Radiation Induced Defects and Thermoluminescence Characteristics in Eu, Dy and Eu/Dy Doped-Quartz Sol-Gel by 2 Gy Beta and 2 MeV $^4$He$^+$ Irradiations

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ABSTRACT

Thermoluminescence (TL) of pure and Eu$^{3+}$ and Dy$^{3+}$ doped synthesis quartz was synthesized and their ion beam and thermoluminescence properties were investigated. The as prepared, doped and co-doped quartz and the effects of imparting 2 Gy beta dose and 2MeV $^4$He$^+$ ion beam irradiation is investigated. The basic model proposed and can explain our observations is that, the dominant signals from the as prepared material arise from the incorporation of the transitions within the RE dopants enhanced by the intensity from the intrinsic or host defect sites within the synthesis quartz network. The complex shape TL glow curves indicate that irradiation causes major distortions to the lattice with the incorporation of extrinsic impurities and RE doping processes, induce perturbations and alter the energy levels pattern of the free ions and assigned transitions probabilities in a manner that that depends on the dopants, their concentrations and the host material. The larger Eu ions stabilize the emission more than that of the Dy ions. The TL peak temperatures are commonly correlated via charge transfer processes and scale with the ions size, in such a manner that the close proximity (or shallow traps) allows lower temperature electron release, whereas the more distant variants (deep traps) are less distorted, but are still able to couple to the higher energy orbitals of the Eu ions.

Keywords: Defects; Ion beam, Rutherford backscattering; Thermoluminescence.

I. INTRODUCTION

Rare-earth elements have generally been recognized to have great demand in the commercial market owing to their unique magnetic, luminescent, catalytic, and electrochemical properties [1], [2]. The ever-growing demand for rare-earth enabled products and technologies has motivated researchers to improve the properties of the existing luminescent materials and to provide new novel materials of desired color, composition and optical properties [3]. Since glasses possess non-crystalline structure it is relatively easy to incorporate varying concentration of the dopant ions in the glass network. The glasses doped with rare-earth ions are of great importance due to their applications in lasers, amplifiers and lighting devices [4]. Owing to the excellent transparent property, silica glass is a key material of particular interest for many optical applications such as optical waveguide, optical components for photolithography. Silica-based glasses offer solubility for rare-earth ions of about $6 \times 10^{20}$ cm$^{-3}$, are transparent in the visible to near-infrared region, and are easily compatible with Integrated Optics, IO- technology [2]. Applications in devices composing a network system use thin layers of amorphous SiO$_2$ (a-SiO$_2$) as a mask for selective ion implantation or insulation between metal and semiconductor layers [5], [6].

In other applications, devices with silica glass are exposed over a broad range of energies to different types of ion irradiations and thus controllably induce electrical, optical, structural, mechanical and chemical properties of materials for a broad range of research and applications, including advanced electro-optical devices and engineered nanostructures[7]-[9]. This, however, requires crucial understanding of the mechanism and processes of structural damage induced by the irradiation beam [10], [11]. Changes, including phase transformations and functional properties near surface regions of materials have been investigated in a series of conferences and proceedings on ion beam modification and analysis of materials (IBMM)-, see e.g. [12], [13]. Commonly, defects can be grouped according to their structure and size as point defects, dislocations (linear defects), and plane defects. The structural damage in crystalline materials include point defects, defect clusters, dislocations and amorphization zones [14]-[16].
literature about irradiation-induced phase transformation and structural modification, have been reported in many previous studies [17]-[20]. Radiation effects in silicate glasses and amorphous SiO$_2$ designate that the energy dissipated in the glass matrix is through the atomic displacements produced by direct nuclear collisions and the ionization damage produced by interactions of the bombarding particles with the bonding electrons. A variety of ionizing conditions including swift proton, electron and gamma irradiation which focus on electronic excitations dominated irradiation processes, induce structural transformations from large ring structure to small three and four, member ring structures resulting with physical disorder to the glass network [21], [22]. Indeed, two types of structural damage have been identified in silica glasses; the intrinsic defects: the E’-centers, the peroxy radical and non-bridging oxygen hole center. The other type of structural damage is the physical disorder, induced by wide distribution of Si-O-Si bond angle. In addition to the defects present with un-paired electron, the limited knowledge of the neutral oxygen deficiency centers (ODCs) have received considerable attention, because they are also essential defects that affect the optical absorption in practical applications [23], [24]. However, ion beam is one of the alternative probes to detect absorption bands corresponding to non-relaxed oxygen vacancy, whereas luminescence measurements during ion irradiation allows one to measure the dynamic processes involved in damage creation and relaxation in the glass network [25], affected by impurities such as OH hydrogen [26], [27].

The interaction of ions with solids results in structural defects and damage to the material through the energy deposition to both the atomic nuclei and electrons in the solid. Energy is transferred to the electronic and atomic structures, and the corresponding response of materials, is divided into three principal energy regimes. At low incident ion energies, the transfer of energy to atomic nuclei (nuclear energy loss) dominates, leading to the displacement of atoms via elastic scattering collisions between atomic nuclei in ballistic collision cascades, while at high incident energies, the electronic energy loss dominates, leading to intense local ionization. At intermediate ion energies, however, nuclear and electronic energy losses are of similar magnitude, which can lead to additive effects on damage production [15]. The presence of impurities may cause the formation of defects and/or lead to the transformation of the existing defects to other types of defect. The distribution of intrinsic defects is usually combined and enhanced by the impurity(extrinsic) defects which activate materials to become novel to be recognized as interesting in the field of radiation dosimetry to explore new features and reveals potential applications, see e.g. [28]-[30].

To this end, the Thermoluminescence (TL) method has emerged as an important technique for understanding the dynamics of electron trapping centers. TL-glow curve analysis methods have been applied to study the kinetics of trapped electrons. Realizing that thermoluminescence (TL) is a defect related phenomenon, information about the presence of intrinsic and extrinsic impurity defects which markedly influence the TL-response and sensitivity of the material, can be pursued. This is possible and constitutes the first step in characterizing the materials under investigation, if the impurities, their concentration, stability, and depth distributions in the near surface regions of solids are determined. On the other hand, the analysis of ion induced luminescence in Rare Earth ions doped silica glass is complicated owing to the simultaneous measurement and dynamicity of the luminescent phenomenon. In the present study, we first examine the characteristics of luminescence activated by the addition of extrinsic impurities, namely Rare Earth- (RE-dysprosium (Dy) and europium (Eu) incorporated within the glass network and then investigate the structural properties. The evolution of radiation induced intrinsic and extrinsic defects on TL characteristics, caused by the energetic irradiation beam (i.e. He$^+$ ions)and changes caused to the glass network initially by the energy deposited to electronic excitations and near the end of the ions track by nuclear collisions is investigated.

II. EXPERIMENTAL

Samples were synthesized using sol-gel method following according to the procedure and technique previously described and reported [31]. Samples used in the measurements were shaped out in the form of circular discs (mass 15 mg), with dimensions: 5mm diameter and thickness about 1mm, under a pressure of 1.0-ton. All samples were then annealed at temperature about 1100 C/2h in a platinum (Pt) crucible.

All measurements which include information about the defect structure and changes in the density and distribution of defect states are determined from the GL-curves followed using thermoluminescence (TL). Samples were measured directly after being subjected to pre-excitation source of a constant dose of 2Gy using $^{90}$Sr-$^{90}$Y-β-particles emission source, supplied by VINTEN Model 623 automatic dosimeter irradiator of nominal activity 1mCi which, delivers the dose at a rate of 2.87μGy s$^{-1}$. Other samples were measured after excitations using 2 MeV He$^+$ beam supplied from the University of Jordan Van de Graff accelerator (JUVAC).

The system employed in TL detection, see, e.g. [32], [33], was a Harshaw Model 3500 TLD reader. The TL-signal representing the intensity of light emitted as function of the simultaneously recorded time and temperature was obtained. All TL glow curves were read using a linear heating rate of 2 °C/s$^{-1}$, from room temperature up to 400 °C, with a preheat temperature set at 80 °C, to eliminate the more rapidly fading low temperature peaks in the TL glow curves and focus on the higher trapping states near the end of TL glow curve. Prior to readout, background signal due to black body radiation was recorded for all samples. The TL glow curves included inherent overlapping peak features, and therefore were deconvolved using total curve fitting technique assuming general order (GO) kinetic processes. The above procedure, however, ensures that peak centroids, intensity, and widths are all not disturbed by the analysis. More
III. RESULTS AND DISCUSSION

A. Characterization of the samples

The TL intensity in general depends on the particles sizes and on their impurities in the lattice of pure and synthesis quartz, Fig. 1 an illustrating diagram for the stages of preparation of silica glass by sol-gel method. Fig. 2 show the energy dispersive spectroscopy (EDS) analysis and the scanning electron microscopy (SEM) micrographs of the synthesis fraction extracted from the whole samples.

They are emphasized that each of these doped samples were de-convoluted to the same number of peaks, in addition to a background signal. Such quantitative measures make the novel doped material excellent candidate to be used in dosimetry that requires high temperatures working environments. In any case, the kinetic parameters for each TL glow curve are listed in Table 1 for comparison and completeness.

The output of the calculation which represents the kinetic parameters, namely the trap depth ($E_t$), thermal or activation energy which is the energy needed to free the trapped electrons, the temperature at maximum ($T_m$), kinetic order ($b$), the frequency factor $s$, the pre-exponential factor and lifetime ($\tau$) are listed in Table 1.

C. Irradiation of Rare Earth doped and co-doped synthesis quartz

The effect of RE-doping: Eu or Dy and co-doping of the synthesis quartz with both Eu and Dy under different ionizing radiation on the TL properties of silica glass doped with 0.2 mol% of Eu, 0.002 mol% of Dy and co-doping with Eu/Dy, respectively, is shown in Fig. 4. The TL glow curves of samples recorded between RT and 400°C, illustrate the effect of 2 Gy β-dose irradiation compared to 2 MeV 4He+ irradiation beam to $1 \times 10^{15}$ ions/cm². The TL glow curves of 2 Gy β-dose irradiation are generally distinguished by a prominent well defined narrow temperature peak centered near 150°C and a varying intensity two broad peak structures detected in the higher temperature range 177-327°C.
Fig. 4. Typical TL GL-curves showing the noted variations of TL-intensity and shapes between samples annealed 1100°C/2h and representing single and double doped synthesis quartz. Measurements are recorded after 2MeV 4He+ irradiation.

Comparing with the 2 MeV 4He+ irradiation beam affected the synthesis quartz network structure in a more complex manner. In fact, the impurity activators that have been stimulated initially by electronic excitation and at the end of the ion track by the atomic displacement of the lattice. The disturbed region is extended to include the low and high temperature peak features indicating that the resulting TL glow curve is complex in structure, shape and analysis. The TL intensity of the prominent peak which is detected near 150°C not only its intensity increased by about eighty folds, but also the satellite peaks near the low and high temperature regions are accompanied by an enormous increase of the whole TL glow curve. The inherent overlapping features observed add to its complexity through the energy deposition to nuclear and electronic excitations of the glass network [17].

The energy transfer processes that produce intrinsic defects within the glass network via electronic excitations \((S_0)\) and atomic displacements \((S_i)\) of 2 MeV He+ onto SiO2. The corresponding total energy loss as well as the depth, and damage distributions induced in the glass network are shown. The curves of Fig.4 indicate opposite energy dependence with the radiation energy but an almost constant total energy loss within the energy range shown. In fact, the similar energy dependence gives evidence that all the three types of intrinsic defects are mainly produced by the nuclear energy loss or elastic collisions and the fact that the absolute value of Sn is smaller than that of Se also implies that Sn is more efficient in producing the damage and hence the intrinsic defect formation. Indeed, comparing the curves of Figs.3, suggests that the more efficient structural modifications of Sn in the formation of intrinsic defects than that of Se. Our results do not eliminate the role played by Se. Indeed, two types of intrinsic defect formation in synthesis quartz by electronic excitations. The first is the cleavage of a single Si-O bond forming E’-center and NBOHC, simultaneously (Eq.1). An alternative mechanism is the displacement of a bridging oxygen atom forming an intestinal oxygen atom and two E’ centers, where both E' centers can bond with each other forming =Si-Si=, (Eq.2)). Thus, the ratio of concentration of E’ center to NBOHC is generally about unity.

This implied that the damage caused by the energetic beam of 2MeV He+ particles are far more efficient in causing damage by electronic processes which indeed exceeds that caused by nuclear processes. Examining such TL glow curves more closely, indicates that the resulted defect structure which is essentially a function of the concentration of activators is mobile. Indeed, Fig.4, gives evidence of shift of the peak maximum towards higher temperatures resulting from increasing the irradiation. One possible explanation is that radiative transition may be quenched at elevated temperatures as a result of an increased contribution of non-radiative transitions in the Eu3+, Dy3+ or Eu/Dy: silica system or through energy transfer from excited RE3+ ions to other ions [34].

It is, however, suggested that special attention and focus is paid towards the progression of the prominent TL-peaks such that analyzing the deconvolved TL-peaks may provide information about the defects and mechanisms of charge carriers and recombination processes. It is suffice at this stage to provide a qualitative description and make an inter-comparison between the TL glow curves which include the prominent peaks characterizing their temperature at maximum positions, intensities and dose response. Such information is facilitated by calculating the parameters that characterize each TL-peak. For such comparison to become meaningful, one additional condition must be imposed on the number of deconvolved TL-peaks inherent in the TL glow curves that must be preserved for possible association with NBOHC. Nonetheless, the recorded experimental GL-curves have been de-convoluted into eight peaks, cf. Fig. 5. For all irradiated samples at 2Gy, the peaks are centered at 123 and 150 °C with full width at half maximum (FWHM) 38 °C, 37 °C for Eu dopants; 157, 183 °C with FWHM 42, 48°C for Dy dopants and finally for both dopants the peaks are centered at 150, 188°C, with similar FWHM of 39 and 39 °C, respectively. On the other hand, with samples irradiated by 2 MeV 4He+ beam, a group of TL-peaks P1(oP1), divalent Si (i.e. peak P2), E’-center (i.e. peak P3) with an extra band for P3-P5 corresponding to the \(\equiv Si-Si \equiv\) are found [23], [34], [35]. Furthermore, literature has reported that there are two major processes for intrinsic defects formation in silica glass by electron excitation. The first one is the cleavage of a single Si-O bond forming E’-center and NBOHC simultaneously, cf. Eq. (1).

\[
\equiv Si \rightarrow O \equiv Si \equiv \equiv Si \cdot (E'\text{center}) + 0^- \equiv Si \equiv NBOHC
\]  

(1)

The second alternative possible mechanism is provided through the displacement of a bridging oxygen atom; thus forming an interstitial oxygen atom and two E’ centers, such that the two E’ centers can bond with each other forming \(\equiv Si-Si \equiv\), cf. Eq. (2), namely:

\[
\equiv Si \rightarrow O \equiv Si \equiv \equiv Si \cdot (E'\text{center}) + 0^0 \rightarrow \equiv Si-Si \equiv + O^0
\]  

(2)
The activation energy of the traps is observed to increase with the center of each trap shifted by some 30 K towards higher temperatures, as shown in Table 2. This seems to be a result of a highly populated trapping state and several recombination centers. The transition probabilities are substantially different from one peak to another due to variations in the trapping cross section. Notice the variation in b values where for all peaks Ps they exhibit a general order kinetic equation.

**TABLE 2: TRAPPING PARAMETERS OF SiO2: Eu, Dy and Eu/Dy As Obtained From Numerical Fitting Technique**

<table>
<thead>
<tr>
<th>Defects</th>
<th># of Traps</th>
<th>RBS (2MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.697</td>
<td>331</td>
</tr>
<tr>
<td>P2</td>
<td>0.909</td>
<td>361.91</td>
</tr>
<tr>
<td>P3</td>
<td>0.977</td>
<td>393</td>
</tr>
<tr>
<td>P4</td>
<td>1.024</td>
<td>426.18</td>
</tr>
<tr>
<td>P5</td>
<td>1.040</td>
<td>462.21</td>
</tr>
<tr>
<td>P6</td>
<td>1.139</td>
<td>502.23</td>
</tr>
<tr>
<td>P7</td>
<td>1.315</td>
<td>547.21</td>
</tr>
<tr>
<td>P8</td>
<td>1.389</td>
<td>602</td>
</tr>
<tr>
<td>Eu(0.2mol%)</td>
<td>0.728</td>
<td>377</td>
</tr>
<tr>
<td>Dy(0.002mol%)</td>
<td>0.886</td>
<td>418</td>
</tr>
<tr>
<td>Eu/Dy</td>
<td>1.063</td>
<td>462.13</td>
</tr>
<tr>
<td>P4</td>
<td>1.349</td>
<td>497.19</td>
</tr>
<tr>
<td>P5</td>
<td>1.396</td>
<td>531.16</td>
</tr>
<tr>
<td>P6</td>
<td>1.727</td>
<td>565.14</td>
</tr>
<tr>
<td>P7</td>
<td>2.101</td>
<td>596.16</td>
</tr>
<tr>
<td>P8</td>
<td>2.218</td>
<td>634.25</td>
</tr>
<tr>
<td>Eu</td>
<td>1.122</td>
<td>378.24</td>
</tr>
<tr>
<td>Dy</td>
<td>1.187</td>
<td>408.18</td>
</tr>
<tr>
<td>Eu/Dy</td>
<td>1.207</td>
<td>441.20</td>
</tr>
<tr>
<td>P5</td>
<td>1.290</td>
<td>472.14</td>
</tr>
<tr>
<td>P5</td>
<td>1.572</td>
<td>505.16</td>
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<td>P6</td>
<td>1.638</td>
<td>536.17</td>
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<tr>
<td>P7</td>
<td>1.664</td>
<td>573.21</td>
</tr>
<tr>
<td>P8</td>
<td>1.748</td>
<td>628.25</td>
</tr>
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</table>

The initial concentration of trapped electrons within the defects centers was however noted to vary. Such variations in the population of electrons within the traps are indications of mobile defect states and charge conversion and/or transfer between defect states such that very shallow states and deep level states are emptying to moderate defect states. This has two main advantages on the efficiency, first; defect

![Image](https://example.com/image.png)

**Fig. 5.** GI-curve deconvolution analysis applied to SiO2 doped with: (a) Eu(0.1mol%) , (b) Dy(0.002mol%) and (c) co-doped: Eu(0.1mol%)/Dy(0.002mol%) after 2MeV He+ irradiation.

By reference the de-convolution procedure carried out, TL characteristics related to trap parameters of different emission TL-peaks are thoroughly explored, which are mostly associated with electron-hole (i.e. exciton) pairs and oxygen defects sites related shallow and deep trap centers [28]. The trapping parameters are listed in Table 2. Comparison between the glow curves of doped and co-doped samples perturbation on the intensity is noted such that the intensity in some cases is doubled. The number of peaks, however, is preserved but there exist changes in their detected positions and perhaps their type. Literature indicates the formation of clusters and complex defect structure proceeding doping. The increase of intensity is solely due to incorporation of Eu, Dy, and Eu/Dy. Oxygen also has a role in enhancing the TL emission process by vacancy type defects [36]. In general, oxygen impurities are known to be first physically adsorbed at the grain boundaries and on the glasses surface. One other hand, oxygen when present at the samples surface and at grain boundaries, it acts as luminescent centers [37]-[39]. In addition, the presence Eu, Dy and Eu/Dy impurities in the samples are trapped as shown at Eq (1) and Eq (2) defects. The defects capture free electrons generated after irradiation by highly energetic particles and act as electron traps.
states are becoming more stable since the temperature at maximum is increased and second; unwanted deep level states as well as surface defect states are minimized or even eliminated.

IV. CONCLUSION

Radiation induced defects and thermoluminescence characteristics in synthesis quartz samples were studied under 2Gy of beta dose and 2MeV ‘He’. The TL-response in the doped Eu³⁺, Dy³⁺ and co-doped Eu/Dy synthesis quartz are very sensitive to type of ionizing radiation. The ionizing radiation also imparted an unstable TL signal which could potentially be beneficial for intrinsic dosimetry.

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REFERENCES