Research Article

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Sapphire irradiation by phosphorus as an approach to improve its optical properties

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Abstract: Ion beam-induced luminescence (IBIL) is a versatile technique used to elucidate the chemical bond's nature and analyze the defects study and impurities present in the material. In this study, IBIL spectra of phosphorus-irradiated sapphire has been analyzed under 2 MeV proton beam as a function of ion dose ranging from 1×10^{14} to 10×10^{14} ions/cm^2 at room temperature in the wavelength range of 200–1,000 nm. The IBIL spectrum shows three kinds of luminescence features. The bands centered at 419 nm as F center and 330 nm as F^+ center are associated with oxygen vacancies. The third kind of luminescence feature located at 704 nm is related to chromium impurities present in the crystal. The luminescence spectrum of the phosphorus-irradiated sapphire has been correlated with the spectrum obtained from pristine sapphire. The finding indicates that the intensity of defects due to phosphorus irradiation is reduced. As the proton ion fluence increases, the F and F^+ center luminescence intensity eventually varies; it turns out that in phosphorus-irradiated sapphire, single crystal defects were reduced and the optical quality was improved.

Keywords: single crystal sapphire, ion beam-induced luminescence, proton beam, defects ratio

1 Introduction

Sapphire (α-Al_2O_3), a good insulator with wide bandgap oxide of about 9 eV, has a wide variety of technological applications because of its unique physical and chemical properties. Due to their high electrical resistance and excellent radiation resistance, they are used as a substrate for integrated microcircuits operating in nuclear power plants and space [1,2]. Optical and luminescent spectroscopy techniques are commonly used to investigate defects of different natures in wide bandgap materials [3,4]. In sapphire, corpuscular irradiation causes point and extended defects that modify their optical properties. The ion beam-induced defect centers in sapphire are mostly F center, F^+ center, F^2 center, F^{2+} center, and F^{22+} center. Thus, the luminescence band located at 415, 330, 518, 385, and 550 nm are related to these centers, respectively [5,6].

Ion beam-induced luminescence (IBIL) is a versatile technique for measuring defects in materials [7,8]. The ion beam is accelerated with high energy that can penetrate up to several microns in most of the materials and give defects and depth profile information. This leads to the critical difference of IBIL from other techniques [9–11]. IBIL is complementary to other techniques like photoluminescence (PL) and UV-visible absorption techniques

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because of its capability to describe point defect mechanism and damage rate in materials [12]. The IBIL of sapphire with an ion beam of different energies and masses under prolonged irradiation has been studied in the literature [13–18]. In the practical application, Jardin *et al.* used IBIL to study the luminescence spectra of sapphire by bombarding different ion species *i.e.*, He^+ and H^+ irradiation [19]. Also, Aoki *et al.* studied the sapphire and ruby (α-Al_2O_3:Cr, Cr_2O_3 content 0.02%) luminescence spectra by bombarding 200 keV He^+ and Ar^+ ion beam at room temperature and discussed the defects and their growth and decay [20]. Furthermore, Malo *et al.* studied IBIL and surface electrical conductivity for three types of alumina by *in situ* measurement to find a correlation between light emissions and enhanced surface conductivity [21]. Moreover, Crespillo *et al.* developed a new IBIL system to provide *in situ* measurements of materials with different ion beams. The real-time, *in situ* ionoluminescence of SiO_2, crystalline quartz, and Al_2O_3 has been studied to obtained information about the interpretation of luminescence with increasing ion fluences at room temperature [14]. Epie *et al.* studied the rate of F-center formation with fluence in 170 keV Ar^+ irradiated single crystals of α-Al_2O_3 at room temperature using ion luminescence and found that the rate of F center formation is due to a dynamic competition between defect formation and recombination, with F center saturation corresponding to an equilibrium state between defect formation and recombination [22]. Harutyunya has used photoluminescence spectroscopy to compare the luminescence and electronic properties of electron and neutron-irradiated Al_2O_3 single crystals with those of unirradiated sapphire crystals to demonstrate the defect behavior of single-crystal sapphire [23]. However, only limited work was reported with the study of ion beam induced defects formed in phosphorus-irradiated sapphire. The use of IBIL is highly efficient to detect defects in materials and has not yet been fully explored.

In this article, the IBIL technique was used for the first time to examine the luminescence of a phosphorus-irradiated sapphire subjected to the irradiation of a hydrogen ion beam that focuses on the behavior of defects such as F^+ and F center.

The rest of the article is organized as follows. The experimental setup of IBIL and material preparation are illustrated in Section 2. The results and discussion of our experimental work are presented in Section 3, and the conclusion is given in Section 4 of this article.

2 Materials and methods

The *in situ* defect study of phosphorus-irradiated single crystal sapphire (α-Al_2O_3) was conducted with a sample size of about 2.2 mm thickness and 10.0 $mm^2 \times 10.0$ mm^2 dimension using IBIL at 5 MV Tandem Accelerator at the National Center for Physics, Islamabad, Pakistan. The pristine sapphire single crystal has been procured from the Nuclear Research Centers of Draria, Algeria. The sample has been prepared for the *in situ* defects study by irradiating pristine single-crystal sapphire with phosphorus ion fluences of 5×10^{15} ions/cm^2 at room temperature by 5 MV Tandem Accelerator.

The *in situ* luminescence spectra of the defective single-crystal sapphire at different proton beam fluences ranging from 1×10^{14} to 10×10^{14} ions/cm^2 at 2 MeV at room temperature were examined. Ion beams were focused through collimator and quadrupoles lens. The chamber working as a Faraday cup to measure the total charge impinging on the sample and the specified beam current of 10 nA in a vacuum chamber (10^{-6} torr). A collimating lens was located at an angle of 45° to the incoming ion beam inside the chamber, which captures the light. Light is then focused on an optical fiber. The vacuum feedthrough guides the light out of the vacuum chamber. Thus, another optical fiber of a larger length is connected with the feedthrough to the outside of the vacuum chamber. The optical fiber then passes light to the ocean FX (QE65000) spectrometer with the entrance slit size of 25 μm, the resolution power of 2 nm, and the wavelength range of collected spectra was 200–1,000 nm. The spectrometer was connected to the PC through a USB cable (RJ45), and data acquisition was controlled by ocean optics software. Figure 1 shows a schematic diagram of the IBIL setup.

3 Results and discussion

The IBIL spectra of the pristine sapphire at 2 MeV proton beam are presented in Figure 2(a). Three different luminescence bands located at 330, 413, and 705 nm were observed in the measured spectrum. The first two bands represent point defects in sapphire, whereas the third band at 705 nm is related to chromium impurity present in the crystal, as mentioned by Jardin *et al.* [19]. The band at 330 nm is related to an oxygen vacancy F^+ center with a

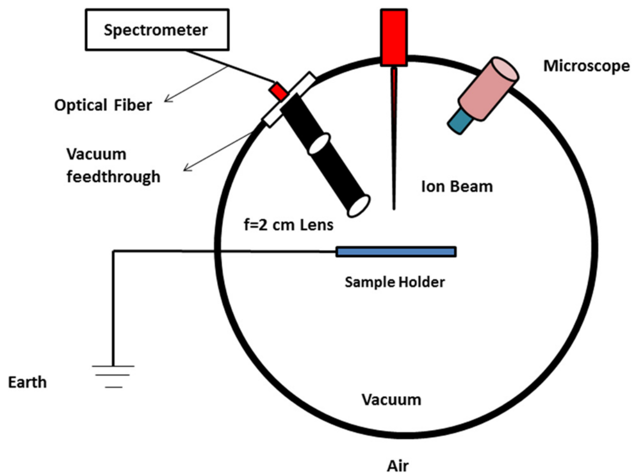

Figure 1: Schematic diagram of the IBIL setup.

Table 1: Intensity value of F and F^+ centers obtained by using a 2 MeV proton beam

Sample	Intensity		
	F^+ (Cts/s)	F (Cts/s)	Cr (Cts/s)
Pristine	941	3,524	352
Phosphorus-irradiated sapphire	196	1,200	155

single trap electron, while the band at 414 nm in the spectrum is related to another oxygen vacancy F center with two tarp electrons [24,25]. The IBIL spectrum obtained with 2 MeV H^+ ion beam for phosphorus-irradiated sapphire is shown in Figure 2(b). The results showed that the luminescence of phosphorus-irradiated sapphire decreased compared to the pristine sapphire spectrum. It was obtained from the result that after phosphorus irradiation, defects concentration is reduced, as shown in Table 1. This may cause the removal of impurities from the crystal by collision cascade effect by phosphorous ion irradiation and recrystallization of single sapphire crystal to reduce defects due to phosphorous ion beam induced local heating along the ions' track [26].

The luminescence spectra were obtained from phosphorus-irradiated sapphire at proton fluence of 1×10^{14} to 10×10^{14} ions/cm^2, as shown in Figure 3. The contribution of the F center to the luminescence spectrum increases as the dose increases, while the luminescence of the F^+ band decreases. When the ion dose increases further, the intensity of the F center decreases, while the F^+ center increases. This shows the creation and annihilation of the F center and F^+ center. This fact indicates that a significant part of the luminescence is due to the defects produced by irradiation and that the intensity of these bands may represent the amounts of the F^+ and F centers [27]. Al Ghamdi and Townsend reported a similar irradiation record for the IBIL of sapphire, in which non-zero values

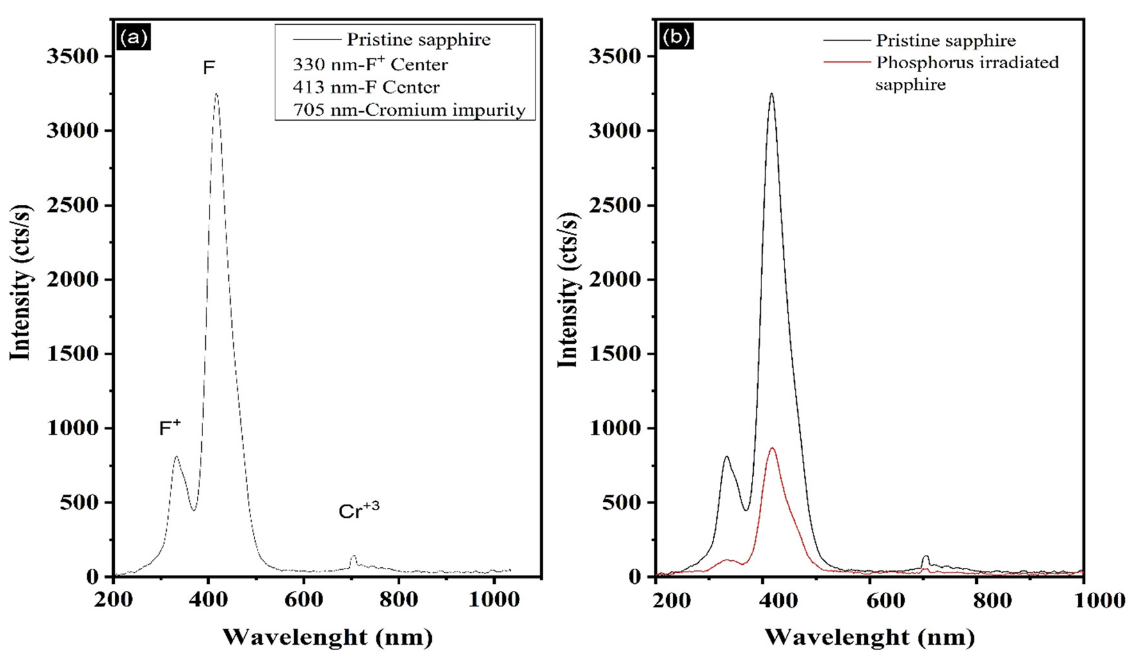

Figure 2: IBIL spectra of (a) the pristine sapphire using 2 MeV proton beam and (b) comparison of the pristine and phosphorus-irradiated sapphire.

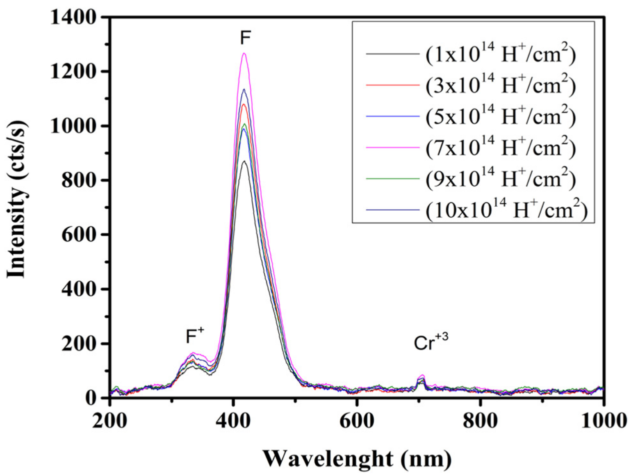

Figure 3: Luminescence spectra analyses of sapphire with different proton fluences.

were observed for the low-fluence luminescence intensity and indicated that the luminescence is from the intrinsic color centers triggered by the excited electrons [28]. On the other hand, almost zero values have been found for the annealed specimens, suggesting that the luminescence occurs from the centers such as F^+ and F produced by the annealed specimens [27]. The radiation fluence often attenuates the Cr^{+3} peak intensity due to proton beam induced local heating along the beam track, which causes undoped Cr atoms doped in the sapphire crystal. The overall luminescence intensity decreases at greater fluence, which may be due to the development of new defect center F^{2+} at higher fluence [29].

Figure 4(a) and (b) shows the behavior of F center and F^+ center as a function of fluence. Initially, the F and F^+ center increases, which shows the creation of defects due to ion beam displacement damage. As the ion fluence increases, the decrease in the intensity of the defects is observed that might be due to the degradation and annihilation of these centers [30,31].

According to the results of the *in situ* study of defective sapphire by proton beam mentioned above, the intensity ratio of $I(F)/I(F^+)$ depends on ion fluence as shown in Figure 5. The result revealed that as the ion fluence increases, variation in the intensity ratio was observed. This shows the creation and annihilation of the F center and F^+ center; by studying the entire spectrum, the F center is dominant over the F^+ center. A similar phenomenon was reported by Skuratov *et al.* in the case of heavy irradiation; the F center contribution to luminescence is higher due to some F^+ center during irradiation following annihilation with interstitial or other defects [10,11]. The intensity ratio between F^+ and F is heavily dependent on the dose rate in the study of electron-irradiated sapphire, the luminescence of F^+ increases with the dose rate, while the luminescence of F decreases [27,32]. Data reported for heavy-ion by Crespillo *et al.* and Malo *et al.* at 45 keV Helium ion, for unirradiated sapphire, showed that it is reasonable to assume interstitial vacancy recombination and vacancy aggregation at the early stage

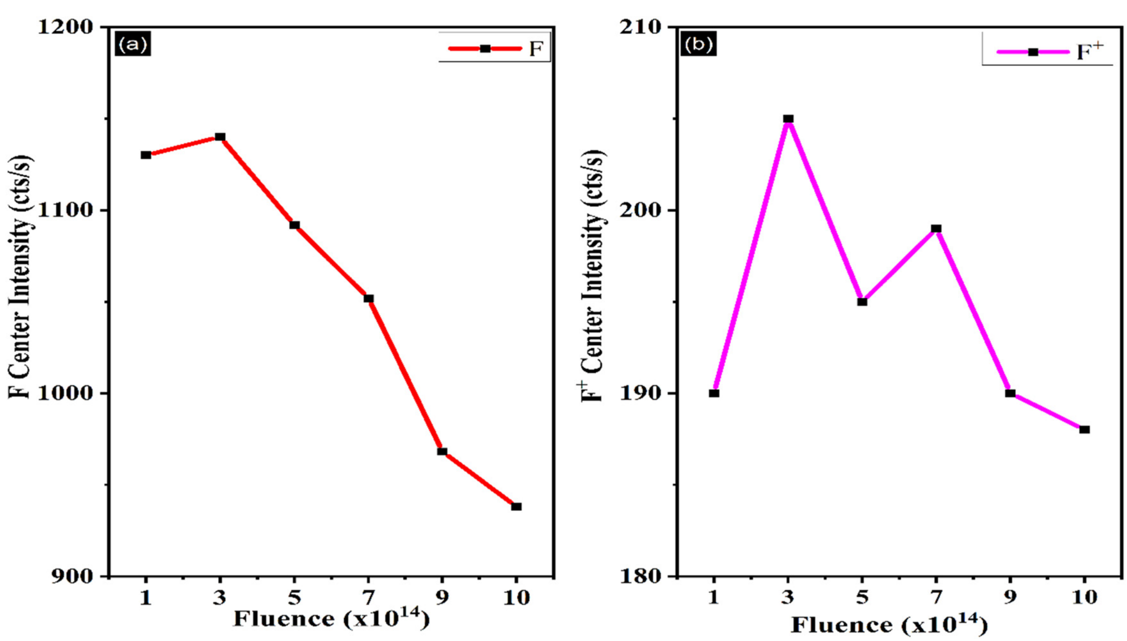

Figure 4: (a) Intensity of F center as a function of ion fluence and (b) intensity of F^+ center as a function of ion fluence.

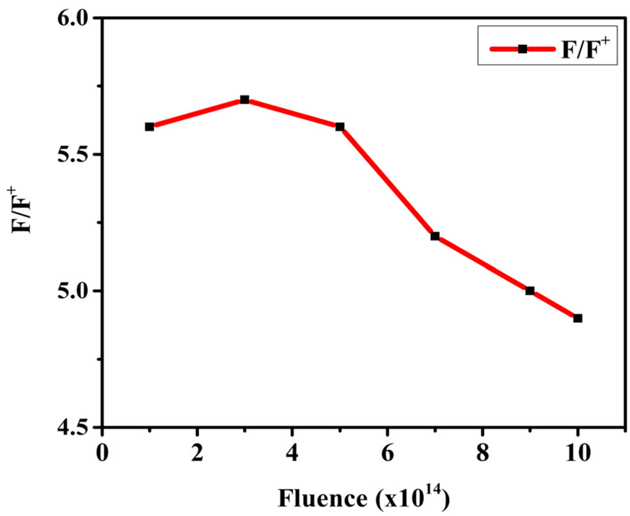

Figure 5: The ratio of (F/F^+) emission intensities on proton fluence at 2 MeV.

of irradiation [14,31]. Crespillo *et al.* stated that two F/F^+ centers are removed by the creation of each F^{2+} center and may account for some of the decreases in the signal from a single vacancy center [14]. However, in the present study, no such higher defects were observed, but the overall decrease in the intensity ratio was observed, that is, recrystallization triggered by electronic energy loss by oxygen ions, as stated by Sina *et al.* [33].

4 Conclusion

This article uses the IBIL technique to examine the *in situ* defects study of phosphorus-irradiated sapphire subjected to the irradiation of a proton beam of 2 MeV at room temperature. The IBIL analysis shows F center, F^+ center, and cr^{3+} luminescence features. The IBIL comparative analysis was presented in pristine sapphire and phosphorus-irradiated sapphire. The observation shows a decrease in the luminescence of defective sapphire to phosphorus irradiation that might be the reason for the removal of impurities from the crystal by collision cascade effect by phosphorous ion irradiation and recrystallization of single sapphire crystal to reduce defects as phosphorous ion beam induced local heating along the ions' track. It was also observed that the intensity of these luminescence features varies as a function of proton ion fluences. On increasing of the proton ion fluence, the ratio F/F^+ gradually increases up to a dose of 3×10^{14} ions/cm^2, but on further increase in the proton ion fluence, the ratio F/F^+ decreases. It was observed that the creation and annihilation of F and F^+ centers occur with varying ion fluence. It turns out to be concluded that defects were reduced in the phosphorus-irradiated sapphire single crystal and the crystal quality was improved. The eventual decrease in the luminescence intensity of F center and F^+ center indicates that IBIL is the best tool to monitor *in situ* material characterization in a high radiation environment to diagnose the inaccessible part of future fusion devices with fission reactors.

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