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FT-IR, RAMAN, PHOTOLUMINESCENCE AND ED-XRF SPECTROSCOPIC STUDIES OF PHYSICO-CHEMICAL ALTERATIONS INDUCED BY NITROGEN ION IRRADIATION ON NATURAL RUBY CORUNDUM FROM PARTS OF SOUTHERN INDIA

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ABSTRACT

Corundum samples of brick red variety from Maragowdanahalli area of Mysore district, Karnataka, Pale pink variety from Lachmanapatti area of Karur district, Tamil Nadu and the colourless or fleshy red coloured from Poovanahalli area of Mysore district, Karnataka are subjected to heavy ion beams of Nitrogen in specific energy and dosage to trigger Physico-chemical changes. Nitrogen ions are irradiated with energy of 120 KeV with a beam current of 1µA, using 150 kV gaseous ion implanter. The implantation is being carried out on all the samples at a dose of $1x10^{17}$ ions/cm^2. The irradiation process has resulted in subtle changes in appearance with respect to colour of the samples. There is seemingly an impartment of purplish hue in the brick red variety, dark bluish tint in the pale pink variety and pinkish tone over the fleshy red variety samples after subjecting to the ion implantation. The capability of Nitrogen ions to alter the elemental configuration is being attempted to understand. The alterations induced in the samples are deciphered with the help of spectroscopic techniques namely FT-IR, Raman, and Photoluminescence, supplemented with the quantified chemistry obtained from ED-XRF study.

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INTRODUCTION

Gemstone variety of corundum show different colours and the presence of trace elements such as chromium (Cr), iron (Fe), titanium (Ti) and vanadium (V) etc makes it desirable to be classified as gem varieties like ruby or sapphire (Nassau K, 1985; Nassau K, 2003; Sinha, J.K. and Mishra, P.K, 2015; Sorokina, E.S *et al*.,2015; Shyam Kumar and Shadakshara Swamy, 2017a; Mehta, B.K.. 2018; Giuliani *et al*. 2018; Pignatelli *et al*. 2019). Ruby variety of Corundum occurences are reported from the states of Karnataka, Tamil Nadu, Orissa, Telangana, Madhya Pradesh, Chattisgarh and Jammu & Kashmir (Indian Minerals Yearbook, 2018) and Kerala (Vidhyadharan *et al*, 2008). Heavy ion implantation or irradiation is an emerging technique in the enhancement of aesthetic value in gemstones. Any irradiation sources can be generally confined to Electromagnetic radiation and Atomic particles. The electromagnetic radiation commonly utilized to change the colour and clarity of the stones are light or ultraviolet light, X-Rays and Gamma rays. The light or ultraviolet light generally have less pronounced coloration. Heavy ion beams are a good candidate of irradiating gemstones, for they are able to bring about both heating effect and introduction of defects, impurities and charges for modification of the optical properties (S. Intarasiri *et al*, 2009)

Nitrogen ion Implantation

In this study the corundum samples are subjected to Heavy ion beams of 'Ni' ions, which are irradiated using Tandetron Accelerator. The target holders were designed with special considerations, aiming at avoiding sputtering contamination on the gem surface as much as possible. Nitrogen ions are irradiated with energy of 120 KeV with a beam current of 1µA, using 150 kV gaseous ion implanter. The implantation is being carried out on all the samples at a dose of $1x10^{17}$ ions/cm^2. Few of the samples analyzed previously are selected for the irradiation experiments. The samples are selected from each of the different categories of rubies that are being ascertained from the preliminary gemological and spectroscopic studies. The samples selected in the study are, brick red coloured sample from Maragowdanahalli area of Mysore district, Karnataka, Pale pink variety corundum from Lachmanapatti area of Karur district, Tamil Nadu and the colourless or fleshy red coloured sample from Poovanahalli area of Mysore district, Karnataka. The accelerated electron beams of varying velocities are implanted on the samples and it has been preliminarily observed to be helpful in producing favorable outcome in terms of colour, transparency and luster, depending upon characteristics of the sample and ions implanted. Outcome of the experiments are being analyzed, with the help of FTIR, Raman Photoluminescence and EDXRF studies.

Physical and Visual Impacts

The Nitrogen iron irradiation process on the selected samples has resulted in subtle changes in its appearance with respect to its colour. In the brownish cherry red sample from Maragowdanahalli area of Mysore district, Karnataka the irradiation process has resulted in the development of purplish hue in them as seen in Fig.1. The pale pink coloued samples from Lachmanapatti area of Karur district, Tamil Nadu, produces a dark bluish tint when subjected to nitrogen ion implantation as shown in the Fig.2. The colourless or fleshy red coloured sample from Poovanahalli area of Mysore district, Karnataka, as shown in Fig.3, also shows proclaimed differences in the appearance after Nitrogen ion implantation. There is development of pinkish tone over the fleshy coloured surface.

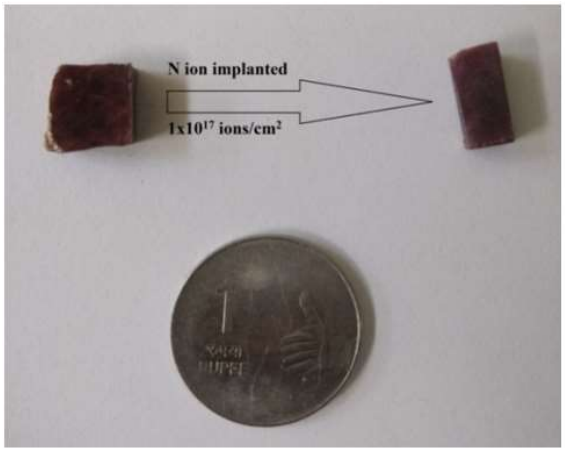

Fig. 1. Depicting the changes induced in the sample from Maradagowdanahalli, Mysore

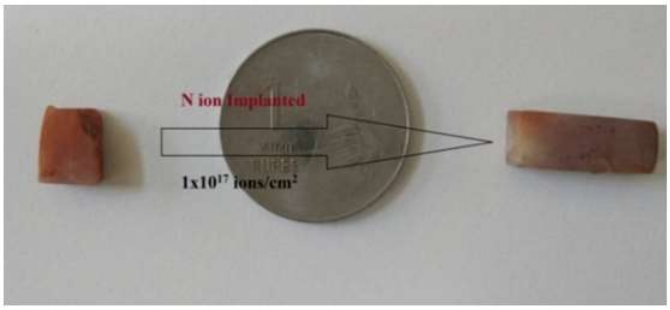

Fig. 2. Depicting the photograph of natural and irradiated sample from Poovanahalli, Mysore

Spectroscopic Implications of Nitrogen ion Implantation

Spectroscopic studies are carried on the samples to understand the effect of ion implantation on the samples subjected to the experiment. The interaction of Nitrogen ions with the molecular structure and atomic arrangement of the crystal have seemingly produced changes in their external appearance. These interactions are being mapped with the help of the advanced spectroscopic studies namely, FT-IR spectroscopy, Raman Spectroscopy, Photoluminescence Spectroscopy and EDXRF studies. The mechanism is looked into with respect to the spectra obtained for each of the analyses in the samples before and after subjecting to the ion implantation experiments.

FT-IR Characteristics: FT-IR studies carried out on the natural and irradiated samples shows subtle differences. Fig.4 shows the FT-IR spectra obtained for the sample from Poovanahalli area of Mysore district, Karnataka. In this sample, the peak does not show much difference. The peaks corresponding to Alumina at 1900 cm^{-1}, 2200 cm^{-1}, 2800 cm^{-1}, 2900 cm^{-1} and 3600 cm^{-1} (Johnson, M.L and Hausladen, P. 1975; Nassau K, 1985; Nassau K, 2003; Kloprogge et al., 2004; Beran and Rossman, 2006) are seen to have very minute decline in the intensity as seen in the figure. This might be due to the dislocations triggered in the Oxygen ion of the aluminum oxide.

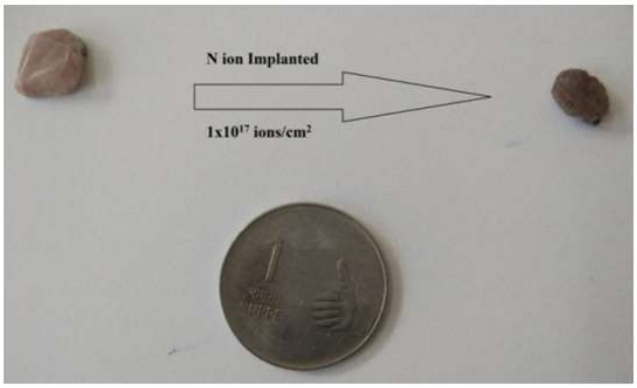

Fig. 3. Depicting the natural irradiated sample from Lachmanapatti, Karur

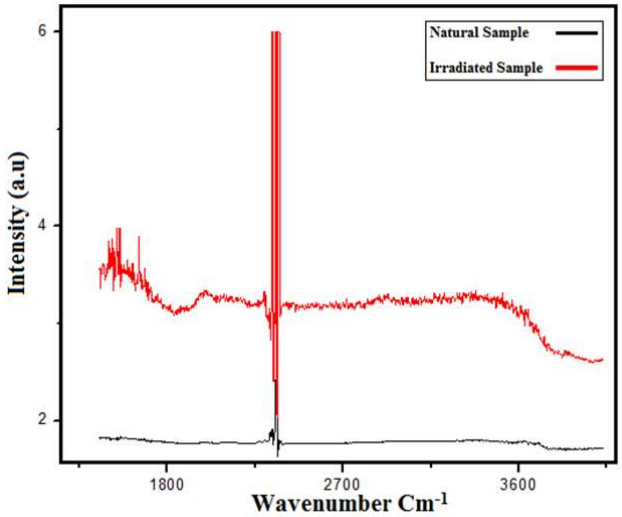

Fig. 4. Showing the spectra obtained for the sample from Poovanahalli, Mysore district, Karnataka

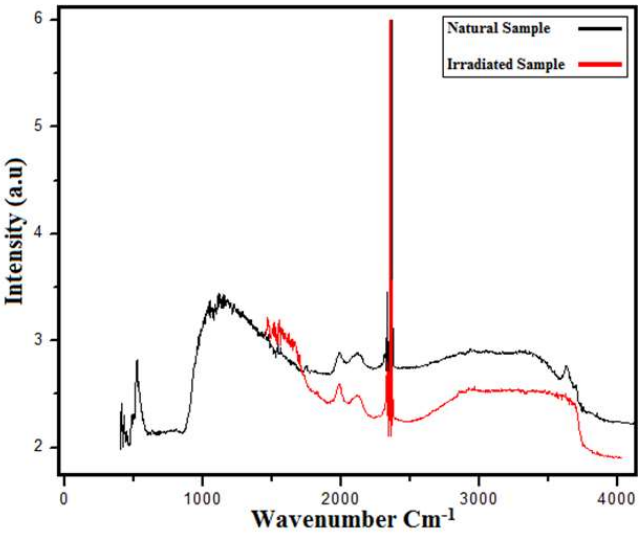

Fig. 5. Showing the spectra obtained for the sample from Maragowdanahalli, Mysore district, Karnataka

The brick red variety sample from Maragowdanahalli area of Mysore district area, Karnataka is subjected to N ion implantation to understand the changes induced in it. In Fig.5, the spectra obtained for both the natural and irradiated sample is shown. In this sample, the overall peaks seen in the spectrum is seen to have increased by certain degree. Such change in the spectrum is produced by the presence of different impurity elements in the crystal that got hydroxylated by the chemical mechanism triggered by the interaction

of Nitrogen ions irradiated in the experiment. Variations seen in the pale pink variety corundum from Lachmanapatti area of Karur district, Tamil Nadu is observed with the help of FT-IR spectroscopy. As shown in Fig.6, the infrared vibrational modes in the corundum sample are seen to have altered precisely. The spectra is seen to be almost unique while the peaks at 1900 cm^{-1} and 2200 cm^{-1} to be increased in magnitude after irradiation. The peaks at 2800 cm^{-1}, 2900 cm^{-1} and 3600 cm^{-1} are seen to be decreased abruptly as seen in the figure.

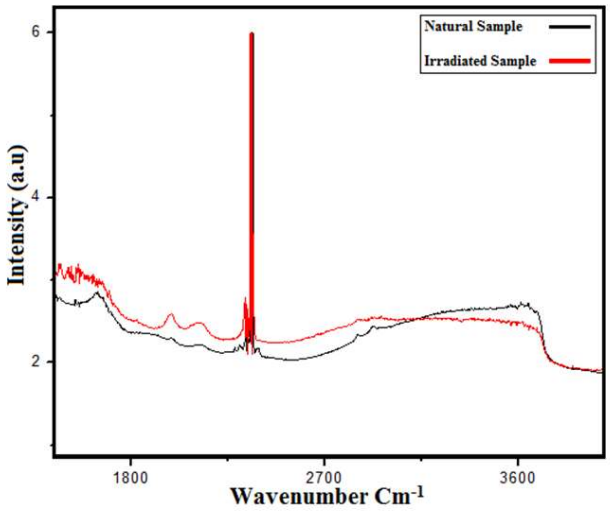

Fig. 6. Showing the spectra obtained for the sample from Lachmanapatti, Karur district, Tamil Nadu

Raman Spectroscopy: The typical Raman active vibrations seen in corundum at 378 cm^{-1}, 418 cm^{-1}, 432 cm^{-1}, 451 cm^{-1}, 578 cm^{-1}, 645 cm^{-1} and 751 cm^{-1} (Porto and Krishnan, 1967; Richet et al. 1993; Xu et al. 1995; Shyam Kumar and Shadakshara Swamy, 2017) are observed closely to understand the changes. The colourless or fleshy red corundum sample from Poovanahalli area of Mysore district, Karnataka is subjected to the Nitrogen ion irradiation and the Raman spectra obtained for the natural as well as treated samples are depicted in the Fig.192.

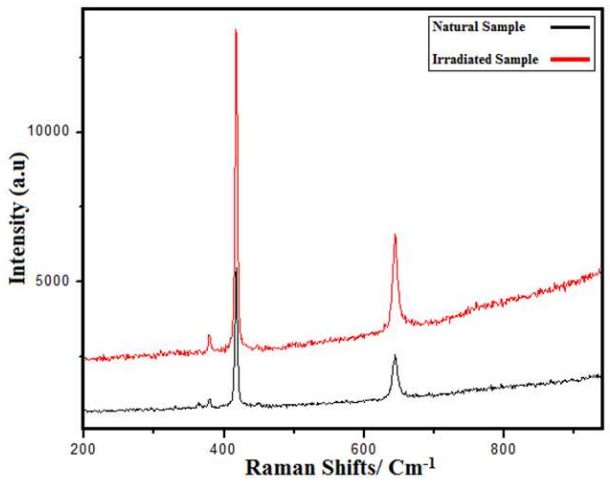

Fig. 7. Showing the spectra obtained for the sample from Poovanahalli, Mysore district, Karnataka

The sample in its natural form is exhibiting peaks corresponding to the Raman active vibrational modes at 418 cm^{-1} and 645 cm^{-1}. On irradiating Nitrogen ions, the intensity of peaks seen at these vibrational modes is seen to have increased appreciably, especially at 418 cm^{-1}. Such an increase might have been caused by the interaction of Nitrogen ion in deoxidizing the impurity molecules. In Fig.8, the affects of Nitrogen irradiation on the Raman characteristics of the sample from Maragowdanahalli area of Mysore district, Karnataka is shown. Raman spectra obtained for the natural sample is present with peaks corresponding to the Raman active vibrational modes at 378 cm^{-1}, 418 cm^{-1} and 645 cm^{-1}. The irradiated sample on the other hand shows an absence in the peaks at 378 cm^{-1} and 645 cm^{-1}, while additional peaks are found to have developed at 432 cm^{-1} and 751 cm^{-1}. The Raman spectra of sample from Lachmanapatti area of Karur district, Tamil Nadu, subjected to the irradiation experiments is shown in Fig.9. The spectrum for natural as well as irradiated sample as seen in the figure is present with distinct vibrational modes. The natural sample is showing considerable peaks at 378 cm^{-1}, 418 cm^{-1}, 578 cm^{-1} and 751 cm^{-1} in the spectrum. All the peaks are being preserved in the sample after irradiating with Nitrogen ions. These peaks appear not to have merely preserved and are markedly intensified after subjecting to Nitrogen irradiation. Such intensification of magnitude may be caused by the removal of abstruse molecules by deoxidization.

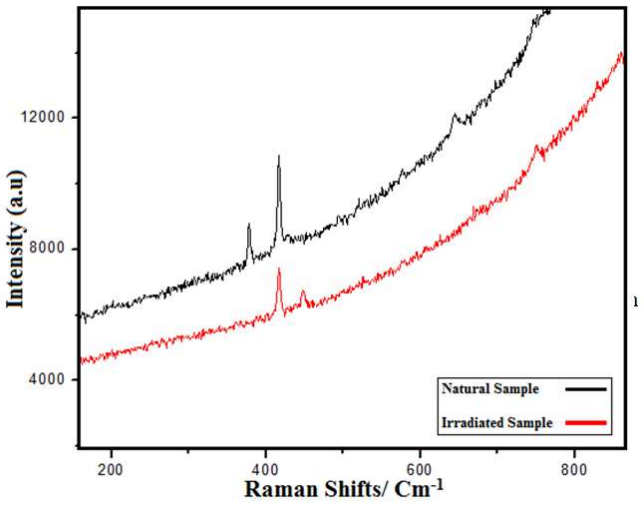

Fig. 8. Showing the spectra obtained for the sample from Maragowdanahalli, Mysore district, Karnataka

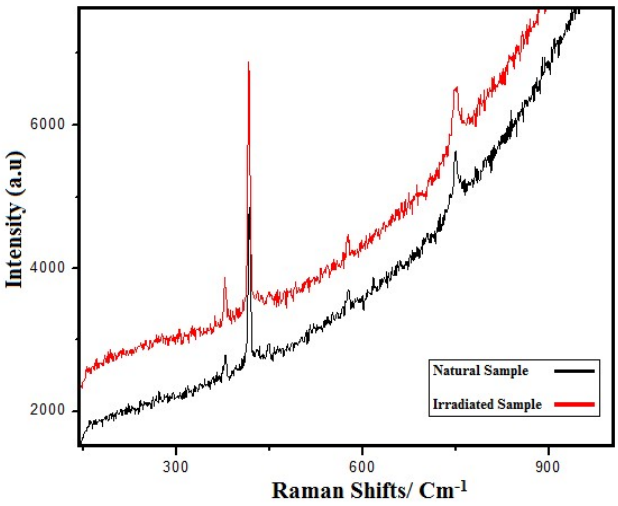

Fig. 9. Showing the spectra obtained for the sample from Lachmanapatti, Karur district, Tamil Nadu

Photoluminescence Effects of Irradiation: Photoluinescence spectra of the samples are observed to understand the alterations associated with the colour causing chromophores in ruby, generally associated with chromium content in them. The emittance peak is observed for the wavelength range between 600nm to 800nm for the samples. The Photoluminescence studies carried out on colourless or felshy red coloured corundum from Poovanahalli area of Mysore district, Karnataka, is shown in Fig.10. The spectrum obtained for the natural sample shows peculiar peaks 692 nm and 694 nm[1]. The Nitrogen irradiation process has caused a slight increase in the intensity of the peaks, particularly at 692 nm. The change in the intensity of

emittance might have resulted from either due to the colour centre effect triggered by the delocalization of Cr ions or due to the deoxidization of the molecular impurities present as oxides. Similar development varying hues of red colour in corundum due to bivalent and trivalent iron and charge transfer also due to heat treatment is previously reported (Majumdar and Mathew, 2012). The spectrum obtained for brick red variety ruby from Maragowdanahalli area of Mysore district, subjected to photoluminescence spectroscopy is shown in Fig.11.

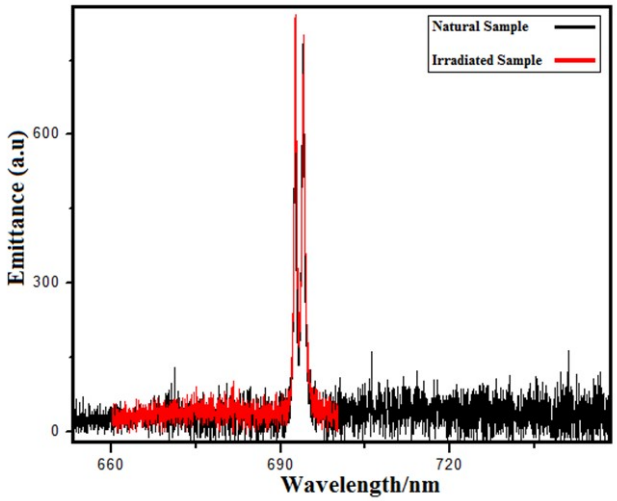

Fig. 10. Showing the spectra obtained for the sample from Poovanahalli, Mysore district, Karnataka

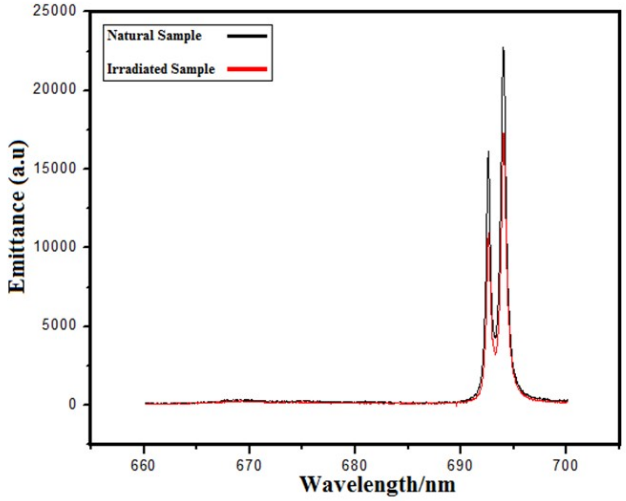

Fig. 11. Showing the spectra obtained for the sample from Maragowdanahalli, Mysore district, Karnataka

The natural as well as Nitrogen ion irradiated samples show the characteristic Raman active vibrational modes at 692 nm and 694 nm. In the natural sample analyzed prior to irradiation, the peaks at these wavelengths are present with a very high magnitude. These peaks are seen to have reduced in intensity by a notable magnitude after the irradiation treatment, which is presumed to be due to the dislocation of Cr ions from the tetrahedral molecular structure, as a result of oxygen atoms released by the interference of Nitrogen ions irradiated. Emittance spectra of the sample from Lachmanapatti area of Karur district, Tamil Nadu is depicted in Fig.12. The differences resulted in the spectrum after irradiation experiment is portrayed explicitly in the spectra. The emittance spectra of the natural sample shows well defined peaks at 692 nm and 694 nm, with a magnitude proportional to the emittance resulted from the Cr ions present as chromophores in them. The spectrum obtained after Nitrogen irradiation has got peaks at these wavelengths in a magnitude higher by several folds than that obtained for the natural sample. Similar cases of development of defect centres due to irradiation, imparting colours in the samples is also noticed in several other studies (Mohanty et al., 2003; Bharadwaj et al.,2004; Intarasiri et al., 2009; Nagabhushana et al., 2009).

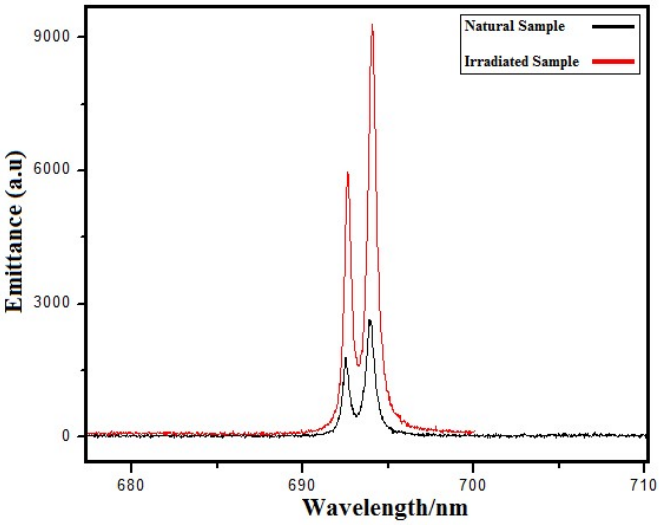

Fig. 12. Showing the spectra obtained for the sample from Lachmanapatti, Karur district, Tamil Nadu

ED-XRF Implications

The Nitrogen ion implantation studies on the samples have resulted in notable differences in the chemistry in terms of major oxides. As the molecular chemistry of corundum is being altered by interaction of the Nitrogen ions with the anions present in the octahedral network, the alterations with respect to Chromophores and impurity inclusions are quantified with the help of Energy Dispersive X-Ray Fluorescence Spectrometer. The Nitrogen ion implantation experiments are known to induce alterations in the molecular structure by creating colour centre and also by causing minor heating effect (Sudheendra Rao et.al, 2016., Mishra, B.K.., 2016., S. Intarasiri et.al, 2009). The variations seen in the concentration of major oxides of the samples are provided from Table.1 to Table 3. The changes induced by Nitrogen ion irradiation on the sample from Maragowdanahalli area of Mysore district, Karnataka is shown in Table 1. The Al_2O_3 concentration is seen to have diminished along with all the other major oxides that are considered in the study, on subjecting to the irradiation experiments, except the Fe_2O_3 and ZrO_2, which are seen to have increased as seen in the table. The negative variation is infinitesimal in case of Cr_2O_3 and Ga_2O_3, while it is seen to be dominant in the case of CaO.

Table 1. Showing the changes in chemistry of the samples from Maragowdanahalli area of Mysore district, Karnataka, after irradiation

Oxide	Natural Sample	Ion implanted sample
Al_2O_3	98.44	97.668
CaO	0.487	0.04
TiO_2	0.018	0.008
V_2O_5	0.02	0.017
Cr_2O_3	0.337	0.333
Fe_2O_3	0.674	0.8
Ga_2O_3	0.021	0.015
ZrO_2	0.001	0.045

Table 2. Showing the changes in chemistry of the samples from Lachmanapatti area of Karur district, Tamil Nadu, after irradiation

Oxide	Natural Sample	Ion implanted sample
Al_2O_3	98.555	97.34
CaO	0.485	1.93
TiO_2	0.106	0.041
V_2O_5	0.005	0.012
Cr_2O_3	0.073	0.055
Fe_2O_3	0.763	0.613
Ga_2O_3	0.003	0.002
ZrO_2	0.01	0.018

The overall development of transperancy and a pinkish red tint on the sample (Fig.1) may be due to the considerable reduction seen in the CaO content due to deoxidization and colour centre defects induced further on. Experimental characteristics of the sample from Lachmanapatti area of Karur district, Tamil Nadu, on subjecting to Nitrogen ion implantation is shown in Table.2. Experimental studies on this sample have resulted in development of dark blue hues in it (Fig.3). The content of CaO, V_2O_5 and ZrO_2 is evidently increased to an extent. Fe_2O_3 and Cr_2O_3 concentration shows a negative trend along with the other oxides like Al_2O_3, TiO_2 and Ga_2O_3. The development of bluish hue may be due to the colour centre defect that would have resulted from the change in oxidation state and the development charge transfer phenomenon between the Fe and Ti ions. The overall decrease in transparency and the development of cloudy appearance may be due to the exponential increase seen in the CaO. Table.3 shows the chemical characteristics of nitrogen ion implantation experiments on the sample from Poovanahalli area of Mysore district, Karnataka. This sample is showing subtle variations in the chemistry after subjecting to irradiation. The experimental studies have resulted in an overall development of a pinkish hue over the sample, as seen in Fig.1. It can be understood from the table that, the concentration of Cr_2O_3 has been increased to an extent after Nitrogen irradiation. The concentration of other oxides like Al_2O_3, Fe_2O_3, CaO, V_2O_5, TiO_2 and Ga_2O_3 are seen to have reduced, still a prominent CaO content is still present in the sample as the decrease seen is quite nominal. As a result, there is no development seen in the sample with respect to its diaphaneity. The increased Cr_2O_3 content and the associated crystal field effect or colour centre formation would have triggered the development of pinkish red hue over the surface of the sample. The elemental chemistry witnesses alterations, in different kinds of treatments for the enhancement of gem quality of corundum (Nassau, K, 1981; Nassau, K, 1984; Nassau, K, 1994.) It is also seen significantly in heat treatment (NASSAU, K., 1981; Themelis, 1992; R.K. Sahoo et al, 2015; Manocha and Ramjibhai, 2012; Sudheendra Rao et.al, 2016) as well.

Table 3. Showing the changes in chemistry of the samples from Poovanahalli area of Mysore district, Karnataka, after irradiation

Oxide	Natural Sample	Ion implanted sample
Al_2O_3	98.257	98.44
CaO	1.241	1.094
TiO_2	0.018	0.008
V_2O_5	0.004	0.001
Cr_2O_3	0.022	0.035
Fe_2O_3	0.447	0.382
Ga_2O_3	0.011	0.04
ZrO_2	0.001	0.001

DISCUSSIONS AND CONCLUSIONS

The Nitrogen Ion irradiation experiments have produced significant changes in the physical outfit of corundum samples. There is an impartment of pinkish, reddish and bluish hues in the samples seemingly after subjecting to the ion implantation. The capability of Nitrogen ions to alter the elemental configuration is being attempted to understand. The contemplations are being carried out with the help of the same advanced spectroscopic techniques deployed in the characterization of annealing experiments, FT-IR Spectroscopy, Raman spectroscopy and Photoluminescence spectroscopy. FT-IR spectroscopic studies on the nitrogen irradiated samples shows subtle differences in the peaks obtained at 1900 cm^{-1}, 2200 cm^{-1}, 2800 cm^{-1}, 2900 cm^{-1} and 3600 cm^{-1}. There is a notable decline in the intensity of the vibrational spectrum at 2800 cm^{-1}, 2900 cm^{-1} and 3600 cm^{-1} in most of the samples subjected to irradiation while those at 1900 cm^{-1}, 2200 $cm^{-1}$are seen to have intensified nominally on the other hand. This paves way to suspect the chance of minor heating effect that would be triggered in the samples due to heavy ion implantation and the elemental rearrangements events induced by nitrogen in crystal, which seems to go hand in hand leading to the dehydroxylation and hydroxylation of Alumina associated impurities. The Raman spectroscopic studies have depicted an overall intensification of Raman active vibrational modes in the samples upon Nitrogen irradiation and most of the vibrational modes present in the natural samples are seen to have preserved after the experiment. At the same time, a sample from Maragowdanahalli area of Mysore district shows seldom diminished spectrum where there is little distortion seen in the Raman active vibrational modes. This sample appears to have developed light pinkish tint after the irradiation, which would have been resulted from the molecular rearrangements as reflected in the Raman spectrum. The Photoluminescence study shows a change in the intensity of emittance peaks corresponding to the chromophores in corundum proportional to the colour inducement in the samples. In a sample from Lachmanapatti area of Karur district, Tamil Nadu, which exhibits pale pink colour in its natural form and seen to have developed dark coloured hue with a bluish tint on Nitriogen ion irradiation, the emittance peaks at 692nm and 694nm are seen to have increased by many folds. The chemical analyses using EDXRF study substantiates the alterations induced in the crystal chemistry from the variations seen in the chemistry of the major oxides, resulted from the minor heating effect or crystal defects induced by the action of Nitrogen ions.

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