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Photoluminescence studies of 100 MeV Ni⁸⁺ ion irradiated Al₂O₃ single crystals

H. Nagabhushana^{a,*}, B. Umesh^b, B.M. Nagabhushana^c, B.N. Lakshminarasappa^d,
Fouran Singh^e, R.P.S. Chakradhar^f

^a Department of PG Studies in Physics, Govt. Science College, Tumkur 572 103, India

^b Department of Humanities, P.V.P. Polytechnic, Bangalore 560 056, India

^c Department of Chemistry, M.S. Ramaiah Institute of Technology, Bangalore 560 054, India

^d Department of Physics, Bangalore University, Bangalore 560 056, India

^e Inter University Accelerator Centre, Aruna Asaf Alimarg, New Delhi 110 067, India

^f Glass Technology Laboratory, Central Glass and Ceramic Research Institute(CSIR), Kolkata 700 032, India

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ABSTRACT

We present the results of photoluminescence (PL) measurements on 100 MeV Ni⁸⁺ ion irradiated Al₂O₃ single crystals in the fluence range 1×10^{11} to 5×10^{12} ions/cm². A sharp PL peaks at ~693, 695, 707 and 730 nm are recorded with an excitation of 442 nm He–Cd laser beam. The sharp emission peaks at 693 and 695 nm are attributed to R₂ and R₁ lines of Cr³⁺ ions, and they are related to the transition from ²E_g → ⁴A_{2g}. The weaker sharp peaks called N lines appear at ~707 nm and its origin is ascribed due to closely coupled pairs of Cr³⁺ ions. The longer wavelength part of the PL spectra at ~730 nm may be due to increase of groups of more than two Cr³⁺ ions. It is observed that the broad emission band (450–650 nm) consists of four bands centered at 470, 518, 547 and 618 nm, respectively. The 470, 518 and 547 nm bands are corresponding to F₂⁺, F₂ and F₂²⁺ defect center, respectively. It is observed that the PL intensity of F₂, F₂²⁺, R and N lines increases with Ni⁸⁺ ion fluence. This can be attributed to increase in concentration of color centers responsible for luminescence through radiative recombination.

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1. Introduction

Sapphire (Al₂O₃) belongs to the R₃C space group where anions are in an approximately hexagonal close-packed (hcp) arrangement and cations occupying two-thirds of the octahedral interstitial sites. It is high band gap (8.8 eV), radiation hard insulator its transmission spectrum extends from about 145 nm to 5.2 μm. Due to the structure and other physical property sapphire is commonly used as substrate for epitaxial growth of various wide band gap materials like III–V and II–VI compounds for LEDs, IR detectors, etc. [1,2]. It finds various applications in novel lasers based on semiconductors or relaxation of active centers due to its peculiar properties like hardness, low temperature dependent refractive index, high thermal conductivity and high transparency. Pure sapphire is colorless and does not show any luminescence at all, but impurities even at concentrations of a few parts per million can cause a remarkable luminescence giving rise to color centers. These color centers or

defects can be induced by ion bombardment [3]. Defects induced in sapphire may be various kinds; single vacancy centers (F and F⁺) and dimmers (F₂, F₂⁺ and F₂²⁺ centers) [4].

Sapphire is an interesting system for the investigation of modification induced by swift heavy ions (SHI). When SHI passes through matter it loses its energy mainly in two ways. One is the electronic energy loss (S_e) due to inelastic collisions with electrons and the other one is the nuclear energy loss (S_n) due to elastic collision with atoms of the solid [5–8]. Over the years, most of the research studies for production of color centers in sapphire have been carried out using low energy (keV range) ion beams, where as the effect of nuclear energy loss is important [9]. There is a lack of research on SHI irradiated induced color centers in sapphire where electronic energy loss plays a major role. There are few reports on PL in sapphire under high electronic excitation [10,11]. Particularly, fluence dependent PL behavior under SHI not available in detail. The defect production mechanism may be understood using PL technique. This is very sensitive compared to optical absorption for the lower concentration of defects. Further, from PL studies one can identify the defects whose optical absorption bands overlap [12]. Here we report the effect of SHI irradiation in Al₂O₃ single crystals using 100 MeV Ni⁸⁺ ions in the fluence range 1×10^{11} to 5×10^{12} ions/cm².

* Corresponding author. Tel.: +91 080 23146895; fax: +91 0816 2260220.

E-mail addresses: bhushanvi@rediffmail.com, sreechakra72@yahoo.com (H. Nagabhushana).

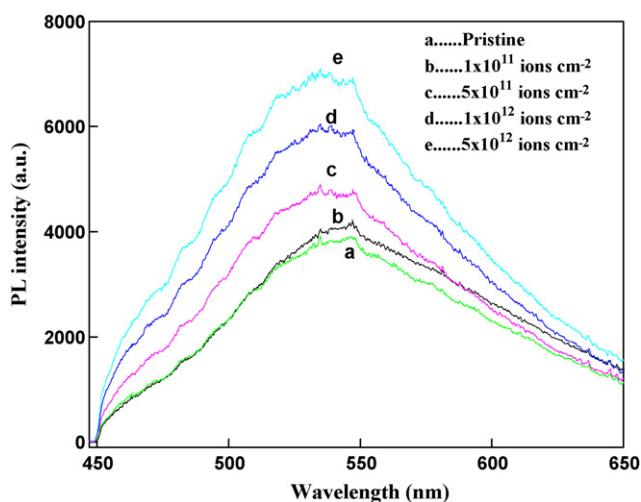


Fig. 1. PL spectra of 100 MeV Ni^{8+} ion irradiated Al_2O_3 : (a) pristine (b) 1×10^{11} ions/cm² (c) 5×10^{11} ions/cm² (d) 1×10^{12} ions/cm² and (e) 5×10^{12} ions/cm².

2. Experimental

Transparent Al_2O_3 single crystals of ~ 0.5 mm thickness and ~ 25 mm² area is obtained by cleaving the block procured from Indian Bureau of Mines (IBM), Bangalore, India. The samples after cleaving were cleaned using ethanol in an ultrasonic vibrator before the irradiation study. For this study, one sample was reserved as pristine in order to compare with the irradiated sample. The crystals were mounted on a vacuum shielded vertical sliding ladder having four rectangular faces. The crystals were irradiated in Material Science Chamber under high vacuum (6×10^{-6} Torr) by using the 100 MeV Ni^{8+} ion beam with appropriate beam current of ~ 2 pA available from 15UD Tandem Pelletron Accelerator at Nuclear Science Center, New Delhi, India [13]. The ion beam fluence was measured by integrating the ion charge on the sample ladder, which was insulated from the chamber. In order to expose the whole target area, the beam was scanned over the x - y plane. Exposure time was selected in such a way to obtain four samples with fluence in the range of 1×10^{11} to 5×10^{12} ions/cm². PL emission spectra of the samples of pristine and ion irradiated were recorded using Kimmon IK series He-Cd Laser system (IK5552R-F) with excitation wavelength of 442 nm and a pre-configured Mechelle (Multichannel Instruments AB, Sweden) spectrograph. The laser light is incident on the sample at 45° and the emitted light is coupled into the spectrograph through an optical input fiber and an SMA-connector. An image detecting system (CCD camera from PCO computer Optics GmbH) attached to the spectrograph records the spectral image (over the range 200–1100 nm). The spectral calibration was done using a mercury pen lamp. The linear spectral resolution in the present configuration was 0.5 nm.

3. Results and discussion

PL spectra of pristine and 100 MeV Ni^{8+} ion irradiated Al_2O_3 single crystals are recorded in the fluence range 1×10^{11} to 5×10^{12} ions/cm². In PL spectra, mainly three features are observed (a) basic electronic defect centers in the region 450–650, (b) R lines of Cr^{3+} ions in the region 690–697 nm, and (c) N lines in the region 705–730 nm, respectively. In the first region (Fig. 1) the spectra exhibit a broad band at ~ 535 nm along with shouldered bands at ~ 470 and 518 nm. In order to visualize these bands clearly, we deconvoluted the spectra using *ORIGIN 8.0* software and shown in Fig. 2. The deconvoluted spectra consist of bands at ~ 470 , 518,

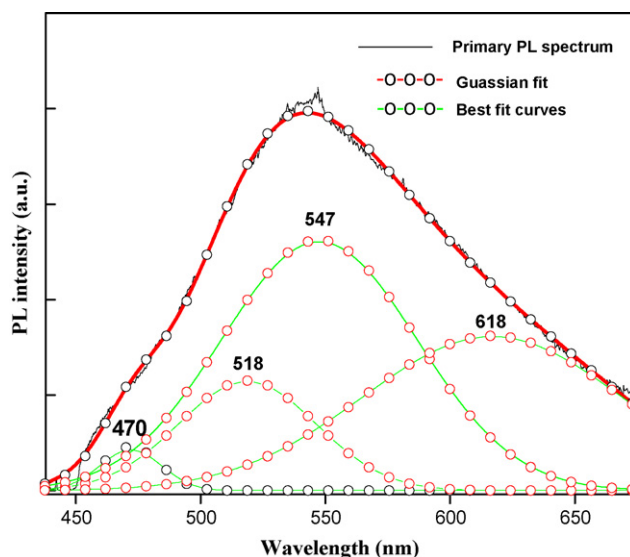


Fig. 2. PL spectrum of Ni^{8+} ion irradiated at a fluence of 1×10^{11} ions/cm² [–]. The line [–o–o–] is a Gaussian fit of the experimental data. The line [–o–o–] represents the Gaussian curves for different bands.

547 and 618 nm, respectively. The emission bands at 470, 518 and 547 nm are due to F_2^+ , F_2 , F_2^{2+} centres, respectively [14–16]. The PL intensity in pristine sample is low when compared to ion irradiated samples. It is observed that, PL intensity at F_2 and F_2^{2+} defect centers increase with increase of Ni ion fluence and shown in Fig. 3. The increase of PL intensity is due to the concentration of primary defect centers (F and F^+) increases as a result of irradiation by energetic ions [17]. These defect centers starts aggregating once their concentration become high on ion irradiation and gives rise to pairs of oxygen vacancies (F_2 -type centers) [18] or one can say that F^+ defect centers act as precursors for the generation of F_2^{2+} defect center [19,20].

In the second region (Fig. 4), we observed sharp emission peaks at 693 and 695 nm are attributed to R_2 and R_1 lines of Cr^{3+} ions and are related to transition from ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$ states. These results are in good agreement with those reported in the literature [21–23]. The R_1 and R_2 lines are known to be originated due to $3d^{3n^*} \rightarrow 3d^{3n}$ transitions of Cr^{3+} . When light is incident on Cr^{3+} ion, electron is raised from its ground state ${}^4\text{A}_2$ to its excited states (${}^4\text{T}_2$ and ${}^4\text{T}_1$)

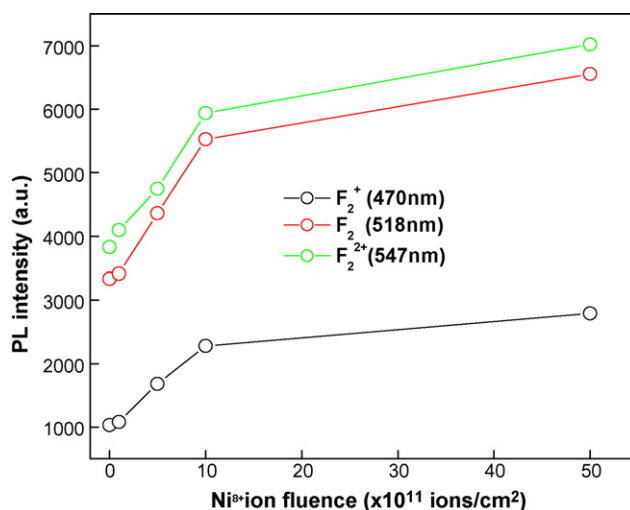


Fig. 3. Variation of intensity at F_2^+ , F_2 and F_2^{2+} defect centers as a function of Ni ion fluence in 100 MeV Ni^{8+} ion irradiated Al_2O_3 single crystal.

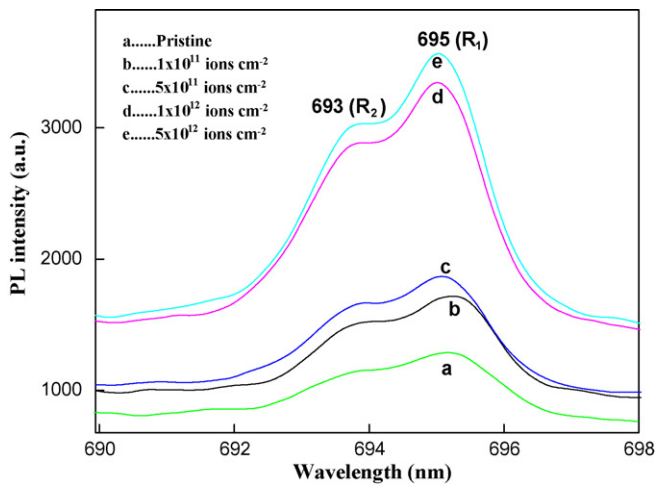


Fig. 4. Magnified view of Cr³⁺ doublet.

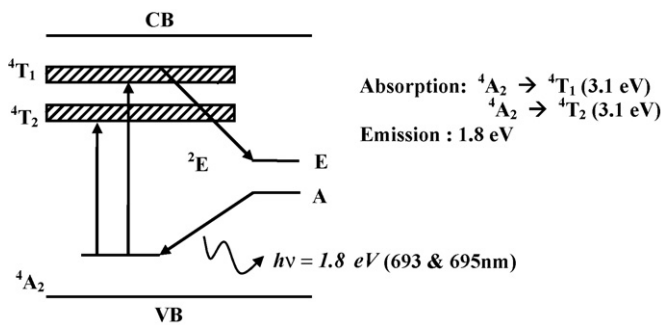


Fig. 5. The Schematic energy level diagram for R lines of Cr³⁺ ions.

lying roughly at 2.2 and 3.0 eV above the ground state ⁴A₂, respectively. These states decay non-radiatively by phonon emission until it ends on its lowest excited ²E metastable state which on transition to ⁴A₂ ground state releases photons of wavelengths 695 and 693 nm. ²E metastable is further splitted in to ²E and ²A states due to spin orbit interaction [21,24]. The schematic energy level diagram for absorption and emission of R lines of Cr³⁺ ions is shown in Fig. 5.

The R₁ and R₂ lines of Cr³⁺ ions at a fluence of 1 × 10¹¹ ions/cm² is fitted using two Gaussian peaks as shown in Fig. 6. It is observed

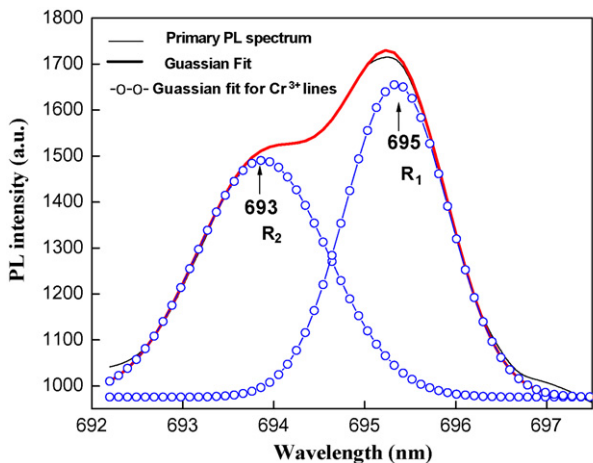


Fig. 6. PL spectrum of Ni⁸⁺ ion irradiated at a fluence of 1 × 10¹¹ ions/cm² [—]. The line [---] is a Gaussian fit of the experimental data. The line [—o—o—] represents the Gaussian curves for Cr³⁺ ions.

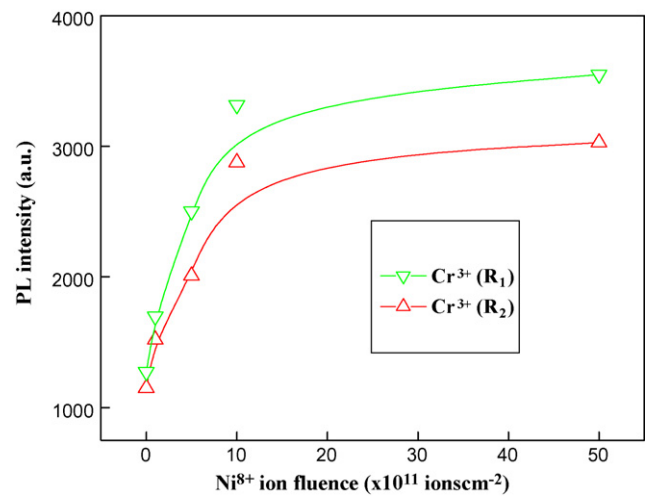


Fig. 7. Variation of R lines intensity as a function of Ni ion fluence in 100 MeV Ni⁸⁺ ion irradiated Al₂O₃ single crystal.

that the R₁ and R₂ lines of Cr³⁺ ions increase with Ni ion fluence (Fig. 7). The growth of R line intensity of Cr³⁺ ions with fluence may be explained in terms of interaction of Cr³⁺ ions with nearby defect centres produced on irradiation [25,26]. At low fluence, F⁺ defect center so produced, participate in the interaction with Cr³⁺ ions (Cr³⁺ + F⁺), which enhances the probability of photon absorption, thereby, ⁴E₂ level starts populating and hence increased intensity is observed.

The increase in PL intensity might also be attributed to photo-absorption in irradiated Al₂O₃ is increased. Ni ions have a high tendency to occupy octahedral position compared to other 3d transition metal ions. Further, from ligand field theory [27] Ni (d⁸) and Cr³⁺ have identical crystal field splitting energy, thereby more absorption of photon occurs. Probably Ni ion transfers its absorbed energy to nearby Cr ion. With this energy Cr ion is excited and decays non-radiatively in its usual way to populate ²E metastable states more efficiently. Thus increase in intensity of R₁ and R₂ lines with Ni ion irradiation can be associated to the formation of their pairing with impurity Cr³⁺ ion in host Al₂O₃ lattice [28].

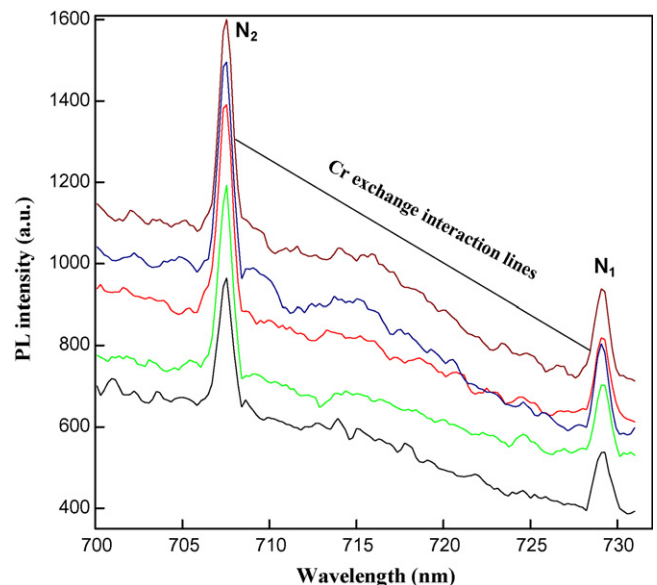


Fig. 8. Cr–Cr interaction lines (N) in Al₂O₃.

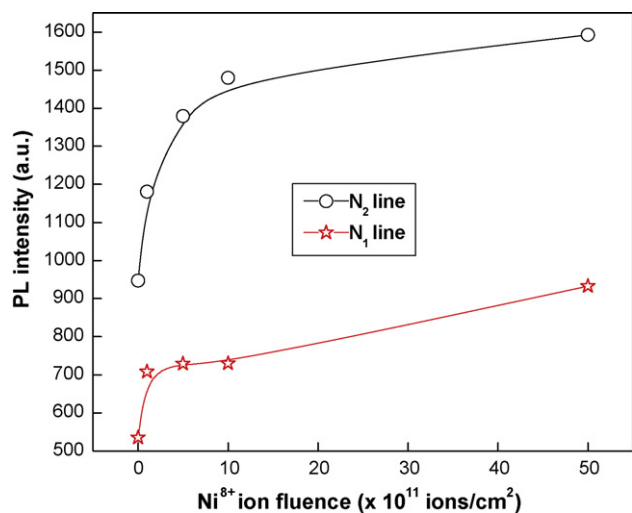


Fig. 9. Variation of N lines intensity as a function of Ni ion fluence in 100 MeV Ni^{8+} ion irradiated Al_2O_3 single crystal.

In the third region (Fig. 8) the two sharp peaks observed at ~ 707 and 729 nm are ascribed to N_2 and N_1 lines, respectively. These lines which arise from second and fourth nearest neighbor exchange-coupled pairs of Cr^{3+} ions, respectively due to the high Cr^{3+} concentration [29–31]. The intensity of N lines is less when compared to R lines of Cr^{3+} ions. The intensity of N lines increases with increase of ion fluence and shown in Fig. 9.

Bharadwaj et al. [28] have studied the Photoluminescence studies on pre- and post-irradiated ruby with 120 MeV Ni^{6+} ions in the fluence at 1×10^{12} and 5×10^{12} ions/cm². They observed R_1 , R_2 , N lines and a broad band at 694.3, 692.9, 704 and 730 nm, respectively. The luminescence yield of R_1 and R_2 lines and other features (N lines) in Ni ion irradiated samples has increased roughly by a factor of 16 at fluence of 1×10^{12} Ni^{6+} ions/cm² and around 80 at fluence of 5×10^{12} Ni^{6+} ions/cm² when compared to the pristine sample. They also noticed the PL yield increases with increase of Ni ion fluence. This increase in PL yield is attributed to the excited state of Ni ion transfers its absorbed energy to the near by Cr^{3+} ion and returns to the ground state. Jheeta et al. [32] have studied the PL and optical absorption studies on sapphire by irradiating with 100 MeV swift titanium ions in the fluence range 1×10^{12} to 5×10^{13} ions cm⁻². They observed the increase of R line intensity of Cr^{3+} ions up to fluence 5×10^{12} ions/cm². Thereafter, the PL intensity decreases with further increase of ion fluence. The increase of R line intensity with fluence may be due to interaction of Cr^{3+} ions with nearby defect centers produced by ion irradiation. At low fluence, F^+ defect centers produced, participate in the interaction of Cr^{3+} ions, which enhances the probability of photon absorption, thereby ${}^4\text{E}_2$ level starts populating and hence increase in intensity is observed. The decrease in Cr^{3+} ions may be due to (1) at higher fluence, Cr^{3+} ions environment is further modified due to the interaction with other defect centres, there by reducing the photon absorption that de-populates the ${}^4\text{E}_2$ level. (2) There is also possibility due to reduction of Cr^{3+} to Cr^{2+} valence state. Same authors [23] have studied PL of sapphire in 100 MeV Ni ions in the fluence range 1×10^{15} to 1×10^{17} ions/cm². Two broad emission bands at 516 and 546 nm are observed. These due to F_2 and F_2^{2+} defect centres, respectively. The intensity of these bands increases up to 1×10^{16} ions/cm² and thereafter it decreases with further increase of ion fluence. The increase in intensity is due to the concentration of primary defect centers increases on Ni ion irradiation. The decrease in intensity is due to the clustering or diffusion of defect centres or their conversion in to F^+ or F_2^{2+} defect centers at higher fluence. Krishnan et al.

[33] have studied plasma sprayed Al_2O_3 coatings using laser irradiation at different output powers ranging from 50 to 200 W with power densities ranging from 2.8 to 11.2 kW cm⁻². They observed sharp R_1 and R_2 lines at 1.785 and 1.789 eV, respectively, with energy difference of ~ 0.004 eV. Song et al. [34] have studied the PL of Al_2O_3 irradiated with 230 MeV Pb ions with an excitation of 350 nm. They reported PL emission with peaks at ~ 380 , 413, 450 and 516 nm. The 450 nm emission is attributed to latent excitation luminescence of F_2^{2+} centers where as PL emission at 380, 413 and 516 nm were attributed to F_2^+ , F and F_2 centers, respectively. Norman et al. [31] have studied PL of Al_2O_3 implanted with Cr ions with energy of 1.31 MeV with fluence 3.68×10^{15} ions/cm² at liquid nitrogen temperature. They observed R_2 and R_1 lines at 693.2 and 691.8 nm, respectively. Above 695 nm a less intense Cr–Cr exchange lines can be observed. In this region of the spectrum, there are series of peaks (N_2 at 704.1 nm and N_1 lines at 700.9 nm) which can all be identified as arising from the exchange interactions. In addition there is a broad spectral feature notably with a peak at ~ 706 nm which is a phonon band.

Fujita et al. [35] have studied room temperature fluorescence for $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ ions from sol–gel method. A sharp R line at 694 nm ascribed to the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition of single Cr^{3+} ions. The two weak peaks observed at around 702 and 705 nm are ascribed to N_1 and N_2 lines, which arise from second and fourth nearest neighbor exchange coupled pairs of Cr^{3+} ions, respectively. Ghamnia et al. [36] have studied the Cathodoluminescence (CL) of Al_2O_3 by 4 keV electron beam irradiation. The main luminescent centres such as F , F^+ and Cr^{3+} ion were observed. The emission intensity at F^+ mainly dependent on the quality of the crystal and divalent impurities such as Ca^{2+} and Mg^{2+} present in the material. Makhov et al. [29] have studied the luminescence spectra of Al_2O_3 in single crystals doped with Cr^{3+} ions irradiated by 50 MeV electrons in the excitation energy 3.75–20 eV. A narrow emission lines around 700 nm which are due to transition from lowest excited state ${}^2\text{E}$ to the ground state ${}^4\text{A}_2$ of Cr^{3+} ions and N lines which are due to emission from near neighbour pairs of Cr^{3+} ions. In addition to these lines broader vibronic structure are observed at the longer wavelength side.

There is one un-reported band at 618 nm was identified in our studies which is difficult to interpret at this stage. However a detailed and more work are required to comment on this band. Optical absorption, electron spin resonance (ESR), Raman spectroscopy studies may throw some light on better understanding of the defects responsible for luminescence. Further experiments are in progress in understanding these aspects in detail.

4. Conclusions

PL of 100 MeV Ni^{8+} ion irradiated Al_2O_3 single crystals have been studied in the fluence range 1×10^{11} to 5×10^{12} ions/cm². Sharp PL emission peaks at ~ 693 , 695, and 707 along with broad emission at ~ 730 nm has been observed upon 442 nm excitation by using He–Cd laser beam. The sharp emission peaks at 693 and 695 nm are attributed to R_2 and R_1 lines of Cr^{3+} ions, and they are related to the transition from ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$. The weaker sharp peaks called N lines appear at ~ 707 nm and its origin is ascribed due to closely coupled pairs of Cr^{3+} ions. The longer wavelength part of the PL spectra at ~ 730 nm may be due to increase of groups of more than two Cr^{3+} ions. The 470, 518 and 547 nm bands are corresponding to F_2^+ , F_2 and F_2^{2+} defect center, respectively. It is observed that the PL yield increases with increase of Ni ion fluence. This can be attributed to increase in concentration of color centers responsible for luminescence through radiative recombination.

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