [22]. Table 1 shows the values of the optical energy gap of the studied binary borate glasses before and after exposing to 60 and 280 kGy of gamma radiation by plotting $(\alpha hv)^n$ versus the incident photon energy (hv) asassumed by the previous relation assumed by Mott and Davis[10].

Figs. 4-6 show the plotting of $(\alpha hv)^{1/2}$ versus(hv) and the linear plots gives the relative values of Eopt that are ranged from 1.51 to 3.02 eV. It is observed from Figs.4-6 and Table 1 that increasing the dose of radiation causesthe decrease in Eopt values where they reveal lower values at 280 kGy than those at 60 kGy.

According to Feifei et al.[23],the increasing in glass bond strengthorigins a larger splitting between the two energetic bands (valence and conduction)leading to a growing in the value of optical band gap. This concept is approvedbyAbo-Naf et al. [24] who supposed that, the more covalent bonds inside the glassy network, not only

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strengthens its structure but also increasesthe bridging oxygens numbersthen higher Eopt values are obtained. However, irradiating glasses causes the alteration in their oxygen bond strength thru increasing the NBO concentration, becauseoxygens displacements from their normal positions lead to the transformation of the bridging oxygens BO into the non-bridging oxygens NBO. This behavior leads to he spin density increase or the unpaired electrons density increase in the unfilled bands.Therefore. morelocalized statesare createdand more electronic transitions occurred causing a declining in Eopt values with the progressive irradiation.

According to density and Eopt values listed in Table1, Eopt values give a compatible manner with the density results before radiation and at the dose of 60 kGy.Because both density and Eopt related directly to the crosslinking between individual atoms of the glass network and the structure compactness, since in the closed and compacted glassy systems, there are large gaps between energy levels and accordingly higher Eopt values. So it would be predicted that the denser and the more compacted glass, has higher Eopt values [5].

However this behavior becomes different at the dose of 280 kGy because glasses density values at

280 kGy are higher than those at 60 kGy although their Eopt values are lower. Also,Eopt values should have an opposite relation against the UV absorbance intensity but at this dose,the results displaylower Eopt values even withthe lower UV absorbance intensity. The last two different behaviors of decreasing Eopt even with the lower UV absorbance and the higher density values at the dose of 280 kGy,may be interpreted according to two assumptions;

(1)The first is correlated to the formingof available non-bridging oxygen's in the network- at this high dose-then the transformation of the triangular borate BO₃to the tetrahedral borate [BO₄] units. Consequently more compacted network or closed systemis produced because the more stable glasses have compacted tetrahedral structures[12]. Oppositely, many electronic transitions are occurred giving lower Eopt with the higher density values as revealed in Table 1.

(2) The secondassumptioniscorrelated to the highly induced disruptions formed at the high dose (280) kGy) like defect color centers; wrong bands [25] or the charge transfer from electrons in the glass matrix to the metal ions. Somany electronic transitions among the orbital sites particularly at the same orbital of the introduced modifier cationmay occur. Subsequently, a narrowing between the localizedstates givinglower Eopt values. Also the possibility of recombination between the formed defectcolor centersdue to reaching to the saturation dose at such high dose (280 kGy) would take place causing the decrease in absorbing UV light and thenlowering in UV absorbance intensity and Eopt values.



Fig. (4): A plot of $(\alpha h v)^{1/2}$ as a function of hv for binary barium borate glasses before and after gamma irradiation.



Fig. (5): A plot of $(\alpha hv)^{1/2}$ as a function of hv for binary calcium borate glasses before and after gamma irradiation.



Fig. (6): A plot of $(\alpha h v)^{1/2}$ as a function of hv for binary strontium borate glasses before and after gamma irradiation.

FTIR Infrared absorption spectra

FTIR spectroscopy is very imperative and helpful tool used in identifying the structural environment of materials and their identified structural groups. Addition of alkaline earth metal oxides to B_2O_3 network causes the alteration of boron coordination numberdue to the formation of BO_4 coordinated boronfrom the BO_3 coordinated boron. This performance is relevant to the change in boron super structural units because alkali ions causes the exchange from broxol ring that involved only BO_3

units to other super structural groups involving higher concentrations of the tetrahedral form $[BO_4]^{-}[26]$.

Fig.7illustrates the FTIR absorption spectra of the studied binary borate glasses beforeirradiation.The spectra shown in Fig. 7 reveal fourbasic active areas in IR spectra region;400-4000 cm⁻¹ as follows;

(1) 460-800 cm⁻¹ revealing peaks at ~ 470- 540, 670-750 cm⁻¹

(2) 800-1200 cm⁻¹ revealing peaks at ~950-980 and 1060 cm^{-1}

(3)1200-1400 cm⁻¹ revealing peaks at~ 1230 and 1380cm⁻¹

(4) Small broad peaks at 2030- 2380, 2700-2980 and 3700-3800 cm^{-1}

The features of the obtained spectral results shown in Fig.7indicate the prevalence of vibrations of different borate groups. Where the small bands in thefar-infrared spectral area at 470- 540 cm⁻¹ represents the vibrations of the introduced metal cations Ba²⁺, Ca²⁺, or Sr²⁺ ions [20] and the area at 670-750 cm⁻¹ represents the IR bending vibrational modes of B-O-B linkages in borate network. While the area at 800-1250 cm⁻¹ reveals the B-O stretching of tetrahedral BO₄ groups [27] and the IR area at 1200-1600 cm⁻¹ reveals the B-O stretching of triangular BO₃ units [28].

Most of the observed IR features were appeared into the mid infrared where region thecentralvibrational modes relatedto borate network were above 500 cm⁻¹. This behavior is attributable to he point that boron has the smallest atomic mass among the other network forming cations. It wasalso noticeable from the spectra before irradiation, that the IR spectral features of

the examined binary borate glasses are relatively similar,demonstrating that the alkaline earth oxides BaO, CaO or SrO behave only as network modifiers and they are located into the network modifying sites [20].

Effect of gamma radiation on the infrared absorption spectra

Figs. 8-11illustrate the FTIR absorption spectra of the studied binary borate glasses after irradiating with 10, 60, 140 and 280 kGy, respectively. The radiation effect on the glassy structure s controlled mainly bythe glass matrix composition in additionto, the energy type of radiation and the total dose. There are two essential interactions of radiation on glasses; ionization of electrons (electron defects) and the direct displacementof lattice atoms. So irradiating the group arrangement of the glass network make it more asymmetrical, thus a weakening of the networkgrouping vibrations and changes the average in bridgingbond angles may occur. Consequently variations in the vibrational peaks on the IR spectrum take place[29].

By comparing FTIR spectra of the studied glasses before and after being exposed to four gamma



Fig.(7): FTIR absorption spectra of the prepared binary borate glasses before irradiation.

radiation doses as revealed in Fig.7-11, it is observed that;

(1) At 10 kGy in Fig.8: the infrared absorption spectra are the same like those before irradiation where the basic vibrated groups havesimilar numbers and positions like the un-irradiated curves. This behavior indicates the stable behavior of the examined glasses against this radiation dose.

(2) At 60 kGy in Fig.9: there are obvious variations because of irradiating glasses by this dosesuch as an insignificant increase in both thesharpness and intensities of the peaks, besides the appearance of some peaks e.g;

(a) Sharp peak at 1230 cm^{-1} related to pyro- and ortho- borate groups.

(b) Sharp peaks at about 1330 and 1380 cm⁻¹corresponded to the asymmetric stretching of B–O bond in $[BO_3]$ and $[BO_2O]^-$ [26].

(c) Asharp absorption peak near 1500 cm⁻¹ correlated to the stretching modes of B–O–B bonds in triangular [BO₃] ⁻ in different borate groups [30].

(d) A small absorption peaks near 1580 and 1750 $cm^{-1}correlated$ to the asymmetric stretching relaxation of B-O bond of BO₃triangular units with NBO [31].

(3) At 140 and 280 kGy in Figs. 10&11, it is obvious that, besides the three main active regions appeared in far and mid- infrared regions before irradiation (460-800, 800-1200 and 1200-1600 cm ¹), peaks at 2030-2980 cm⁻¹ and 3600-3800 cm⁻¹ are appeared more obviously near the infrared region after irradiating glasses with either 140 or 280 kGy, where they represent the vibrational modes of H₂O, OH groups and/or B-OH groups [32, 33]. The appearance of these near IR peaks more obviously at the highest radiation doses, may berelated to the accumulativecreation of more NBO on account of the persistentradiation process. This behavior indicates that the structures of the examined glasses are highly affected because of irradiation with these two high doses which is indicated also by shifting major peaks to lower wavenumbers.

The FTIR Figs.7-11reveal a general observation due to the effect of radiation on the prepared glasses; where the concentration increase of the same modifier ion leads to the increase in absorbance intensity of peaks at 850-1200 cm⁻¹ conversely the decrease of the peaks at 1200-1600 cm⁻¹. This behavior indicates the creation of more NBO with the increase of the introduced modifier cation concentration, then the transformation of the triangular BO₃ into the tetrahedral BO₄⁻ units demonstrating the participation of the introduced metal cationsBa²⁺, Ca²⁺ or Sr²⁺ as modifiers inside the glass network [12].



Wave number "cm⁻¹"

Fig.(8): FTIR absorption spectra of the prepared binary borate glasses after gamma irradiation with 10 kGy.



Fig. (9): FTIR absorption spectra of the prepared binary borate glasses after gamma irradiation with 60 kGy



Fig. (10): FTIR absorption spectra of the prepared binary borate glasses after gamma irradiation with 140 kGy.



Fig. (11): FTIR absorption spectra of the prepared binary borate glasses after gamma irradiation with 280 kGy. *Arab J. Nucl. Sci. & Applic.* **Vol. 53,** No.2 (2020)

Electron Spin Resonance spectra (ESR)

ESR spectroscopy is studied to identify the irradiation-induced changes concerning to the paramagnetic defectslikecenters with unpaired electrons.So the detected signals obtained from ESR spectra can give information about the natures and kinetics of the structural alterations taking place at the defects sites. Therefore ESR technique is considered as a fingerprintfor the paramagnetic centers formed because or radiation[34]. Figs.12-14demonstrate the ESR spectra of the un-irradiated and irradiated alkaline earth borate glasses with four gamma radiation doses.Where there are no real peaks appeared for the un-irradiated and 10 kGy irradiated glasses however, there is onesignal with small intensity (not real ESR peak) appeared for 60 kGy irradiated glasses. But two obvious ESR signals with high intensity are appeared at the doses of 140 and 280 kGy.

Before irradiation and at the first radiation dose (10 kGy), the ESR data for all the glasses reveal diffuse resonance spectra without any distinct signals reflecting the high stability of the prepared glasses against the relative low dose of radiation. This effect continues when the glasses are

irradiated with 60 kGy where a small neglected signal wasperformedindicating the relatively start of radiation effect. Conversely,when the glasses are irradiated with either 140 or 280 kGy,high intensity distinctive signals are appeared because ofcreating more defects, NBO and/or atomic displacements. Accordingly theaccumulation of unpaired ions and capturing of electrons or positively charged holes that cause a clear distinction of the paramagnetic centers at such high doses.

The last behavior is combatable with the Eopt values that are decreased with increasing the radiation dose.Because, when the glasses are irradiated withthe highest doses of radiation (e.g. 280 kGy),forming of defect centers and NBO are enhancedand more electronic transitions are taken place causing alowering in Eopt values. In other words,the progressive irradiating of glasses with the high doses (140 or 280 kGy) enhances the changing in oxygen bond strength by increasing OPD that gives higher chance to the photons to pass throughout the material andcausingthe creation of more free radicalsthen a typical ESR signals.



Fig. (12): ESR spectra of binary barium borate glasses before and after gamma irradiation.



Fig. (13):ESR spectra of binary calcium borate glasses before and after gamma irradiation.



4. Conclusion

Studying of some physical and spectroscopic properties of the prepared alkaline earth binary borate glasses before and afterdifferent doses of radiation reveal the following gamma interpretations; The density values of glasses increase with increasing the mass of the introduced modifier ions Ba^{137.33}> Sr^{87.62}> Ca^{40.08} and also with increasing the introduced modifier ion progressive concentration because of the conversion of triangular BO3 units to the more compacted tetrahedral BO₄ groups. Also, the OPD values give an agreement with the density results. After irradiation, the high dose (280 kGy) gives relatively higher density and OPD values than those at 60 kGy for all the examined glasses.

The UV–visibleabsorption spectra reveal a strong UV bands at~ 230-350 nm which is correlated to the electron transfer mechanism of Fe^{3+} ions that present as impurities in the raw materials used in

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preparingglasses. After gamma irradiation, the growing of these bands is owing to the photooxidation process comingfrom the transformation of Fe^{2+} ions into Fe^{3+} ions. While the additional broad visible band at about 580-620 nm are generated due to the induced defects of boron hole centers or non-bridging hole centers. Eopt values revealed an obvious decrease with increasingthe radiation dose because of the effect of radiation in enhancing the formation of NBO and increasingthe unpaired electrons density in the unfilled bands allowing more electronic transitions to take place. In spite of the low UV absorbance and high density values at the highest radiation dose (280 kGy),Eopt values are decreased because of creating more NBO and the transformation of $[BO_3]$ into the more stable tetrahedral borate $[BO_4]$, thus more closed structures with higher density are produced. In addition to the probability of recombining the formed defect color centers through reaching to the saturation dose causing a decrease in theUV absorbance intensity.

The FTIR spectral features of the studied glasses show three active bands;(1) at $460-800 \text{ cm}^{-1}$ representing B-O-B linkages of borate network vibrations or the vibrations of introduced metal cations Ba^{2+} , Ca^{2+} , or Sr^{2+} ions,(2) at 800-1250 cm⁻ representing the B-O stretching of tetrahedral 1200-1600 BO_4 units and (3)at cm⁻¹ representing the B-O stretching of triangular BO₃ units. The relative similarity in IR spectra of unirradiated glasses indicates the behaving of BaO, CaO or SrO as network modifiers only. After irradiation, FTIR spectra displayrising in peaks absorbance intensity at 850-1200 cm⁻¹ corresponding to the decrease of the peaks at 1200-1600 cm⁻¹ because of creating more NBO and the transformation of the triangular BO₃ into the tetrahedral BO₄⁻ units as a result of irradiation.

ESR spectra demonstrate a similar effect of the studied glasses towards the different gamma irradiation doses as they reveal a stable behavior against the approximately low radiation doses up to 60 kGy, however they are highly affected at the higher radiation doses (140 and 280 kGy).

The overall view obtained from this study recommendedusing the prepared alkaline earth binary borate glasses as gamma radiation shielding materials for only the low radiation doses before 60 kGy but not suggested for shielding the higher doses.

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