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Gemological modification of local natural gemstones by ion beams

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ABSTRACT

Ion implantation was applied as an effective method to gemological modification of Thai local natural corundum including sapphire and ruby for enhancement of the essential qualities of the gemstones. Oxygen and nitrogen ions at medium and low energies to various fluences were implanted to the natural gemstones. The heavy ion irradiation modifies the color to desirable colors and improves the color distribution, transmission and lustre. These modifications lead to the improvement of quality of gemstones and thus the market value. Possible mechanisms of these modifications have been proposed. The main cause for these modifications could be the changes in oxidation states of impurity metals, induction of charge transfer from one metal cation to other and the production of color centres.

1. Introduction

Ion beam technology has been extended to the application on gemology. Heat treatment is the most popular technique commercially used for the improvement of quality of gemstones [1]. Heat treatment mainly [2,3] modifies color, unifies inclusions, increases transmittance and improves luster. However, heat treatment is expensive and is not an efficient process to bring about desirable changes in the properties of gem stones. For example, it involves annealing at 1000 °C and above for periods ranging from few hours to few days depending on the type of gemstones. Different types of gemstones cannot be treated simultaneously. Alternative treatments are exposing the gemstones to energetic particle beams and laser beams. Laser beams do not produce localized heating, whereas low mass particles such as electrons produce localized but yield poor coloration. Neutron irradiation makes gemstones radioactive. 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 [4], as well as treat individually different gems. In the past ion implantation on sapphires has been investigated from the point of view of improving their optical and mechanical properties [5–10] for the application on optics, optoelectronics, photonics and tooling [11,12]. Many studies have dealt with understanding basic and applied aspects of ion beam modifications of sapphire but not many have focussed on developing industry-ready technology. The present work aims at developing heavy ion beam irradiation process for enhancing the quality of gemstones and thus increasing their market values. The quality and beauty [1] of gem stones are determined using the established grading system followed by gemologists [13].

2. Experiments

2.1. Gem materials

Gem materials were corundums coming from local occurrences of Thailand (Siam) and Myanmar (Burma). The typical chemical compositions of the gemstones have been published in many literatures (e.g. [1]), nevertheless, we used in-house X-ray Fluorescence (XRF) and Particle Induced X-ray Emission (PIXE) to analyze the gems [14] (Fig. 1). The analysis showed that the corundums were mainly composed of Fe, Cr, Ti and Ga with traces of V, Hf, As, Se and Br; the quantities of the major coloring elements such as Fe in blue sapphire and Cr in red ruby were determined to be in the ranges of 0.02–1.62% and 0.14–2.26%, respectively. 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.

2.2. Ion implantation

Ion implantation was carried out using various ion beam facilities at Chiang Mai University, including a 150-kV mass-analyzed heavy ion implanter [15], a 150-kV non-mass-analyzed high-current N-ion implanter [16], and a 20-kV multicusp high-intensity plasma source ion implanter [17]. The target holders were designed with special considerations, aiming at avoiding sputtering contamination on the

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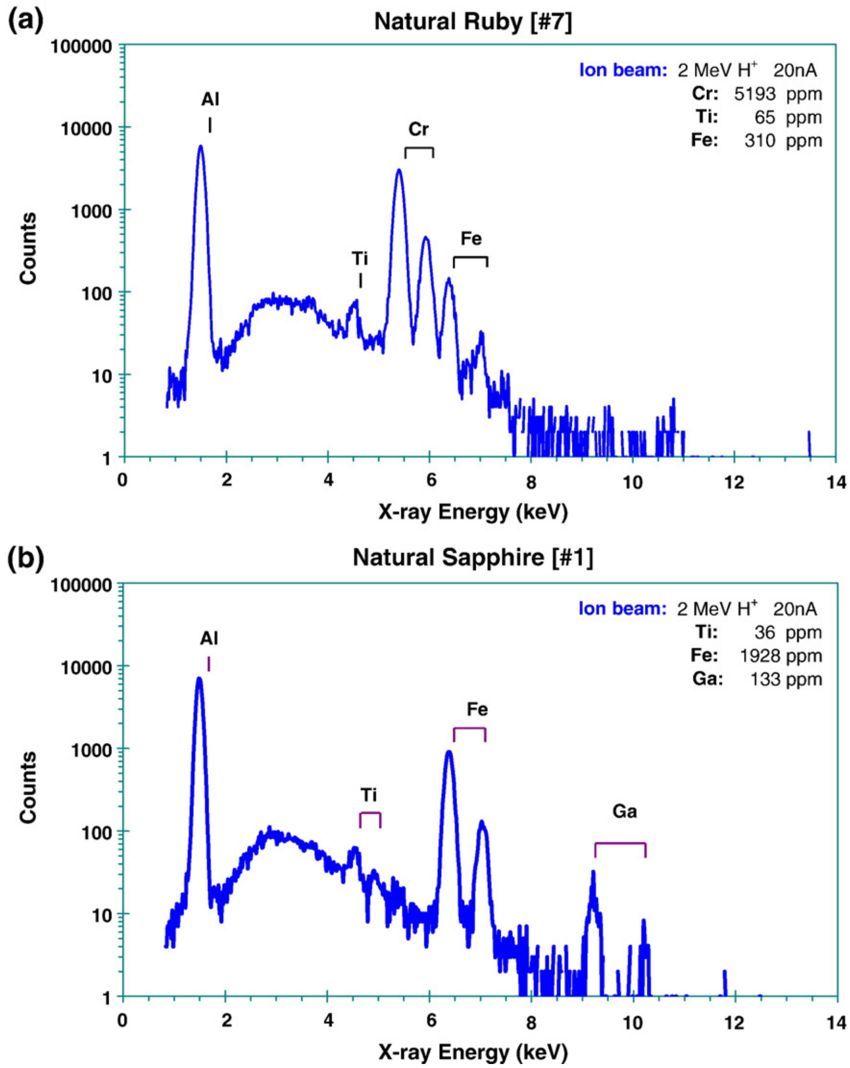

Fig. 1. PIXE spectra of Thai local natural (a) ruby and (b) sapphire.

gem surface as much as possible. The holders were made from ceramics, instead of metal, in a two- or three-needle structure, which was able to fix regularly or irregularly shaped specimens, for reducing the contacting areas between the holder and the gems. Oxygen and nitrogen ions at 120 keV, 60 keV or 20 keV were implanted to the gem specimens with beam currents of 0.1 to a few mA to fluences ranging from 10^{18} to a few 10^{19} ions/cm^2. The operating pressures in the target chambers were about 10^{-3}–10^{-4} Pa. The target temperatures during ion implantation were measured using an infrared thermometer to be stabilized at about 200–600 °C, depending on the size of the specimen and the ion implantation conditions. No post treatments were deliberately done on the ion-implanted gems.

2.3. Judgments

The ion beam-treated specimens were observed under either gemologist-professional binocular microscopes (Zeiss, Germany) or directly the natural lights. The grades of the gemstones were judged by authorized gemological professionals [18].

3. Results and discussion

Here we present selected examples of the results from many experiments in our laboratory. Fig. 2 shows a comparison on the appearance between the ion-implanted and unimplanted natural ruby. The specimen was implanted with 120-keV atomic O-ions with a current 100 μA to a fluence of about 2×10^{18} ions/cm^2. The virgin gem with the original color of red + purple has shown less blue and more pure red color after implantation. The clarity and luster have also been improved. Fig. 3 shows a comparison between the implanted and unimplanted natural blue sapphire. The gem was implanted with atomic N-ions in the same conditions as above. The original color in blue + green of the virgin gem has turned to be in more pure blue and less green after ion implantation. Fig. 4 shows a comparison between the implanted and unimplanted natural yellow sapphire. The gem treated by oxygen plasma ion implantation under the conditions of 20 kV, a few mA and 3×10^{19} ions/cm^2 has shown more yellow at its one end and colorless at the center.

The causes of color in gemstones can be many (about 16) [1,2,18,19]. Among them, transition metal impurities, charge transfer, color centers, and defect electrons may mostly are related to the effects of ion implantation. Ion implantation can introduce metal impurity ions into the gems. Various metallic elements at certain oxidation states give rise to different colors in different gems. For example, Cr^{3+} (<1%) in ruby colors red, $Fe^{2+} + Ti^{4+}$ in ruby blue, Fe^{3+} in sapphire yellow, Fe^{2+} in sapphire blue, $Fe^{3+} + Ti^{3+}$ in sapphire blue, etc. However, in our application, gaseous nonmetal ions (oxygen and nitrogen) were implanted, and thus the mechanism of charge

(a)
(b)

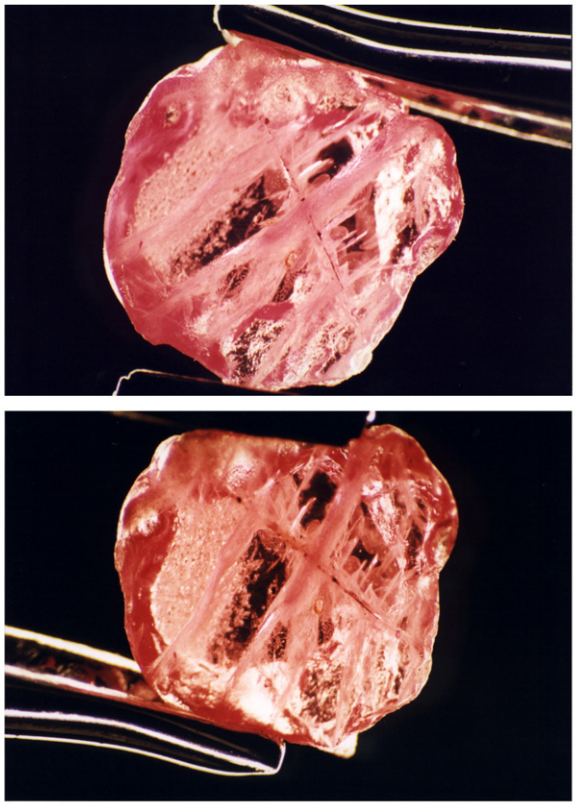

Fig. 2. Natural ruby. (a) Unimplanted, and (b) implanted with 120-keV atomic O-ions with a current 100 μA to a fluence of about 2×10^{18} ions/cm^2.

(a)
(b)

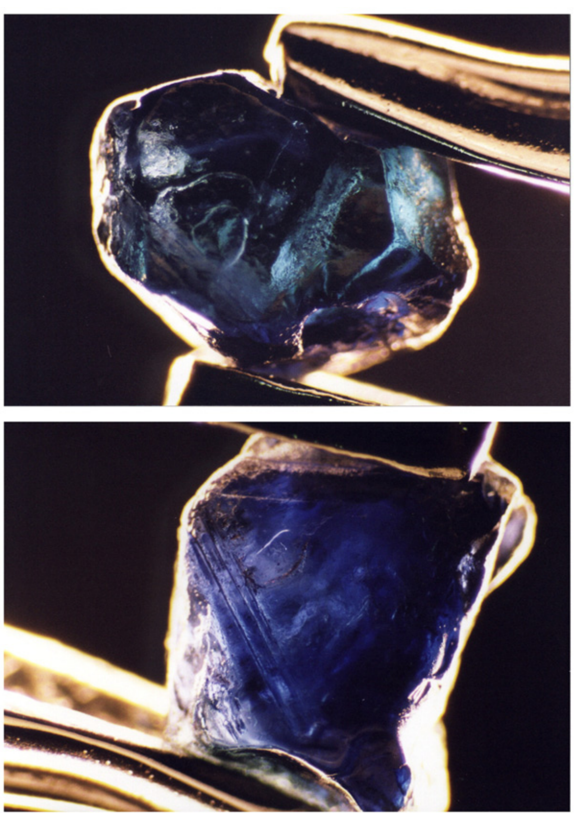

Fig. 3. Natural blue sapphire. (a) Unimplanted, and (b) implanted with 120-keV atomic N-ions with a current 100 μA to a fluence of about 2×10^{18} ions/cm^2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(a)
(b)

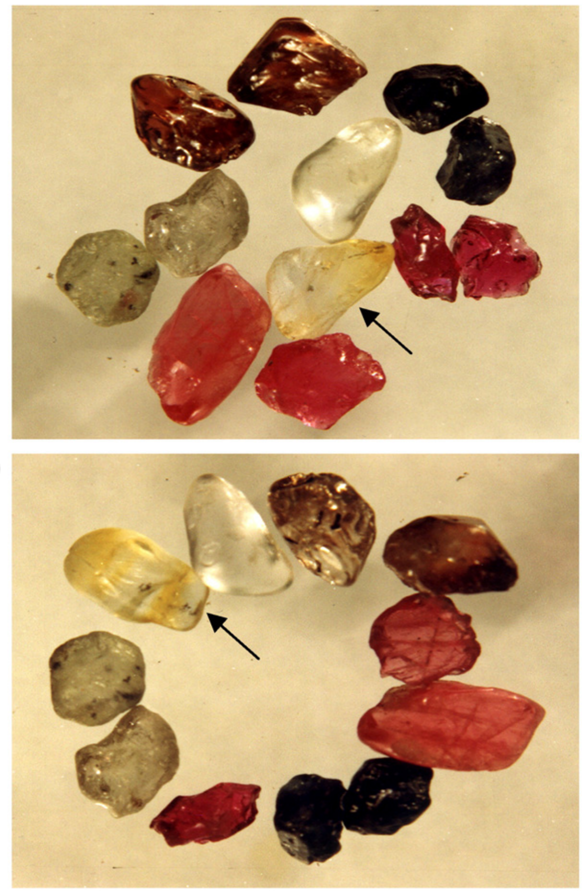

Fig. 4. Natural yellow sapphire (as pointed by the arrows). (a) Virgin, and (b) treated by oxygen plasma ion implantation using a voltage of 20 kV, current of a few mA and fluence of 3×10^{19} ions/cm^2. Other stones are only for color contrast. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

transfer might be involved. There are two cases. In the case of O-ion implantation, introduction of oxygen leads to oxidation processes, such as [20]

$$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-},$$

$$\text{or } 4FeO + O_2 \rightarrow 2Fe_2O_3,$$

$$\text{or } 2Al_{2-2x}Fe_{2x}O_{3-x} + xO_2 \rightarrow 2Al_{2-2x}Fe_{2x}O_3.$$

Both the above processes result in an electrically neutral state containing only Fe^{3+} in corundum; the result now corresponds to Fe_2O_3 present in Al_2O_3, having a pale-to-medium yellow color, depending on the concentration [20]. Therefore, original color of red + purple coming from Cr^{3+} (showing red) and $Fe^{2+} + Ti^{4+}$ (showing blue) after ion implantation turned less blue and pure red [21]. In the case of N-ion implantation, there are two possibilities, namely intervalence charge transfer (IVCT) and color center formation. Compared with oxygen, nitrogen is non-reactive [22] and thus ion energy deposition effect is more dominant. The ion energy deposited can 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) → Fe^{3+} (in cation site 1) + Fe^{2+} (in cation site 2). The color change in the case of N-ion implantation of sapphire is probably attributed to the reversed IVCT of $Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+}$ [23], hence more Fe^{2+} contributes blue while less Fe^{3+} reduces green. N-ion implantation can produce another

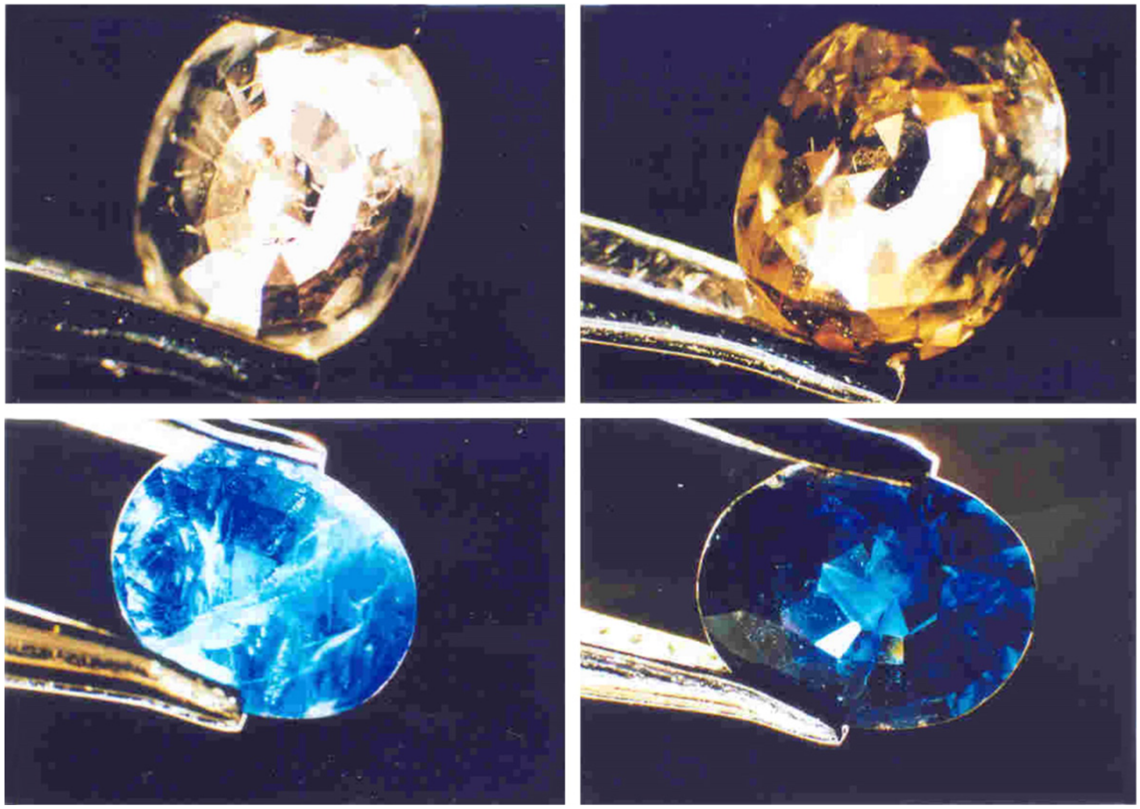

Fig. 5. Cut sapphires with either yellow (up) or blue (down) toning implanted with high-current (a few mA) 20-keV O-ions to a fluence of about 5×10^{19} ions/cm^2 (right), compared with the virgins (left). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

effect in terms of the N-ion knocking out the O atom from its site in Al_2O_3 to form a color center, which is associated with certain absorption bands [24], thus the color is changed. We have found that the role in changing color played by N-ion implantation in sapphire is unique and O-ion implantation plays no effect on changing color in sapphire. This fact supports the color-center contribution. The yellow color in sapphire comes from not only Fe^{3+} but also the vacancy or interstitial electrons [2]. When high-fluence ions were implanted, the implanted ions might fill the vacancies thus reduce the yellow color. For the third example mentioned above (Fig. 4), since the central area received a higher fluence of the ions due to a Gaussian-like distribution of the beam profile, it then became more colorless.

Besides changing colors, ion implantation has other useful effects on optical qualities of the gems. Fig. 5 shows two examples of the ion implantation effect on color toning. The sapphires with either yellow or blue toning were implanted with high-current (a few mA) 20-keV O-ions to a fluence of 5×10^{19} ions/cm^2. The color tones have been greatly increased. Fig. 6 shows that the sapphire implanted with 120-

(a)
(b)

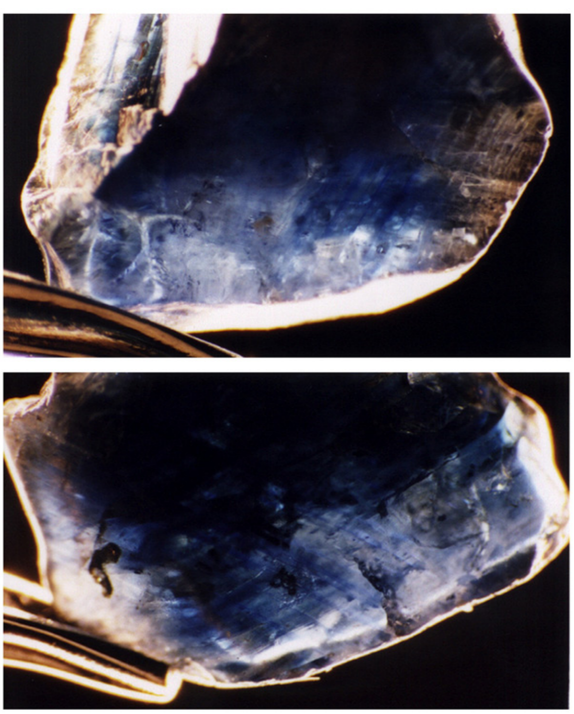

Fig. 6. Natural sapphire. (a) Virgin, and (b) implanted with 120-keV mixed (atomic and molecular) nitrogen ions at a current of 0.4 mA to a fluence of about 1×10^{19} ions/cm^2 (right). The higher transmittance can be seen at the edge of the ion-implanted gem (actually the whole gem exhibits the higher transmittance, but at the thicker parts the phenomenon cannot be displayed).

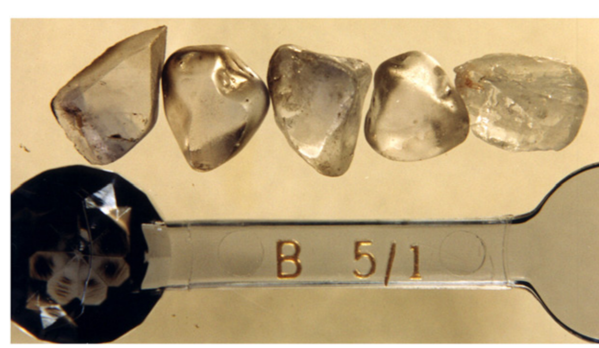

Fig. 7. An example of the ion-fluence dependent glittering of the blue sapphire treated by the 120-keV mixed N-ion beams with the current of 0.4 mA to the fluences of 2, 4, 6, 8×10^{18} ions/cm^2. The specimens are arrayed from the left to right in the direction of increasing of the ion fluence (the most left one is virgin). A gemological grading tool of Grade B 5/1 is shown at the lower part of the photograph, used to grade the gemstones.

Table 1
Examples of grading of the gemstones.

Gem sample	Treatment	Color	Tone	Saturate
Ruby	Unimplanted	stpR	4	4
	O-ion implanted	oR	4	4
White sapphire	Unimplanted	Colorless	–	–
	O-ion implanted	B	4	4
Blue sapphire	Unimplanted	B	4	7
	N-ion implanted	bV	4	8
White sapphire	Unimplanted	B	1	3
	O-ion implanted	B	2	4
Blue sapphire	Unimplanted	B	4	7
	N-ion implanted	vB	4	7
White sapphire	Unimplanted	Colorless	–	–
	O-ion implanted	Y	2	2
Green sapphire	Unimplanted	G	1	5
	O-ion implanted	bG	3	7
Zircon	Unimplanted	yO	3	3
	O-ion implanted	oY	3	3

The grading letters of color indicate the color; the larger grading number of tone, the stronger the color tone; the larger grading number of saturate, the more the color saturated. In the color grading, stp: strongly purplish, R: red, B: blue, V: violet, Y: yellow, G: green, O: orange; the capital letter indicates the major color, while the small letter indicates the minor color.

keV mixed (atomic and molecular) nitrogen ions at a current of 0.4 mA to a fluence of 1×10^{19} ions/cm^2 has obtained a more homogeneous color distribution and a higher transmittance (as seen at the edge). Fig. 7 shows the ion-fluence dependent glittering of the blue sapphire treated by the 120-keV mixed N-ion beams with the current of 0.4 mA to the fluences of 2, 4, 6, 8×10^{18} ions/cm^2. It is seen that the glittering and brilliance of the sapphire are improved as increasing of the fluence. Additionally, a focused ion beam could cure a color flaw on the gemstone to be perfect (result not shown).

Table 1 lists examples of gemological grading of the ion beam-treated gemstones together with those untreated. The color has been graded to be changed in most of the cases, particularly those colorless becoming colored. The tone (or the color strength) and the saturation (or the color plentifulness) have been found to be more favorable (the tone is evaluated only for the same color). It has been known that, in some cases, a modest 5% increase in the overall appearance of rubies after heating will result in a 25% or more price increase [2]. Therefore, it has no doubt that ion implantation brings the corresponding increases in benefits to the treated gemstones. We should also point out that experimentally no residual radioactivity has been detected from the ion-implanted corundum and the appearance improvements have remained fairly stable. Compared with the heat treatment, the cost of ion implantation is competently lower, thanks to its considerable shorter treatment time, about 1/10 to 1/100 of that of heat treatment, without high-temperature heating and its secure equipment.

4. Conclusion

We have developed application of ion implantation on gemological modification of gemstones for enhancement of the gem qualities. Inexpensive ion implantation using gaseous ion species, such as oxygen and nitrogen, has been carried out to serve as the cause of improvement of color features for local corundum including ruby and sapphire. It has proved that the qualities of the corundum treated by ion implantation have been indeed upgraded.

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