



Color improvement of rubies by ion beam technique



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ABSTRACT

Ion implantation technique has been used for improving the quality of natural ruby. The implantation was performed by using 90 keV N₂-ion and 50 keV O-ion beams. Either kind of ion species could eliminate tiny inclusions in the ruby as observed from an optical microscope. The red color of the ruby was intensified after O-ion implantation. N₂-ion implantation changed the color of red ruby to be violet-red. UV–vis and X-ray absorption spectroscopic techniques were employed for investigating the mechanism behind the optical quality improvement of the ruby. The results from both measurement techniques are reported and discussed.

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1. Introduction

A gemstone is the naturally occurring crystalline form of a mineral, which is desirable for its beauty, valuable in its rarity and durable enough to be enjoyed for generations. Corundum mineral is a crystalline form of Al₂O₃. A perfect crystalline Al₂O₃ is colorless. The color is originated from the traces of impurities existing in corundum. The red variety of corundum is known as ruby, and all other colors of corundum are known as sapphires. Ruby is generally known as the most valuable of all color gemstones that exhibit apparent color from pink to blood-red. For ruby, the red color is caused mainly by the presence of a small percentage of chromium (Cr). Price of ruby is primarily determined by its color. Although the discoveries of natural gemstones are found from time to time in many parts of the world, only relatively small amount of high quality gem material can typically be produced comparing to a much larger quantity of low quality gem material recovered from a given mining locality. Thus, huge efforts have been spent to develop methods to treat this lower-quality material to enhance its appearance and thereby its marketability for gem purposes.

Heat treatment is the most popular technique and commercially used for the improvement of quality of gemstones in such ways to modify color, unify inclusions, increase transmittance and improve luster [1, 2, 3]. However, the main drawback of the heat treatment is that it involves annealing at rather higher temperatures (typically above

1000 °C) for various periods ranging from few hours to few days depending on the type of gemstones, and thus different types of gemstones cannot be treated simultaneously. Alternative treatments are exposure of gemstones to energetic particle beams or laser beams. Among different types of irradiating beams, a heavy-ion beam is a promising candidate as it is able to bring about both local heating effect and to directly introduce defects, impurities that have direct effects on the modification of the optical properties [4]. Moreover, the ion beam can be used to treat different gems individually.

In the past, research activities of ion implantation on corundum were either the improvement of optical and mechanical properties [5, 6, 7, 8, 9, 10], or the applications in optics, optoelectronics, photonics and tooling [11, 12]. Most of the previous works focused mainly on basic understandings of ion beam modifications of sapphire. Our recent work demonstrated the potential of ion implantation technique for quality enhancement of several gems in the corundum family [13]. The present work aims not only at the development of a heavy ion beam irradiation process for enhancing the quality of rubies but also the understanding of mechanism behind the optical quality improvement of the rubies. Different measurement techniques were employed in this work. Particle Induced X-rays Emission (PIXE) technique was used for determine the concentration of the trace elements. Raman spectroscopic technique was used for investigating the disorders in ruby related to the formation conditions [14, 15]. UV–vis absorption spectroscopy, as a common technique to study the mechanisms of coloration caused by transition metal in gemstones, was also used [16]. In addition, X-ray absorption spectroscopy [17], which is a powerful technique for chemical analysis, was also

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employed to investigate the information about the oxidation state of the transition metals in ruby before and after ion implantation.

2. Experimental details

The ruby investigated in the present work is from the mining in Mozambique. The gem specimens were either naturally virgin or well cut and polished, and their sizes varied from a few mm to almost 1 cm in specific diameters.

The ruby specimens were implanted by N_2^- and O-ions. N_2^- -ion implantations were performed by using a 200-kV Varian ion implanter equipped with a Freeman ion source at Chiang Mai University in Thailand. While O-ion implantations were carried out by using a Danfysik ion implanter equipped with a magnetic multicusp plasma discharge ion source at Uppsala University in Sweden. Both implanters are equipped with a beam scanning system to ensure the uniform distribution beam with an area over 6-in. in diameter. It is noted that the ion species and energy were chosen from the optimal performance of each ion implanter since rather high ion fluences were required in this work. N_2^- -ion implantations were performed with an ion energy of 90 keV and a fluence of $\sim 5 \times 10^{17}$ ions/cm². While O-ion implantations were performed with an ion energy of 50 keV and a fluence of $\sim 4 \times 10^{17}$ ions/cm². Each of gemstones was fixed on the carbon tape which attached to the sample holder directly in a way to prevent a colliding of the ion beam to the carbon tape. The target temperature during ion implantation was measured using a pyrometer and found to be stabilized below 200 °C. The operating pressures in the target chambers were $\sim 10^{-5}$ – 10^{-6} Torr. Surface cleaning by oxygen plasma was subsequently done after ion implantation.

The ion beam-treated specimens were observed under either gemologist-professional binocular microscopes (Zeiss, Germany) or directly in natural light. The photos were taken under the dark field with the magnification of 3.75 and the inclusions were recorded under the bright field with the magnification of 35. The photo recording systems were kept in the same manner, especially variations in lighting conditions, throughout the whole experiment without any interruption from other activities. Moreover, before the photos of samples after ion implantation were taken, the background was set to be the same as before ion implantation. All color changes of implanted samples were described by the authorized gemologist professionals, i.e. B. Wanthanachaisaeng [18], based on the color grading system [19]. The values of the gemstones were judged based on overall performance of 20 samples in each group by both authorized gemological professionals and specialist from business company, i.e. C. Rookkajinda [20].

The trace elements in the ruby samples were analyzed using PIXE based on a 2-MeV proton beam produced by a 1.7 MV tandem Tandetron accelerator at Chiang Mai University [21]. The optical absorption spectroscopic study was carried out by using a Perkin Elmer Lambda 950 UV/vis Spectrometer which recorded over the range from 300 to 800 nm. The ordinary ray (o-ray) and extraordinary ray (e-ray) of samples were previously identified by the Polariscopes [22]. All absorption measurements in this work were carried out at room temperature. A Jobin Yvon spectrometer HORIBA (T64000), equipped with a triple monochromator, 532 nm solid state excitation laser, and a focused spot size of about 0.8 μ m by a 100 $\times$ objective (NA = 0.9), was used for the Raman measurements. It has been known that corundum is, after all, very chemically heterogeneous and one can expect different optical and physical properties on different parts of the stone even without any sort of treatment [22]. Therefore, we marked the position for measurements of both UV–vis and Raman spectra to ensure that the measurement results did not differ only because of non-uniformity in nature of the stone.

Measurements of X-ray absorption near edge structure (XANES) spectra of the ruby with and without ion implantations were carried out at the Synchrotron Light Research Institute of Thailand using the X-ray absorption spectroscopy beamline (BL8) [23]. The measurements

were performed in fluorescence mode using a 13-element Ge detector. The intensity of the incident X-ray beam was measured by an ionization chamber located in front of the sample. The photon energy scan was carried out using a Ge(111) double crystal monochromator to cover the K-edge of Fe and Cr. XANES spectra taken from a metallic Fe foil, FeO and Fe₂O₃ were used as the references for the +0, +2 and +3 oxidation states of Fe, respectively. For Cr K-edge, a metallic Cr foil and Cr₂O₃ were used as the references for the +0, and +3 oxidation states, respectively.

3. Results

Fig. 1 shows the appearance of ruby for before and after 90 keV N_2^- -ion implantation to a fluence of $\sim 5 \times 10^{17}$ ions/cm². Under dark field, it was seen that the color tone become darker (Fig. 1a). Moreover, it observed, by increasing the optical magnification, that some tiny inclusions, marked by oval figure, were removed (Fig. 1b–e). These inclusions might be small features near surface which were broken up by ion beams irradiation. Note that the elemental analysis by PIXE revealed the quantity of Cr, Fe and Ti in this sample to be 6230, 4010 and 72 ppma, respectively. The color grading system indicates that the overall color of rubies treated by N_2^- -ions implantation changed from red (R) to strongly purplish red (StpR).

Fig. 2 shows the appearance of ruby for before and after 50 keV O-ion implantation to a fluence of $\sim 5 \times 10^{17}$ ions/cm². It was seen that its color tone slightly lightened up, thus, the color become slightly redder after treatment (Fig. 2a). It was observed, by increasing the optical magnification, that some tiny inclusions, marked by oval figure, have also been removed. Note that, from PIXE analysis, the concentrations of Cr, Fe and Ti in this sample were found to be 12,020, 5243 and 89 ppma. The color grading system indicates that the overall color of rubies treated by O-ions implantation changed from red (R) to orangy red (oR).

Fig. 3a and b show the optical absorption spectra for the N_2^- -ion and O-ion implanted rubies, respectively, comparing to the rubies before the implantation. In the visible spectral region, there were two large absorption bands centered at ~ 400 and 560 nm which were assigned to the transition associated with Cr. These two bands were corresponding to the spin-allowed $^4A_{2g} \rightarrow ^4T_{1g}$ and $^4A_{2g} \rightarrow ^4T_{2g}$ transitions, respectively [24]. In addition, the spectra generally displayed a strong “background absorption” starting around 600 nm and increasing towards the UV spectral edge. The Cr “doublet” at 694 nm [22] was visible for both before and after ion implantation.

After N_2^- -ion implantation, as shown in Fig. 3a, it is obvious that the overall absorption was greatly changed. However, the absorption along the o-ray and e-ray has been differed significantly by the ion implantation. It might be due to the fact that the ions were implanted into only one direction, resulting in the non-uniformity. In the vicinity of green region (500–600 nm), after ion implantation, it was an increase in the absorption of the o-ray but vice versa of the e-ray, implying that the shade of color differed significantly. However, the overall absorbance is higher at longer wavelength (600–800 nm). As proportionately more absorption is noticed in the 600–800 nm (red and near IR) bands, the sample appears slightly darker.

While for O-ion implantation, the overall absorption spectrum was not much changed after the ion implantation. However, in the green region (500–600 nm), the overlapping of Cr^{3+} and $Fe^{2+}-Ti^{4+}$ bands, was increased significantly. This implies that the yellow color increases and the sample hue becomes orange-red.

It is noted that the absorption spectra of samples are, in general, combination spectra showing the Cr^{3+} absorption features together with a pronounced contribution of Fe^{3+} and Fe^{3+}/Fe^{2+} bands at 377/388 nm and 450 nm respectively [25]. More rarely seen was a combination of the Cr^{3+} features with the $Fe^{2+}-Ti^{4+}$ charge-transfer (IVCT) band of sapphire at around 560 nm [25]. It is unfortunate that, in our measurements, due to strong absorption behavior of Cr^{3+} in ruby, some of these peaks are difficult to identify and compare. Therefore, it

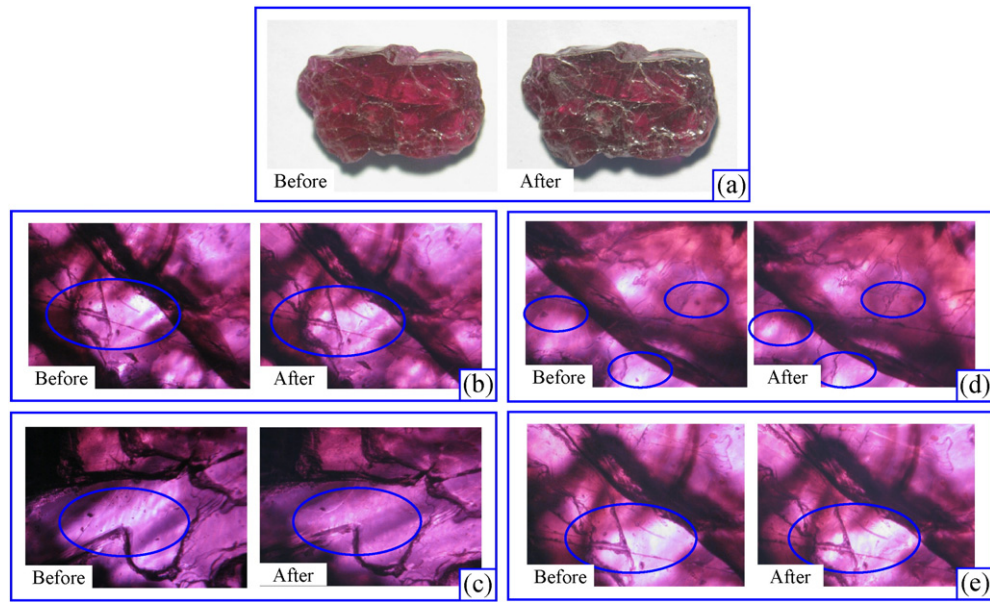


Fig. 1. Images of natural ruby; (a) dark field (magnification 3.75), (b)–(e) bright field (magnification 35) before and after 90 keV N_2 -ion implantation.

is not possible to decipher explicitly the cause of color change due to ion implantation by only using these absorption spectra.

Fig. 4 displays the Raman spectra of ruby before and after ion implantation. Based on theoretical analysis, Bhagavantam and Venkatarayudu [26] expected seven Raman active frequencies ($2A_{1g} + 5E_g$) for corundum. Porto and Krishnan [27] presented that these Raman vibrational modes were at 378 (E_g), 418 (A_{1g}), 432 (E_g), 451 (E_g), 578 (E_g), 645 (A_{1g}), 751 (E_g) cm^{-1} . In our measurements, both samples exhibited the main peak (A_{1g}) at 417 cm^{-1} indication of Al–O vibrations of corundum. However, some other modes were missing from the spectra and also difference for both samples. The crystal structure of corundum consists of dense, closest packed layers of oxygen and octahedrally coordinated aluminum. In the structure of corundum, edge and face sharing of the Al-octahedra cause distortion, resulting in appreciable polarization of the atoms and intense Raman peaks [27].

Therefore, it might point out that both samples have been cut slightly off the c-axis and also difference for both of them. In our measurements, the Raman band positions remain unchanged after ion implantation for both N_2 -ions and O-ions implantation (Fig. 4a and b respectively). However, the peak intensities of N_2 -ions implantation reduced significantly. This might be the indication of surface damage. It was reported that differences in absorption band strengths are noted for implantation in crystals of different orientation [28]. This should take into account in our case.

Fig. 5a and b show, respectively, the Fe K-edge XANES spectra taken from the standard samples and from the natural ruby before and after N_2 -ion implantation. Because of the differences in the local structure around the Fe atom, the Fe K-edge XANES spectra of a metallic Fe foil, FeO and Fe_2O_3 are obviously distinguishable, as shown in Fig. 5a. It is obvious that the absorption edge shifts towards lower photon energy

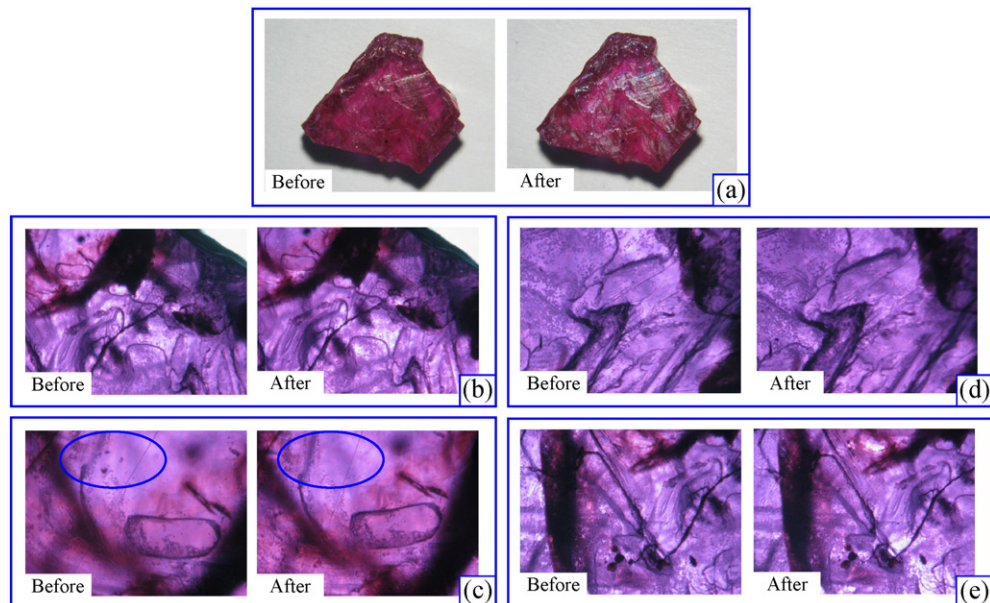


Fig. 2. Images of natural ruby; (a) dark field (magnification 3.75), (b)–(e) bright field (magnification 35) before and after 50 keV O-ion implantation.

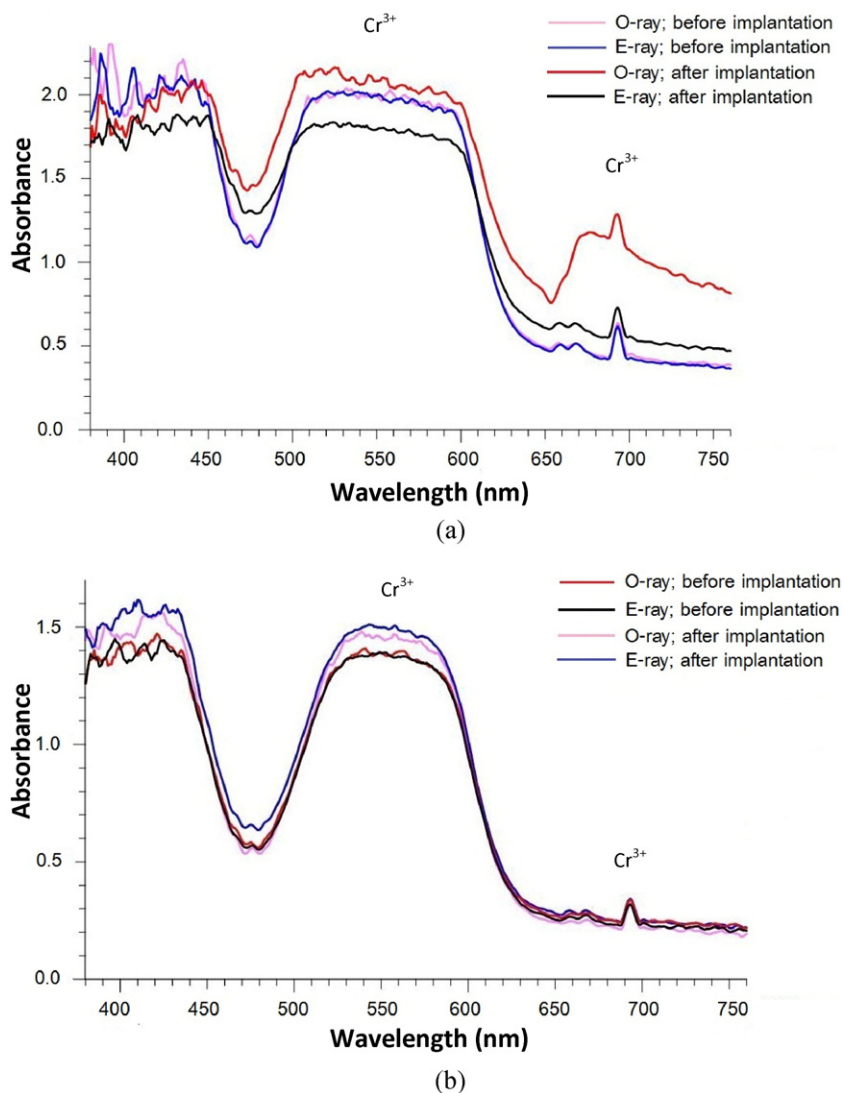


Fig. 3. Uv-vis absorption spectra of natural ruby before and after; (a) 90 keV N_2 -ion implantation, (b) 50 keV O-ion implantation.

when the oxidation state of Fe reduces. The pre-edge and the edge positions of the XANES spectrum of the natural ruby before N_2 -ion implantation are located the same positions as those of Fe_2O_3 , indicating that oxidation state of Fe in the natural ruby is +3. The features of the XANES spectrum of the natural ruby before N_2 -ion implantation are very similar to those of Fe_2O_3 . This suggests that the local structure around Fe in the ruby is similar to that in the standard Fe_2O_3 sample. The noticeable discrepancies between the Fe K-edge XANES spectra taken from the standard Fe_2O_3 sample and the natural ruby indicating the slight differences in the local structure around the Fe atom in both samples. There are big differences in the XANES spectra of the ruby before and after N_2 -ion implantation. For the implanted sample, the pre-edge peak at 7111 eV becomes pronounced. In addition, the absorption edge shifts towards lower photon energy, suggesting that the oxidation state of some Fe atoms was changed to be lower numbers. It is noted that the probed depth of XANES (tens of micron) is well below the thickness of the ion implanted layer. Thus the measured XANES spectra are a combined result from the implanted layer and from the region below the ion range. This results in multiple absorption edges for the implanted ruby. By comparing to the standard spectra, the XANES spectrum of the implanted ruby is from Fe with oxidation states +2 and +3. The Fe^{+3} may be from the region with the depth below the implanted layer and the Fe^{+2} may be from the implanted layer.

It is noted that there are no differences in the Cr K-edge XANES spectra taken from the natural ruby before and after N_2 -ion implantation. This suggests that the oxidation of Cr in the ruby was not altered by the N_2 -ion implantation. The oxidation state of Cr in the ruby samples was deduced by comparing the XANES of the ruby and the standard samples. The most likely oxidation state number is +3, which is in agreement with a previous report [29]. It is also interesting to note that XANES spectra of the natural ruby samples taken before and after O-ion implantation are very similar for both Fe K-edge and the Cr K-edge (the spectra are not shown).

4. Discussions

Colors in corundum can be originated from many different mechanisms [1,2,30,31,32]. The well-known basic causes of color are the followings: Cr^{3+} generates pale pink through deep red as its concentration increases, Fe^{3+} generates a pale yellow and Fe^{2+} - Ti^{4+} pairs generate blue through the intervalent charge transfer (IVCT) mechanism. The chemical information obtained from XANES measurements allowed us to focus on the major mechanism caused by the presence of Cr and IVCT of the trace elements existing in ruby (mainly Fe and Ti) before and after ion implantation.

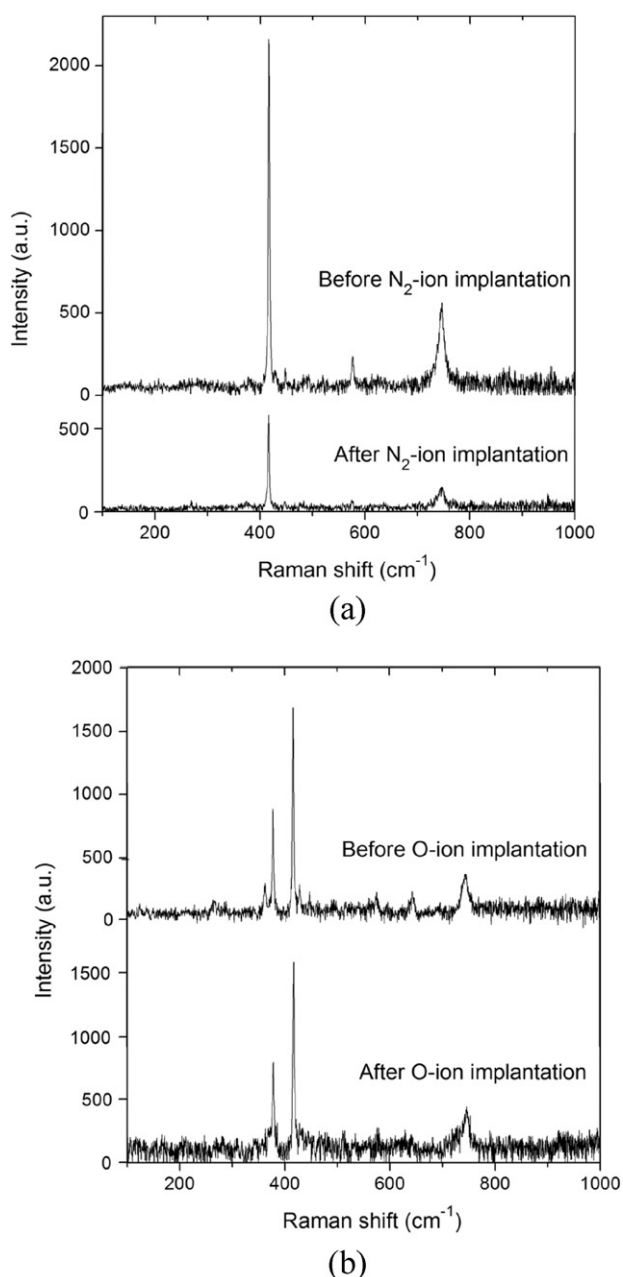


Fig. 4. Raman spectra of natural ruby before and after: (a) 90 keV N_2 -ion implantation; (b) 50 keV O-ion implantation.

For ruby, it is well understood that the cause of color is due to Cr^{3+} in trigonal distorted octahedral site in corundum lattice. Haeger [33] has pointed out that Cr^{3+} is an independent coloring element and does not influence the valance of the other trace elements. It is also not possible to change the content and valance of Cr^{3+} in the corundum lattice by heating. Our XANES measurements also show that the ion implantations could not change the number of oxidation state of Cr. Thus, the alterations of color in ion implanted rubies were not related to the modification of Cr^{3+} .

The number of the oxidation state of Fe in ruby remains +3 after O-ion implantation. The mechanism behind the origin of color in the O-ion implanted ruby may be similar to the situation found in the Mong Hsu ruby in a way that blue marks on the ruby was diminished when heating up to 1300 °C in air [34]. It was suggested that this happened as a result of the separation of Fe^{2+} - Ti^{4+} pairs, and Fe^{2+} was found to be oxidized to Fe^{3+} . That results in the characteristic yellow color

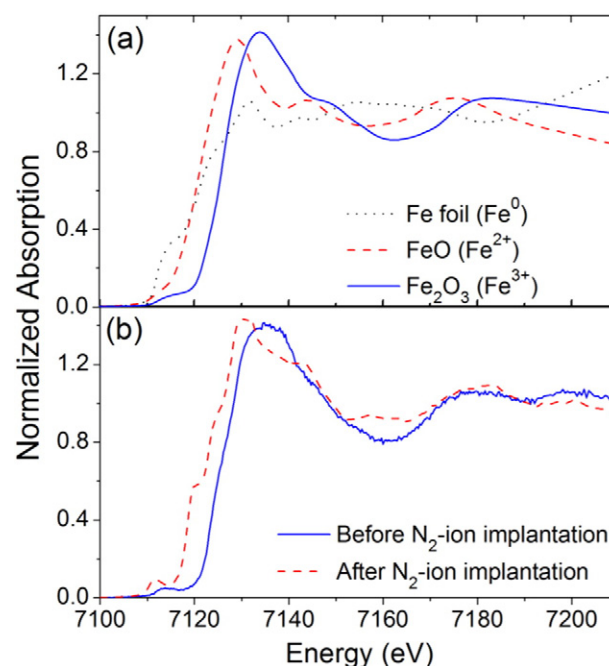


Fig. 5. Fe K-edge XANES spectra taken (a) from the standard samples and (b) from the natural ruby before and after N_2 -ion implantation.

emission, and while red color comes from Cr^{3+} ions, the superposition of the two colors (yellow and red) leads to an overall orange red color with luster for the ruby.

Nitrogen is non-reactive [35] and thus ion energy deposition effect is more dominant. The ion energy deposited may stimulate a transfer of an electron between two adjacent metal ions, such as the commonly found interaction of Fe^{2+} (in cation site 1) + Fe^{3+} (in cation site 2) $\rightarrow$ Fe^{3+} (in cation site 1) + Fe^{2+} (in cation site 2) and the actual colors of corundums are dependent on the concentration fraction of those 2 species [36]. It is interesting to emphasize that, from the XANES measurements, the oxidation state of Fe was obviously reduced from 3+ to 2+ after N_2 -ion implantation. The increase in the concentration of Fe^{2+} might also increase the number of Fe^{2+} - Ti^{4+} pairs, and thus blue color was intensified in the N_2 -ion implanted ruby. This turns the ruby to be violet, which is a combination of the intensified blue and unchanged red [37].

5. Conclusions

This work demonstrates that low- and medium-energy nitrogen and oxygen ion implantations are capable to improve the quality of natural ruby. Tiny inclusions near the surface can be eliminated. The red color of the ruby was intensified after 50 keV O-ion implantation. 90 keV N_2 -ion implantation can change the color of red ruby to be violet-red. From XANES measurements, N_2 -ion implantation reduces the oxidation state of Fe from +3 to +2 while causes no changes in the oxidation state of Cr. For the O-ion implantation, no changes in number of the oxidation state of Fe and Cr were observed. The changes in color of the ion implanted rubies may be governed by the interplay of the intervalent charge transfer between Fe and Ti atoms. Unfortunately, XANES spectra of Ti K-edge could not be obtained due to the low concentration. Thus, this issue will be a topic for further investigation after the improvement of detection sensitivity of the XANES set up.

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