



# Ionoluminescence and photoluminescence studies of $\text{Ag}^{8+}$ ion irradiated kyanite

H. Nagabhushana<sup>a,\*</sup>, S.C. Prashantha<sup>a</sup>, B.N. Lakshminarasappa<sup>a</sup>, Fouran Singh<sup>b</sup>

<sup>a</sup>Department of Physics, Bangalore University, Bangalore 560 056, India

<sup>b</sup>Inter University Accelerator Centre, Aruna Asaf Alimarg, New Delhi 110 067, India

Received 13 October 2006; received in revised form 17 April 2007; accepted 20 April 2007

Available online 4 May 2007

## Abstract

Ionoluminescence (IL) of kyanite single crystals bombarded with 100 MeV swift  $\text{Ag}^{8+}$  ions with fluences in the range  $1.87\text{--}7.5 \times 10^{11}$  ions/cm<sup>2</sup> has been studied. A pair of sharp IL peaks at  $\sim 689$  and 706 nm along with broad emission in the region 710–800 nm are recorded in both crystalline and pelletized samples. Similar results are recorded in Photoluminescence (PL) of pelletized kyanite bombarded with same ions and energy with fluences in the range  $1 \times 10^{11}\text{--}5 \times 10^{13}$  ions/cm<sup>2</sup> with an excitation of 442 nm laser beam. The characteristic pair of sharp emission peaks at 689 and 706 nm in both IL and PL is attributed to luminescence centers activated by  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. The reduction in IL and PL bands 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.

© 2007 Elsevier B.V. All rights reserved.

PACS: 32.50.F; 41.80.G; 07.65.G

Keywords: Ionoluminescence; Photoluminescence; Swift heavy ions; Kyanite

## 1. Introduction

Ion beam-induced luminescence (IBIL) or simply known as ionoluminescence (IL) is a luminescence phenomenon, which is caused by energetic ions interacting with solid matter. The light emitted under ion irradiation originates from electron transitions followed by recombination processes within the outer electron shells of the sample atoms. The IL method provides the information for rapidly identifying the different types of minerals, oxidation states of rare earth elements (REEs), sample size in the order of micrometers and identification of natural minerals from synthetic ones [1–5]. A lot of IL data was reported on certain natural minerals [6,7], insulators [8–12], semiconductors [13], thin films [14] and synthetic minerals [15]. However, a limited work has been carried out on IL and PL of natural kyanite using ion irradiation [16]. Natural kyanite, a crystalline aluminum silicate ( $\text{Al}_2\text{SiO}_5$ ) is one of

the silicate groups of mineral used in the production of non-fusion cast tank blocks, in the manufacture of spark plugs and as mineral specimens. It is a polymorph with three minerals—andalusite, sillimanite and mullite [17–19]. Kyanite, a triclinic occurs in long thin blade form, semi-transparent, blue in color and iron is found to be major impurity present in the sample. In the present paper, an attempt has been made to study the oxidation states of iron present in the sample and also effect of SHI on irradiation on kyanite sample was studied using the techniques of IL and PL.

## 2. Experimental

Natural kyanite single crystals of  $\sim 0.4$  mm thickness and area  $\sim 25$  mm<sup>2</sup> are obtained by cleaving the long thin block procured from Indian Bureau of mines (IBM), Bangalore. The pellets of similar area and thickness are also prepared by grinding the long thin crystals using pestle and mortar. The samples were irradiated at room temperature by  $\text{Ag}^{8+}$  ions with energy of 100 MeV for different ion fluences in

\*Corresponding author. Tel.: +91 9945954010.

E-mail address: [bhushanvi@rediffmail.com](mailto:bhushanvi@rediffmail.com) (H. Nagabhushana).

the range  $1.87 \times 10^{11}$ – $7.50 \times 10^{11}$  ions/cm<sup>2</sup>, using a 16 MV Tandem Van de-Graaf-type Electrostatic Pelletron Accelerator at the Nuclear Science Centre (NSC), New Delhi, India [20]. The dose rate for 100 MeV Ag<sup>8+</sup> ions was  $\sim 5 \times 10^9$  ions/cm<sup>2</sup>/s. The samples were mounted on a copper target ladder with a silver paste giving good thermal and electrical conductivity between them. This prevents sample heating during SHI irradiation. The ion beam was magnetically scanned on a 10 mm  $\times$  10 mm area on samples surfaces for uniform irradiation. For IL studies, the detailed experimental set up was described elsewhere [21]. 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. In Mechelle system, 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

Fig. 1 shows the IL spectra of kyanite single crystals bombarded with 100 MeV Ag<sup>8+</sup> swift ions for fluences in the range  $1.87$ – $7.50 \times 10^{11}$  ions/cm<sup>2</sup>. A pair of IL bands with peaks at  $\sim 689$  and 706 nm along with broad emission in the range 710–800 nm are recorded. Also, similar results are obtained in the case of pelletized kyanite bombarded with same amount of ion fluence as shown in Fig. 2. It is observed that the IL intensity is found to be reduced with increase of Ag<sup>8+</sup> ion fluence (Fig. 3). The pair of sharp

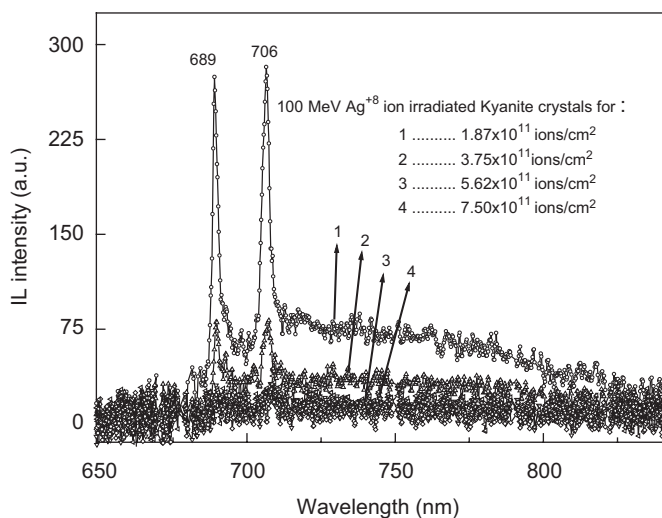


Fig. 1. Ionoluminescence spectra of kyanite single crystals irradiated with 100 MeV Ag<sup>8+</sup> ions for (1)  $1.87 \times 10^{11}$  ions/cm<sup>2</sup>, (2)  $3.75 \times 10^{11}$  ions/cm<sup>2</sup>, (3)  $5.62 \times 10^{11}$  ions/cm<sup>2</sup> and (4)  $7.50 \times 10^{11}$  ions/cm<sup>2</sup>.

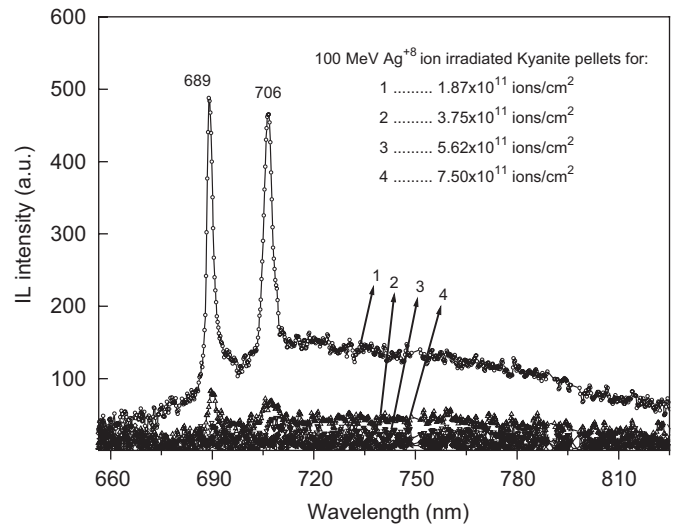


Fig. 2. Ionoluminescence spectra of kyanite pellets irradiated with 100 MeV Ag<sup>8+</sup> ions for (1)  $1.87 \times 10^{11}$  ions/cm<sup>2</sup>, (2)  $3.75 \times 10^{11}$  ions/cm<sup>2</sup>, (3)  $5.62 \times 10^{11}$  ions/cm<sup>2</sup> and (4)  $7.50 \times 10^{11}$  ions/cm<sup>2</sup>.

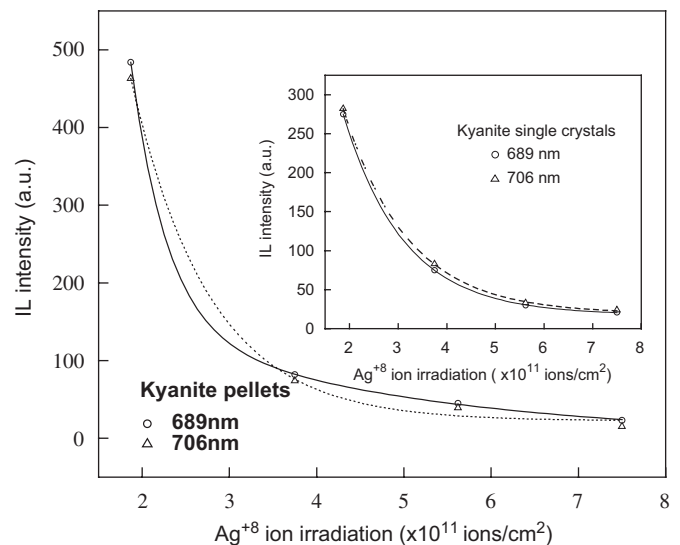


Fig. 3. Variation of IL intensity at 689 and 706 nm peaks as a function of Ag<sup>8+</sup> ion fluence in kyanite pellets and single crystals.

peaks observed at 689 and 706 nm is attributed to luminescence centers activated by Fe<sup>2+</sup> and Fe<sup>3+</sup> ions [22]. These two luminescent centers having almost equal intensity, which signifies the charge exchange between the two iron ions. The characteristics of the center giving rise to sharp emission in kyanite might be due to the fact that optically active electron involved in the luminescence emission is within 3d shell which is partially shielded by the outer most electrons 3S<sup>2</sup> 3P<sup>6</sup> [3]. The peak positions of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in our results are in very good agreement with that analyzed by IL and CL studies of plagioclase feldspars [6]. The FWHM of the IL spectrum for our measurement was about 0.11 eV, which is much less than the interval of 0.40 eV for the two chemical states of Fe<sup>2+</sup> and Fe<sup>3+</sup>, the two peaks of Fe<sup>2+</sup> and Fe<sup>3+</sup> are distinctly

separated. Usually the difference of energy levels for different chemical states is about 1 eV and hence the FWHM of the IL spectrum is good enough to analyze the chemical states of the elements as an impurity in crystals or in some kinds of geological samples [6]. It is found that the IL intensity in pelletized kyanite is observed to be more when compared to crystalline samples. This might be due to surface roughness of the sample [23]. A single  $\text{Fe}^{3+}$  peak was observed in different origin plagioclase mineral by Ryan using IL method [5].

The decrease of sharp IL peaks at 689 and 706 nm with increase of  $\text{Ag}^{8+}$  ion fluence might be due to disorder produced by dense electronic excitation under SHI irradiation [24]. If the concentrations of impurities including rare earths (Fe, K) and transitional metal ions increased in the kyanite sample, the crystal structure may change and play an important role in the extrinsic luminescence process. Although kyanite is a natural mineral containing iron as the major impurity in the crystal and the same is confirmed from electron spin resonance (ESR), energy-dispersive X-ray analysis results [25]. Pure minerals often do not show luminescence at all, but impurity ions  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  present in the sample usually acts as luminescence quenchers [1]. However, the impurity concentrations are too high they may act as self-quenchers. Wang et al. [16] have observed the amorphization of kyanite irradiated with 1.5 MeV  $\text{Xe}^+$  ions with fluence of  $1.88 \times 10^{14}$  ions/cm<sup>2</sup> using selected area diffraction (SAD) pattern. Amorphization in the system ( $\text{Al}_2\text{SiO}_5$ ) as each incident ion may create one or more several displacement cascades which become amorphous as a result of rapid quenching, and then cascades eventually overlap to form an amorphization of solid. In the present studies, complete amorphization was not achieved and it requires some more fluence to study the complete amorphization. Brooks et al. [10] have studied the IL of plagioclase feldspar bombarded with  $\text{H}^+$  and  $\text{He}^+$  with 3 MeV. They observed that IL intensity decreases with increase of ion fluence. This decrease in intensity is due to variation in the bond distances of Fe–O. However, Zuk et al. [11] have studied the IL of ultra-pure porous silicon bombarded with 250 keV  $\text{H}^+$  ions. They observed that IL intensity increases with increase of ion dose. A rapid growth of intensity is due to increasing number of simple defects induced into the sample by  $\text{H}^+$  ion bombardment. In our earlier studies of IL of kyanite with 100 MeV  $\text{Ni}^+$  ions shows a similar kind of results [17]. The IL intensity is more in  $\text{Ag}^{8+}$  ions when compared to  $\text{Ni}^{8+}$  ions. The IL intensity depends on type of ion implantation, luminescence activators/quenchers.

Photoluminescence spectra of pelletized kyanite bombarded with 100 MeV swift  $\text{Ag}^{8+}$  ions for fluences in the range  $1 \times 10^{11}$ – $5 \times 10^{13}$  ions/cm<sup>2</sup> followed by 442 nm laser beam excitation are recorded and the results obtained are shown in Fig. 4. In order to avoid the effect of pristine part in irradiated part, only top surface of the irradiated sample was carefully separated using a new stainless-steel blade. A part of it was used for PL measurements and the remaining

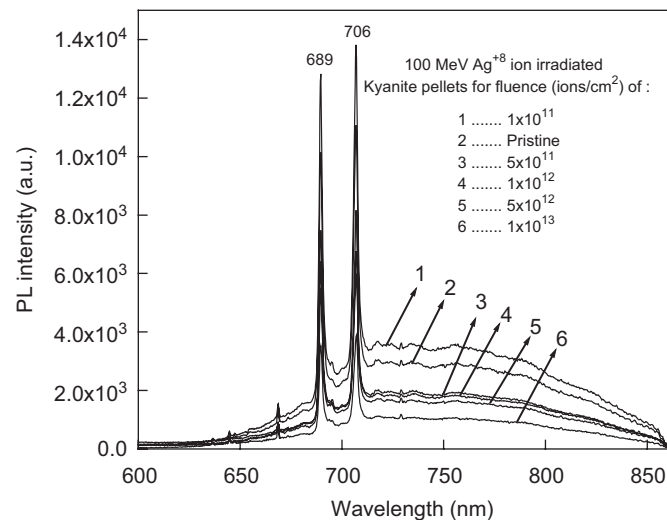


Fig. 4. Photoluminescence spectra ( $\lambda_{\text{excit}}$  442 nm) of 100 MeV  $\text{Ag}^{8+}$  ion-irradiated kyanite pellets for fluence (1)  $1 \times 10^{11}$  ions/cm<sup>2</sup>, (3)  $5 \times 10^{11}$  ions/cm<sup>2</sup>, (4)  $1 \times 10^{12}$  ions/cm<sup>2</sup>, (5)  $5 \times 10^{12}$  ions/cm<sup>2</sup> and (6)  $1 \times 10^{13}$  ions/cm<sup>2</sup>.

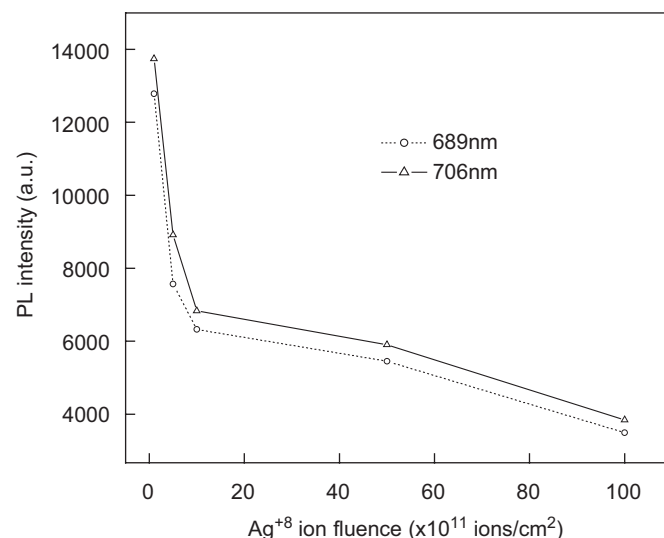


Fig. 5. Variation of PL intensity at 689 and 706 nm peaks as a function of  $\text{Ag}^{8+}$  ion fluence in kyanite pellets.

part was used for IR studies. The detailed sampling process after irradiation was described elsewhere [26]. A pair of sharp PL emission bands with peaks at 689 and 706 nm along with a broad emission in the range 700–850 nm are recorded in the entire samples. These results are in very good agreement with those recorded in IL measurements. It is found that PL intensity at 689 and 706 nm peaks decreases with increase of  $\text{Ag}^{8+}$  ion fluence (Fig. 5). The decrease in intensity might be attributed to the destruction of the surface chemical species because of the energy deposited through  $S_e$  during SHI irradiation and formation of defects leading to non-radiative recombination centers at higher fluences [27]. In order to study the destruction of surface chemical species, we performed infrared absorption studies of pristine and ion irradiated kyanite pellets with 100 MeV  $\text{Ag}^{8+}$  ions with fluences in the range

$1 \times 10^{11}$ – $5 \times 10^{13}$  ions/cm<sup>2</sup>. The results revealed the presence of silicates and water molecules before irradiation of the sample. The characteristic absorption band in the range 2325–2725 cm<sup>-1</sup> corresponds to Si–O ( $2\nu_3$ ) mode [28,29]. This mode decreases with increase of Ag<sup>8+</sup> ion fluence. The reduction in IL and PL intensity at 689 and 706 nm in the present studies might be attributed to degradation of Si–O ( $2\nu_3$ ) mode. The irradiation effects may lead to the restructuring of the surface chemical species because of the energy deposited through electronic energy loss during the process of SHI irradiation and formation of ion-induced defects leading to non-radiative recombination centers. These two processes are simultaneous consequences of irradiation and they compete with each other. Enhancement or degradation in the IL and PL in the present studies might be due to the balance between these two effects [30]. In the present investigations, optical absorption measurements were not carried out, since, the sample is not transparent. Optical absorption or photoacoustic measurements of this sample will give more information about the nature of defects centers.

#### 4. Conclusion

The IL technique is highly informative and provides information about type of impurity, oxidation state, etc. In the present study, the sharp IL and PL emission bands with peaks at 689 and 706 nm corresponds to luminescence centers activated by Fe<sup>2+</sup> and Fe<sup>3+</sup> ions. The reduction in IL and PL bands 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 also might be due to disorder produced by dense electronic excitation under SHI irradiation. Optical absorption/photoacoustic studies will through light on the nature of defects centers in kyanite.

#### Acknowledgments

The authors wish to express their thanks to Dr. D.K. Avasthi, Nuclear Science Centre (NSC), New Delhi, for useful discussion, besides his constant encouragement in the work. One of the authors (H.N.) thanks NSC for the award of research fellowship under UFUP scheme.

#### References

- [1] K.G. Malmqvist, M. Elfman, G. Reymond, C. Yang, Nucl. Instrum. Methods B 109–110 (1996) 227.
- [2] C. Yang, K.G. Malmqvist, M. Elfman, P. Kristiansson, J. Pallon, A. Sjoland, R.J. Utui, Nucl. Instrum. Methods B 130 (1997) 746.
- [3] N.P.O. Homman, C. Yang, K.G. Malmqvist, Nucl. Instrum. Methods A 353 (1994) 610.
- [4] A.A. Bettiol, K.W. Nugent, D.N. Jamieson, Nucl. Instrum. Methods B 130 (1997) 734.
- [5] C.G. Ryan, Nucl. Instrum. Methods B 104 (1995) 377.
- [6] Y. sha, P. Zhang, G. Wang, X. Zhang, X. Wang, Nucl. Instrum. Methods B 189 (2002) 408.
- [7] C. Yang, N.P.O. Larsson, E. Swietlicki, K.G. Malmqvist, Nucl. Instrum. Methods B 77 (1993) 188.
- [8] F. Jaque, P.D. Townsend, Nucl. Instrum. Methods B 182–183 (1981) 781.
- [9] A. Logiudice, G. Pratesi, P. Olivero, C. Paolini, E. Vittone, C. Manfredotti, F. Sammiceli, V. Rigato, Nucl. Instrum. Methods B 210 (2003) 429.
- [10] R.J. Brooks, D.E. Hole, P.D. Townsend, Nucl. Instrum. Methods B 190 (2002) 136.
- [11] J. Zuk, T.J. Ochalski, M. Kulik, J. Liskiewicz, A.P. Kobzev, J. Lumin. 80 (1999) 187.
- [12] V.A. Skuratov, K.J. Gun, J. Stano, D.L. Zagorski, Nucl. Instrum. Methods B 245 (2006) 194.
- [13] E.J. Teo, A.A. Bettiol, T. Osipowicz, M. Hao, S.J. Chua, Y.Y. Liu, J. Cryst. Growth 268 (2004) 494.
- [14] R.J. Brooks, D.E. Hole, P.D. Townsend, Z. Wu, J. Gonzalo, A. Suarez-Garcia, P. Knott, Nucl. Instrum. Methods B 190 (2002) 709.
- [15] A.A. Bettiol, C.G. Ryan, D.N. Jamieson, S. Prawer, Nucl. Instrum. Methods B 181 (2001) 225.
- [16] S.X. Wang, L.M. Wang, R.C. Ewing, Nucl. Instrum. Methods B 127–128 (1997) 186.
- [17] H. Nagabhushana, B.N. Lakshminarasappa, F. Singh, D.K. Avasthi, J. Radiat. Meas. 36 (2003) 643.
- [18] H.H. Read, Rutleys Elements of Minerology, Thomas Murphy Co., 1953.
- [19] A.V. Milovsky, O.V. Kononov, Minerology, Mir Publishers, Moscow, 1985.
- [20] D. Kanjilal, S. Chopra, M.M. Narayanan, S. Indira, Nucl. Instrum. Methods A 328 (1993) 97.
- [21] F. Singh, D.K. Avasthi, Ravikumar, D. Kanjilal, Proceedings of National Seminar on Lumin. and its Applications, Hyderabad, India, 2000, p. 96.
- [22] D.J. Marshall, Cathodoluminescence of Geological Materials, Unwin Hyman, London, 1988, p. 119.
- [23] O.V. Kalantaryan, V.T. Kolesnik, S.I. Kononenko, V.I. Muratov, V.E. Storizhko, Nucl. Instrum. Methods B 129 (1997) 79.
- [24] L.H. Abu-Hassan, P.D. Townsend, Nucl. Instrum. Methods B 32 (1988) 293.
- [25] H. Nagabhushana, B.N. Lakshminarasappa, Proc. Natl. Semin. on Lumin. and its Appl. Jabalpur, India, 2001, p. 164.
- [26] H. Nagabhushana, Ph.D. Thesis, Bangalore University, 2002, p. 32.
- [27] C. Trautmann, M. Toulemonde, J.M. Costantini, J.J. Grob, K. Schwartz, Phys. Rev. B 62 (2000) 13.
- [28] H. Nagabhushana, B.N. Lakshminarasappa, F. Singh, D.K. Avasthi, Nucl. Instrum. Methods B 211 (2003) 545.
- [29] H. Nagabhushana, B.N. Lakshminarasappa, S.C. Prashantha, K.R. Nagabhushana, F. Singh, D.K. Avasthi, Nucl. Instrum. Methods B 244 (2006) 31.
- [30] T.M. Bhave, S.S. Hullavarad, S.V. Bhoraskar, S.G. Hegde, D. Kanjilal, Nucl. Instrum. Methods B 156 (1999) 121.