***In-situ* luminescence monitoring of ion-induced damage evolution in SiO₂ and Al₂O₃**

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Abstract

Real-time, *in-situ* ionoluminescence measurements provide information of evolution of emission bands with ion fluence, and thereby establish a correlation between point defect kinetics and phase stability. Using fast light ions (2 MeV H and 3.5 He MeV) and medium mass-high energy ions (8 MeV O, E=0.5 MeV/amu), scintillation materials of a-SiO₂, crystalline quartz, and Al₂O₃ are comparatively investigated at room temperature with the aim of obtaining a further insight on the structural defects induced by ion irradiation and understand the role of electronic energy loss on the damage processes. For more energetic heavy ions, the electronic energy deposition pattern offers higher rates of excitation deeper into the material and allows to evaluate the competing mechanisms between the radiative and non-radiative de-excitation processes. Irradiations with 8 MeV O ions have been selected corresponding to the electronic stopping regime, where the electronic stopping power is dominant, and above the critical amorphization threshold for quartz. The usefulness of IBIL and its specific capabilities as a sensitive tool to investigate the material characterization and evaluation of radiation effects are demonstrated.

Keywords: Ion beam induced luminescence; ion-solid interaction; irradiation effects; silica; quartz; alumina

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1. Introduction

Luminescence [1] is very sensitive in comparison with other optical techniques, such as optical absorption, Raman spectroscopy, and electron paramagnetic resonance. The technique has a factor of $\sim 10^5$ higher sensitivity in comparison to optical absorption, and it permits the detection of 10^{10} defect/cm². It is often applied for characterization of dielectric and semiconductor materials. Luminescence provides information about the upper electronic levels of a material (near the Fermi level), particularly for intra-gap levels associated with impurities and defect centers, such as those introduced by irradiation. The luminescence induced by ion-beam irradiation, commonly named ionoluminescence or ion beam-induced luminescence (IBIL), is a technique capable of acquiring information about intrinsic or preexisting defects in materials as well as *in-situ* information about the microscopic processes accompanying the generation of damage from energetic ions, their kinetic evolution with the accumulation with increasing ion fluence, the formation of color centers, and their recovery with thermal annealing [2-14]. The visible light produced during luminescence is a result of outer shell transitions. Detection of these transitions gives information about the nature of normal chemical bonds in materials, perturbations to the local chemical environment due to defects or trace substitutional impurities, and to the microstructural feature of the material [15].

An important difference between IBIL and other luminescence techniques is that, with IBIL, it is possible to reach penetration depths of several microns in most materials as the ions can be accelerated to energies on the order of several MeV or more [16]. In comparison with photoluminescence (PL), the energetic ions provide high intensity electronic excitation along their trajectories, similar to femto-second (fs) pulsed laser irradiations. Through the choice of ion species and ion energy, the energy deposition can be made to occur almost entirely in the electronic system (as with PL, cathodoluminescence (CL), radioluminescence (RL), etc.). Unlike other luminescence techniques however, energy transfer directly to atomic nuclei is also possible, making IBIL applicable to the investigation of material modification in both nuclear and electronic energy loss regimes, or as a real time problem to provide insights of defect formation and kinetics. All of the aforementioned features make IBIL a valuable tool for monitoring

material modifications during irradiation. IBIL is complimentary to other ion beam analysis (IBA) techniques such as Rutherford backscattering spectrometry (RBS) and particle-induced X-ray emission (PIXE), as it describes defect structures in insulators and semiconductors that are invisible to RBS or PIXE [17]. However, IBIL is far less used than other IBA techniques because the analysis of the data generally requires additional information from electronic structure calculations or from measurements using other optical techniques, such as optical absorption and photoluminescence, in order to obtain physically meaningful information [18]. Other luminescence methods involve excitation with photons (PL), X-rays (RL), and electrons (CL). CL and RL rely on electronic excitations via ionizing radiation whereas PL requires excitation at the absorption bands of defects followed by emission.

Silicon dioxide (SiO_2), both in its crystalline (quartz) or amorphous (silica) forms, is a technologically important compound abundant in nature. It is used in many applications in a variety of fields ranging from photonics and microelectronics to geological dating and archaeology. In several of these applications, both materials are subject to high fluxes of ionizing radiation such as photons in laser technology, or neutrons and charged particles in spacecraft, accelerators and nuclear fission and fusion facilities [19, 20]. The use of the radiation induced light emission, such as IBIL, as a remote method to monitor material modification would be of great interest in fusion devices as it may permit *in-situ* monitoring of material performance [13, 14]. Therefore, significant effort has been devoted to understanding the effects of ion irradiation on the atomic and electronic structures of crystalline and amorphous SiO_2 . Previous work has mainly focused on the effect of UV light, X-rays, electrons, neutrons and ions on amorphous silica [5, 7, 21-23]. Less attention has been paid to irradiation effects on quartz [24-26]. Interest in the damage produced by high-mass, high-energy (i.e. swift heavy) ions has increased recently because ion damage in the electronic energy loss regime may dominate over elastic nuclear collisions, and the induced damage presents a considerable number of differential features not yet sufficiently understood [27-34].

Recently, a new ion beam induced luminescence (IBIL) system has been successfully developed in the multipurpose end-station in the L3 beamline of the Ion Beam Materials Laboratory (IBML) at the

University of Tennessee, Knoxville, (IBML, <http://ibml.utk.edu/>) [35] in order to provide insights on radiation damage mechanisms and perform *in-situ* material characterization during irradiation. Examples of experiments conducted in the new system are presented here to illustrate the potential for characterizing radiation effects in ceramic materials with fusion applications using IBIL.

This work focuses on a comparative study of ionoluminescence in crystalline quartz and amorphous silica by irradiation with several ions (H at 2 MeV, He at 3.5 MeV and O at 8 MeV) in the electronic stopping regime. Protons and He ions were selected because their electronic energy loss falls below the amorphization threshold and their low mass induces little sample modification through elastic collisions (hence the H and He ions are used for quasi-nondestructive analysis). On the other hand, O was selected to observe, *in-situ*, direct amorphization above the electronic stopping power critical threshold value, estimated to be about 2 keV/nm at the sample surface [9, 36, 37].

IBIL is also demonstrated in α -Al₂O₃ and used to monitor the dynamic processes of material modification under ion irradiation. Changes in the light emission during irradiation reveal the formation of oxygen vacancies (F and F⁺ centres), F centre aggregation (F₂), and a dynamic charge balance between the vacancy sites.

2. Experimental methods

High-purity synthetic quartz (z-cut), UV fused silica (OH nominal concentration < 1000 wt. ppm) and sapphire (0001) crystals with low defect concentrations used in this work were provided by MTI Corporation. Two-side polished samples with dimensions of 1x10x10 mm were irradiated at room temperature under a vacuum of 5×10^{-5} Pa, at the Ion Beam Materials Laboratory (IBML) [35]. They were tilted 5° with respect to the incident ion beam to avoid ion channeling. Adjustable beam slits were used to define an irradiation area of 3×3 mm² on the sample surface. Beam homogeneity was verified to within 10% by measuring the spatial ionoluminescence signal induced in a sample of amorphous silica using a 12-bit charge-coupled device (CCD) camera mounted on the end-station. Irradiations were performed with 2 MeV H, 3.5 MeV He, and 8 MeV O with beam currents in the range of 70-100 nA to avoid beam

heating and electrical arcs on the samples. The ion flux was kept constant ($5 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$) during the irradiations. The irradiation parameters for the ions and materials used in this work, calculated using Stopping and Range of Ions in Matter (SRIM) full-cascade simulations (version 2012) [38, 39], are shown in **Table 1**, assuming threshold displacement energies of 25 eV and 50 eV for the Al and O atoms, respectively [40], and a sample density of 3.98 g cm^{-3} for $\alpha\text{-Al}_2\text{O}_3$.

A schematic diagram of the in-situ luminescence experimental setup is shown in **Fig. 1**. The light emitted from the samples is transmitted through a sapphire window port at 150° with respect to the ion beam direction, and collected via a 25-mm-diameter, 4-cm-focal-length silica lens into a silica optical fiber of 1 mm diameter located outside of the vacuum chamber. The magnification of the optical system at the entrance of the optical fiber is around 0.25. The light was fiber-coupled to an imaging spectrometer, which consists of a monochromator (Acton Research Corp. SpectraPro-2556 with 500 mm focal length and fitted with a 600 lines/mm grating blazed at 500 nm) and a liquid nitrogen-cooled back illuminated UV enhanced CCD camera multichannel array detector (Princeton Instruments, Spec-10: 2KBUV). The evolution of the IBIL spectrum was monitored in spectroscopic mode with Full Vertical Binning (FVB) for wavelengths from 250 to 1000 nm. The spectral resolution is better than 0.05 nm. Commercial WinSpec/32 (v 2.5.23) software from Princeton Instruments was used for IBIL spectra acquisition. The spectrometer wavelength calibration was performed using Ne (Model 6032) and Hg(Ar) (Model 6035) spectral lamps from Newport Instruments.

Static IBIL spectra were recorded using an integration time between 1 and 5 s, depending on the sample. For damage evolution kinetics measurements, 0.2 s was used as the integration time. The combination of high photon collection efficiency and a very sensitive CCD permits rapid (hundreds of milliseconds) acquisition of luminescence spectra with low ion beam currents. The observed luminescence intensity was found to be proportional to the incident ion flux and energy. The ion-induced luminescence intensity was normalized to the incident current density, energy and acquisition time. For the beam current normalization, variations in the ion flux were assumed to change linearly over the

acquisition time. Thus, to first order, the normalized yields presented here may be considered proportional to the photons per excited electron-hole (e-h) pair. Furthermore, the IBIL corrected spectra have been converted from wavelength (originally in units of $I(\lambda)d\lambda$) to energy space ($I(E)dE$) by multiplying the measured counts by λ^2 . This conversion is required to represent the relative photon yields between different emission peaks [41, 42]. Due to the high sensitivity of the IBIL against small ion current fluctuations (around 1 nA), it was necessary to record the real-time evolution of the current in order to discriminate variations in the IBIL produced by the kinetics of damage evolution from those associated with current changes.

3. Experimental results and analysis

3.1 Silica and quartz

Figure 2 shows typical ion induced luminescence spectra from silica (a) and quartz (b) under 2 MeV H, 3.5 MeV He and 8 MeV O ion irradiation at various fluences at room temperature. For both samples, broad luminescence peaks were observed at around 1.9 eV and 2.7 eV. In **Fig. 3**, representative IBIL spectra for silica (**Fig. 3(a)** and **(c)**) and quartz (**Fig. 3(b)** and **(d)**) irradiated with He and O ions show, in more detail, the deconvolution into specific emission bands. The observed color of the irradiated samples changes with material and fluence as illustrated in the corresponding inset photos accompanying the spectra. Light emission under irradiation results from the recombination of e-h pairs at certain suitable recombination centers related to impurities or defects previously existing in the sample or related to the damage products. Thus, the light yield is proportional to the local density of excited e-h pairs (the ionization density along the ion track) and to the density of luminescent centers interacting with the e-h pairs through the recombination cross-section [43]. It follows [44] that the luminescence yield (Y) of a certain band will be proportional to the ion flux (ϕ), the energy of the incident ion (E), and the concentration, ($N(\phi)$), of available recombination sites (luminescent centers). In other words, $Y(\phi) \propto \phi EN(\phi)$. This suggests that $Y(\phi)/\phi E$ is the best normalization for the purpose of comparing the IBIL yields

from the same bands of different spectra, and it can be used to monitor the concentration of recombination centers for a certain emission band generated by the irradiation [43].

The spectra here have been indexed according to identifications of color centers made in the literature. The band at 1.65 eV is ascribed to Fe^{3+} substitutional impurities [45]. 1.9 eV is due to non-bridging oxygen hole color centers (NBOHCs) [5, 6, 24, 46, 47]. The 2.26 eV band originates from the radiative recombination of self-trapped excitons (STEs) at E' centers [47]. The origin of the 2.7 eV band is still a matter of debate. It has been variously attributed to STE recombination at strained Si-O bonds [24, 37, 46, 48-51], the ODC-II center (a non-relaxed diamagnetic oxygen-deficient center) [52], and the E'-center (a paramagnetic oxygen vacancy with a trapped hole) [53]. In this manuscript, the 2.7 band is generally identified with an extrinsic recombination of the STEs at ODC-II centers produced by irradiation. It is worth bearing in mind, however, that luminescence from this band could also be attributed to other mechanisms, such as STE recombination at strained bonds that is supported by experiments under irradiation [46] and by theoretical considerations [49, 51, 54], which predict efficient self-trapping of excitons in silica, where Si-O bonds are strongly distorted, but not in crystalline quartz. The following discussion focuses on the two main broad emission bands lying at 1.9 eV (652 nm) and 2.7 eV (459 nm), which are far more intense than other two bands centered at 1.5 and 2.26 eV (**Fig. 3**). These bands are hereafter referred to as the red (1.9 eV) and blue (2.7 eV) bands.

The blue band in silica is clearly dominant over the red band both under light ion irradiation (H and He) and under O irradiation (**Fig. 2(a), 3(a) and 3(c)**). For quartz, however, the red band dominates under the “non-destructive” He and H irradiations, while the blue band grows under O irradiation (**Fig. 2(b), 3(b) and 3(d)**). It should be noted that, while the initial difference between the two structures is evident from the relative band intensities in the initial spectra (**Fig. 3(a) and (b)**), they converge to a common spectrum upon O irradiation (**Fig. 3(c) and (d)**). Moreover, with further O irradiation, a decrease in luminescence yields of both bands is observed in silica (**Fig. 3(a) and (c)**). In quartz, the red emission is initially dominant but is gradually taken over by blue emission with further damage accumulation. The blue emission becomes overwhelmingly dominant in the highly damaged quartz. Furthermore, the red

band exhibits similar behavior as for silica, rapidly increasing to a maximum yield followed by a more gradual decrease. The maximum yield for quartz, however, is higher than for silica in the low damage stage (around 10 times). The maximum yield in the quartz upon O irradiation is slightly higher than for silica. Differences in light collection efficiency between both samples, sample geometries, the presence of an amorphous/crystalline layer structure in the quartz sample, and differences in non-radiative recombination rates in each material may all influence the total light output however.

A detailed study of the damage kinetics with ion fluence provides better understanding into the luminescence mechanisms under irradiation. Normalized yield vs. fluence data has been calculated by fitting Gaussian functions to the emission bands of the $I(E)dE$ spectra at each time step. No significant shifts or broadening of the emission bands were observed during the acquisitions.

The evolution of the normalized yields for the red (Y_R) and blue (Y_B) bands, stimulated by each of the ion beams (H, He and O), is shown in **Fig. 4(a)** and **(c)** for silica and in **Fig. 4(b)** and **(d)** for quartz. A qualitative difference exists in the evolution of the emission bands with damage accumulation between light ions (H and He) and O ion irradiation. In both materials, both red and blue emission bands increase monotonically under light ion irradiation. In the case of He, the emission reaches a saturation stage after a certain fluence (around 1.0 to $1.5 \times 10^{14} \text{ cm}^{-2}$ for silica, and $4 \times 10^{15} \text{ cm}^{-2}$ for quartz). The bands have higher intensity under He irradiation than under H irradiation. Moreover, in silica, light ions produce more intense bands than those obtained with O ions.

Under O irradiation, all the curves show a clear transition between two kinetic regimes separated by a critical fluence. Initially all curves exhibit rapid growth followed by gradual decay, ultimately converging to a steady state intensity. For silica, the maximum intensities are obtained at a fluence in the range of 1.5 to $3.5 \times 10^{12} \text{ cm}^{-2}$. The intensities then decrease with a slower time constant to a smaller steady state value. In silica, both bands follow qualitatively similar kinetics being the blue band clearly dominant over the red one. In quartz, the red band exhibits similar behavior as in silica, peaking at a maximum yield value at an approximate fluence of $5.5 \times 10^{12} \text{ cm}^{-2}$, followed by a gradual decrease to a steady state value. Similar to the red band, the blue band undergoes a rapid growth up to the critical

fluence around $5.5 \times 10^{12} \text{ cm}^{-2}$. Unlike the red band, it however continues to grow, albeit with a slower time constant, before it reaches a steady state (again around $1.0\text{-}1.5 \times 10^{14} \text{ cm}^{-2}$). Above a fluence of $1 \times 10^{13} \text{ cm}^{-2}$ the blue emission overwhelms the red one, being very close in value to the fluence when the maximum yield in the red band is reached. In the steady stage the blue band yield appears close to the value reached in silica. This behavior suggests that after enough fluence both materials reach an equivalent “damaged” phase.

Figure 5 shows the ratio between the peak area intensity of the blue and red peaks (Y_B / Y_R) for silica and quartz. This calculation allows the comparison with other experimental results being independent of the experimental setup. There is a clear difference in the behavior observed with the damage accumulation when the irradiation is carried out under light ions compared to O ions. For silica, and quartz irradiated with O ions, there is an initial rapid growth with increasing ion fluence up to a saturation value. However, in the case of quartz irradiated with He ions, there is a gradual decrease reaching a steady value after a fluence of $\approx 4 \times 10^{14} \text{ cm}^{-2}$. The relative growth rate of the blue peak with respect to the red one strongly depends on both, the material and the stopping power, being 10 times faster for the silica in comparison to quartz during the irradiation with O ions (**Fig. 5 (a, b)**). In silica, the critical fluence for reaching the saturation stage seems to be inversely proportional to the electronic stopping power. The saturation state is reached at higher fluence in quartz than in silica. The Y_B/Y_R ratio is roughly constant for silica and reaches a close value as in quartz under O irradiation showing a certain comparable “highly disordered” phase.

For silica, in order to determine whether the main contribution to the production rate of recombination centers for blue emission is nuclear or electronic in origin, the H and He kinetics curves were prepared using two alternative normalization schemes for the fluence. In the first, the fluence was converted to total ionization. In the second, the fluence was converted to total displacements. The conversion factors were calculated by integrating the ionization and damage event profiles along the projected range of the incident ions. Ionization and damage profiles were obtained with SRIM 2012 [38, 39]. The kinetics curve under each normalization scheme are presented in **Fig. 6 (a, b)**.

3.2 Sapphire

Fig. 7 presents a typical IBIL spectra of α -Al₂O₃ under 2 MeV H, 3.5 MeV He and 8 MeV O ion irradiation at various fluences. The inset figure shows the IBIL of the sample during 2 MeV H⁺ ion irradiation. All spectra have been decomposed into several emission bands previously reported in the literature, as seen in **Fig. 8** and **9**. The bands at 3.01 eV and 3.76 eV can be assigned to optical transitions involving F (oxygen vacancies with two trapped electrons) [55-57] and F⁺ centers (oxygen vacancies with one trapped electron) [55-57], respectively. The origins of the emission bands centered at 1.54 eV and 1.78 eV are connected with intrinsic defects (impurities) Ti³⁺ (²E→²T) [58] and Cr³⁺ (²E₂→⁴A₂) [55-57], respectively. A small emission band can be also observed at 2.48 eV that is ascribed to optical transitions of F⁺⁺ centers (oxygen vacancies without trapped electrons), although the stability of such centers is still a subject under investigation. Irradiation with He, or heavier O ions, produces similar features, but with an additional emission band at 3.32 eV, associated with the F₂⁺ center (di-vacancy aggregates) [55-57].

The IBIL spectra taken during light ion (H and He) irradiation exhibits higher intensity bands than for O irradiation, (when the intensities have been normalized by ion beam flux and energy) (**Fig. 7** and **8**). For 2 MeV H irradiation, the intensity of the main emission bands are a factor two higher than for 3.5 MeV He ions. This result is in agreement with McCarthy et al. [4] where the absolute efficiency of several luminescent materials was compared in terms of light yield (i.e., number of photons emitted per incident H and He ion as a function of ion energy) for low mass ions. Additionally, the IBIL intensities from α -Al₂O₃ samples was found to be several orders of magnitude higher than that of a-SiO₂ and quartz, in agreement with the present results. **Figure 9** shows IBIL spectra at different stages during the 8 MeV O ion irradiation, where the evolution of defect centers (F, F⁺ and F₂⁺) as a function of ion fluence is observed. The overall intensities decrease with increasing ion dose and the F⁺ band dominates since low fluences. The F band decreases rapidly when increasing the fluence, disappearing after certain fluence, where F and F₂⁺ emission bands still remain.

Figure 10 shows the evolution of the emission band intensities as a function of fluence for the main emission bands (F, F⁺, F₂⁺, Cr³⁺) during 8 MeV O irradiation. Both F and F⁺ bands follow similar kinetics, but the F⁺ band is clearly dominant at all fluences. The band intensities first increase with fast time constants to a maximum value ($3 \times 10^{13} \text{ cm}^{-2}$ for F⁺ and $1.5 \times 10^{13} \text{ cm}^{-2}$ for F) then decay with slower time constants. The F⁺ emission band reaches a certain saturation value after $1 \times 10^{15} \text{ cm}^{-2}$, but the F centre emission decreases to zero. Note that the F and F⁺ intensities start from non-zero values. This indicates that an initial population of oxygen vacancies is present in the material before irradiation. **Figure 10 (b)** shows, in detail, more rapid kinetics occurring at low fluences. During this early stage of the irradiation (fluence $\leq 1.5\text{-}2 \times 10^{13} \text{ cm}^{-2}$) F₂⁺ centers (aggregates of two oxygen vacancies) were observed to form and reach a quasi-steady state concentration. Unlike the oxygen vacancy centers, the initial concentration of F₂⁺ centers is zero (or at least below detection limits). Note that the saturation kinetics of the F₂⁺ band is correlated with the buildup and decay kinetics of the F band. Similar evolution behavior of the F, F⁺, and F₂⁺ centres at low ion fluence has also been reported by M. Malo *et al.* [14]. The ratio between the intensity (as calculated by the Y_{F^+}/Y_F area ratio) of the F⁺ and F bands (not shown) exhibits exponential growth in the low fluence stage, but at about $1 \times 10^{15} \text{ cm}^{-2}$ it saturates at a value of 45. The Cr³⁺ emission yield also exhibits buildup and decay kinetics, reaching a maximum yield at a fluence of around $1 \times 10^{14} \text{ cm}^{-2}$.

4. Discussion

4.1 Silica and quartz

The evolution of the two main emission bands – the red band (1.9 eV) and the blue band (2.7 eV) – that were observed in the IBIL spectra for silica and quartz, corroborate previous results available in the literature. The red band is attributed, by most authors, to non-bridging oxygen hole centers (NBOHC) [5, 24, 46]. These centers have an unpaired electron in the 2p orbital along a broken Si-O bond. Their concentration depends on the amount of precursor peroxy linkages and the concentration of hydroxyl

groups (OH) [11, 59, 60]. As mentioned previously, a certain controversy exists as to the specific mechanism responsible for the emission of the blue band. It has been variously attributed to ODC II centers (non-relaxed oxygen vacancies), intrinsic recombination of STEs (non-defect mediated), STE recombination at E' centers, or emission from STEs located at strained bonds [37, 48-51]. Finally, the authors suggest to consider an alternative interpretation, where the 2.7 eV emission band could be associated to an extrinsic recombination of the STEs at ODC-II centers produced by irradiation. The nature of the STE in quartz and silica is still not obvious. Some calculations have concluded that the STE is localized on a broken Si-O bond with the hole located on the O and the electron located on the Si in a sp^2 configuration [49].

As seen in the results, both emission bands in silica and quartz exhibit a single kinetics regime under He and H irradiation but two kinetic regimes under O irradiation with a transition between the regimes for a fluence on the order of several 10^{12} cm^{-2} , where a saturation of defective centers takes place. The structural damage appearing under irradiation plays an important role in modifying the STE dynamics. Altered STE migration rates, lifetimes, diffusion lengths and populations of competing recombination centers affect the balance between the recombination rates at those competing centers.

In silica, the large number of strained bonds accounts for the intense blue band that is predominant over the red band for all ions and fluences. Although certain differences can be distinguished in the blue to red ratio (**Fig. 5(a)**) associated to a monotonic trend between electronic energy loss of the ion species and energy, in general, they show a quite similar behavior. Furthermore, it should be noted that the creation of emission centers and their activation by the generation, transport and recombination of e-h pairs depends on the specifics of both nuclear and electronic energy loss mechanisms for each ion in an extremely complex way, being more relevant this effect for the light ions.

4.1.1 Fast light ions in silica

In silica, it has been shown by Nagata *et al.* [43] that the energy normalized intensity of the blue band decreases with increasing H ion energy (between 0.1 and 3 MeV), while it is independent of incident

energy for He ions. In other words, the luminescence efficiency is proportional to the electronic energy deposition for H ions but saturates at higher energies for He ions. This saturation behavior has been attributed to long-lived excited states [43]. Because the blue band is thought to be related to triplet excited states, the decay time could be as long as ms [61]. Energetic He ions transfer energy more densely to the electronic system than H ions. Presumably, the localized production of e-h pairs and STEs in the He ion track can outpace the de-excitation of the relatively stable triplet excited states. Hence de-excitation from the color centers is a rate limiting process and saturation results. In our case the ratio between the luminescent efficiency for 3.5 MeV He and 2 MeV H ion irradiation is around 4.5 in agreement with McCarthy *et al.* [4].

A rate theory model based on a competition between the creation and annihilation of the luminescent centers (strained Si-O bonds, ODC-II centers, or E' centers) during the ion irradiation was employed [43] in order to explain the higher emission intensity from He ions. The fitting parameters from our experimental data for 3.5 MeV He and 2 MeV H ions are in agreement with the values presented in the original paper [43]. The ratio of the production rate to the annihilation rate constant is larger for He than for H. This result is not surprising because He, having larger nuclear and electronic stopping powers, can produce more defects (either through nuclear elastic scattering or via ionization and bond breaking).

As seen in **Fig. 6** the He and H kinetics are in better quantitative agreement when the fluence is normalized by displacements. This suggests that the production of blue emission centers occurs primarily by knock-on damage (nuclear elastic collisions). Physical factors that go into the annihilation rate constant could be difficult to determine because, in principle, there are more competing mechanisms that affect the observed steady state. These factors could include (but are not limited to): point defect migration and recombination, competition between ionization induced annealing (recovery) of color centers and generation of higher density of e-h carriers (enhancing emission intensity), and the aforementioned saturation of excited centers by He ions.

Furthermore, emission from the blue and red bands can be affected by impurities such as OH. Blue emission is enhanced in lower-OH content silica glasses, while the red band, attributed to the

NBOHC centers, is more prominent in high-OH silica [5, 6]. The higher intensity of blue light is a consequence of the larger amount of strain present in Si-O bonds in lower OH silica glass. Although this explanation implies that the emission process is mainly described by STE recombination at strained bonds, such bonds can also be easily broken forming oxygen vacancy related defects (ODC-II or E'). In high-OH content silica, the structure is more relaxed (less strained bonds) and the formation of NBOHCs from silanol groups is enhanced by ion dissociation of OH. Hence the ratio of the red to blue intensities is greater. The structure will be more relaxed and the blue emission will be lower. In the present work, the silica samples had an intermediate OH concentration, explaining the moderately large ratios seen in **Fig. 5 (a)**.

Although additional data are needed to develop a more complete understanding, these example experiments demonstrate how IBIL is used to measure the dynamic process involved in damage creation in and relaxation of the silica glass network. On the other hand, the analysis of ion induced luminescence in SiO₂ glasses is complicated owing to simultaneous damage processes and luminescence phenomena that appear in the measurements.

4.1.2 Oxygen irradiation in silica

It has been reported in synchrotron radiation studies, using photons above the band-gap energy for SiO₂ [46], that the 1.9 eV emission band accompanies the 2.7 eV emission band during STE decay. This has been interpreted as follows. The NBOHC is created in an excited state following Si-O bond breaking associated with the formation of the self-trapped excitons. This explanation is consistent with the present data, which shows that the blue to red intensity ratio is mostly constant during the entire irradiation. The growth and decay kinetics appearing at several 10¹² cm⁻² agree with results from [8]. The transition from growth to a lower concentration steady state is not fully understood as the structure remains amorphous throughout the irradiation [31, 62, 63]. However, [8] attributed this behavior to a densification effect induced by irradiation in silica. Irradiation-induced densification occurs at fluences where the individual ion tracks overlap (on the order of ~ 10¹² cm⁻²) [31]. These are similar fluences to

those at which the light yield was observed to decrease. In the denser structure, closer to a damaged quartz, average bond strain is reduced [64] reducing the exciton trapping rate and hence the intensity of the red and blue light [49, 51].

4.1.3 Fast light ions in quartz

According to the scarce published literature on the origins of the blue emission band in irradiated quartz, it has been attributed to the recombination of electrons at oxygen vacancies [65]. While heavy ion implantation does generate oxygen vacancies, the effects of nuclear elastic scattering on the production of strained bonds must also be considered. Initially, few strained bonds are available for STE recombination, as the fluence increases a saturation stage is reached.

The most prominent difference between the IBIL spectra of quartz and silica is the dominance of the red band in quartz. Similar observations have been reported in both CL and IBIL studies showing the defect structure of quartz is extremely radiation sensitive. Those results were attributed to the formation of NBOHCs as peroxy linkages are broken and radiolysis of hydroxyl groups occurs [60, 66]. Similar emission behavior, observed under 3 MeV H^+ ion irradiation, was also attributed to NBOHC formation [11]. Since the red band appears to be related to an electronic energy loss mechanism (radiolysis), the blue band has been attributed to nuclear energy loss mechanisms, and for light ions, electronic energy loss greatly exceeds nuclear (**Table 1**), the observed dominance of the red band over the blue band, at all fluences, is compatible with the proposed mechanisms for formation of red and blue color centers in quartz.

4.1.4 Oxygen irradiation in quartz

Under oxygen irradiation in quartz, the red emission, though initially dominant, is eventually overcome by blue emission. This behavior is attributed to self-trapped exciton recombination at heavily strained Si-O bonds, such as those present in silica or in a damaged quartz crystal [8]. Experimental results show that STE recombination can occur in pristine quartz crystal [26, 67]. Theoretical calculations

also show that self-trapping is stabilized at strained bonds [49, 51, 54]. The IBIL kinetics for the blue band is qualitatively different to that observed for silica; instead of paralleling the decreasing yield in the second stage of the kinetics, the blue increases, albeit with a slower time constant. The blue band carries the main structural information, particularly on the initial linear region of the curves, before more complex processes take effect.

For swift ions with electronic stopping power above a critical amorphization threshold, each ion generates an amorphous track of nanometer diameter [28, 29]. The energy deposition from 8 MeV O at the sample surface is above the threshold for quartz (~ 2 keV/nm) [36, 37, 68]. The track formation process proceeds as follows: the passing ion transfers energy to the electronic structure (0.1-1 fs time scale), a non-equilibrium energized e-h cloud with a width on the order of nanometers undergoes electron-electron interactions to repartition the energy [69], and eventually reaches thermal equilibrium [28] in about 10^{-14} s. As the hot electron cloud cools, it can couple to the lattice resulting in localized melting and formation of amorphous zones or columns. The distribution of electrons and holes extends over a distance scale on the order of the carrier diffusion length, L_D (several tens of micrometers) [9]. These remnant e-h pairs, though too dispersed and too cool to cause significant local heating, can annihilate via radiative recombination modes or form bound states (excitons). The excitation density (e-h density) efficiency generated by swift heavy ions decreases with increasing electronic stopping power [44]. The reason for this appears to be the high rate of initial non-radiative e-h recombination in the dense e-h pair cloud near the core of the ion track.

Light emission under irradiation results from the recombination of e-h pairs at suitable recombination centers related to defects [70]. The slope (Y_B/ϕ) in the initial linear region of the blue light yield vs. ion fluence can be used to monitor the generation of recombination (STE) centers under irradiation. Following [9], the evolution of the normalized IBIL yield was compared with the amorphization kinetics derived from Rutherford-backscattering spectra under channeling conditions (RBS/C) for 4 MeV O and 15 MeV F. The electronic stopping power of 8 MeV O lies in between these

two ion energy combination ($S_e = 2.1$ keV/nm for 4 MeV O and 2.3 keV/nm for 15 MeV F, at the surface) [71].

In this regime of ion mass and stopping power, the material reaches an amorphous state at a fluence of $\sim 2 \times 10^{14} \text{ cm}^{-2}$. The blue yield saturates at this fluence. At this point, strong recombination from the strained bonds reflects an amorphous state (**Fig. 4(b)**). The marked change in the slope of the blue band above $\sim 5 \times 10^{12} \text{ cm}^{-2}$ indicates the accumulation of strained bonds. In other words, it follows the growth of the amorphous volume fraction in the material as amorphous tracks begin to overlap each other. During swift ion irradiation in other dielectric materials, a systematic increase the thickness of the amorphous layer has been observed. This increase is believed to be a cumulative effect of the ion tracks [33, 34, 72]. The resulting IBIL spectra of the quartz at an O fluence of $3 \times 10^{15} \text{ cm}^{-2}$ is virtually indistinguishable from that of silica (**Fig. 3 (c, d)**) indicating that the structure has been totally amorphized.

The red band presents a behavior similar to that of silica, rapidly growing followed by a slow decrease. These results are comparable to those obtained for quartz in [8], where a clear correlation between the evolution of the red and blue bands is not observed. Competition between recombination centers, either NBOHC or STE, can be invoked to explain the behavior. At the start of the irradiation few strained bonds are available for STE recombination (blue band). Therefore, most recombinations take place at NBOHC centers (red band), already present in the material or induced by ion irradiation. With the accumulation of the structural damage, the STE recombination channel grows with concomitant growth of the blue emission band.

The blue to red intensity ratio increases more rapidly in silica than in quartz, as can be observed from **Fig. 5**. This could be explained by the presence of a large number of pre-existing strained bonds in the amorphous structure. Furthermore, the onset of the steady state behavior occurs at a higher fluence in quartz than in silica. Indeed, the ratio increases as the ion tracks begin to overlap. At the maximum fluence ($3 \times 10^{15} \text{ cm}^{-2}$), this ratio becomes approximately 12. The ratio is 11.5 in silica and it is more or less

constant throughout irradiation suggesting that the constant ratio of the two recombination rates is characteristic of the amorphous structure.

4.2 Sapphire ($\alpha\text{-Al}_2\text{O}_3$)

Prior luminescence studies of sapphire identified the F and F^+ bands with oxygen vacancy related defect sites. According to the data presented here, the major luminescence features caused by ion irradiation arise from point defects. Strong single-vacancy related peaks luminescing at the onset of irradiation correspond to defects present before irradiation and not generated by the incident ions. As the irradiation takes place, new oxygen vacancies and interstitials are continuously produced due to ionization and atomic displacement, as evidenced by the initial increase in the F and F^+ emission intensities. F-center luminescence grows faster than F^+ -center probably due to the dense ionization induced by 8 MeV O and the oxygen vacancy configuration, which might be more stabilized in the form of F-center than F^+ -center in the very early stage of irradiation [73]. The F and F^+ intensities decrease at later stages of the irradiation and the F emission yield is suppressed (**Fig. 10**). This might be attributed to various mechanisms such as: the loss of single vacancies to defect complexes/aggregates, an effect of stress introduced by irradiation producing minor changes in lattice symmetry, or competition from non-radiative recombination mechanisms (loss in radiative efficiency) [10]. The F_2^+ band appears during irradiation with heavier ions (oxygen) (**Fig. 10**). Clustered defects are more likely to form from dense collision cascades characteristic of heavy ions at the end of their ion range than along the ion path where the displacement damage density is low. The appearance of the F_2^+ band could be attributed to vacancy clustering occurring at the end of the O ion range.

The sapphire lattice is remarkably stable and its crystallinity is preserved to He ion fluences in excess of 10^{17}cm^{-2} [10]. Low-dose, light-ion implantations or electron irradiations primarily induce isolated point defects. Canut *et al.* [74] have experimentally measured an amorphization threshold of 21 keV/nm in $\alpha\text{-Al}_2\text{O}_3$ for producing extended defect creation along the amorphous ion track due to collective electronic excitations. High-energy, heavy-ion irradiations induce both point defects and

extended defect clusters, where the major fraction of these point defects (such as F and F⁺ centers) and aggregates are created by elastic processes in the nuclear energy loss regime. In the present data, with 8 MeV O irradiation, the electronic stopping power ($S_e = 3.13$ keV/nm, see **Table 1**) is well below the amorphization threshold. Thus, only point defects and small clusters may be formed along the ion path and most of the defects are to be found at the end of the ion range. It should be noted, however, that electronic damage is cumulative in the sense that, even below the amorphization threshold, point defects can accumulate through successive ion track overlapping [33, 34].

At the early stages of irradiation ($\leq 1.5\text{-}2 \times 10^{13}$ cm⁻²), it is reasonable to expect vacancy-interstitial recombination and also vacancy aggregation. This latter process has been confirmed by both the IBIL (**Fig. 9(a)**) and optical absorption spectra [14]. The formation of every F₂⁺ centre removes two F/F⁺ centres, and could account for some of the reduction in the signal from single vacancy centres. On the other hand, although the F and F⁺ bands continue to decrease, the kinetics shows no further increase in the F₂⁺ emission. Instead a steady state is reached. According to M. Malo *et al.* [14] the F₂⁺ centre is an essential precursor to higher oxygen vacancy aggregates (F₃, F₄, etc.) and is a well-known nucleation site for aluminum colloids. During nucleation, the colloids act as effective sinks for oxygen vacancies. Hence single oxygen vacancies are also being removed by higher order vacancy clusters and colloids. Meanwhile, the generation of F₂⁺ centers by clustering is balanced by the removal of F₂⁺ centers by higher order clustering and colloid nucleation. These processes explain both the steady state observed in the F₂⁺ population as well as the apparently continuous loss of single vacancies.

5. Conclusions

An ion beam induced luminescence (IBIL) system has been developed and installed at the multifunctional Ion Beam Materials Laboratory at the University of Tennessee, Knoxville in partnership with Oak Ridge National Laboratory on one of the multipurpose end-stations to provide in-situ characterization capabilities of materials undergoing radiation damage and ion beam modification. The apparatus for photon detection has been fully integrated into the existing ion beam analysis set-up to facilitate simultaneous acquisition of IBIL and Rutherford Backscattering spectra. A correlation between the evolution of the defect bands and the microstructural modifications is clearly demonstrated.

The comparative study of the IBIL induced by fast light ions (He and H) and heavy ions (O) in silica and quartz was presented. The observations are consistent with the assignment of a 1.9 eV red band to non-bridged oxygen hole centers (NBOHC). A 2.7 eV blue band was associated with recombination of STEs, either at heavily strained Si-O bonds or at oxygen vacancies. In silica, a reduction in the yield of both bands under O irradiation was attributed to the densification of the Si-O-Si network. In quartz, the O irradiation response indicates a shifting competition between recombination at NBOHC centers and strained bonds that changes as the material becomes amorphized along O ion tracks.

Due to the important roles of oxygen vacancies (F and F^+ centres), di-vacancy aggregation (F_2^+ centres) and their complex dynamic balance in the kinetics of the damage evolution, the emission peaks from these defect centers can be used as indication for monitoring material modifications during ion irradiation.

High sensitivity of the IBIL technique can provide insights on the kinetics of radiation-induced defect production and microstructural evolution during ion irradiation even from very low fluences. The usefulness of IBIL and its applicability to *in-situ* material characterization in extreme radiation environments could be implemented in diagnosing inaccessible components in future fusion devices and present fission reactor components, as well as an important characterization tool in fundamental research.

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Tables

Table 1. Irradiation parameters for the ions and materials used in this work, calculated using Stopping and Range of Ions in Matter (SRIM) full-cascade simulations (version 2012) [38, 39], where S_e is the electronic stopping power at the surface, $S_{e \text{ max}}$ is the maximum value of the electronic stopping power, S_n is the maximum value of the nuclear stopping power and R_p is the projected ion range. The average dose in dpa (displacements per atom) was estimated under full-cascade simulations for the ion range avoiding the damage peak region (90% R_p) for the specific irradiation fluences used. In the case of Al_2O_3 , $\langle dpa \rangle$ is calculated for fluences shown in **Fig. 7** and **8**.

Ion	Energy (MeV)	S_e (keV/nm)	$S_{e \text{ max}}$ (keV/nm)	S_n (keV/nm)	R_p (μm)	$\langle dpa \rangle$
<i>Silica</i>						
H	2.0	0.03	0.10	6.7×10^{-5}	49.2	5.3×10^{-5}
He	3.5	0.19	0.34	2.0×10^{-3}	14.0	4.6×10^{-4}
O	8.0	1.78	1.82	4.2×10^{-2}	6.20	5.4×10^{-2}
<i>Quartz</i>						
H	2.0	0.03	0.12	7.7×10^{-5}	40.5	5.5×10^{-5}
He	3.5	0.23	0.41	3.0×10^{-3}	12.0	5.7×10^{-4}
O	8.0	2.14	2.19	5.0×10^{-2}	5.10	6.0×10^{-2}
<i>Al_2O_3</i>						
H	2.0	0.05	0.17	1.1×10^{-4}	27.2	1.0×10^{-5}
He	3.5	0.33	0.59	3.4×10^{-3}	8.25	1.4×10^{-4}
O	8.0	3.13	3.18	6.1×10^{-2}	3.50	1.2×10^{-3}

Figure Captions

Fig. 1. Schematic experimental setup for online IBIL measurements.

Fig. 2. IBIL spectra from silica (a) and quartz (b) under 2 MeV H, 3.5 MeV He and 8 MeV O ion irradiation at various fluences.

Fig. 3. IBIL spectra and the corresponding component bands from silica (a and c) and quartz (b and d) under 3.5 MeV He and 8 MeV O ions. The dashed curves represent the emission bands used to deconvolute the spectra. The inset color photos accompanying the spectra show the luminescing samples during 3.5 MeV He ions irradiation ($I=80$ nA, spot area= 3×3 mm²).

Fig. 4. Evolution of the luminescence intensity of the blue (2.7 eV) and red (1.9 eV) bands plotted as a function of incident ion fluence for silica (a and c) and quartz (b and d) under 2 MeV H, 3.5 MeV He and 8 MeV O ion irradiations.

Fig. 5. Area ratios between the intensities of the blue (2.7 eV) and red (1.9 eV) peaks (Y_B/Y_R) for silica (a) and quartz (b) for 2 MeV H, 3.5 MeV He and 8 MeV O ion irradiations.

Fig. 6. Normalized intensity of the IBIL corresponding to the blue emission band (2.7 eV) for silica under 2 MeV H and 3.5 MeV He ion irradiations, in the initial rapid linear growth regime, plotted as a function of (a) ionization ($\phi \times S_e$) and (b) displacements ($\phi \times d_{pi}$). The upper x-axis shows the incident H ion fluence for reference.

Fig. 7. IBIL spectra and emission bands from α -Al₂O₃ under 2 MeV H, 3.5 MeV He and 8 MeV O ion irradiation at various fluences. The inset color photograph accompanying the spectra shows the luminescence of the sample during 2 MeV H ion irradiation ($I = 200$ nA, spot area = 3×3 mm²).

Fig. 8. IBIL spectra and the corresponding component bands from α -Al₂O₃ under 3.5 MeV He (a) and 8 MeV O (b) ion irradiation. The dashed curves represent the emission bands used to decompose the spectra. The solid red line represents the global fit of the spectrum.

Fig. 9. Evolution of the α -Al₂O₃ IBIL spectra showing the defect centers evolution (F, F⁺ and F₂⁺) as a function of ion fluence during irradiation with 8 MeV O ions. The dashed curves represent the emission bands used to decompose the spectra. The solid red line represents the global fit of the spectrum.

Fig. 10. Evolution of the luminescence intensity of the emission bands associated with F, F⁺, F₂⁺, Cr³⁺ defect centers as a function of the irradiation fluence under 8 MeV O irradiation for α -Al₂O₃. (b) Detailed emission intensities in the low fluence regime.

Figures

Fig. 1. Schematic experimental setup for online IBIL measurements.

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Fig. 7. IBIL spectra and emission bands from α - Al_2O_3 under 2 MeV H, 3.5 MeV He and 8 MeV O ion irradiation at various fluences. The inset color photograph accompanying the spectra shows the luminescence of the sample during 2 MeV H ion irradiation ($I = 200 \text{ nA}$, spot area $\approx 3 \times 3 \text{ mm}^2$).

Fig. 8. IBIL spectra and the corresponding component bands from $\alpha\text{-Al}_2\text{O}_3$ under 3.5 MeV He (a) and 8 MeV O (b) ion irradiation. The dashed curves represent the emission bands used to decompose the spectra. The solid red line represents the global fit of the spectrum.

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