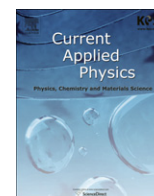




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Ionoluminescence studies of combustion synthesized Dy³⁺ doped nano crystalline forsterite

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ABSTRACT

Ionoluminescence (IL) of nano crystalline Mg₂SiO₄:Dy³⁺ pellet samples bombarded with 100 MeV Si⁺⁸ ions with fluences in the range $(1.124\text{--}22.480) \times 10^{12}$ ions cm⁻² have been studied. Two prominent IL bands with peaks at ~480 nm and ~580 nm and a weak band with peak at ~670 nm are recorded. The characteristic peaks are attributed to luminescence center activated by Dy³⁺ ions due to the transitions ⁴F_{9/2} → ⁶H_{15/2}, ⁶H_{13/2} and ⁶H_{11/2}. It is found that IL intensity initially decreases rapidly and then continuous to decrease slowly with further increase in ion fluence. The reduction in the ionoluminescence intensity with increase of ion fluence might be attributed to degradation of Si–O (2ν₃) bonds present on the surface of the sample and/or due to lattice disorder produced by dense electronic excitation under heavy ion irradiation.

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1. Introduction

Researchers exploited energetic ion beams in different ways in the field of materials science. Its effect on the materials depends on the ion energy, fluence and ion species. When an energetic ion penetrates a solid material, it loses its energy mainly by two nearly independent processes: (i) elastic collision with the nuclei known as nuclear energy loss which dominates at an energy of 1 KeV/amu and (ii) inelastic collisions of the highly charged projectile ion with the atomic electrons of the matter known as electronic energy loss which dominates at an energy of about 1 MeV/amu or more [1].

Ionoluminescence also known as Ion beam induced luminescence (IBIL) is a technique used for material analysis and defect studies. An ion beam is used to excite atoms in a target and visible light emitted from the target material is analyzed with a fiber optic spectrophotometer. Since visible light results from outer shell transitions, it gives information about the nature of chemical bonds in materials and also IBIL is sensitive to the local chemical environment of compounds and trace substitutes and to the microstructures of the network [2,3]. IL technique can be applied for characterization and also materials modification with heavy ion beams in order to follow the creation of intrinsic defects. Also, it is possible to reach higher electronic levels because of amount of ion energy supplied during irradiation (order of MeV) whereas, it is not possible with other luminescence techniques [4].

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IL studies on various materials like natural and synthetic materials, insulators, semi-conductors, thin films, etc are reported earlier [5–7]. However, no such studies are reported on Forsterite also known as magnesium silicate (Mg₂SiO₄) system to understand mechanism involves in light emission during heavy ion irradiation. Rare earth luminescent materials are considerable practical applications involving the production of different visible fluorescent colors such as cathode ray tubes, lamps, X-ray detectors etc [8,9]. Forsterite (Mg₂SiO₄) is a member of the Olivine family and has orthorhombic crystalline structure, which has extremely low electrical conductivity that makes it an ideal substrate material in electronics. It has high surface area, low thermal expansion, good chemical stability and excellent insulation properties even at high temperatures [10–12]. In the present work, an attempt is made to study mechanism of luminescence caused by heavy ion irradiation on Mg₂SiO₄:Dy³⁺ system by IL technique.

2. Experimental

Nanocrystalline Mg₂SiO₄:Dy³⁺ powder used in this experiment was synthesized through low temperature combustion synthesis (LCS) method based on procedure discussed elsewhere [13]. The stoichiometry of the redox mixture used for combustion process was calculated using the total oxidizing and reducing valencies of magnesium silicate. Synthesized Mg₂SiO₄:Dy³⁺ powder was grained into a fine powder using an agate mortar and was calcined at 800 °C for 3 h. The sample is characterized by PXRD (Philips PW 1050/70, Cu–Kα radiation with Ni Filter). The samples were made

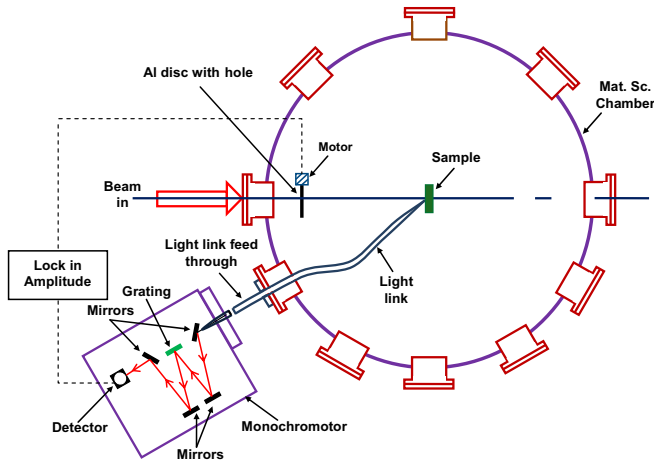


Fig. 1. Schematic experimental setup for online Ionoluminescence studies.

into pellets of 8 mm diameter and ≈ 1 mm of thickness using an homemade pelletizer. The samples were irradiated at room temperature with 100 MeV Si^{+8} ions for fluences in the range $(1.124\text{--}22.480) \times 10^{12}$ ions/cm² using 15UD pelletron accelerator (16 MV Tandem Van-de Graff type electrostatic) at Inter University Accelerator Centre (IUAC), New Delhi, India. The broad beam was scanned over 5 mm² area using a magnetic scanner with a beam current of 1.5 pA. The detailed Ionoluminescence setup used is discussed elsewhere and its schematic diagram is shown in Fig. 1 [14,15].

3. Results and discussion

The phase purity and crystal structure of the synthesized $\text{Mg}_2\text{SiO}_4:\text{Dy}^{3+}$ were examined by PXRD using $\text{Cu-K}\alpha$ radiation of wavelength 1.54056 Å. Fig. 2 shows the XRD patterns of pure and Dy doped Mg_2SiO_4 synthesized by combustion technique. The pattern was compared with JCPDS file No. 34-0189. The XRD pattern was found to match exactly with those reported in the literature [16]. The average particle size (D) was estimated to be in the range 50–60 nm from the line broadening in X-ray powder using Scherrer's formula, $D = (K\lambda) / \beta \cos\theta$, where, 'K' is a constant (0.9 for spherical shape [17]), ' λ ' wavelength of X-rays, and ' β ' FWHM [18].

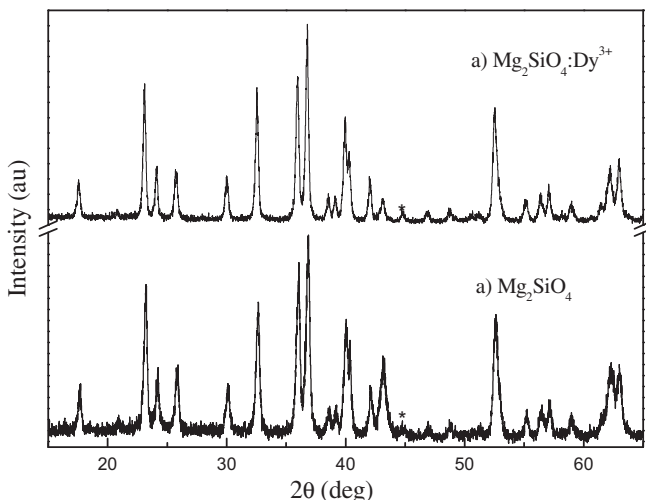


Fig. 2. PXRD Patterns of (a) pure and (b) Dy^{3+} doped Mg_2SiO_4 .

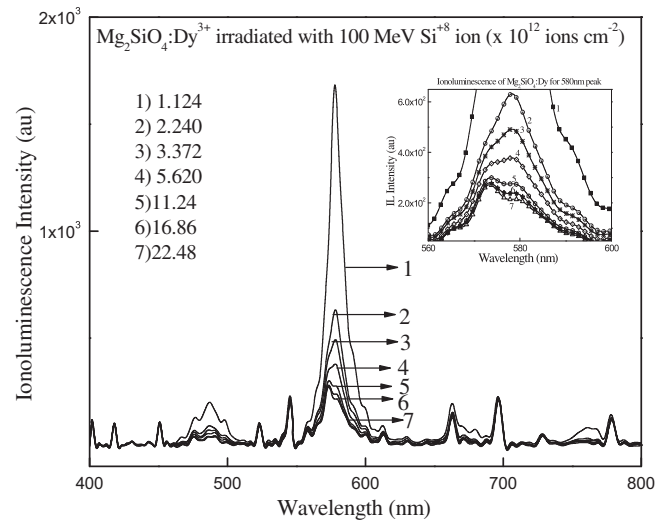


Fig. 3. Ionoluminescence spectra of $\text{Mg}_2\text{SiO}_4:\text{Dy}^{3+}$ irradiated with 100 MeV Si^{+8} ions.

The Ionoluminescence spectra of $\text{Mg}_2\text{SiO}_4:\text{Dy}^{3+}$ doped with samples bombarded with 100 MeV Si^{+8} ions with fluences in the range 1.124×10^{12} to 22.480×10^{12} ions cm⁻² is shown in Fig. 3. A sharp and prominent emission with IL peaks at 580 nm is recorded. Also, weak IL emissions with peaks at 488 nm, 545 nm, 665 nm, 695 nm and 780 nm are observed as can be seen from Fig. 3. The characteristic peak at 488 nm, 580 nm and 665 nm in IL spectra is attributed to the luminescence centers activated by Dy^{3+} ions. The weak emission bands at 545 nm, 695 nm and 780 nm may result from the host material and might be due to $\equiv\text{Si}-\text{Si}\equiv$ oxygen vacancy. It is caused due to singlet to singlet or singlet to triplet transitions [19,20]. The IL intensity depends on ion species, luminescence activators/quenchers. At the beginning of the ion irradiation the IL intensity increases rapidly, stabilizes, decreases and remains almost steady with higher fluences. The rapid increase in IL intensity is caused due to the increasing number of intrinsic defects produced by ion irradiation and the decrease in IL intensity with Si^{+8} ion fluence might be due to the disorder produced by dense electronic excitation under swift heavy ion (SHI) irradiation [21].

The variation of IL emission intensity with peaks at 488 nm, 580 nm and 665 nm with ion fluence are shown in Fig. 4. It is observed that IL emission initially very high particularly for the

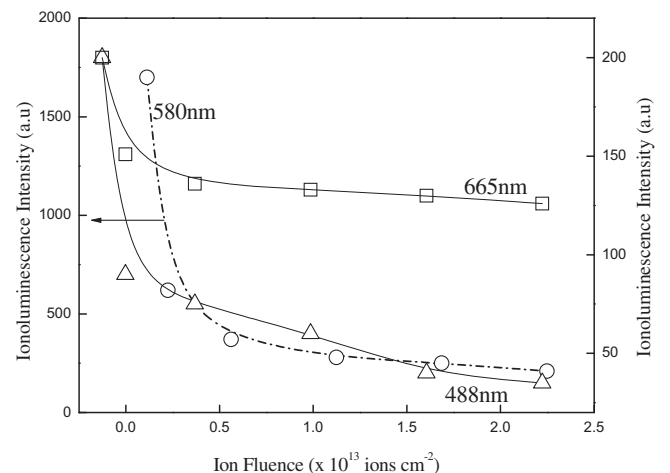


Fig. 4. Variation of IL intensity with ion fluence at (1) 580 nm peak, (2) 480 nm peak and (3) 670 nm peak.

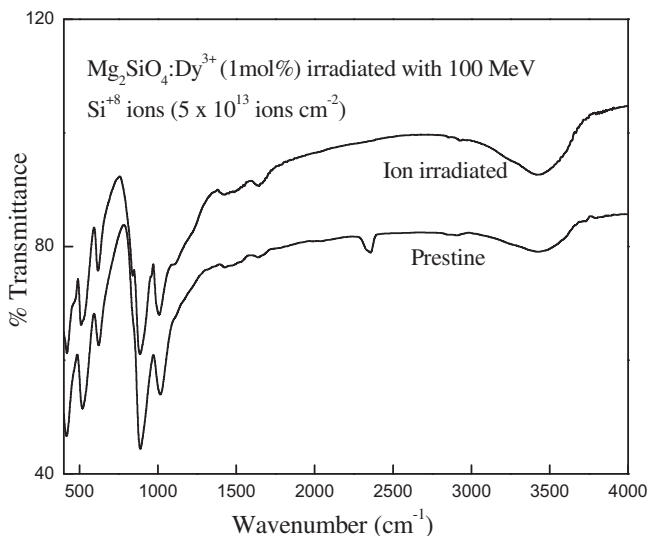


Fig. 5. FTIR spectra of pristine and SHI (5×10^{13} ions cm^{-2}) irradiated $\text{Mg}_2\text{SiO}_4:\text{Dy}^{3+}$.

peak at 580 nm and then it decreases with increase on ion fluence. This might due to amorphization of the material and it may be explained on the basis of thermal spike model. When the heavy ion strikes the lattice of the material, most of its energy is employed for the creation of an excited electron cloud. The excited material then stabilizes by emitting energy in different forms. There are two important mechanisms suggested. (i) Non-radiative emission of phonons from the lattice. This process would increase the temperature in the crystal if the irradiation is continuous *i.e.*, increase in ion fluence and would lead to amorphization of the crystalline (ii) Alternatively the radiative emission by an impurity atoms located in the matrix of the crystal takes place from their excited levels to the ground level. This emission is very sensitive towards the valence state, coordination and distance from the emitting atom to the element to which it is coordinated. The light emission generated in this way fades with the ion fluence and an increment in temperature is observed. A proton beam colliding in a crystalline material (lattice + impurities) generates some electron cloud that appears localized in the lattice and the impurities thus having an excited lattice and excited impurities. Certain different relaxing mechanisms are available for the material to return to its ground state, namely non-radiative and radiative emissions coming either from the lattice or from the impurities. These mechanisms are dependent on irradiation time. The final effect is that of the heating of the lattice that thermally quenches all the forms of emission [22]. Also, the reduction in IL intensity with increase of ion fluence might be attributed to degradation of Si–O ($2\nu_3$) bonds present on the surface of the sample and it is confirmed by FTIR

Table 1
Assignment of the bond positions of the infrared spectra of pristine and 100 MeV Si^{+8} ion irradiated $\text{Mg}_2\text{SiO}_4:\text{Dy}^{3+}$

Absorption peak (cm^{-1})	Pristine sample	Irradiated sample
420	MgO_6 octahedral	MgO_6 octahedral
525	Si–O(ν_4)	Si–O(ν_4)
618	Si–O (bending)	Si–O (bending)
680	Mg–O	Mg–O
890	Si–O (stretching)	Si–O (stretching)
1020	CO and Si–O(ν_3)	CO and Si–O(ν_3)
1250	C–H	C–H
1384	NO_3	NO_3
2350	Si–O ($2\nu_3$)	–
3450	–OH (stretching)	–OH (stretching)

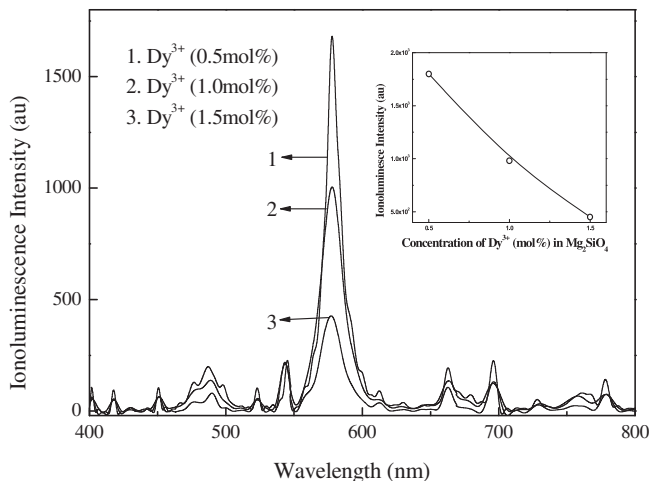


Fig. 6. IL spectra of (0.5 mol %, 1.0 mol % and 1.5 mol %) Dy^{3+} doped Mg_2SiO_4 irradiated with 100 MeV Si^{+8} for fluence of 1.124×10^{12} ions cm^{-2} .

studies of pristine and irradiated samples and is shown in Fig. 5 and the data obtained are summarized in Table 1. The irradiation effect may lead to the restructuring of the surface chemical species because of the energy deposited through electronic energy loss during the process of heavy ion irradiation and formation of ion induced defects leading to non-radiative recombination [23].

The effect of Dy^{3+} ion concentration in an Ionoluminescence of Mg_2SiO_4 is studied. Fig. 6 shows the IL spectra of Mg_2SiO_4 doped with 0.5 mol%, 1.0 mol% and 1.5 mol% of Dy^{3+} and bombarded with 100 MeV Si^{+8} ions with fluence 1.124×10^{12} ions cm^{-2} . It is observed that the IL intensity decreases with increase in the concentration of Dy^{3+} ion in the host material as can be seen from the same figure (see also inset).

The Ionoluminescence lines of Dy^{3+} are observed in various regions as can be seen from Fig. 3. The blue emission in the region 470–500 nm region due to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ transition is magnetically allowed which varies a little with the crystal field strength change around the Dy^{3+} ion and the yellow emission in the 570–600 nm region due to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition is a forced electric dipole transition with $\Delta j = 2$, which is strongly influenced by the host environment. In $\text{Mg}_2\text{SiO}_4:\text{Dy}^{3+}$ sample the emission with peaks at 480 nm and 580 nm are assigned to $5\text{D} \rightarrow 4\text{F}$ transitions. The secondary emission of the Dy^{3+} ions are also observed at 665 nm is due to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ transition. It is

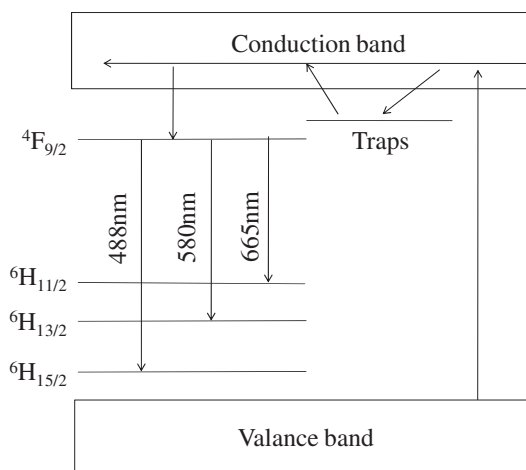


Fig. 7. Energy level diagram for the Dy^{3+} in Mg_2SiO_4 .

observed that IL intensity decreases with increase in ion fluence. Although the intensity of the luminescence changes relatively rapidly, the changes in the luminescence profile are restricted to a broadening of the multiplets. It might be due to the formation of greater populations of defect-stabilized Dy^{3+} sites as elastic nuclear collisions generate greater numbers of displaced atoms [24–26].

Dy^{3+} has proper traps which can capture part of the excitation energy during heavy ion irradiation. At room temperature thermal stimulating induced persistent energy transfer from electron traps to the state $^4\text{F}_{9/2}$ of Dy^{3+} ions which would create the characteristic emissions of Dy^{3+} ions and corresponding energy level diagram shown in Fig. 7. Also, Dy^{3+} ion is well known as an activator dopant for many different inorganic lattices producing white light emission by suitably adjusting blue and yellow emissions. In addition, Dy^{3+} acts as a most sensitive probe ion because the fluorescence from Dy^{3+} ions originates from the $5\text{D} \rightarrow 4\text{F}$ transition and the 5D state is easily affected by the outer crystal field [27–29].

4. Conclusions

Ionoluminescence is a sensitive and versatile tool for the study of beam modification effects in luminescent inorganic materials. The sharp IL emission peaks observed at 488 nm, 580 nm and 670 nm in $\text{Mg}_2\text{SiO}_4:\text{Dy}^{3+}$ are tentatively attributed to the transitions $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{11/2}$ of Dy^{3+} ions, and they are the characteristic $5\text{D} \rightarrow 4\text{F}$ transitions of Dy^{3+} ion. The decrease in IL intensity might be due to the destruction of the surface chemical species because of the energy deposited through electronic energy loss during heavy ion irradiation and formation of defects leading to non-radiative recombination centers at higher fluences. Further, the decrease in IL intensity might be attributed to lattice disorder produced by dense electronic excitation under heavy ion irradiation and Si–O ($2\nu_3$) species destroyed due to amorphization. The decrease in IL intensity during irradiation may be due to the formation of point defects near Mg^+ ions quenching the emission feature or blocking the charge migration to the activation ions.

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