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Analysis and modification of blue sapphires from Rwanda by ion beam techniques

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ABSTRACT

Blue sapphire is categorised in a corundum (Al_2O_3) group. The gems of this group are always amazed by their beauties and thus having high value. In this study, blue sapphires from Rwanda, recently came to Thai gemstone industry, are chosen for investigations. On one hand, we have applied Particle Induced X-ray Emission (PIXE), which is a highly sensitive and precise analytical technique that can be used to identify and quantify trace elements, for chemical analysis of the sapphires. Here we have found that the major element of blue sapphires from Rwanda is Al with trace elements such as Fe, Ti, Cr, Ga and Mg as are commonly found in normal blue sapphire. On the other hand, we have applied low and medium ion implantations for color improvement of the sapphire. It seems that a high amount of energy transferring during cascade collisions have altered the gems properties. We have clearly seen that the blue color of the sapphires have been intensified after nitrogen ion bombardment. In addition, the gems were also having more transparent and luster. The UV–Vis–NIR measurement detected the modification of their absorption properties, implying of the blue color increasing. Here the mechanism of these modifications is postulated and reported. In any point of view, the bombardment by using nitrogen ion beam is a promising technique for quality improvement of the blue sapphire from Rwanda.

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 aluminum oxide (Al_2O_3). It is naturally clear, but can have different colors when different chemical types of impurities are present. The red variety of corundum is known as ruby, all the other colors of corundum are known as sapphires. Although new occurrences of natural gemstones are found from time to time in many parts of the world, these localities combined with historically important gem deposits have not always provided the best quality material in sufficient amounts to meet the current demand for gemstones among consumers. Besides the relatively small amount of high quality gem material typically produced at a given mining locality, there is also recovered a much larger percentage of lower quality material that has little market value. Therefore, individuals continue to strive to develop methods to treat this lower-quality material in the laboratory to enhance its appearance and thereby its marketability for gem purposes.

Heat treatment is the most popular technique commercially used for the improvement of quality of gemstones [1]. Heat treatment mainly modifies color, unifies inclusions, increases transmittance and improves luster [2]. However, heat treatment is expensive, difficult to control, 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 [3], as well as treat individually different gems. In the past ion implantation

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on sapphires has been investigated from the point of view of improving their optical and mechanical properties [4–9] for the application on optics, optoelectronics, photonics and tooling [10,11]. 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. We have reported recently that ion beam irradiation has potentials to enhance several gems in corundum family [12].

Blue sapphire deposits is widely distributed in a variety of geologic conditions, allowing gem-quality stones to be unearthed in greater amounts and in significantly greater sizes than the other members of the corundum family. The blue color of sapphire may be found in many evocative shades, ranging from the soft pastel of cerulean to richly saturated indigos. The origin of a gemstone can have a profound impact on its market value. In the case of blue sapphires, the most highly reputed and valued stones are the sapphire from Kashmir and Sri Lanka. Top-quality sapphires from these sources typically achieve the highest per-carat price at auction [13]. Recently, a small amount of blue sapphire from Rwanda came to Thailand by the Thai merchants. The color quality of them seems to below the high grade blue sapphire. The present work, therefore, aims at documenting the fingerprint base on ion beam analysis technique and developing heavy ion beam irradiation process for enhancing the quality of blue sapphire from Rwanda and thus increasing their market values.

2. Experimental details

2.1. Gem materials

The blue sapphires from Rwanda for about 100 samples were selected for the present study. 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 beam analysis

In the study, the elemental compositions of the gemstones samples were analyzed using PIXE based on a 2-MeV proton beam produced by a 1.7 MV tandem Tandetron accelerator at the Plasma and Beam Physics Research Facility of Chiang Mai University, Thailand. The proton beam was collimated to a diameter of ~1 mm, and the beam current on the sample was 10 nA. The X-rays were detected by a Si(Li) detector. A 74-μm mylar foil with 0.38% relative hole area was placed in front of the detector as an absorber in order to reduce the count rate caused by impurities of low atomic numbers. Base pressure in the vacuum chamber was $\sim 6 \times 10^{-6}$ mbar. Quantitative analysis of PIXE spectra, the elemental composition ($Z \geqslant 13$) in the samples, was achieved using the GUPIXWIN code [14]. The quantitative calibration included the normalization at $(100\% - x)$ of the oxide sum, while the value of x is a sum of Na_2O and MgO determined by EDS.

2.3. Ion implantation

Ion implantation was carried out using a self-constructed compact ion implanter [15]. The target holders were designed with special considerations, aiming at avoiding sputtering contamination on the gem surface as much as possible. Nitrogen ions at 70 keV were implanted to the gem specimens with beam currents of a few mA to a fluence of $\sim 1 \times 10^{18}$ ions/cm^2. The operating pressures in the target chambers were $\sim 10^{-5}$–10^{-6} Torr. The target temperatures during ion implantation were measured using an infrared thermometer to be stabilized below 200 °C. No post treatments were deliberately done on the ion-implanted gems.

2.4. Justification

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 [16]. Blue sapphires are evaluated based on the purity of their primary hue. Purple, violet, and green are the most common secondary hues found in blue sapphires [17]. Violet and purple can contribute to the overall beauty of the color, while green is considered to be distinctly negative. Gray is the normal saturation modifier or mask found in blue sapphires. Gray reduces the saturation or brightness of the hue and therefore, has a distinctly negative effect [17]. The color of fine blue sapphires may be described as a vivid medium dark violet to purplish blue where the primary blue hue is at least 85% and the secondary hue no more than 15%, without the least admixture of a green secondary hue or a gray mask [17].

3. Results and discussions

3.1. Color grading

Color in gemstones breaks down into three components: hue, saturation, and tone. “Hue” is most commonly understood as the color of the gemstone. “Saturation” refers to the vividness or brightness of the “hue”, and “tone” is the lightness to darkness of the “hue” [17]. In order to investigate the color characteristics of the blue sapphire from Rwanda, the Gem Dialogue system [18] is used for describing and grading the blue sapphire samples. We observe that Rwanda sapphire exists in various mixtures of its primary (blue) and secondary hues, various tonal levels (shades) and at various levels of saturation (vividness). Their hue are found for example, B = blue, bV = bluish violet, bP = bluish Purple, vB = violetish Blue, V = Violet, rP = reddish Purple, PR/RP = Red-Purple or Purple and vstgB = very strongly greenish Blue. Table 1 shows some examples.

3.2. Ion beam analysis

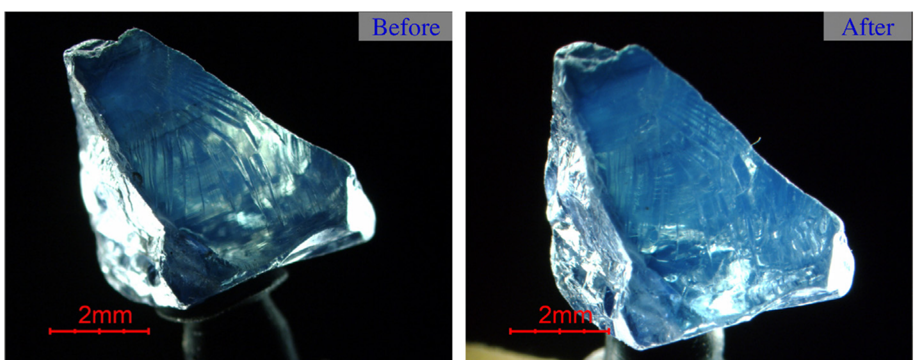
In our experiment, about 100 samples of blue sapphire from Rwanda were selected to measure their chemical compositions by PIXE. The analysis showed that the sapphires were mainly composed of Fe, Cr, Ti and Ga with traces of V, Ca, Mn, Ni and Si. The quantities of the major coloring elements such as Fe, Ti, Cr, V, and Ga in the sapphire were determined to be in the ranges of 0.088–15.352 wt% for Fe, 0.002–0.065 wt% for Ti, 0.001–6.700 wt% for Cr, <0.003 wt% for V and <0.036 wt% for Ga. The literature reported that [19] the blue color of the sapphire sample changes to darker as the contents of total Fe and Ti increase. The blue color of the sapphire sample is more pure as the content of total Fe is 0.02–0.75%, the content of Ti is 0.006–0.040% and the content ratio of total Fe to Ti is 10–30. When more than these ranges, the color of the sapphire sample is usually green or purple hue. We calculated our results and found that the ratio of total Fe to Ti is above 30. This estimation indicates that the blue color of sapphire from Rwanda is not deep enough, requiring the color enhancement treatment.

3.3. Ion beam induce color change

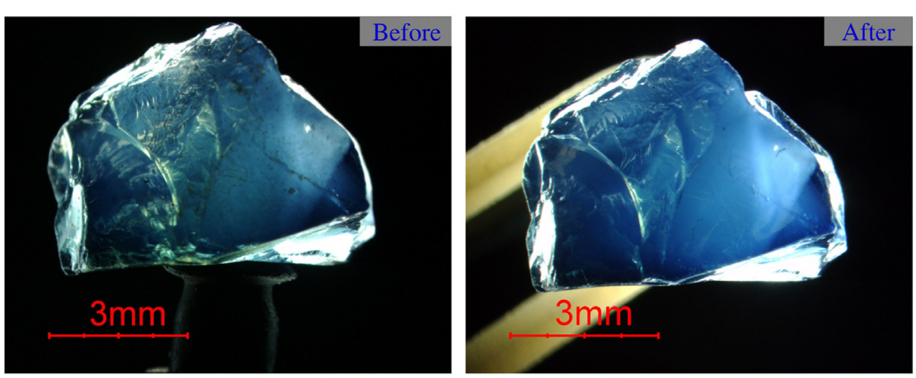
Since we have already found that nitrogen ions have potential to enhance color quality of corundum, especially for blue sapphire [13]. Therefore, N-ion implantation was carried out for the blue sapphires from Rwanda. We enthusiastically notice that optical properties of sapphires were modified by ion implantation. The

Table 1
Selected example of blue sapphire from Rwanda and their color altering by N-ion implantation at 70 keV to a fluence of $\sim 1 \times 10^{18}$ ions/cm^2.

Sample	Before ion implantation				After ion implantation			
	Color	Hue	Tone	Saturation	Color	Hue	Tone	Saturation
A1	bV 8/3	Bluish violet	Very dark	Very slightly grayish	bP 7/4	Bluish purple	Dark	Moderately strong
A2	bV 8/3	Bluish violet	Very dark	Very slightly grayish	bP 7/4	Bluish purple	Dark	Moderately strong
B1	B 7/4	Blue	Dark	Moderately strong	B 8/3	Blue	Very dark	Very slightly grayish
B2	bP 6/5	Bluish purple	Medium dark	Strong	bP 7/4	Bluish purple	Dark	Moderately strong
C1	bP 6/3	Bluish purple	Medium dark	Very slightly grayish	bP 7/4	Bluish purple	Dark	Moderately strong
C2	bP 6/3	Bluish purple	Medium dark	Very slightly grayish	bP 7/4	Bluish purple	Dark	Moderately strong
D1	bP 6/3	Bluish purple	Medium dark	Very slightly grayish	bP 7/4	Bluish purple	Dark	Moderately strong
D2	bp 6/3	Bluish purple	Medium dark	Very slightly grayish	bP 7/4	Bluish purple	Dark	Moderately strong
E1	B 5/3	Blue	Medium	Very slightly grayish	B 8/3	Blue	Very dark	Very slightly grayish
E2	B 5/4	Blue	Medium	Moderately strong	B 8/3	Blue	Very dark	Very slightly grayish
F1	B 6/2	Blue	Medium dark	Slightly grayish	B 8/3	Blue	Very dark	Very slightly grayish
F2	B 7/2	Blue	Dark	Slightly grayish	B 8/3	Blue	Very dark	Very slightly grayish
G1	B 7/2	Blue	Dark	Slightly grayish	B 8/3	Blue	Very dark	Very slightly grayish
G2	B 5/2	Blue	Medium	Slightly grayish	B 7/2	Blue	Dark	Slightly grayish
G3	V 7/4	Violet	Dark	Moderately strong	V 8/1	Violet	Very dark	Grayish
H1	B 7/2	Blue	Dark	Slightly grayish	B 8/3	Blue	Very dark	Very slightly grayish
H2	B 7/2	Blue	Dark	Slightly grayish	B 8/3	Blue	Very dark	Very slightly grayish
I1	vstgB 5/2	Very strongly greenish blue	Dark	Slightly grayish	vstgB 7/2	Very strongly greenish blue	Dark	Slightly grayish
I2	bV 4/3	Bluish violet	Medium light	Very slightly grayish	vB 7/3	Bluish purple	Dark	Very slightly grayish
J1	B 6/2	Blue	Medium dark	Slightly grayish	B 7/2	Blue	Dark	Slightly grayish
J2	vstgB 6/4	Very strongly greenish blue	Medium dark	Moderately strong	vstgB 7/2	Very strongly greenish blue	Dark	Slightly grayish
K1	vstgB 6/4	Very strongly greenish blue	Medium dark	Moderately strong	vstgB 7/2	Very strongly greenish blue	Dark	Slightly grayish
K2	vstgB 5/2	Very strongly greenish blue	Medium	Slightly grayish	vstgB 7/2	Very strongly greenish blue	Dark	Slightly grayish
L1	B 4/2	Blue	Medium light	Slightly grayish	B 5/1	Blue	Medium	Grayish
L2	B 5/1	Blue	Medium	Grayish	B 6/2	Blue	Medium dark	Slightly grayish



(a)



(b)

Fig. 1. Photographs of (a) SBM-01 and (b) sample SBM-09 of the blue sapphires from Diago, Madagascar, for before (left) and after (right) ion implantation at 70 keV to a fluence of $\sim 1 \times 10^{18}$ ions/cm^2, the gems become vivid blue.

results show that the tone of the samples changed to darker when being ion implanted. Table 1 summarized modification of samples after ion implantation at 70 keV to a fluence of $\sim 1 \times 10^{18}$ ions/cm^2. It is clear that the color hue was almost not changed, while the color tone was dramatically increased, and the color saturation was slightly modified. For example tone of sample B2 of bluish purple changed from medium dark to dark and the saturation become slightly moderately, said from [bP 6/5] to [bP 7/4] in gemological color grading system.

Blue sapphires with any amount of green as a secondary hue are not considered to be fine quality. We, therefore, performed ion implantation to the sapphires of this group, We have found that, in case of very strong greenish blue sapphire, such as sample J2, the tone changed from medium dark to dark, but the saturation became slightly grayish, said from [vstgB 6/4] to [vstgB 7/2]. This is somewhat distinctly negative effects of N-ion implantation. Gray reduces the saturation or brightness of the hue, but it is the normal saturation modifier or mask found in blue sapphire [17]. However we have clearly noticed that the greenish is reduced and the sapphire became more pure blue. The introduction of grayish to sapphire is also found on blue sapphire, such as, sample G1. The hue was not changed, but the tone changed from dark to very dark and the grayish became higher saturation, said from [B 7/2] to [B 8/3]. However, in some case, grayish saturation can be removed by N-ion implantation, for example sample D1 of bluish purple sapphire. The hue was not changed, but the tone changed from medium dark to dark, said from [bP 6/3] to [bP 7/4]. The very interesting result is for sample A1 of bluish violet, the hue changed to bluish purple, and the tone changed from very dark to dark, said from [bV 8/3] to [bP 7/4]. This is somewhat the best results of our program on N-ion implantation to blue sapphire from Rwanda. It is a good example demonstrating that the hue or color of blue sapphire can also be modified.

With this light, we, therefore, run other experiment to confirm the finding by ion implantation of blue sapphires from other origins, i.e., from Diago, Madagascar with the same treatment conditions. It is clear that N-ion implantation has significantly improved their color properties, as a results, the gems become vivid blue as seen in Fig. 1.

As known, heat treatment is considered to be a practical approach for color enhancement of blue sapphire. However, during treatment, the stone is heated to very high temperatures (approximately 1600 °C) causing inclusions, chemical elements, and other impurities to reform themselves and become unnaturally. We have examined our ion implanted samples by high magnification microscope and found that the solid solubility and fingerprint were not deformed during ion implantation as seen in Fig. 2, indicating of a low temperature processing.

For clarifying our results, UV–Vis–NIR spectroscopy was applied to investigate the ion implanted samples. It is clear that the absorption spectra of ion implanted sapphires at 70 keV to a fluence of $\sim 1 \times 10^{18}$ ions/cm^2 has been modified as seen in Fig. 3. The overall spectra imply that the gems become vivid blue.

The causes of color in gemstones can be many [1,2,20,21]. Among them, transition metal impurities, charge transfer, color centers, and defect electrons may mostly are related to the effects of ion implantation. Various metallic elements at certain oxidation states give rise to different colors in different gems. For example, Cr^{3+} (<1%) in ruby colors red, $Fe^{3+} + Ti^{3+}$ in sapphire yellow, $Fe^{2+} + Ti^{4+}$ in sapphire blue, etc. In our application, gaseous non-metal ions were implanted, and thus the mechanism of charge transfer might be involved. In the case of blue color in sapphire, it is governed by the intervalence charge transfer (IVCT); $Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+}$ [22].

Nitrogen is non-reactive [23] 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

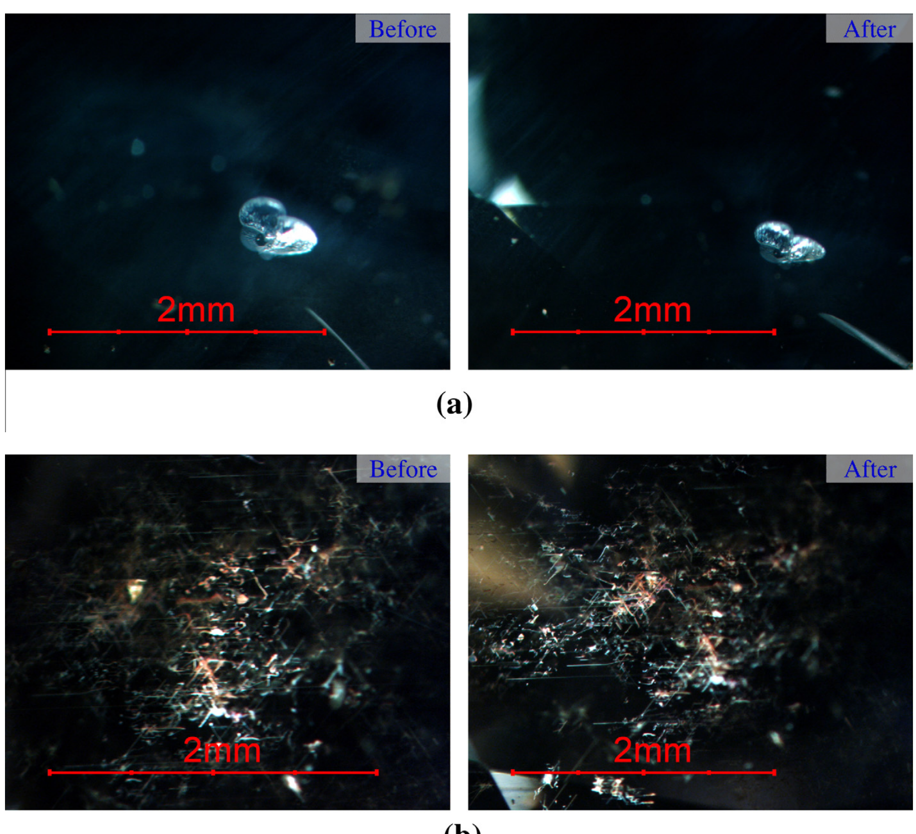


Fig. 2. (a) Solid solubility and (b) fingerprint of blue sapphires were not deformed during ion implantation at 70 keV to a fluence of $\sim 1 \times 10^{18}$ ions/cm^2, indication of low temperature processing.

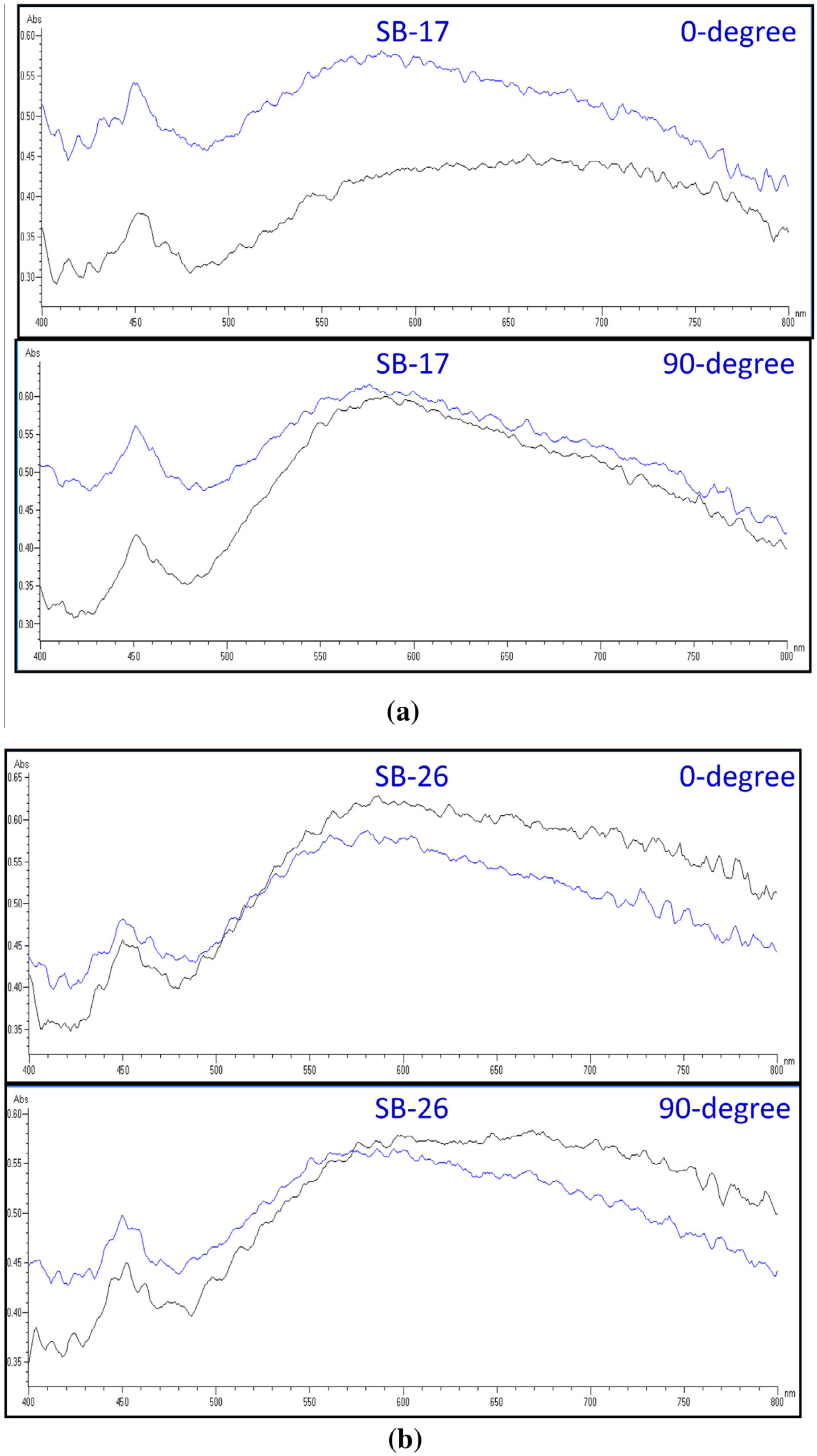


Fig. 3. Absorption spectra of sample (a) SB-17 and (b) SB-26 for before (black) and after (blue) ion implantation at 70 keV to a fluence of $\sim 1 \times 10^{18}$ ions/cm^2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

1) + Fe^{3+} (in cation site 2) → Fe^{3+} (in cation site 1) + Fe^{2+} (in cation site 2) and the actual colors of corundums are depending on the concentration fraction of those 2 species [24]. We believe such transferring can be found in Ti, such that Ti^{4+} (in cation site 1) + Ti^{3+} (in cation site 2) → Ti^{3+} (in cation site 1) + Ti^{4+} (in cation site 2). Thus color of corundums can be engineered.

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+} reduce yellow. Therefore, blue color is intensify, thus paler blue sapphire become darker blue. Another explanation is that the energy deposition might stimulate the replacing of $Fe^{2+} + Ti^{4+}$ to the Al^{3+} site in Al_2O_3. This finding supports to our previous results [13] in case of blue sapphire, that the original color of greenish in core due to the yellow or orange coloration, has turned to be in more pure blue and less green after N-ion implantation.

In the case of N-ion implantation, there are two possibilities, namely intervalence charge transfer (IVCT) as explained above and color center formation. N-ion implantation can produce another 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. 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.

4. Conclusions

The present study reports on ion beam analysis and modification of blue sapphire from Rwanda. Ion beam analysis technique, i.e. Particle Induced X-rays Emission (PIXE) is an effective tool to detect a few amounts of trace elements in the gems. The effect of ion implantation on the gemological modification with respect of optical properties change have been studied and proposed. The heavy ion irradiation modifies the optical properties and improves the color distribution, transmission and luster. These modifications lead to the improvement of quality of gemstones and thus the value added. Changing in color from appearance of the ion implanted gemstone making it lively and brilliant. Sapphire color of blue/green originated turned into those having a more vivid blue color and less green after nitrogen-ion implantation. The possible mechanism for these modifications could be due to the changes in oxidation states of impurity metals, induction of charge transfer from one metal cation to other and the production of color centers.

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References

[1] P.G. Read, Gemmology, Butterworth-Heinemann Ltd., Oxford, 1995.
[2] T. Themelis, The Heat Treatment of Ruby and Sapphire, Gemlab Inc., USA, 1992.
[3] K. Nassau, Am. Mineral. 63 (1978) 219.
[4] G.W. Arnold, G.B. Kreft, C.B. Norris, Appl. Phys. Lett. 25 (1974) 540.
[5] C.J. McHargue, P.S. Sklad, J.C. McCallum, C.W. White, A. Perez, E. Abonneau, G. Marest, Nucl. Instr. Methods B46 (1990) 74.
[6] K. Sickafus, N. Yu, R. Devanathan, M. Nastasi, Nucl. Instr. Methods B106 (1995) 573.
[7] Y. Aoki, N.T. My, S. Yamamoto, H. Naramoto, Nucl. Instr. Methods B114 (1996) 276.
[8] J.N. Mitchell, R. Devanathan, N. Yu, K.E. Sickafus, C.J. Wetteland, V. Gopalan, M.A. Nastasi, K.J. McClellan, Nucl. Instr. Methods B141 (1998) 461.
[9] N.K. Huang, B. Tsuchiya, K. Neubeck, S. Yamamoto, K. Narumi, Y. Aoki, H. Abe, A. Miyashita, H. Ohno, H. Naramoto, Nucl. Instr. Methods B143 (1998) 479.
[10] Y. Saito, H. Horie, S. Suganomata, Nucl. Instr. Methods B59/60 (1991) 1173.
[11] M. Ikeyama, M. Tazawa, H. Morikawa, A. Chayahara, in: J.S. Williams, R.G. Elliman, M.C. Ridgway (Eds.), Proc. of the 9th Int. Conf. on Ion Beam Modification of Materials, Canberra, Australia, Feb. 5–10, 1995, North-Holland, Elsevier Science B.V, Amsterdam, 1996, p. 1077.
[12] S. Intarasiri, D. Bootkul, L.D. Yu, T. Kamwanna, S. Singkarat, T. Vilaithong, Surf. Coat. Technol. 17–18 (2009) 2788.
[13] R.B. Drucker, Venue and value: the wide-ranging prices of sapphires and emeralds, Jeweler's Circular Keystone 170 (3) (1999) 174.
[14] GUPIXWIN Version SRIM-2008.04. University of Guelph, Canada, 2005.
[15] S. Intarasiri, A. Wijaikhum, D. Bootkul, D. Suwannakachorn, L.D. Yu, U. Tippawan, S. Singkarat, Appl. Surf. Sci. 310 (2014) 94.
[16] R. Hansawek, Miner. Resour. Gazette 45 (2000) 19–33.
[17] R.W. Wise, Secrets of the Gem Trade, the Connoisseur's Guide to Precious Gemstones, pp. 18–22.
[18] J.M. King, T.M. Moses, J.E. Shigley, Y. Liu, Color grading of colored diamonds in the GIA gem trade laboratory, Gems Gemol., Winter (1994) 220.
[19] Z.W. Tang, L.P. Li, J. Gems Gemmol. 02 (2009) 919.
[20] D.F. Nelson, M.D. Sturge, Phys. Rev. (1965) A1117.
[21] C. Sorell, Gemstone Technology Workshop, Nov.–Dec. 1999, Bangkok and Chiang Mai, Thailand, under World Bank Loan 4160-TH/Aus-AID Contract 5869.
[22] K. Nassau, The Physics and Chemistry of Color, Wiley, New York, 1983.
[23] K. Nassau, Gemstone Enhancement, second ed., Butterworth-Heinemann Ltd., Oxford, 1994. p. 34.
[24] R.W. Hughes, Ruby & sapphire. RWH publishing, Fallbrook, 1997 <http://www.ruby-sapphire.com>, 2008.