



X-ray diffraction and thermodynamics kinetics of SiB_6 under gamma irradiation dose

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Abstract

The silicide hexaboride (B_6Si) was irradiated with ^{60}Co at room temperature to study the structural changes and weight kinetics. The B_6Si samples were irradiated using a gamma source with a dose rate (D) of 0.27 Gy/s. At adsorption dose range of 9.7, 48.5, 97, 145.5 and 194 kGy. The samples were analysed using X-ray diffraction (XRD) and Energy dispersive spectroscopy (EDS) to study the microstructural and composition changes. The XRD results showed the crystalline structure for the sample before and after irradiation (with gamma irradiation dose 9.7, 48.5 and 97 kGy). Amorphization of the sample began at the gamma irradiation dose of 145.5 kGy. Increase in gamma irradiation dose had an inverse effect on the activation energy and had a directly proportional effect on the lattice volume.

Keywords Gamma irradiation dose · X-ray diffraction · Boron compound · Silicide hexaboride · Amorphization · Crystal structure

1 Introduction

Different boron compounds such as BSi_n , B_nC , SiBC , BC-ZrC and BSi-ZrC are used in nuclear technology. The use of boron compounds is due to their exceptional physical and chemical properties when compared with other compounds [1, 10]. Furthermore, B-Si composites are used in the production of photoelectric converters in electronic systems [8, 17]. Current studies are focusing on the investigating the physical and mechanical properties of B_6Si compounds for use in nanotechnology application [14]. These studies focused on high thermodynamic parameters [7, 19], 20 GPa pressure resistance of B-Si binary system and little friction coefficient of the ceramic

systems which are used to create B_6Si compound with metal oxides in the aquatic environment [20]. Researches have shown that B_6Si lacks wear resistance in various environments, thus have spark great interest in studying the B_6Si combination [12]. Studies have also intensively investigated “self-healing components” [18] properties of B_6Si components [9, 13, 15]. The study of the crystal structure of B_6Si compound by X-ray diffraction method in a number of scientific researchers showed that, $Pnmm$ has an orthomorph symmetry of the spatial group. Lattice parameter values of: $a = 14.397(7)$, $b = 18.318(9)$, $c = 9.911(7)$ Å and, determined which electron density appears to contain 43 silicon atoms and 238 boron atoms [16]. It is known that changing the structure parameters will also change the physical properties [3, 20]. There are two major causes for the structural degradation of silicide hexaboride compound namely: Oxidation with influence of temperature and amorphous process with gamma irradiation. Under the influence of the temperature, the information about the mechanism of oxidation in the B_6Si compound is given [2, 11]. However, under the influence of gamma radiation, the mechanism of the process is different from that occurring under the influence of the temperature. The created active centres are subjected to non-covalent with oxygen and carbon atoms, which is up to the temperature of 1200 K. The gamma irradiated samples create active centres and defects in the

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B_6Si structure. In both processes, the value of the temperature factor is required for the breakdown of communications between the B-Si atoms and the dose boundary value of the radiation. The initial value for the activation of the active B and Si communication with the effect of the temperature is 810 K. Most studies focused on the structural properties of the silicide hexaboride (B_6Si) compound with the effect of the temperature, but the effect of radiation on the crystal structure of B_6Si compound has not been studied sufficiently. This study focused on the effect of irradiation of B_6Si and determining the energy state of the system before and after irradiation.

2 Materials and Methods

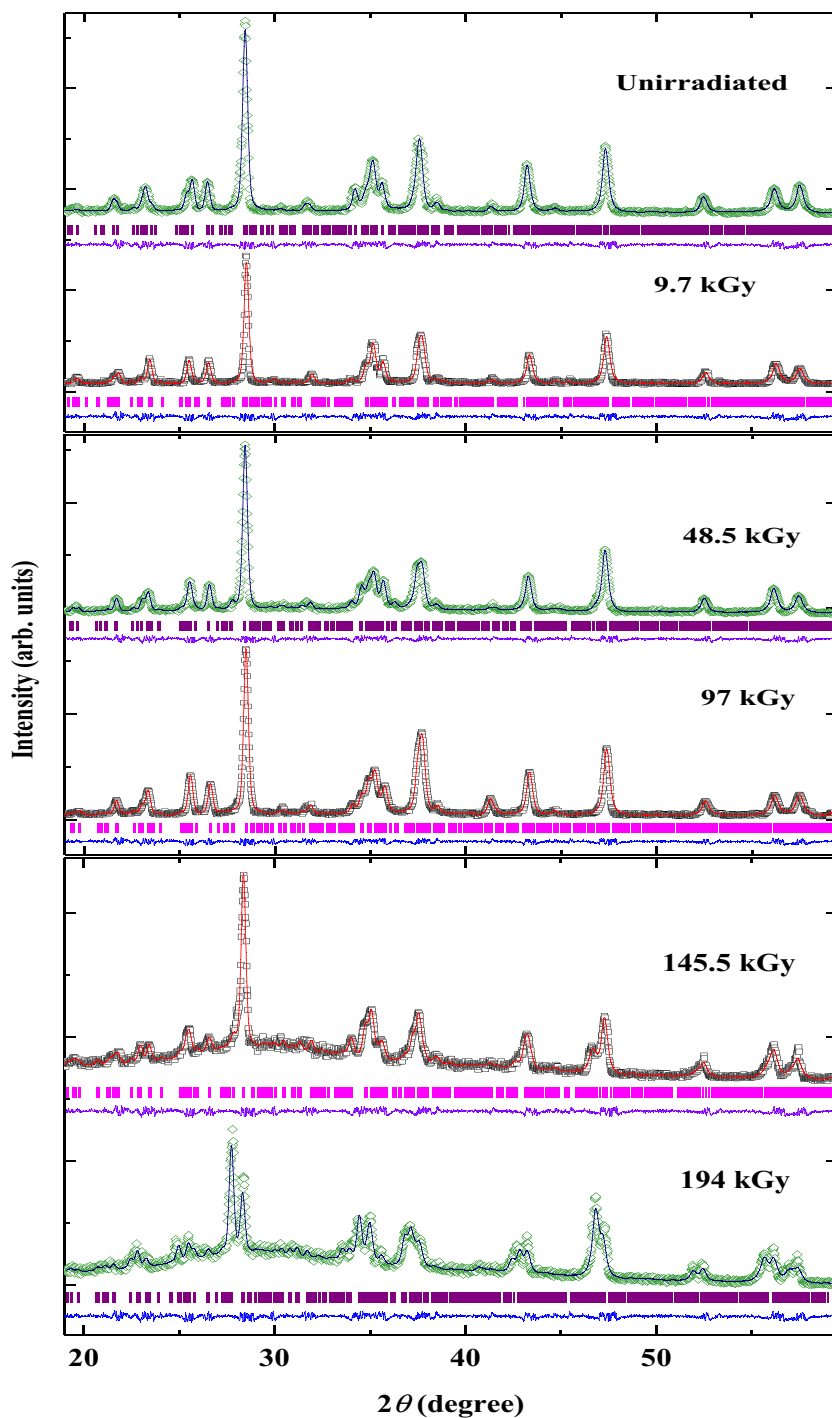
Silicide hexaboride (B_6Si) compound with a density of 2.43 g/cm³ and a purity of 99.5% (US Research Nanomaterials, Inc., TX, USA) was used. The sample was irradiated with ⁶⁰Co source with energy of 1.17 MeV at a K-25 radiation-chemical facility, (High Technologies Centres, Azerbaijan National Academy of Sciences) by gamma rays at dose rate $D = 0.27$ Gy/s at different adsorbed doses of 9.7, 48.5, 97, 145.5 and 194 kGy.

The phase analysis was performed using D8 ADVANCE X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 1.5406$ Å), at operating voltage and current of 40 kV and 40 mA respectively. In order to carry out X-ray diffraction studies, powder samples were prepared from the B_6Si crystal samples. The obtained diffractograms were processed by the Rietveld method using the FullProf program [6, 21]. Scanning Electron Microscope, ZEISS, Σ IGMA VP) EDS component was used to perform the surface morphology and microcircular analysis. The analysis was measured at the 300 K standard room temperature. The error of determination did not exceed 1% at 300 K. The electron source of SEM was zirconium tungsten ring. For processing thermo emotion, the given resistance range from 100 V to 30 keV was used. The distance of electronic source to sample was ≤ 10 mm. The experiment was performed under vacuum condition of 10^{-7} Pa generated by turbo-molecular pumps. With the SE2 detector energy was used to investigated particle size and microstructure. Thermal studies were carried out using the Perkin Elmer, Simultaneous Thermal Analyser, STA 6000 [22–25]. The effect of the temperature on the kinetics processes taking place in the sample have been studied by the experimental thermal analysis. In the thermal analysis, the sample was heated from 300 K to 850 K at a heating rate of 5 K/min and at Ar gas flow rate of 20 ml/min. After heating the sample for 110 min, it was then cooled in the PolyScience analyser cooling system.

3 Results and Discussion

The B_6Si samples were gamma irradiated with different absorption doses at room temperature and the XRD pattern for the samples before and after irradiation is shown in Fig. 1. The unirradiated B_6Si XRD pattern indicated the structure of the sample to be crystalline. The lattice parameters values for the unirradiated sample were: $a = 14.0605(5)$ Å, $b = 18.0279(2)$ Å and $c = 9.2692(7)$ Å. The results showed that under atmospheric pressure and room temperature, the B_6Si has an orthomorph symmetry and crystalline structure of $Pnmm$ spatial group. Our results were in agreement with results from previous studies [6, 16]. A change in the peak intensity on the XRD pattern for the samples which were gamma irradiated with an adsorption dose range of $0 \leq D \leq 97$ kGy was observed. The B_6Si peak intensities were seen to fluctuate with increase in irradiation fluence from $0 \leq D \leq 97$ kGy. This change in the peak intensity can be explained to be due to the crystal structural changes of the samples. That is, crystals (atoms) rearrange themselves during irradiation process causing a change in the crystal structure of the material. However, the silicide hexaboride compound keeps its $Pnmm$ orthogonal structure. When the gamma adsorption dose was increased to $D \geq 145.5$ kGy, it resulted into a decrease in most of the peaks intensities when compared to the lower irradiation gamma dose. This decrease affects the gamma quantum (1.2 MeV energy) and changes the lattice parameter values (of some atoms relate to their ideal position). The B_6Si samples gamma irradiated with adsorption dose $D \geq 145.5$ kGy also showed partial amorphization of the sample. To determine the amorphousness of silicide hexaboride the area in the XRD peak of unirradiated sample is divided by the XRD peak area of the irradiated samples. Figure 2 showed amorphization of silicide hexaboride before and after gamma irradiation dose. About 54% of the sample was amorphized for the 145.5 kGy irradiated sample. Further decrease in the peak intensity and further amorphization was observed for the samples irradiated with adsorption dose of $D = 194$ kGy and 69% for the 194 kGy sample. The lattice parameter and volume change of the elementary lattice of irradiated B_6Si is listed in Table 1. The result in Table 1 indicates that the lattice parameters increase with irradiation dose. The lattice parameter for a before irradiation was 14.060 Å. After the sample was irradiation at 48.5 kGy and 194 kGy, the lattice parameter a changed to 14.096 Å and 15.224 Å respectively. Consequently, the volume of the samples increased with increase in irradiation dose, from 2349 Å³ before irradiation to 2356 Å³ and 2380 Å³ after irradiating at 48.5 kGy and 194 kGy respectively. The increase in the lattice volume and lattice parameters indicates the material is experiencing stress and strain. To

Fig. 1 XRD pattern for B₆Si before and after gamma irradiation with adsorption dose of 9.7 kGy, 48.5 kGy, 97 kGy, 145.5 kGy and 194 kGy



determine the dependence of lattice parameters (*a*, *b* and *c*) on gamma adsorption dose of B₆Si, a graph of lattice parameter and adsorption dose was plotted and studied (see Fig. 3). The irradiation constant was calculated using Eq. (1) by taking the slope of the graph in Fig. 3.

$$k_i = \left(\frac{1}{a_{i0}} \right) \left(\frac{da_i}{dD} \right)_{P,T} \tag{1}$$

where,

- k_i* coefficient of expansion
- a_{i0}* lattice parameters of unirradiated sample
- a_i* lattice parameters of irradiated sample
- D* adsorption dose

The resulting *k_i* values (lattice expanding the lattice parameters) were *k_a* = 6.2 × 10⁻⁵ kGy⁻¹, *k_b* = 2.3 × 10⁻⁶ kGy⁻¹, and

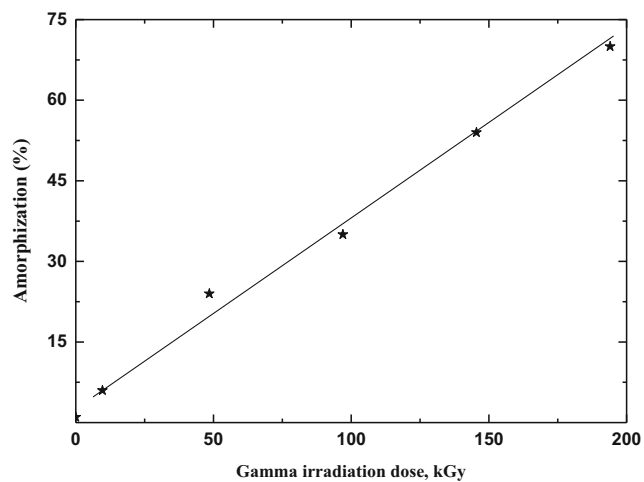


Fig. 2 Amorphization of silicide hexaboride with increase in gamma irradiation dose

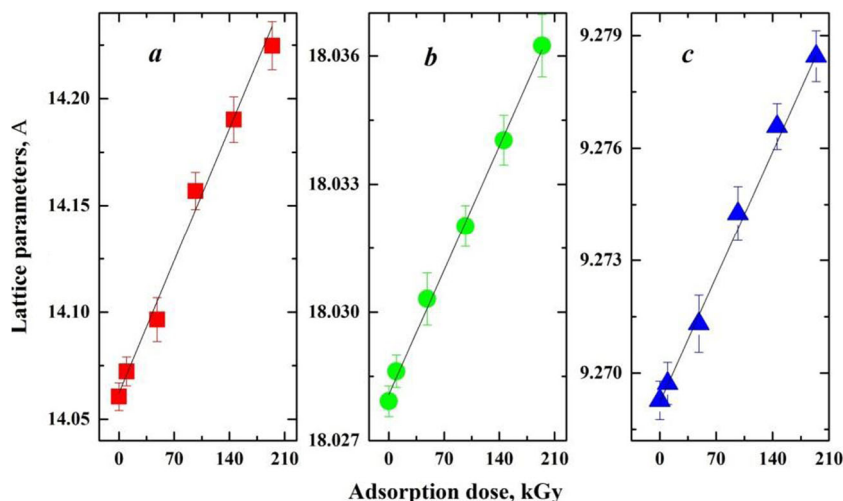
$k_c = 5.2 \times 10^{-6} \text{ kGy}^{-1}$. As stated on the latter paragraph, increase in gamma irradiation results in increase in the lattice volume of B_6Si . Furthermore the lattice volume increased from $V_0 = 2349.6 \text{ \AA}^3$ to $V_{194 \text{ kGy}} = 2380.5 \text{ \AA}^3$, which is equivalent to percentage lattice volume increase of 1.31%. [20] reported on unirradiated B_6Si samples having different lattice structures in just a single sample. The effects of gamma irradiation in each lattice structure occurred in the condensation and phase passage. Because the intensity and energy of gamma irradiation change the location of atoms in the lattice and regularity is violated. At high adsorption dose, gamma irradiation created different point defects and active centres, which may migrate in the sample. The surface morphology and microstructural analysis of B_6Si before and after irradiation was investigated. The distribution of chemical elements on the surface of the sample was statistically characterized. Figure 4 showed the EDS results indicated the presence of B, Si, Al, Fe and Ni on the unirradiated and irradiated sample. The quantity of Ni, Al and Fe remained the same regardless of the change in irradiation dose. An increase in adsorption dose led to a parallel increase in the surface value. The oxygen atoms in active centres showed statistical growth of the oxidation process during the increase in adsorption dose. The temperature and weight axis was divided into two regions.

The linear range $T \leq 470 \text{ K}$ and $T \geq 470 \text{ K}$ showed poor decrease range of weight kinetics. When the gamma adsorption dose was increased, a parallel decrease of weight kinetics was observed. Figure 5 shows a shift in temperature to the high region and at maximum radiation, this difference is 25 K. This shows that, in high irradiation doses defects have high recombination rate and changes place to the high temperatures. The value representing the weight kinetics during the gamma irradiation is based on the following model. The first model: increase in adsorption dose causes an increase in temperature of the sample up to 420 K. As the sample cools down (cooling process), defects and active centres are created. The active centres on the surface are more active than the active centres deep in the material. OH group is chemisorbed on the active centres. And with the influence of temperature degradation which OH groups of dipole interaction. It should be noted that these values were not measured during the gamma irradiation but post-irradiation measurement at room temperature were taken. This is because taking measurements during radiation is a very difficult process. Therefore, experiments are performed after irradiation. During radiation, the number of defects is slightly higher. Chemisorption and recombination is difficult to accurately analyse. Have been adsorption characterization of ceramics materials [4, 5]. The second model is, “the defects concentration is dependent on the adsorption dose of gamma irradiation.” That is, increase in gamma irradiation adsorption dose leads to increase in defects concentration. Furthermore, depending on the temperature, defects recombination will have a different value. The two models play a major role in the processes observed in these results (created defects and recombination rate process). The activation energy calculated was seen to decrease with increase in gamma irradiation adsorption dose, see Table 2. as C/T^k (where $T(K)$ is the measurement temperature, C and k are the constants for each sample). For the unirradiated B_6Si , the parameter C is equal to 1, and it was reported that k decreases with the increase in gamma irradiation dose. Adsorption dose and activation energy for B_6Si sample are listed in Table 2. Activation energy was calculated from the Arrhenius approach in Fig. 3. To determine the values of activation energy during chemisorption and recombination processes [5]. At elevated

Table 1 Lattice parameters and lattice volume for B_6Si before and after gamma irradiation with different gamma irradiation dose at room temperature

Gamma irradiation dose (kGy)	Lattice parameters and lattice volume			
	$a, \text{ \AA}$	$b, \text{ \AA}$	$c, \text{ \AA}$	$V, \text{ \AA}^3$
0	14.060(6)	18.027(9)	9.269(2)	2349.(6)
9.7	14.072(2)	18.028(6)	9.269(7)	2351.(8)
48.5	14.096(5)	18.030(3)	9.271(3)	2356.(4)
97	14.156(9)	18.032(2)	9.274(2)	2367.(5)
145.5	14.190(2)	18.034(2)	9.276(5)	2373.(9)
194	14.224(7)	18.036(2)	9.278(4)	2380.(5)

Fig. 3 Gamma irradiation dose dependences of lattice parameters of the orthorhombic phase of silicide hexaboride at room temperature. Solid lines are interpolation of the experimental data by linear functions polynomials



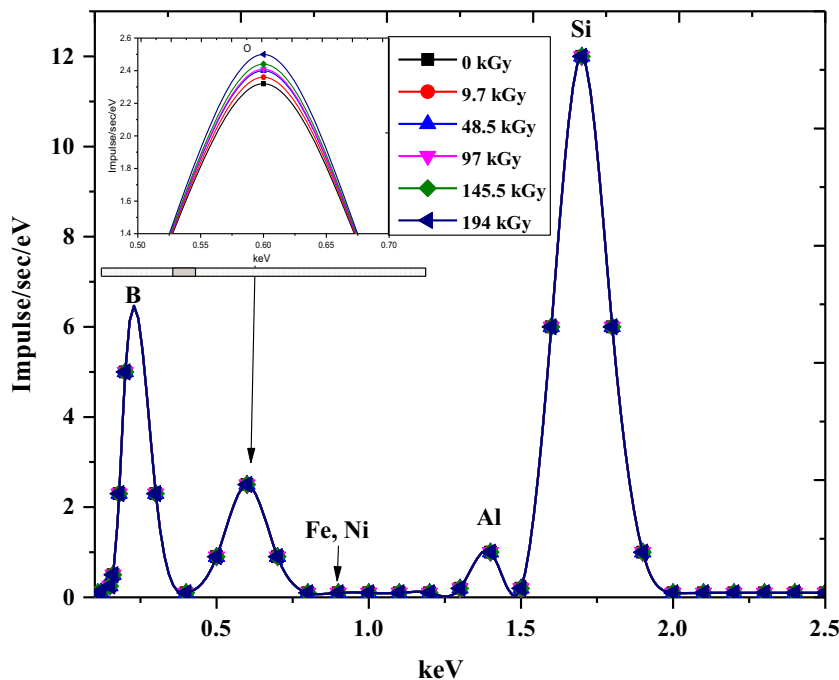
temperatures point defects migrate in the solid. The diffusion of defects can be expressed as thermal activated jumps of atoms from their lattice site to another lattice sites. Silicide hexaboride samples which were gamma irradiated with different adsorption dose created two different energy levels (which are suitable). The first energy barrier changed from 0.14 eV at 0 kGy to 0.26 eV at 197 kGy and second energy barrier changed from 0.22 eV at kGy to 0.46 eV to 197 kGy at room temperature. The formation of the two energy levels in silicide hexaboride the location of the point defects in the deeper levels of energy and is located to the valence zone closer. Increase in irradiation (adsorption dose) led to increase in oxygen content present during the initial irradiation of the

sample. The first time it was determined that silicide hexaboride compound $D \geq 145.5$ kGy irradiation dose has been omorphization.

4 Conclusions

The effect of irradiation of B_6Si and determining the energy state of the system before and after gamma irradiation was investigated. XRD and EDS were used to analyse the microstructural changes. A change in the lattice parameters was observed due to irradiation. The lattice volume of the B_6Si sample was observed to increase with increase in gamma

Fig. 4 Unirradiated and irradiated of sample distribution of chemical elements of silicide hexaboride



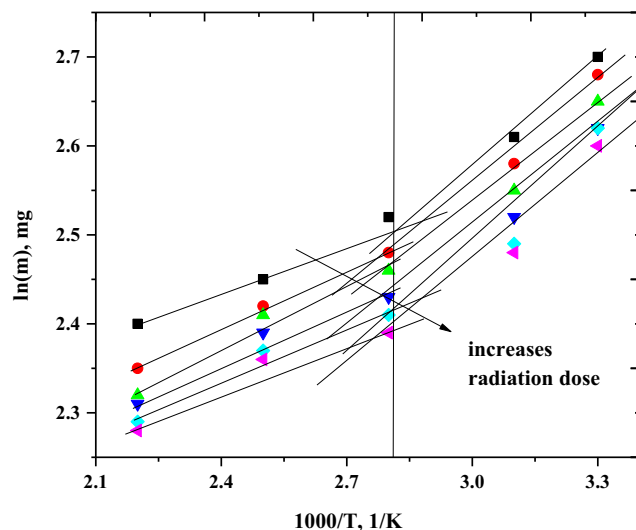


Fig. 5 Variation in the activation energy of silicide hexaboride sample with temperature from 300 K to 830 K. The organic binder was removed in an Ar atmosphere

Table 2 Gamma irradiation dose and activation energy for silicide hexaboride sample

Sample	Gamma irradiation dose (kGy)	Activation energy (eV)	
		T ≤ 470 K	T ≥ 470 K
B ₆ Si	no irradiated	0.22	0.14
	9.7	0.41	0.21
	48.5	0.38	0.23
	97	0.38	0.21
	145.5	0.42	0.24
	194	0.46	0.26

irradiation dose. The increase in volume was attributed to the stress/stain experienced by the samples due to increase in gamma irradiation dose. A structural change from crystalline to amorphous state after irradiation was observed. Low irradiation dose (9.7 kGy, 48.5 kGy and 97 kGy) retained the crystalline structure while 145.7 kGy partial amorphization of the material was observed. Irradiating at 194 kGy led to an increase in amorphization on the B₆Si. At 145.5 kGy a processes of oxygen chemisorption was observed to increase by 1.5%. After gamma irradiated of the samples, two energy barrier states were created. The first energy barrier changed from 0.14 eV (0 kGy) to 0.26 eV a(197 kGy) and second energy barrier changes from 0.22 eV (0 kGy) to 0.46 eV (197 kGy) at room temperature.

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