STUDY OF THE OPTICAL BAND GAP ENERGY ASSOCIATED TO OPTICAL MATERIALS EXPOSED TO LOW DOSES OF GAMMA-RAYS

A. CELAREL, C. TUTA, G.-V. IOAN*

Horia Hulubei National Institute for Nuclear Physics and Engineering,
30 Reactorului Street, P.O. Box MG-6, RO-077125 Bucharest-Magurele, Romania,
*Corresponding author: igabriel@theory.nipne.ro

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Abstract. In this paper, the analysis of the absorption spectra and the experimentally determination of the forbidden band structure associated to a batch of optical materials with high potential to be used in ionizing radiation environments was studied. The present study was focused on the low absorbed gamma-ray doses region (<105 Gy) and the chosen optical materials were BK-7 and ZF-7 glasses. The variation of the optical band gap energy, for the direct and respectively indirect types of optical absorption, as a function of the absorbed dose value is presented. For the dense flint ZF-7 type glass, a relative decrease of 2.7% of the optical band gap energy for the direct transition, respectively 2.9% for the one corresponding to the indirect transition were determined. In the case of borosilicate BK-7 type glass, the relative decrease of the optical band gap energy was found to be 7.8% for the direct transition and 4.8% for the indirect one. These kinds of studies allow obtaining more complex information regarding the optical phenomena occurring at the propagation of the light through optical glass materials, phenomena that influence the optical parameters of the studied materials. The main goal of the present study was to investigate, in an more complex manner, the fundamental properties of the two chosen types of optical materials when interacting with ionizing radiation and, as a result, to characterize their radiation hardness and the possibility of being used in gamma-ray dosimetry.

Key words: gamma-ray, glass browning, absorbance, absorption coefficient, optical band gap.

1. INTRODUCTION

Glass is an outstanding versatile optical material that has plenty of applications in all kinds of fields, including nuclear physics related activities. Due to its wide range of applications, the study of glass's optical properties is a very important task to be fulfilled [1–4]. All materials show direct and indirect transitions on the electronic structure bands, leading to the absorption of the light passing through them. In regular standard conditions, the presence of impurities or defects in the structure of materials (resulted from the manufacturing processes) leads to absorption of the incident light. In this case, the energy of the absorbed light produces transition of the electrons between the discrete energy levels and the conduction or valence bands. In the case of exposing glass materials to ionizing radiations, the presence of impurities in their structure, even in a low quantity, leads to an increased vulnerability of them, by activating the absorption centers (color centers). This phenomenon is also known as „glass browning” or *radiation induced absorbance* (RIA). The occurrence of this phenomenon leads to the deterioration of the performances (optical parameters) of the exposed materials [5–9]. As well as all the solid state materials, the glass shows a specific configuration of its corresponding energy bands. This fact determines and explains the absorption processes occurring in the frame the intimal interaction between photons and the material. Due to this dependence between absorption processes and the energy bands corresponding to a studied material, the knowledge of the optical absorption is able be used as an experimental manner of analyzing the energy bands structure (direct or indirect).

The incident energy transported by the electromagnetic radiation, E_λ, absorbed by an optical material leads to a multitude of dominant specific physical processes: absorption of light on impurities (indirect transition, $E_\lambda < E_g$) and fundamental absorption (direct transition, $E_\lambda > E_g$). In these cases, the energy transported by the incident photons is high enough to be able to produce transitions of the electrons from the valence band to the conduction band, which is expressed by the wavelength-dependent absorbed light spectra, $\alpha(\lambda)$. In the case of exposing the optical materials to ionizing radiation, the absorption spectra are also dependent to the absorbed dose [10–16].

2. METHODS AND MATERIALS

An optical material can be characterized through a series of observables that can be determined experimentally by spectrophotometrical measurements. These observables are determined starting from measurements of direct observables, as reflectance (R), transmittance (T) and absorbance (A), and by correlating them with the optical constants (fundamental optical constant, absorption coefficient, initial and absorbed energies) of the studied samples.

In this study, six samples of each of the two chosen optical materials (ZF-7 and BK-7 glasses) were exposed to gamma-rays provided from a Co-60 source ($E_{mean} \sim 1.25$ MeV) at Horia Hulubei National Institute for Nuclear Physics and Engineering (IFIN-HH), Romania. The maximum absorbed dose value was 105 Gy, accumulated at a dose rate of 27 mGy/s. The absorbed dose rate was determined using a calibrated 30006 type “Farmer” ionization chamber. The absorbed dose values and their corresponding uncertainties are presented in Table 1.

Table 1

Absorbed dose values and their associated uncertainties

Absorbed dose values						
D [Gy]	3.2	6.4	12.8	25.6	54.3	105.0
σD [Gy] (k=2)	0.1	0.2	0.4	0.8	1.7	3.3

The absorbance spectra of the BK-7 and ZF-7 (67% lead content) glasses were obtained using an UV-VIS SP-SM242 type spectrophotometer from Spectral Products. The absorption spectra corresponding to the two chosen types of optical materials (ZF-7 and BK-7 glasses) are presented in Fig. 1.

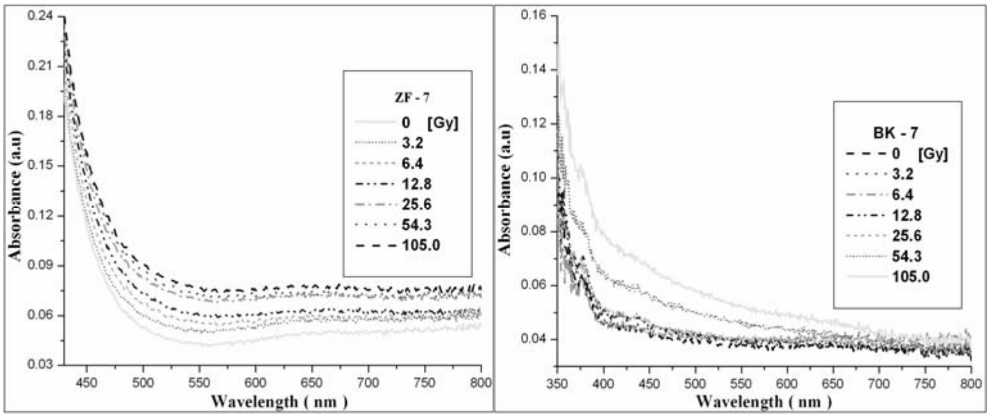

Fig. 1 – Absorbance spectra corresponding to ZF-7 (left) and BK-7 (right) studied glass types.

In Fig. 1, a narrower optical spectral band of the ZF-7 dense flint related to the one corresponding to the BK-7 borosilicate glass can be observed. For the ZF-7 type optical materials, the variance of the absorbance is quasi-constant on the (550–800) nm wavelengths range, while for the BK-7 type ones the quasi-constant region was found to start from 700 nm.

At the photon-sample interaction, following the absorption and for a low reflection (transparent materials), the intensity of the light along with the *x* distance through material vary according Lambert-Beer law [17]:

$$I = I_0 \cdot \exp(-\alpha \cdot x) \tag{1}$$

where: I – intensity of light at *x* distance;
I_0 – initial intensity of the light;
α – absorption coefficient;
x – sample's thickness.

In order to obtain the expression of the absorption coefficient, the relation (1) becomes, [18, 19]:

$$\alpha = \frac{1}{x} \cdot \ln \frac{I_0}{I} \tag{2}$$

The direct optical absorption is the most important mechanism by which the main quantity of energy of the incident light is absorbed by the passed through optical material (high probability of occurrence), involving transitions for which the maxim value of the valence band and the minim value of the conduction band are situated in the same point in the space of the wave vector. The indirect optical absorption is the phenomenon with a lower probability of occurrence than the direct one, involving transitions for which the maxim value of the valence band and the minim value of the conduction band are situated in different points in the space of the wave vector. In an optical material, depending to elemental composition, impurities content and the structure of the main matrix, both types of transitions may appear.

The analytical expression between the absorption coefficient, the incident energy and the energy of the optical band gap is (3):

$$\alpha \cdot E_{\lambda} = c \cdot (E_{\lambda} - E_{g})^{n} \tag{3}$$

where n is the number characterizing the optical transition process (0.5 for direct transitions and 2 for indirect transitions) [20]. In the case of the optical materials studied in this paper, both types of transition were considered, as follows, [21, 22]:

$$(\alpha \cdot E_{\lambda})^{2} = c^{2} \cdot (E_{\lambda} - E_{g}) \quad \text{– direct transition} \tag{4}$$

$$(\alpha \cdot E_{\lambda})^{0.5} = c^{0.5} \cdot (E_{\lambda} - E_{g}) \quad \text{– indirect transition} \tag{5}$$

where: E_{λ} – incident photon energy (wavelength dependent);
E_g – optical band gap energy of the material;
α – optical absorption coefficient;
c – constant (independent of energy).

From the graphics representing $(\alpha \cdot E_{\lambda})^{0.5}$ and $(\alpha \cdot E_{\lambda})^{2}$ as a function of E_{γ}, the value of the energy of the optical band gap, E_g, is obtained by extrapolating the nonlinear intervals.

The relation (4) is applicable for high energy photons, while the relation (5) is appropriate for the low energy photons. This approach describes the difference between optical band gap energies, meaning that the optical band gap energy for the direct transitions is higher than the one for indirect transitions.

By fitting the experimental points representing the dependence of the energy of the variation of the optical band gap to the different well known gamma-rays absorbed dose values, the expressions of the two possible dosimetric parameters is obtain. The general expression is given by relation (6), [3], as follows:

$$E_{gi} = a_{E_{gi}} + b_{gi} \cdot \log(D_{d_i}) \tag{6}$$

where: E_{gi} – determined optical band gap energy for direct transitions (i = 1) and indirect transitions (i = 2);
$(a_{Eg})_i$, $(b_{Eg})_i$ – fitting parameters;
d – number associated to each absorbed value.

By applying the law of propagation of uncertainties to relation (6), the following relation is obtained (7):

$$\sigma^2_{E_{gi}} = \sigma^2_{a_{E_{gi}}} + \left(\log(D_{d_i})\right)^2 \cdot \sigma^2_{b_{E_{gi}}} + \left(\frac{b_{E_{gi}}}{2.3 \cdot (D_{di})}\right)^2 \cdot \sigma^2_{D_{di}} \quad (7)$$

By rewriting the relation (6), the general form of the equation representing the estimation of the absorbed, D_{di}, is obtained as:

$$D_{d_i} = 10^{\frac{E_{gi} - a_{E_{gi}}}{b_{E_{gi}}}} \quad (8)$$

The concrete form of the law of propagation of uncertainties associated to equation (8) is given by the following equation:

$$\sigma^2_{D_{di}} = \left(2.3 \cdot b_{E_{gi}} \cdot D_{d_i}\right)^2 \cdot \left[2 \cdot \sigma^2_{a_{E_{gi}}} + \left(\left(\log(D_{d_i})\right)^2 + \frac{x_i - a_{E_{gi}}}{b_{E_{gi}}}\right) \cdot \sigma^2_{b_{E_{gi}}} + \left(\frac{b_{E_{gi}}}{2.3 \cdot D_{di}}\right)^2 \cdot \sigma^2_{D_{d_i}}\right] \quad (9)$$

All the quantities associated to Eqs. (8) and (9) are known.

3. RESULTS AND DISCUSSIONS

For optical materials, the marginal value from where the absorption is starting to appear (direct or indirect) may be used in order to obtain the optical band gap energy, E_g, following Davis and Mott theory [23]. The band corresponding to the difference between conduction and valence bands can be obtained using the position of the edge of the absorption spectrum. This parameter provides information regarding the modification of the electrons distribution as a result of exposing an optical material to ionizing radiation. The energy of the optical band gap as a function of the incident photons energy, for the non-irradiated ZF-7 and BK-7 optical materials is presented in Fig. 2.

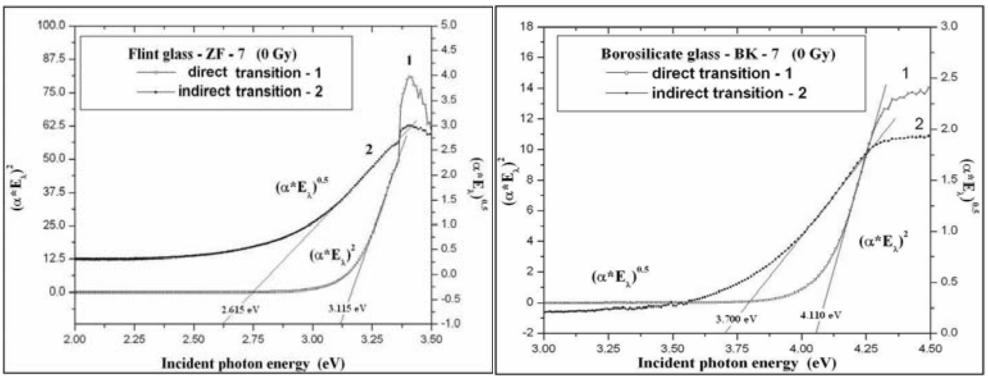

Fig. 2 – Optical band gap energy *vs*. incident photon energy (ZF-7 and BK-7; non-irradiated sample).

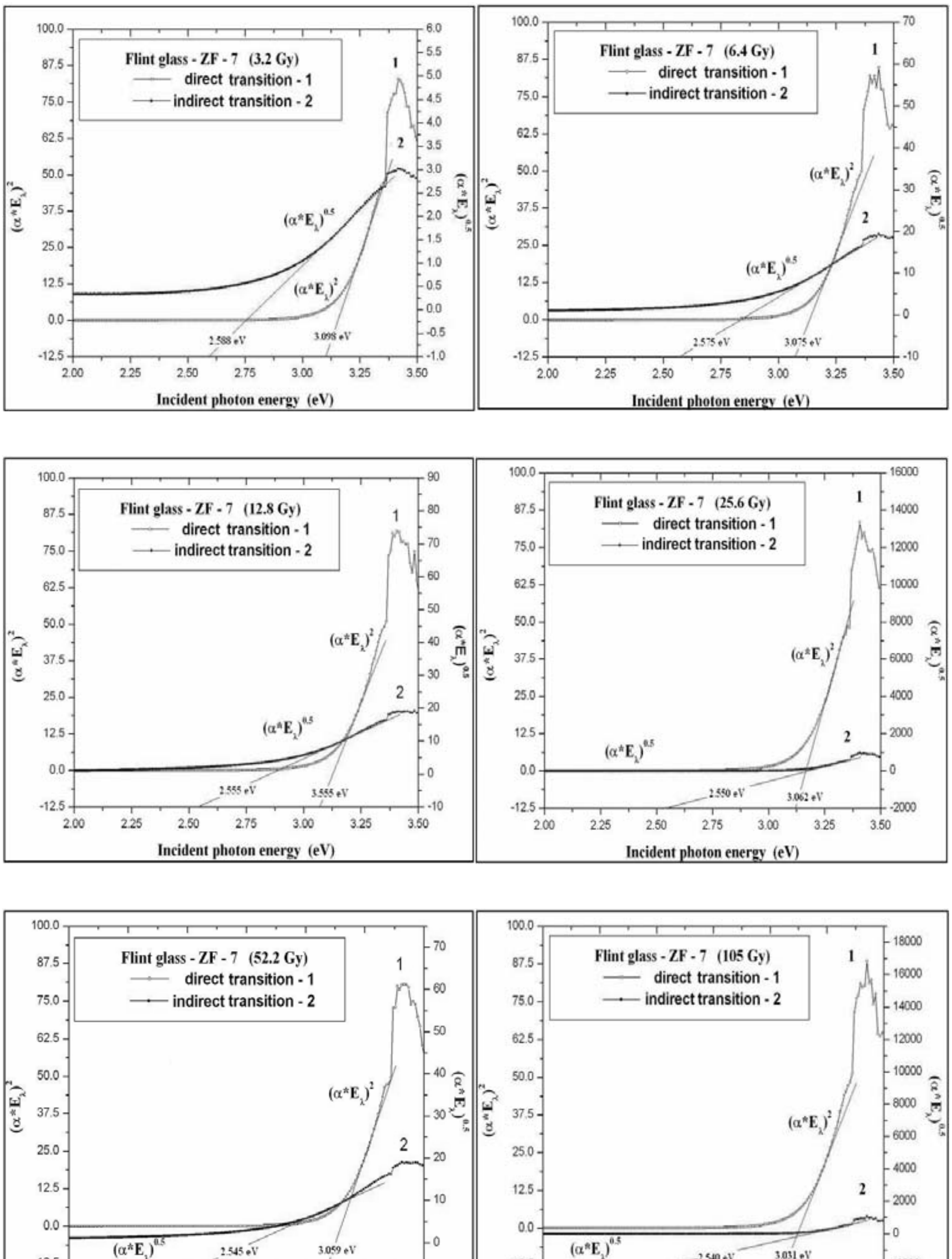

Fig. 3 – Optical band gap energy of ZF-7 glass *vs.* incident photon energy (the six absorbed dose values).

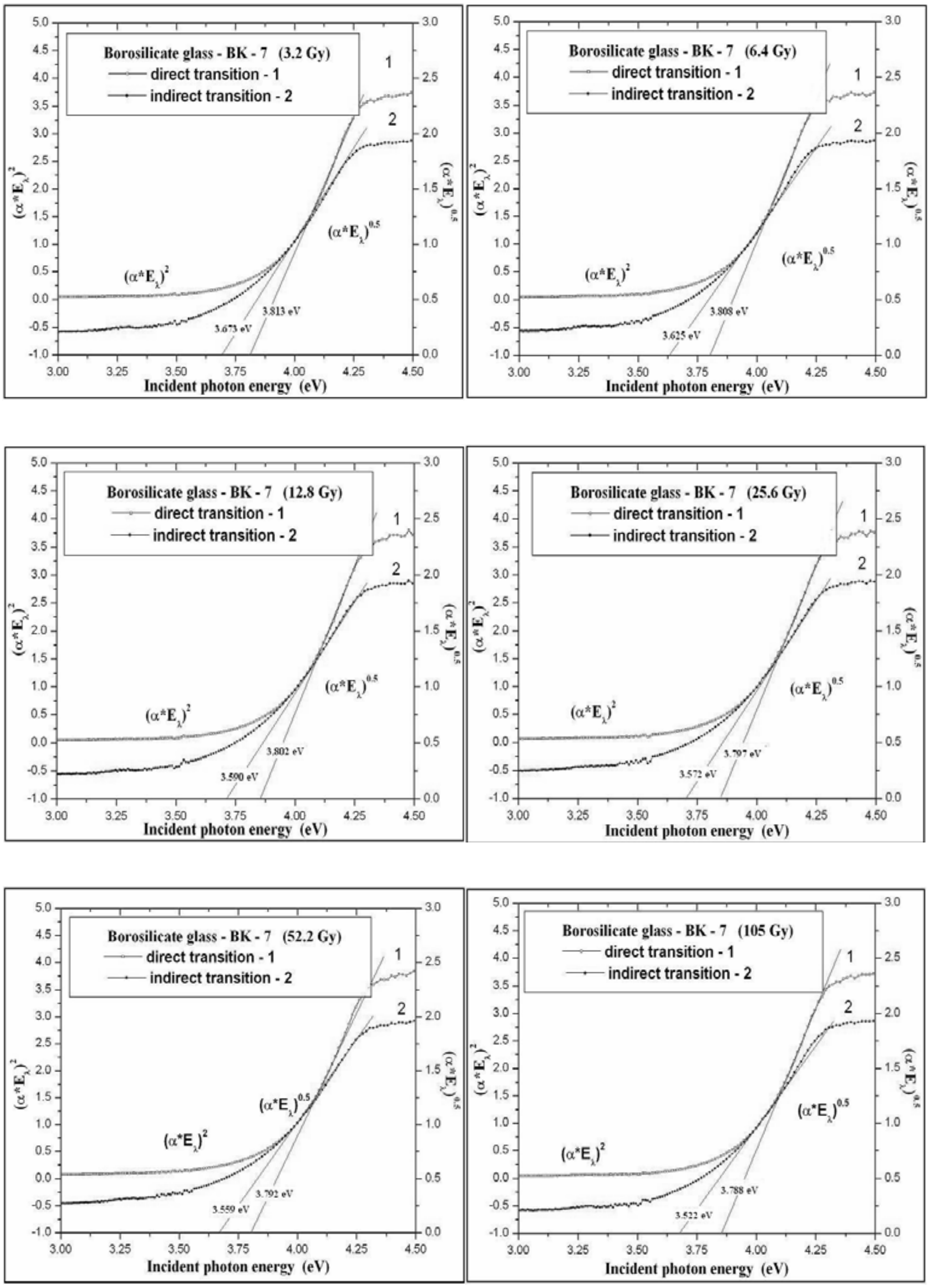

Fig. 4 – Optical band gap energy of BK-7 glass *vs.* incident photon energy (the six absorbed dose values).

As it can be seen from Fig. 2, for the non-irradiated ZF-7 glass the value of optical band energy corresponding to the direct transition was found to be of 3.1 eV, which is with about 3.3% smaller than the one found in literature, of 3.5 eV [24]. In the case of the BK-7 glass, the value of optical band energy corresponding to the direct transition was found to be of 4.11 eV, which is with about 3.9% smaller than the one found in literature, of 4.28 eV [23]. In both cases, the small differences are probably due to the differences between the batches used in this paper and the ones used for obtaining the data in references.

The energy of the optical band gap as a function of the incident photons energy, for the six absorbed dose values, is presented in Fig. 3 for the ZF-7 glass and in Fig. 4 for the BK-7 glass.

The optical band gap energies corresponding to the ZK-7 and BK-7 glasses as a function of the absorbed dose are presented Fig. 5. For both glass types, the optical band gap energy for direct transitions was obtain from the graphic corresponding to Equation (4) and the one for indirect transitions was obtain from the graphic corresponding to Equation (5).

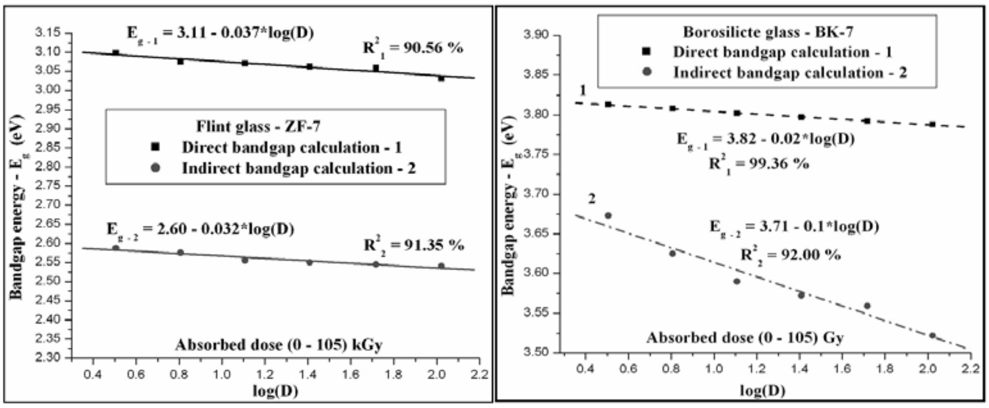

Fig. 5 – Optical band gap energy of ZF-7 (left) and BK-7 (right) glass *vs.* absorbed dose.

In Fig. 5 (left), a relative decrease of 2.7% of the optical band gap energy for the direct transition and one of the 2.9% for the indirect one as a function of the absorbed dose value are observed. In Fig. 5 (right), a relative decrease of 7.8% of the optical band gap energy for the direct transition and one of the 4.8% for the indirect one as a function of the absorbed dose value are observed. These decreases are due to the exposure to increased gamma-rays absorbed dose values.

Due to its proportionality with the absorbed dose value, the optical band gap energy is suitable to be used as dosimetric parameter. In this paper, for the glass types used, the linearity interval was validated only for the (0–105) Gy interval. This interval can be extended using other thicknesses of glass or other optical materials. The relation between the optical band gap and absorbed dose is given by equation (8), with the associated uncertainty (9). The fitting parameters associated to relation (8) and their uncertainties are presented in Table 2. One of the most important aspects giving the accuracy of the method is the calibration process, mainly in the very low region of the absorbed dose values [25, 26].

Table 2

Fitting parameters associated to relation (8) and their uncertainties

The absorbed dose range 0–105 [Gy]	Fitting parameters	a_{Egi}	b_{Egi}	σ_{aEgi}	σ_{bEgi}
Optical band gap energy ZF-7	E_{g1}	3.11	0.037	0.008	0.006
	E_{g2}	2.60	0.032	0.007	0.005
Optical band gap energy BK-7	E_{g1}	3.82	0.02	0.0007	0.0005
	E_{g2}	3.71	0.1	0.01	0.009

4. CONCLUSIONS

An UV-VIS spectrophotometer was used to obtain the absorption spectra of two types of optical materials (ZK-7 glass and BK-7 glass). The results showed that the absorption was increased as the samples were exposed to increasing values of absorbed dose. The dependence between the two quantities was found to be linear on the absorbed dose interval considered, (0–105) Gy.

For the optical materials, the optical band gap energy E_g was determined for both direct and indirect transitions, using Davis and Mott theory. For the direct transitions and for both types of studied optical materials, the relative differences between the determined values of the optical band gap and the ones found in literature were within 5%. The decrease of the energy of the optical band gap as a function of the gamma-rays absorbed dose values is the property suitable to be used in dosimetry.

From the experimental data, it can be observed that edge from where the absorption starts occurring (optical band gap) is sensitive to exposure time (absorbed dose value). This aspect can be attributed to the modification of the electronic configuration due to the absorption of the energy provided by the gamma-rays. For the ZF-7 glass, relative decreases of 2.7% of the optical band gap for the direct transition and of 2.9% for the indirect transitions were found. In the case of BK-7 glass, relative decreases of 7.8% of the optical band gap for the direct transition and of 4.8% for the indirect transitions were determined.

These conclusions highlight the suitability of the optical band gap to be used as parameter in gamma-rays dosimetry. The presented results were validated only for the studied optical materials and only for the studied (0–105) Gy dose interval.

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