



Investigation on modification of ion implanted natural corundum by UV–Vis–NIR spectroscopy



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ABSTRACT

Natural corundum, a crystalline form of aluminium oxide (Al_2O_3) with impure elements, is an allochromatic mineral whose color varies based on the presence of impurities in the composition. Ion implantation technology can be utilized for enhancing the optical properties of corundum by selecting the implanted ion type leading to modification of the composition and defects. As for the appearance of corundum depending on many factors including brilliance, color, fire (light dispersion), and luster, this research attempted to find out an alternative method for improving the optical appearance and color enhancement of corundum by using ion implantation. Ion beam treatments with 70 keV nitrogen and argon ions and 23 keV oxygen ion at fluence of 10^{17} ions/cm² were applied to ruby and sapphire from Thailand, Myanmar, Cambodia, Sri Lanka, Africa, and USA. Additionally, ion beam analysis techniques, i.e., particle-induced X-ray emission (PIXE), together with conventional gemological observations such as optical microscope and UltraViolet-Visible and Near Infrared (UV–Vis–NIR) spectroscopy were applied to understand the phenomena observed. The results revealed the possibility of color changing by ion beams resulting from variation in the ionic stage of trace elements as seen from UV–Vis–NIR absorption spectra. The advantages of ion implantation appear to be new and sustainable for improving corundum properties.

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1. Introduction

Corundum is a crystalline form of aluminium oxide (Al_2O_3) in hexagonal structure which is naturally clear, yet it can show certain colors when some chemical types, structure and quantity of elements emerge. The color is produced by certain wavelengths of light reflected or transmitted by the crystal lattice while others absorbed. Those wavelengths of light reflected or transmitted are perceived by the viewer and hence the property of color is exhibited. Corundum is an allochromatic mineral whose color varies based on the presence of impurities in the composition and on defects in the structure [1]. For examples, few ppm of chromium (III) ions which replace aluminium ions in corundum – natural colorless – provide the red color appearance and the mineral is called ruby, while the yellow color in sapphire is caused by iron (III) ions. The intervalence charge transfer (IVCT) is also indispensable formalism for blue color produced in sapphire especially for valence electrons between Fe^{2+} and Ti^{4+} transferring [2]. The color is a variable and unpredictable property of corundum which can be described by many coloration mechanisms.

Although the corundum market is growing, sources of good quality materials tend to be insufficient. This is why gems traders try to improve corundum's characteristics such as strength, color and transparency by various methods. However, treating gems by some techniques especially heat treatment, which is a thermionic radiation process below corundum's melting point directly effecting corundum properties via volumetric expansion by temperature dependence [3], is problematic. These treatments cause transformation of crystalline to be unnatural, crack, cleavage, fracture, and undesired oxide such as silicate or calcite [1], or to be temporarily thermal stability [4]. Moreover, the results often depend on several complicated conditions such as oxidation partial pressure, heating process, temperature, etc. In addition, the radiation treatment has been introduced for modifying gemstones. This treatment only affects the color in gems, caused by the color center mechanism, and thus, corundum is inappropriate for this treatment. Foregoing, a new standard and reliable technique for improving the corundum properties is still required.

Ion implantation can produce energetic ions bombarding the material and easily control the accurate factors such as ion species, ion current, ion direction, fluence, and time. This enhancement technique is one of the favorite methods for many applications such as doping semiconductor, modifying thin films, etc. The mechanical, chemical, electrical, and optical properties of the target materials can also be modified

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by this technique. It is well known that hundreds of keV ion can not only penetrate into a matter about a micron, but also transfer enormous of energy to the target. As a result, the charge state existence of element can be altered by these factors, and the enhancement is based on thermal spike causing the atomic translation and phase transformation in corundum. Then, this technique is an interesting method for enhancing the optical quality of corundum. In this aspect, there have been some researches about modification of ruby and sapphire using various ion beam techniques and conditions [5–7].

As for analytical technique, ultraviolet–visible spectroscopy or ultraviolet–visible spectrophotometry (UV–Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet–visible spectral region. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in which fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state [8]. UV–Vis absorption spectroscopy is a common technique to study the mechanisms of coloration caused by transition metal in gemstones [9].

In our study, we concentrated on applying basic principles of ion implantation to enhance the optical properties of corundum. The method appears to be new and sustainable for improving gemstones properties. The study on ion implantation technique was focused on the effects of ion types on a variety of corundum via the altering of the absorption phenomena of the sample. In this report, we would not only mention the positive effect, but also discourse on every detectable modification in corundum after ion implantation.

2. Experimental

Typically, small particles on the surfaces of all corundum including natural ruby and sapphire from various deposits were eliminated by dispersing with ethanol in an ultrasonic bath. If a significant number of calcium or silicon particles existed on any corundum surfaces, they were soaked in hydrofluoric acid for ~24 h. Then, an optical microscope was used for observing the samples and recording at 10× magnification. The specimens were measured for the absorption properties by using ultraviolet–visible–near-infrared (UV–Vis–NIR) spectroscopy.

Prior to treatment, the trace element compositions of corundum were analyzed by particle-induced X-ray emission (PIXE) technique with a 2-MeV proton beam generated from a Cs-sputter ion source using the 1.7 MV tandem accelerator system at Chiang Mai University [10]. During measurement, energetic proton beam collided and penetrated into corundum at a depth of ~15 μm (calculated by SRIM code [11]) and induced X-ray emissions. Each measurement was taken for approximately 10 min. Thereby, one could quantitatively analyze the trace elements in corundum by fitting curve with GUPIXWIN software

[12] and the trace element concentrations as parts per million (ppm) are reported in Table 1.

In case of ion implantation, the samples were treated in two main patterns including positive and negative ions. In the first pattern, we chose nitrogen and argon positive ions, using a 200 kV ion implanter, generated from a Freeman ion source. Then, the beam was deflected by a 90° electric-dipole magnet for classifying the required ions. The beam was scanned on both horizontal and vertical directions to be a rectangular cross section with 10 × 10 cm² size, followed by measuring the ion beam current at four corners to adjust the uniform beam distribution. Consequently, the remaining ion beam was collimated to a circular cross section at the target section. Each corundum sample was fixed on the carbon tape which was attached to the sample holder directly, avoiding being collided by ion beam. Subsequently, the holder was laid on the target system consisting of a hole of ~7 mm at the center for ion beam current measurement, normally about 3 μA for N₂-ion beam and 8 μA for Ar-ion beam, respectively. In the second pattern, we utilized 23-keV oxygen negative ions generated from a Cs-sputter ion source for negative ion implantation. The ion beam was not cut off, dissimilar to the first pattern. We developed the beam quality, focusing the beam at the horizontal–vertical directions, by using a steerer and an Einzel lens. A mass analyzing magnet sorted and purified the required ions. The ion beam was ~1 cm in diameter at the target chamber. Each sample was set similar to the first pattern, but the former holder was replaced by a flower-like holder. It has nine petals which could turn around to meet the beam line, but avoiding ion beam hitting the carbon tape. For ion beam current measurement, a Faraday cup with a 2-cm diameter was placed in front of the target system, which could lean out before ions bombardment, and the beam current was regularly about 10–20 μA.

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. All absorption measurements in this work were carried out at room temperature. It 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 [13]. Therefore, we have marked the position for taken UV–Vis spectra to ensure that the measurement results are not differed only because of non-uniformity in nature of the stone.

3. Results and discussion

Before ion implantation, raw samples were characterized by PIXE and reported in Table 1. For example, it was found that rubies from all deposits contained the fabulous of chromium which was related to the red appearance. The yellow sapphire from Montana, USA contained rich iron in the trivalent state causing the yellow color. The blue sapphire contained both iron and titanium to cooperate the blue color.

Table 1

The concentrations of Ti, V, Cr, Fe and Ga in each type of corundum, in parts per million (ppm) by weight as measured by PIXE technique.

Type of corundum	Trace elements concentrations (ppm)				
	Ti	V	Cr	Fe	Ga
(A)	221 ± 224	12 ± 12	90 ± 64	4629 ± 2654	98 ± 88
(B)	210 ± 165	22 ± 24	313 ± 208	11,288 ± 9330	63 ± 36
(C)	146 ± 70	22 ± 11	2220 ± 935	4510 ± 886	30 ± 16
(D)	372 ± 306	11 ± 7	78 ± 96	4119 ± 8311	50 ± 14
(E)	134 ± 111	18 ± 11	160 ± 178	6860 ± 3759	154 ± 70
(F)	449 ± 533	18 ± 16	29 ± 22	1230 ± 1051	69 ± 45

Note:

(A) refers to yellow sapphire from Montana, the USA.

(B) refers to dark-blue sapphire from Pailin, Cambodia.

(C) refers to ruby from Bo rai, Thailand.

(D) refers to blue sapphire from Sri Lanka.

(E) refers to blue green sapphire from Bang Kacha, Thailand.

(F) refers to pale blue sapphire from Sri Lanka.

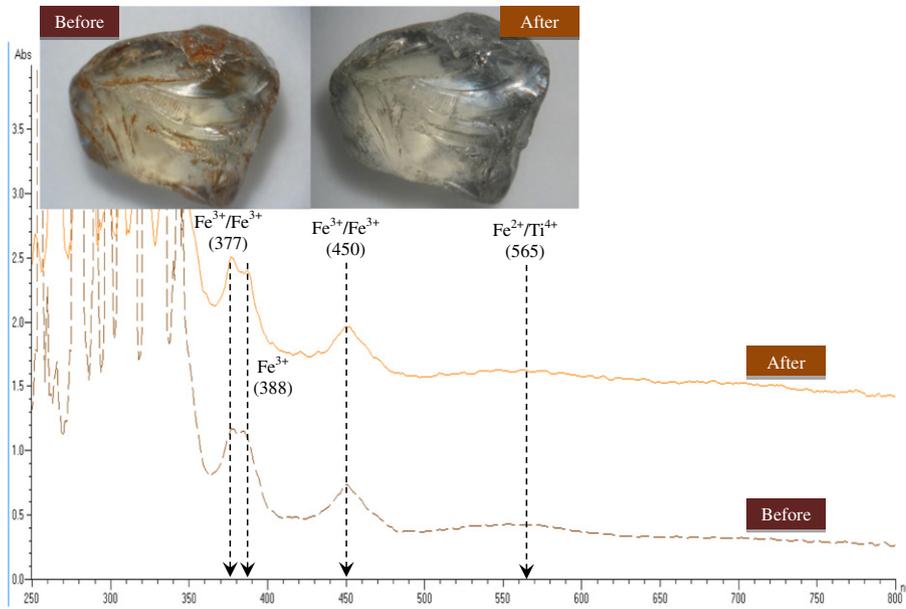


Fig. 1. Optical microscope images of yellow sapphire from Montana (U.S.A.) for before and after ion implantation by a 70 keV N_2^+ to a fluence $\sim 5 \times 10^{17}$ ions/cm² and their UV-Vis spectra.

Moreover, the dull white sapphire did not show any significant amount of the transition element concentration.

We observed several alterations in corundum, mainly by optical microscopic recording, after ion implantation. The results are shown as below.

3.1. Nitrogen ion implantation

A variety of rubies and sapphires were treated by 70 keV N_2^+ beams. As N_2 gas is the main content in the air, the environment at the sample surface during implantation became N-rich, or, in other word, was discrimination of oxygen. This circumstance was known as “reducing” in heat treatment method, in such case the coloration element reduced the charge state such as iron (from Fe^{3+} to Fe^{2+}). For example, the UV-Vis-NIR absorption spectrum was altered with the pair of

Fe^{3+}/Fe^{3+} peak centered at 450 nm decreased dramatically after heat treatment [14]. As for ion implantation, one interesting example observed in yellow sapphire, Fig. 1 showed that the original yellow color was altered to blue-green after ion implantation. Another example is that the color of the blue sapphire from Cambodia became intensely deeper blue as seen in Fig. 2. In both cases, the overall absorption spectra were rising, implying that the samples were darker. However, their peak intensities did not change significantly.

3.2. Oxygen ion implantation

This treatment condition resembled the oxidizing condition in the traditional heat treatment. In this case, we used the O^- with high electron affinity in the general atmosphere. Vast kinetic energy of ions was enough for attracting the divalent electrons from the positive

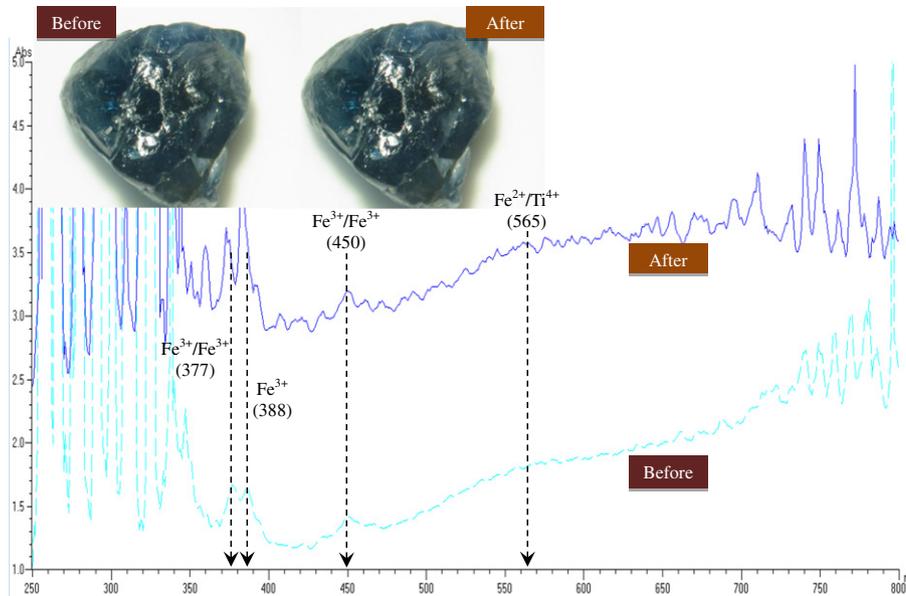


Fig. 2. Optical microscope images of blue sapphire from Cambodia for before and after ion implantation by a 70 keV N_2^+ to a fluence $\sim 5 \times 10^{17}$ ions/cm² and their UV-Vis spectra.

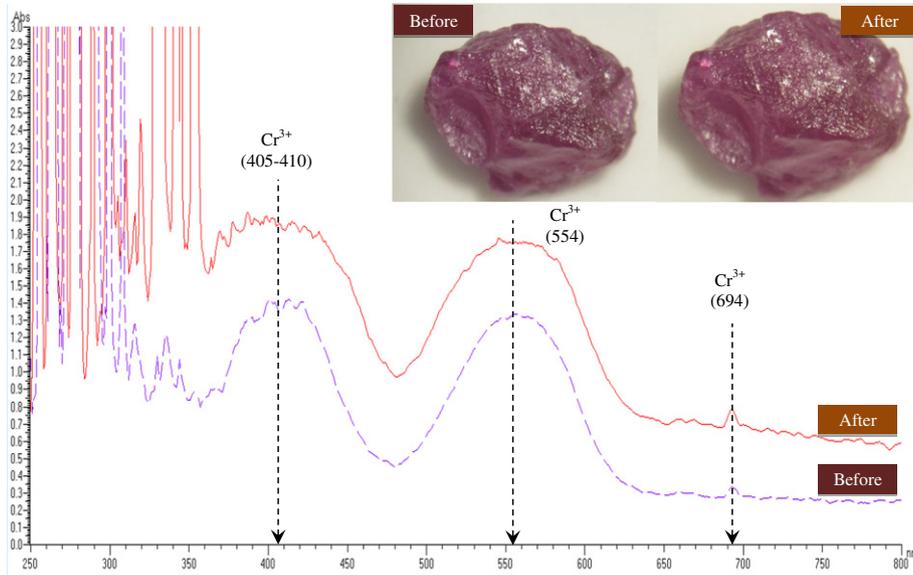


Fig. 3. Optical microscope images of ruby from Bo Rai (Thailand) for before and after ion implantation by a 23 keV O^- to a fluence $\sim 5 \times 10^{17}$ ions/cm² and their UV-Vis spectra.

transition ions in the matter with the charge state of +2. The interesting result, occurring in ruby from Bo Rai, Thailand, was that the Cr^{3+} -dominant concentration corundum modified the reddish saturation, and thus became more vivid as shown in Fig. 3. We observed the same modification for pink sapphire that the pale violet tint, a combination of more red and less blue, was enhanced by the oxidizing of iron. As the titanium concentration was slightly low, the Fe^{2+} could not solely produce the significant color and the Fe^{3+} maintained producing yellow nearby the reddish tone, and therefore the reddish tone appeared dominantly. In other words, the combination of red color and blue color produced purple tint. If the blue color was reduced, the red color became dominant ultimately. The UV-Vis-NIR spectroscopy showed the same trend that the absorption peaks of Cr^{3+} became overshadowed. Fig. 4 shows that the brownish tint and pale blue of blue sapphire from Sri Lanka became intensively blue and less brownish tint, as a result that the yellow-color-related Fe^{3+} was enhanced. The UV-Vis spectroscopy

illustrates that the blue region is less transmission after implantation, indicating the deep blue tone of the sapphire.

3.3. Argon ion implantation

The third condition selected for this investigation is using positive argon ion (Ar^+) beam. Both N_2^+ and Ar^+ have very good performance to capture the electrons because their valence electron configurations have partial space. We achieved significant alteration of clarity from Ar^+ beam treatment. As seen in Figs. 5 and 6, the clarity of blue-green sapphire and pale blue sapphire was modified. We believe that it is because of the decomposing of the non-chromophoric element or inclusions due to Ar^+ implantation. In our experiment, we used atomic Ar^+ and molecular N-ions at the same energy for ion implantation. As well known, in the case of molecular ion species, the molecular ion, N_2^+ in this case, will be broken to be atomic ions, N^+ , when hit the sample

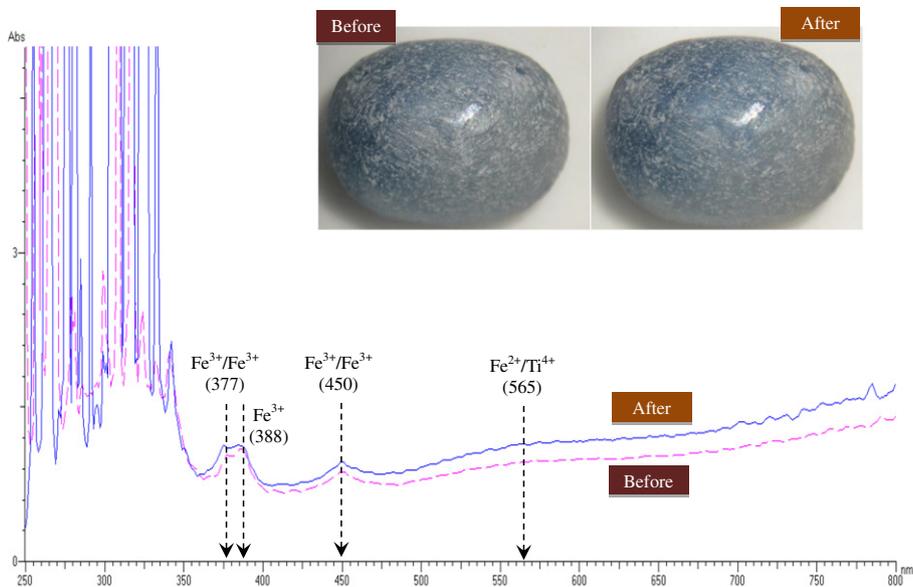


Fig. 4. Optical microscope images of blue sapphire from Sri Lanka for before and after ion implantation by a 23 keV O^- to a fluence $\sim 5 \times 10^{17}$ ions/cm² ion and their UV-Vis spectra.

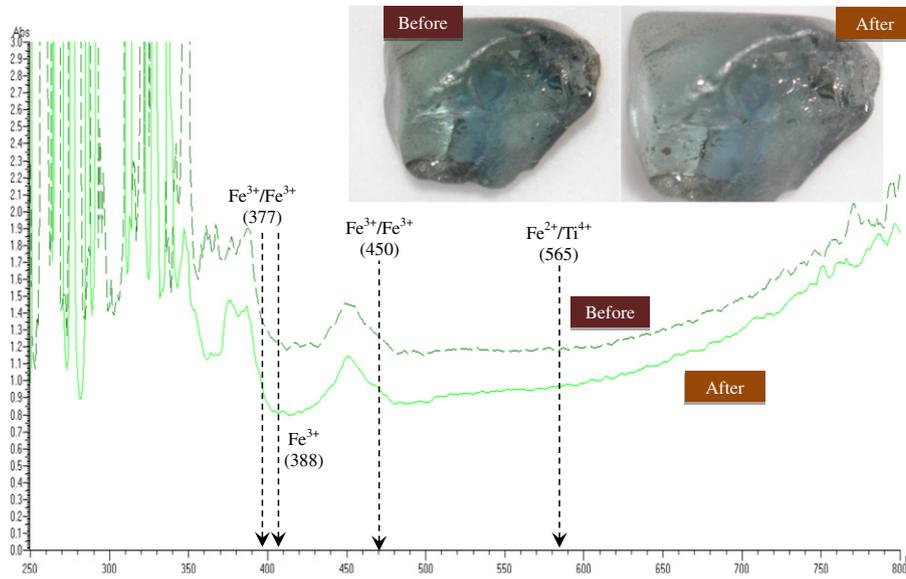


Fig. 5. Optical microscope images of blue-green sapphire from Bang Kacha, Thailand for before and after ion implantation by a 70 keV Ar^+ to a fluence $\sim 5 \times 10^{17}$ ions/cm² and their UV-Vis spectra.

surface and energy will be divided to half for each of them. As a result of Ar having higher mass than N, the momentum of Ar^+ was nearly twice that of N^+ when they have the same energy, meaning a more interaction probability. Therefore, this implies that the opportunity to modify the clarity in corundum by Ar^+ implantation could be increased dramatically with higher momentum. Localized atoms in the target could also be removed by ion implantation, subsequently, permitting the intensely external light to transmit through the gems. In addition, as Ar^+ has higher sputtering yield than N^+ , the treated corundum by Ar^+ exhibited more clarity than that treated by N_2^+ . The less absorption of samples after Ar^+ implantation, as seen from UV-Vis-NIR measurements, confirms this postulation. The coloration altering in the case of Ar^+ implantation was similar to that of nitrogen ion implantation, but Ar^+ implantation was less significant in color changing compared to N_2^+ implantation, probably due to the non-reactive nature of Ar.

3.4. Discussions

There are a few investigations on quality improvement of corundum by ion implantations [14–16]. High current (μA) energetic heavy ions can penetrate into micron-thick layer of corundum and transfer kinetic energy via atomic collision for crystalline rearrangement. Ion implantation is a non-equilibrium process in oxide crystal materials. Radiation-induced damage in oxide crystal can occur as a result of displacement, collisions or ionization, followed by defects formation. Some properties of oxide crystal such as electrical and optical properties are correlated with the defects formed in it. Particularly, changes of optical properties are affected by point defects (color centers). The factors - energy, time, ion beam direction, temperatures and ion species - are influential to efficiency of irradiation to corundum [17].

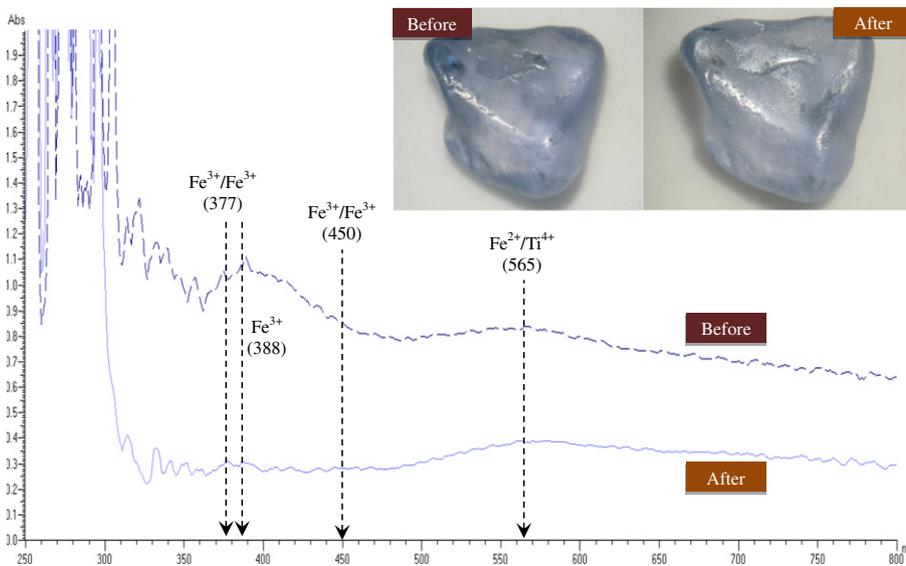


Fig. 6. Optical microscope images of pale blue sapphire from Sri Lanka for before and after ion implantation by 70 keV Ar^+ to a fluence $\sim 5 \times 10^{17}$ ions/cm² and their UV-Vis spectra.

Another interesting effect is that inclusions gradually diffused to the material bulk to make up the sample with more clarity. This process was developed by the kinetic energy transfer from the energetic ions to the loosely bound part of the bulk during bombardment. In addition, ion implantation, or ion bombardment, gave the samples with the smooth surface by sputtering of the rough surface and filling out the cracks, fractures or cavities on the surface region [18]. Therefore, we could observe the sample becoming more clear and vivid.

As for UV–Vis spectroscopy, it may not be sensitive to account the surface phenomena. Therefore, it is not possible to decipher explicitly the cause of color change due to ion implantation by only using these absorption spectra.

4. Conclusions

Ion implantation was very powerful for the low-quality corundum enhancement. The energetic ions could strongly interact with the localized impurity, resulting in clarity enhancement. The other significant effect was the charge state alteration, reduction or oxidation, controlled by the oxygen partial concentration of the environment. The reducing condition was very useful for blue color intensification in blue sapphire or changing the yellow tone to the greenish tone. As Fe^{2+} was produced, it was more likely to incorporate with Ti^{4+} for creating blue color. Some less useful modifications were also found such as ruby becoming more violet tint. The oxidizing condition affected the ruby and the reddish tone sapphire making them less violet tint but more reddish tone. Moreover, the vivid yellow could be enhanced by the enriched oxidizing iron (Fe^{3+}). This process could be applied to lighten the dark tone of blue sapphire for increasing its market value. For the higher ion momentum case, the energetic ions could transfer the kinetic energy to the impurity and dissolve the impurity including inclusion, fissure, cavity, etc. into the bulk corundum. Eventually, light could further pass through the corundum, resulting in more clarity. Thus, our experiment demonstrates that the optical properties of corundum can be controlled by adjusting the ion beam treatment condition. Therefore, the value of modified corundum can be increased by using the proper method.

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