Formation of color centers and concentration of defects in boron carbide irradiated at low gamma radiation doses

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Abstract

In the present work, boron-carbide (B_4C) samples (purity of 99.5% and density of 1.80 g/cm^3) were irradiated by using gamma radiation from a ^{60}Co gamma source. Gamma irradiation of the samples was carried out at doses 48.5, 97, 145.5 and 194 kGy. The samples were analysed using a UV-V Gary 50 Scan spectrophotometer. The effect of different irradiation doses on the defects created in the B_4C samples was investigated. In the B_4C samples, the formation processes for color centers depended on the gamma irradiation dose. The calculated activation energies at room temperature essential for the formation of F and F^+ color centers ranged from 1.89 – 2.05 eV.

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1. Introduction

A number of methods, such a X-ray irradiation, electron irradiation, *etc*, are used to produce color centers in samples. The interest in color centers is due to their distinctive properties, which are used in applications such as the realization of broad-band emitting lasers and amplifiers in the optical domain operating at room temperature [1]. Gamma irradiation is one of those methods used [2–4]. In most materials, the gamma irradiation energy is converted into heat while a small part induces radiation damage [5–8]. Color centers in boron-carbide have been extensively investigated using different irradiation methods so as to identify the best method to be employed for inducing them [9,10].

Gamma irradiation of boron-carbide induces the formation of F color centers. The irradiation of a boron-carbide compound results in the formation of defects, and the defects generated are pairs of F and H color centers [11]. After gamma irradiation of the boron-carbide

crystal structure, ions are ejected from their normal lattice sites to form cracked boron and carbon atoms (H-color centers). The H-centers are easily trapped because of their high mobility. At temperatures above 30 °C, as is the case of heat producing waste, the mobility of primary defects is increased [12]. The difference in the radiation damage created depends highly on the temperature of the applied irradiation, the level of impurities present, the dose rate and the total dose [13]. Even though radiation damage in boron carbide has been extensively studied, no studies have been done for low gamma irradiation doses. This study investigated the formation of color centers and the concentration of defects in boron carbide when irradiated by gamma radiation at different low doses.

2. Computational Methods

The B_4C (US Research Nano Materials Inc.) samples were irradiated at room temperature by using 1.17 MeV gamma radiation from a ^{60}Co gamma source at four different irradiation doses. Gamma irradiation of the samples was conducted at the K-25 radiation-chemical facility located at High Technologies Centres, Azerbaijan National Academy of Sciences. A gamma dose rate D of 0.27 Gy/sec and total gamma irradiation doses ranging from 48.5 to 194 kGy were used [14–17]. All the gamma irradiated boron-carbide samples had diameters d of 7 μm, thicknesses h from 200 to 500 nm and an average grain size of 10 μm. For irradiation, the samples were mounted on a sample holder placed at an angle of 90° relative to the gamma ray beam, which had a scan rate of 600 nm/min.

Optical absorption measurements on the samples were performed using a UV-V Gary 50 Scan spectrophotometer (Varian). The optical absorption spectra were collected within the wavelength scanning range from 200 nm to 800 nm because the absorption bands of the F color centers are found at about 460 nm and there of the M color centers at 700 nm. The volume concentration of the defects in the samples was calculated using the semi-empirical Smakula formula given by [18,19]

$$N_{\mathrm{CCs}}\left(\mathrm{cm}^{-3}\right) = \mathrm{Abs} \times \frac{\ln 10}{t} \times \frac{10^{16}}{2.06 \cdot f}, \tag{1}$$

$$\alpha = \frac{\ln 10}{t}\,\mathrm{Abs}, \tag{2}$$

where N_{CCs} is the number of F-centres per cm^3, t is the thickness in cm, Abs is the maximum absorbance of the material, f is the oscillator strength between 0.8 to 0.9, and α is the absorption coefficient in cm^{-1} [20]. The absorption coefficient can be written in terms of the optical density OD by using

$$\alpha = \frac{\mathrm{OD}}{\log_{10}^{e} \cdot R} = 2.3 \cdot \frac{\mathrm{OD}}{R}, \tag{3}$$

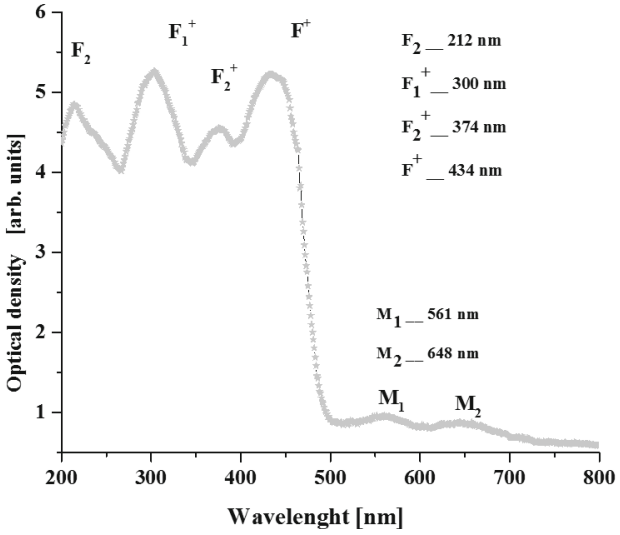

Fig. 1. Absorption spectrum of the unirradiated boron-carbide sample.

where R is the range of the gamma ray in the material.

The diffusion of point defects in the sample occurs when atoms jump from one lattice site to another due to an increase in temperature. The defect concentration N_{F}, which changes with temperature T and time t, can be calculated using

$$\frac{N_{\mathrm{F}}}{N_0} = \exp(-\nu t), \tag{4}$$

where N_0 gives the defect concentration after gamma irradiation. The diffusion frequency at room temperature is given by

$$\frac{N_{\mathrm{F}}}{N_0} = \exp\left(-\nu_0 t \cdot \exp\left(-\frac{E_{\mathrm{A}}}{k_{\mathrm{B}} T}\right)\right), \tag{5}$$

where ν_0 is a frequency factor (0.012 ± 0.004), E_{A} the activation energy for formation of vacancies and k_{B} the Boltzmann constant [20].

3. Results and Discussion

Figure 1 shows the absorption spectrum of unirradiated boron-carbide sample. From this boron-carbide spectrum, four F^+ color centers at wavelengths of 212 nm, 300 nm, 374 nm and 434 nm with an activation energy of about 1.89 eV were observed. From the same absorption spectrum, two M color centers, one each at 561 nm and 648 nm, with an activation energy of 0.1 eV were also observed. The absorption of F^+ color centers increased when the samples were gamma irradiated at 48.5 kGy (see Fig. 2). A continuous increase in the absorption F^+ color centers with increasing gamma irradiation dose was generally observed as indicated in

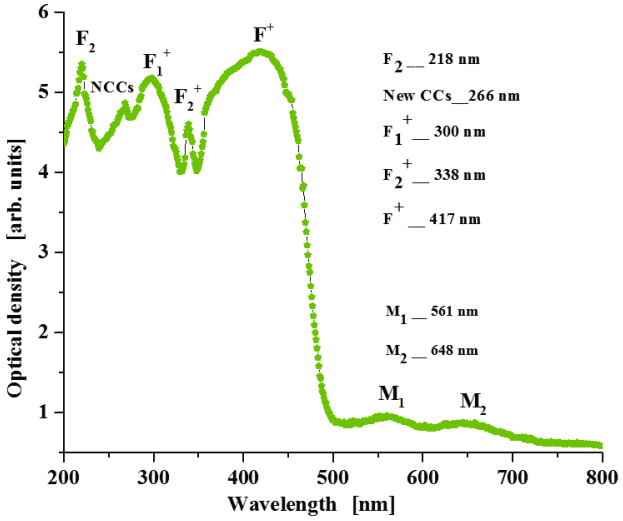

Fig. 2. Absorption spectrum of the boron carbide sample gamma irradiated at a 48.5 kGy dose.

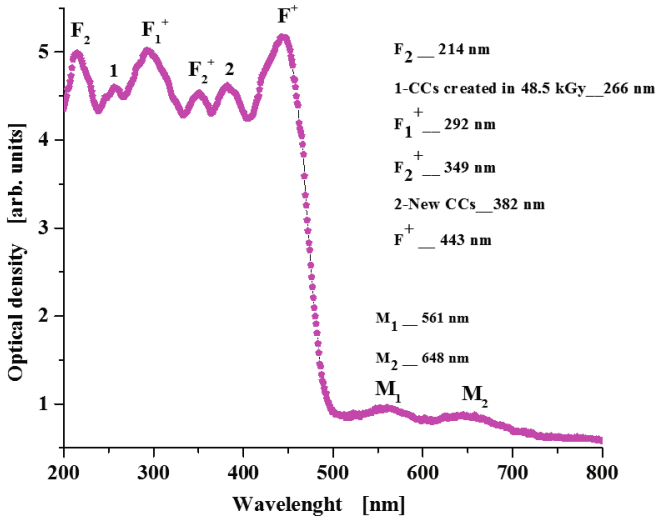

Fig. 3. Absorption spectrum of the boron-carbide sample gamma irradiated at a 97 kGy dose.

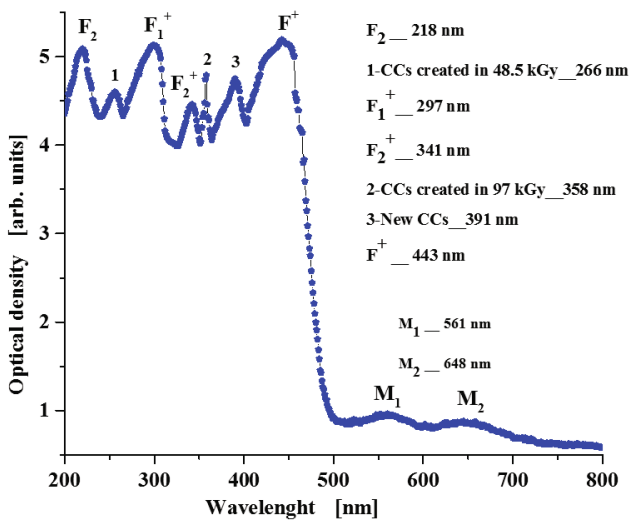

Fig. 4. Absorption spectrum of the boron-carbide sample gamma irradiated at a 145.5 kGy dose.

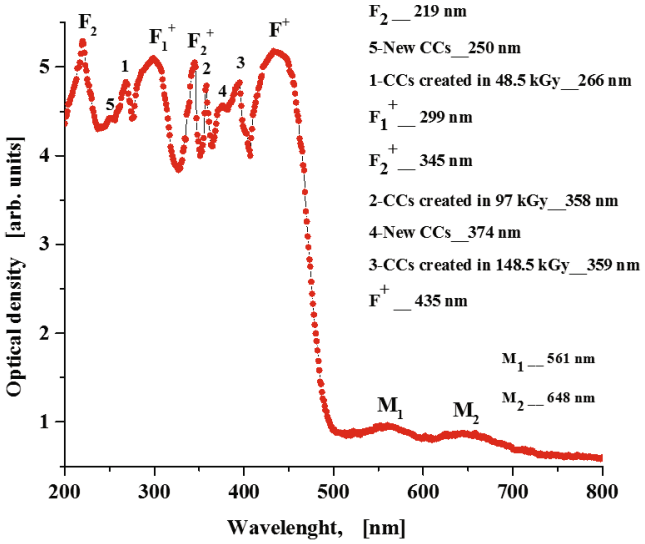

Fig. 5. Absorption spectrum density of the boron-carbide sample gamma irradiated at a 194 kGy dose.

Figs. 3 - 5. When the gamma irradiation dose increased from 145.5 to 194 kGy, the absorption of the F^+ color centers increased rapidly. In summary, the absorption of the F^+ color centers increased with increasing gamma irradiation dose. This increase was more rapid at higher irradiation doses. In this experiment, no change in the color center from F to F^+ take place at low gamma irradiation doses because the irradiation was done at room temperature for the samples.

The reader remembers that the samples for this study were irradiated at room temperature and atmospheric pressure. However, when the samples are gamma irradiated at different doses, an increase in sample temperature occurs (which is roughly around 370 K to 420 K depending on the particle flux) [18, 21–23]. Previous studies have reported that samples with a strong absorption band form color centers in an energy band from around 2.4 to 6.0 eV. In this experiment, F-affiliated centers showed an absorption band between 210 nm and 460 nm. The concentration of color centers was quantified from the absorbance of each band by using Eq. (1).

1. Defect concentration in a boron-carbide sample gamma irradiated at a dose of 48.5 kGy

Figure 2 presents the absorption spectrum of the boron-carbide sample irradiated at a dose of 48.5 kGy. Clearly for the absorption band at 266 nm, the forma-

Table 1. Positions of the color centers in the absorption spectrum and defect concentrations in boron-carbide samples irradiated at different gamma irradiation doses.

	Unirradiated sample	Gamma irradiation dose, 48.5 kGy	Gamma irradiation dose, 97 kGy	Gamma irradiation dose, 145.5 kGy	Gamma irradiation dose, 194 kGy
Wavelength (nm)	Defect concentration, cm^{-3}				
213	$8.92 \cdot 10^{20}$	0.00	0.00	0.00	0.00
220	0.00	$1.01 \cdot 10^{21}$	constant	constant	constant
249	0.00	0.00	0.00	0.00	$8.39 \cdot 10^{20}$
268	0.00	$1.34 \cdot 10^{20}$	constant	constant	constant
297	0.00	$9.81 \cdot 10^{20}$	constant	constant	constant
302	$1.05 \cdot 10^{21}$	0.00	0.00	0.00	0.00
340	0.00	$8.75 \cdot 10^{20}$	constant	$8.47 \cdot 10^{20}$	constant
350	0.00	0.00	$8.62 \cdot 10^{20}$	constant	constant
358	0.00	0.00	0.00	$9.11 \cdot 10^{20}$	constant
375	$8.54 \cdot 10^{20}$	0.00	0.00	0.00	0.00
381	0.00	0.00	$8.46 \cdot 10^{20}$	constant	constant
390	0.00	0.00	0.00	$9.02 \cdot 10^{20}$	constant
418	0.00	$1.05 \cdot 10^{21}$	constant	constant	constant
437	$9.68 \cdot 10^{20}$	0.00	0.00	0.00	0.00

tion of a new type of defect was observed. The color center at 266 nm was not present in the unirradiated concentration of sample. However, these color centers had a small in the sample around 1.34×10^{20} cm^{-3}. The concentrations of defects were calculated for all absorption bands and were found to be 1.01×10^{21} cm^{-3}, 1.34×10^{20} cm^{-3}, 9.81×10^{20} cm^{-3}, 8.75×10^{20} cm^{-3} and 1.05×10^{21} cm^{-3} at 218 nm, 266 nm, 300 nm, 338 nm and 417 nm, respectively; all had activation energy of about 1.92 eV. In all the colors centers, these defects were located at the designated energy levels.

2. Defect concentration in a boron-carbide sample gamma irradiated at a dose of 97 kGy

Figure 3 shows the absorption spectrum of the boron-carbide sample irradiated at a dose of 97 kGy. The samples irradiated at a dose of 97 kGy resulted in the formation of two new color centers in the wavelength range 332 nm - 404 nm. For the 48.5 kGy irradiation dose, only one new color center was found. After the sample had been irradiated at a 97 kGy irradiation dose, the wavelength interval was divided into two regions. The concentrations of defects for the two additional color centers formed were 8.62×10^{20} cm^{-3} and 8.75×10^{20} cm^{-3}at 350 nm and 381 nm, respectively, all at an activation energy of about 1.98 eV. The concentrations of color centers created for other frequencies wavelengths were stable. This means that new energy levels had emerged.

3. Defect concentration in a boron-carbide sample gamma irradiated at a dose of 145.5 kGy

Figure 4 shows the absorption spectrum of the boron-carbide sample gamma irradiated at a dose of 145.5 kGy. The increase in gamma irradiation dose led to an increase in the samples defect concentration. The new color centers in the sample were formed at wavelengths between 239 nm - 266 nm and had a defect concentration of 8.83×10^{20} cm^{-3}. Although three (F and F^+) color centers already existed in the wavelength range between 332 nm - 404 nm, the concentrations of defects in the created color centers were at one level of energy. These concentrations were 8.47×10^{20} cm^{-3} at 341 nm, 9.11×10^{20} cm^{-3} at 358 nm and $9.02 \cdot 10^{20}$ cm^{-3} at 390 nm, with an activation energy of about 2.01 eV.

4. Defect concentration in a boron-carbide sample gamma irradiated at a dose of 194 kGy

Figure 5 shows the absorption spectrum of the boron-carbide sample irradiated at a dose of 194 kGy. The absorption spectrum in Fig. 5 shows that the color centers in the irradiated sample were formed at nine energy levels. The wavelength range was divided into two parts, *i.e.*, 238 nm - 275 nm and 249 nm, which created other new color centers with a defect concentration of 8.39×10^{20} cm^{-3}. In the 332 nm - 404 nm wavelength range, five color centers were formed with defect concentrations increasing from 8.1×10^{20} cm^{-3} to 9.59×10^{20} cm^{-3}.

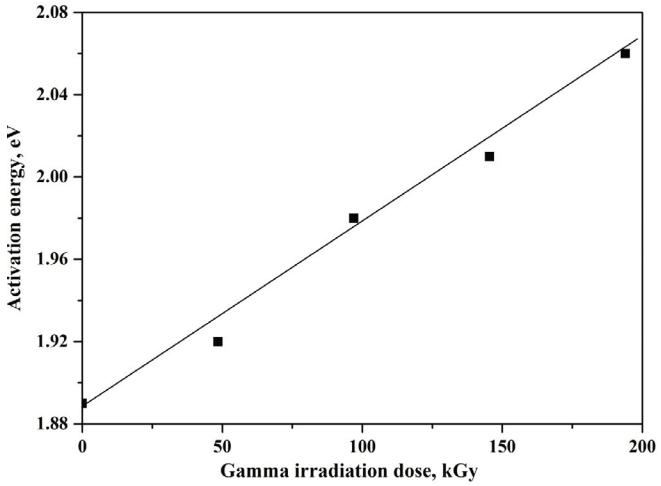

Fig. 6. Dependents of different gamma irradiation dose of activation energy.

The absorption spectrum for a 48.5- to 194-kGy dose was divided into two parts. In the first part, the color centers were created in the 220-nm to 270-nm wavelength range, and in the second part, the color centers were created in the 332 nm to 404 nm wavelength range. The color centers in the 200 nm to 270 nm wavelength range formed at gamma irradiation dose below 145.5 kGy were at two energy levels whereas for the wavelength range from 332 nm to 404 nm, the energy levels depended on the gamma irradiation dose and the concentration of defects divided into a few parts. It can state that the color centers for and at low gamma irradiation doses occur in the 220 nm to 404 nm wavelength range at different energy levels. Figure 6 shows the change in activation energy of the defects in the boron-carbide samples at different gamma irradiation doses. Depending on the irradiation dose, the energy level approaches the zoning region and defects migrate to different energy levels. When the samples were irradiated at doses from 48.5 kGy to 194 kGy, color centers were observed to shift towards higher energy levels. The positions of the color centers in the absorption spectrum and the defect concentrations in boron-carbide samples irradiated at different gamma doses are presented in Table 1. This is the displacement of energy levels as a result of the effects of irradiation.

4. Conclusion

Boron-carbide was irradiated at room temperature with gamma rays at different doses. A UV-V Gary 50 Scan spectrophotometer was used to study the formation of color centers (defects). The concentration of color centers was calculated using the Smakula formula and was found to increase with increasing gamma irradiation dose. The absorption spectra can be divided into two wavelength parts, the first one reaching from 220 nm to 270 nm and second one reaching from 332 nm to 404 nm. For F- and F^+- color centers, the activation energies for unirratiated sample was 1.89 eV. After gamma irradiation at different doses, the activation energy for color centers increased from 1.89 eV to 2.05 eV. Color center degradation as a result of gamma irradiation was observed.

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