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# Ionoluminescence of fused silica under swift ion irradiation

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ABSTRACT

Ion beam induced luminescence spectra have been in-situ recorded during $He^+$ (2.5 MeV), $O^{4+}$ (13.5 MeV) and $Si^{4+}$ (24.4 MeV) irradiations for three vitreous silica grades with different OH content (KU1, KS-4V and Infrasil 301). Remarkable changes in the ionoluminescence spectra of the three silica grades were observed for low ion fluences. $He^+$ irradiated samples exhibited higher luminescence than equivalent ones irradiated with heavier $O^{4+}$ and $Si^{4+}$ ions. KU1 samples with the highest OH content showed the lowest blue luminescence. Blue luminescence maximum during ion irradiations with $O^{4+}$ and $Si^{4+}$ ions is correlated with structural changes.



## 1. Introduction

Fused silica is a relevant material both from the fundamental (as model for the study of glasses), as well as the applied point of view, due to its uses in many different technological fields like optics, electronics, energy or space. Irradiation effects on optical properties of vitreous $SiO_2$ are a demanding issue, since optical absorption and light emission impose severe limitations on the use of optical materials within a radiation field. Optical and electrical properties of silica glasses are strongly influenced by point defects, which are introduced during the manufacturing process or produced by energetic photons (UV light, X-ray or $\gamma$ radiation) and/or particles (ions, electrons or neutrons) [1]. Besides, it must be considered that the damage in glassy silica is also due to radiation-induced changes of the structural disorder through site-to-site modification in bridging angle of $SiO_4$ tetrahedral units, i.e., in the distribution of Si–O–Si bond angles.

Ion implantations are widely used as a relatively low-cost and rapid means of simulating the neutron irradiation damage in materials. Implanted ions lose their incident energy by two processes: inelastic collisions that produce electronic excitations and elastic collisions in which substrate atoms are displaced. Research interest about the damage produced by swift ions into silica and other insulators has increased recently, since electronic mechanisms may dominate over elastic nuclear collisions and the induced damage presents features not yet sufficiently understood [2–5]. Several physical models (thermal spike, Coulomb explosion, bond weakening, exciton self-trapping) have been proposed to understand the latent tracks created by swift heavy-ions, differing in how and how fast the excited electrons transfer their energy to the atomic network. Furthermore the self-trapped exciton (STE) is regarded as a significant mechanism of energy localization and relaxation of the glassy lattice in the excitonic model. The formation of STEs entails Si–O bond breaking, emission of luminescence in the photon energy range near or below 3 eV, formation of Frenkel pairs and modification of local lattice structures [2,3].

Well-known radiation-induced point defects in amorphous silica are the paramagnetic silicon and oxygen dangling bond pair from a Si–O–Si bond, E′ (≡Si·) and the non-bridging oxygen hole center (NBOHC, ≡Si–O·). Frenkel defect processes from regular and strained Si–O–Si bonds give rise to oxygen deficient center (ODC(I), ≡Si–Si≡) and to interstitial oxygen ($O^0$). ODC(II), twofold coordinated silicon =Si··, another type of oxygen deficiency, is readily formed from ODC(I), due to interconversion reaction between these diamagnetic defects. Interstitial $O^0$ dimerizes into $O_2$, or can be incorporated into the network to form ≡Si–O–O–Si≡ (POL, peroxy linkage) and ≡Si–O–O· (POR, peroxy radical). The above notation ≡ represents three bonds with other oxygen atoms in the glass network and · denotes an unpaired electron.

The optical properties of point defects in silica have been reviewed by Skuja et al. [6,7] and defects related luminescence by Salh [8]. Kajihara et al. [9] reported the mechanisms of intrinsic defect formation in amorphous $SiO_2$ by electronic excitation.

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Formation of electron–hole pairs and their self-trapping following band-to-band excitation, caused by the strong $SiO_2$ electron-lattice interaction, allow transient dangling bond pairs creation. STEs are converted to stable defects at heavily distorted sites in $SiO_2$ network, such as the strained Si–O–Si bonds. Also the self-trapped holes (STH, ≡Si–O·–Si≡) can participate in the radiolysis processes, playing an important role, not only at low temperature but also at room temperature, as it has been pointed out in the extensive revision about STH made by Griscom [10,11], and recently an alternative model for ODC(II) in silica glass has been also suggested by Griscom [12]. Trukhin in a short review on luminescence of localized states in pure synthetic silica KS-4V under excimer laser irradiation considers that recombination of separated electrons and holes leads to recombination luminescence, being the main luminescent bands determined by oxygen deficient centers [13]. A complex temperature, dose rate and dose dependence of the radioluminescence behavior for electron irradiated KS-4V is discussed in the work of Moroño and Hodgson, also involving STE recombination [14].

The ionoluminescence in vitreous silica irradiated by light (H, He) and heavier ions ($N^+$, $O^+$), was presented in earlier papers by Jaque, Townsend and Chandler [15,16]. In-situ luminescence measurements were made by Moritani et al. [17–19] to obtain the reaction kinetics of radiation-induced defects under ion beam (2 MeV $He^+$) irradiation in vitreous silica with different OH content, showing additionally the formation of clusters defects of oxygen deficient centers (ODCs). Also irradiations by H and He ions with energies from 0.2 to 3 MeV in silica with different OH concentration were made by Nagata et al. [20–22], and the ion-beam induced luminescence was measured to study the formation and annihilation behavior of the oxygen vacancies. A recent work concerning the roles of the OH content and the ion stopping power on ion induced luminescence in silica [23], concludes a strong luminescence kinetics dependence on incident ions stopping power.

X-ray absorption technique (XAFS) was applied to study the local structure of silica glasses irradiated in a nuclear reactor [24], the results suggest appearance of Si precipitates. The possibility of Si precipitates by irradiation with $H^+$ ions accelerated to 13 keV was also considered analyzing the in situ luminescence from high and low OH silica glasses [25].

The present work aims to gain insight of the dynamical processes involved in damage creation and relaxation in a glass lattice affected by impurities and network modifiers. The OH content is the most relevant impurity and samples luminescence was measured in the course of ion irradiation.

## 2. Experimental methods

Optically polished silica samples with different OH and impurity content have been studied: KU1 (OH 820 ppm) and KS-4V (OH < 1 ppm) high purity synthetic silica grades, candidate materials for optical components in fusion devices for their radiation hardness; and Infrasil 301 (from Heraeus), with metallic and metalloid impurities (Al ~ 20 ppm, Ge) and hydroxyl content below 8 ppm. Samples of around 1 mm thickness were covered by a copper mask during implantation, to avoid electric arcs and to define an irradiation area of $5 \times 5$ mm$^2$. Ion bombardment was performed at the Centre for Micro Analysis of Materials (CMAM) in Madrid (UAM) using a 5 MV tandem accelerator within a standard discharge chamber at a vacuum of $10^{-4}$ Pa. Room temperature irradiations were carried out with $He^+$ (2.5 MeV), $O^{4+}$ (13.5 MeV) and $Si^{4+}$ (24.4 MeV), using beam currents of 45 nA and 1 nA to avoid possible overheating of the samples. Fluences were determined by direct current integration from the target using electron suppression. Experimental fluences varied between $5 \times 10^{12}$ and $1.6 \times 10^{15}$ ion/cm$^2$.

Depth profiles of energy loss of ions, in both electronic and nuclear processes, were estimated using SRIM 2008 code [26], with displacement energies of 35 eV for Si and 20 eV for O [27] and a target material density of 2.21 g/cm$^3$. With the energies used in this work the estimated projected range of ions was 9 μm and the predominant damage mechanism was electronic excitation. The electronic stopping power assessed at the samples surface were 3.5 keV/nm for silicon, 1.6 keV/nm for oxygen and 0.3 keV/nm for helium irradiations.

During ion irradiation the ionoluminescence (IL) emission was transmitted through a silica window port (placed at 45° with respect to the ion beam), then collected and focused with a lens into an optical fiber located outside of the discharge chamber. The light was guided to a compact spectrometer QE 6500 (Ocean Optics Inc.) configured with a multichannel array detector that measured simultaneously the whole spectrum in the range 200–850 nm. The spectra were recorded in $I(\lambda)d\lambda$ units, using an integration time of 3 s, and were converted to $I(E)dE$ multiplying the measured counts by $\lambda^2$ [28,29]. Details and a schematic of the experimental setup can be consulted in Ref. [30].

## 3. Results and discussion

### 3.1. Ionoluminescence for low and high experimental fluences

The analysis of ion-induced luminescence (IL) is complicated due to the concomitant creation, excitation and recombination processes giving rise to luminescent signals and the modification of the glass lattice during irradiation.

In Figs. 1 and 2 is shown the ionoluminescence spectra of KU1, KS-4V and I301 silica samples irradiated with $He^+$ 2.5 MeV and $Si^{4+}$ 24.4 MeV at low and high fluence. The main IL bands detected for the three silica grades were the 1.9 eV (650 nm) red band due to non-bridging oxygen hole centers (NBOHC) [17,20], a 2.3 eV band (540 nm) of small intensity attributed to STE [30,31], and a 2.7 eV (460 nm) blue band that is ascribed to recombination of the self-trapped exciton (STE) and to the triplet-singlet emission of ODC(II) defect creation [17,20]. Self-trapped excitons can cause a transient or permanent rupture of the Si–O–Si bond [32,33]

$$\equiv Si{-}O{-}Si\equiv \rightarrow \equiv Si{-}Si\equiv + O_{int} \equiv 2(=Si^{\cdot\cdot}) + O_{int} \quad \text{(Frenkel-like mechanism)} \tag{1}$$

resulting in the creation of ODC(I) (≡Si–Si≡) and consequent ODC (II) (=Si··). The near infrared luminescent band at 1272 nm, the spectroscopic signature of interstitial $O_2$ [34], could not be detected under our experimental setup.

The red IL band increases quickly at the beginning of the irradiation for highest OH content silica (KU1 grade) due to creation of NBOHCs from OH bonds cleavage [17,20]

$$\equiv Si{-}OH \rightarrow \equiv Si{-}O^{\cdot} + H^{\cdot} \quad \text{(OH bonds radiolysis)} \tag{2}$$

and then decreases up to a steady intensity at higher fluences. For low OH content silica glasses, the red band steady intensity could be due to NBOHCs created from strained bonds breakage

$$\equiv Si{-}O{-}Si\equiv \rightarrow \equiv Si{-}O^{\cdot} + {\cdot}Si\equiv \quad \text{(dangling bond defect pairs NBOHCs and E′)} \tag{3}$$

At high irradiation fluence the three silica types presents similar red band intensity for He and heavier ions $O^{4+}$ and $Si^{4+}$.

A small but noticeable blue shift of the red signal (from 1.91 towards 1.94 eV) was detected for O and Si ion fluences between maximum intensity and steady intensity in KU1 samples. This can be explained by the creation of NBOHCs (≡Si–O·) from different precursors (from the radiolysis of OH or from strained