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Development of vertical compact ion implanter for gemstones applications

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ABSTRACT

Ion implantation technique was applied as an effective non-toxic treatment of the local Thai natural corundum including sapphires and rubies for the enhancement of essential qualities of the gemstones. Energetic oxygen and nitrogen ions in keV range of various fluences were implanted into the precious stones. It has been thoroughly proved that ion implantation can definitely modify the gems to desirable colors together with changing their color distribution, transparency and luster properties. These modifications lead to the improvement in quality of the natural corundum and thus its market value. Possible mechanisms of these modifications have been proposed. The main causes could be the changes in oxidation states of impurities of transition metals, induction of charge transfer from one metal cation to another and the production of color centers. For these purposes, an ion implanter of the kind that is traditionally used in semiconductor wafer fabrication had already been successfully applied for the ion beam bombardment of natural corundum. However, it is not practical for implanting the irregular shape and size of gem samples, and too costly to be economically accepted by the gem and jewelry industry. Accordingly, a specialized ion implanter has been requested by the gem traders. We have succeeded in developing a prototype high-current vertical compact ion implanter only 1.36 m long, from ion source to irradiation chamber, for these purposes. It has been proved to be very effective for corundum, for example, color improvement of blue sapphire, induction of violet sapphire from low value pink sapphire, and amelioration of lead-glass-filled rubies. Details of the implanter and recent implantation results are presented.

1. Introduction

In Thailand, the gem industry has been an important local industry for national revenue. A gemstone is the naturally occurring crystalline form of a mineral, which is desired for its beauty, valuable in its rarity and durable enough to be enjoyed for generations. Corundum is one type of gemstones where, in general, its popularity, value and hardness are second only to diamond. It is a crystalline form of aluminum oxide (Al_2O_3) which is naturally clear, but can have different colors that depend on chemical types of impurities within. 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 still found from time to time in many parts of the world, these localities combined with all historically important gem deposits have not always provided sufficient high quality material to meet the current demand. On the contrary, each mine owns plenty of low quality gemstones, e.g. those that have poorer clarity, color or size, thus having low market value. Accordingly, there is always an attempt to develop techniques for treating these low quality gems in private laboratories in order to enhance their appearance and thereby their marketability.

Heat treatment is the most popular technique commercially used for the improvement of gemstone quality [1]. The technique mainly modifies color, unifies inclusions, increases transmittance and improves luster [2,3]. However, heat treatment is time consuming and expensive and is not an efficient process to fulfill desirable

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changes in the properties of gemstones. For example, it involves a continuous annealing in a gas oven or electrical oven at 1000 °C or even above for a period ranging from few hours to few days depending on the type of gemstones. Different types of gemstones cannot be treated together. Alternative treatments are the exposure of gemstones to energetic particle beams or laser beams. A laser beam does not produce localized heating, whereas low mass particles such as electrons generate localized heating but yield poor coloration. Electron beam irradiation suits topaz more than corundum. Neutron irradiation makes gemstones radioactive. Last but not least, heavy ion beams seem superior to all the other candidates. The heavy ion beams have multiple potential in providing necessary tools for gem optical property improvement such as localized kinetic energy transfer or localized heat, defects, impurities and charges [4], as well as the capability to treat different gems individually. The limited availability and high cost of high-quality natural gemstones mean that their potential use for other applications, such as in high technology area, is also restricted.

In the past ion implantation on sapphires had been investigated from the point of view of improving their optical and mechanical properties [5–10] for the applications on optics, optoelectronics, photonics and tooling [11,12]. Several studies had dealt with understanding of basic and applied aspects of ion beam modification of sapphire but not many had focused on developing industry-ready technology. Our work aims at developing a heavy ion beam irradiation process for enhancing the quality of natural gemstones and thus increasing their market values. We have found recently that ion implantation is able to serve as a unique treatment for improving gemstone qualities [13]. However, the former ion implanter, originally designed for semiconductor applications, was inconvenient for gemstone treatment and too expensive to afford and too complicated to handle, from the customer's point of view. Therefore, a 100 kV vertical compact ion implanter becomes necessary and the program to develop such an ion implanter has been carried out. The design of the machine was aimed at providing our customers with simple operation, convenient in maintenance and low-cost machine for gem improvement, which would eventually contribute to the basic research and gem-industry developments. Details of the implanter along with some examples of particular challenges for the optical modification of gem materials are reported below.

2. Experimental details

2.1. Vertical compact ion implanter

In our efforts to develop ion beam technology for novel applications in gemology (one of the most important research programs of the country), a 100 kV vertical compact ion implanter was developed. The designing of the machine was aimed at providing our customers with a user friendly, convenient and low cost machine. The machine, as shown in Fig. 1, was designed in a vertical configuration so that the gem samples of irregular shapes and sizes could simply be placed in a horizontal tray at the target chamber without any need of glue.

The total length of the implanter is only 1.36 m. It consists of, from top to bottom, a duoplasmatron ion source, an einzel lens, a 100-kV(max) accelerating tube, a beam diagnostic chamber and a target chamber. In the first phase of development program, the $x-y$ scanner has not yet been included in front of the target chamber although the scanner and its power supply are available already. All power supplies were ready-made products purchased for us by the International Atomic Energy Agency (IAEA, Vienna). The beam line is evacuated by a powerful diffusion pump system. To prevent return-flow of the pumping fluid and enable the

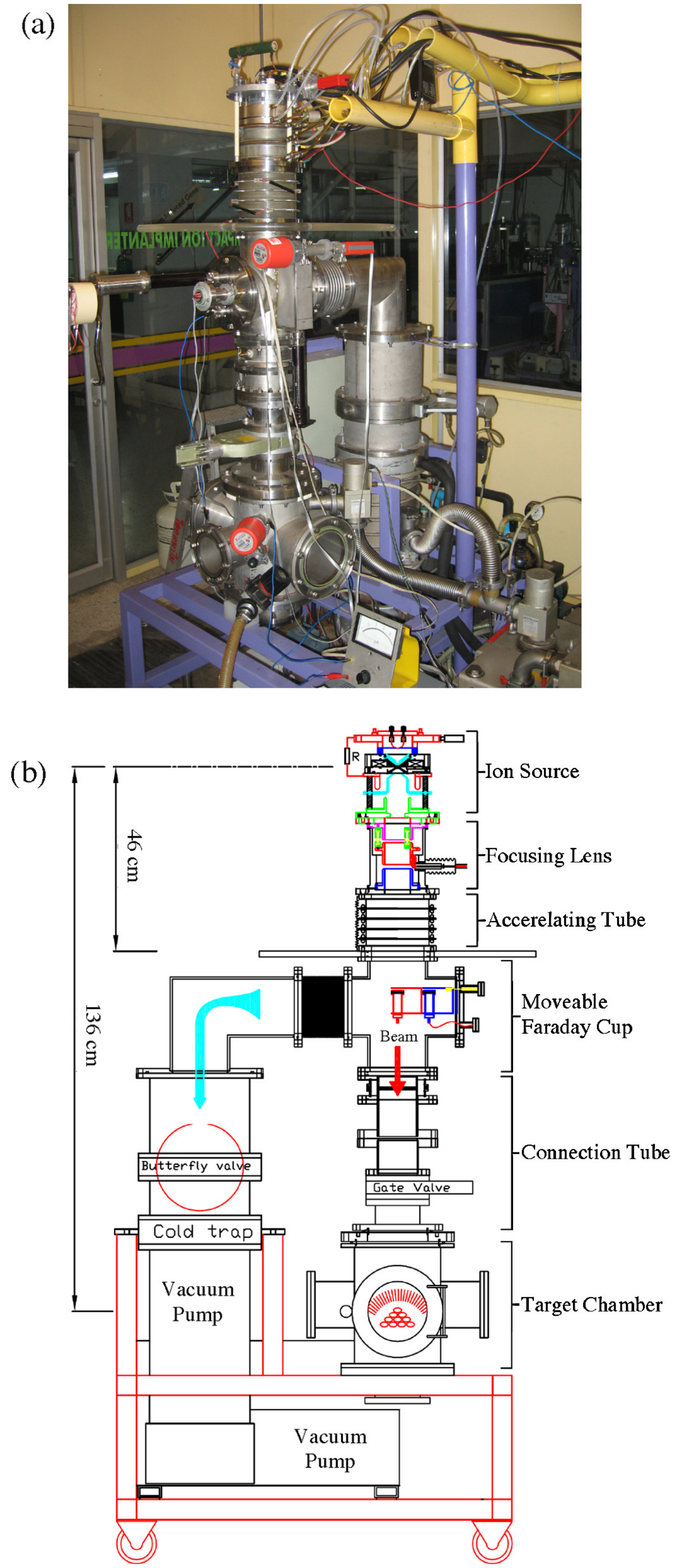

Fig. 1. (a) A photograph and (b) schematic diagram of the high-current vertical compact ion implanter.

diffusion pump to pump the system down to its ultimate possible, a cold trap was installed in front of the pump. The ion source was of a duoplasmatron type with certain modifications for high ion current performance. The ion source could be separated into two parts, a plasma generator and an extraction system. The first part included a

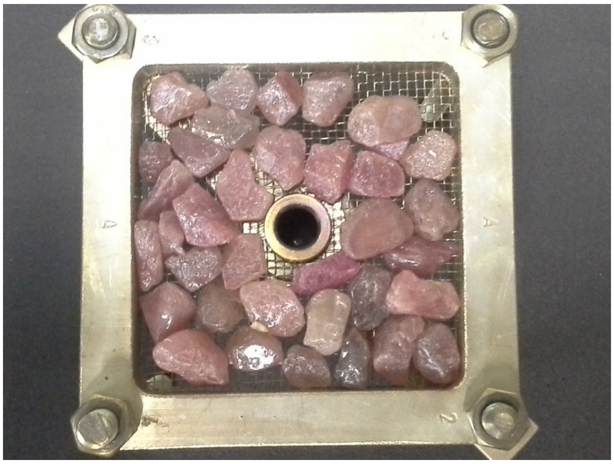

Fig. 2. A photograph of the sample tray with rubies.

filament cathode, an intermediate electrode and an anode. The second part consisted of two or three electrodes which were anode, extractor and ground. In order to find optimized operation conditions, both parts were intensively investigated. After testing the ionization process, the nitrogen plasma was stable for about 60 min with an arc current of 2.0 A and an arc voltage of 80–85 V, and the arc pressure was 6×10^{-1} Torr which was related to the sufficiency of the gas supply rate. The extraction voltage was normally fixed at 6 kV after optimization though its capacity was 15 kV. The accelerating tube was only 15 cm long. The beam emittance [14], the average spread of particle coordinates in the position-and-momentum phase space in a unit of length × angle, was measured based on the transformation matrix theory [15] using a pepper pot plate [16] at the beam diagnosis chamber to be ε_x = 1.62 mm mrad. This number is acceptable for our application. Our implanter is able to accelerate ion beams such as nitrogen and argon at the maximum voltage of 100 kV with a maximum current of about 1 mA which is enough for ion beam modification of gemstones. The 30 cm diameter target chamber was purposely made relatively small for saving pumping time but big enough to incorporate a 8 cm × 8 cm sample

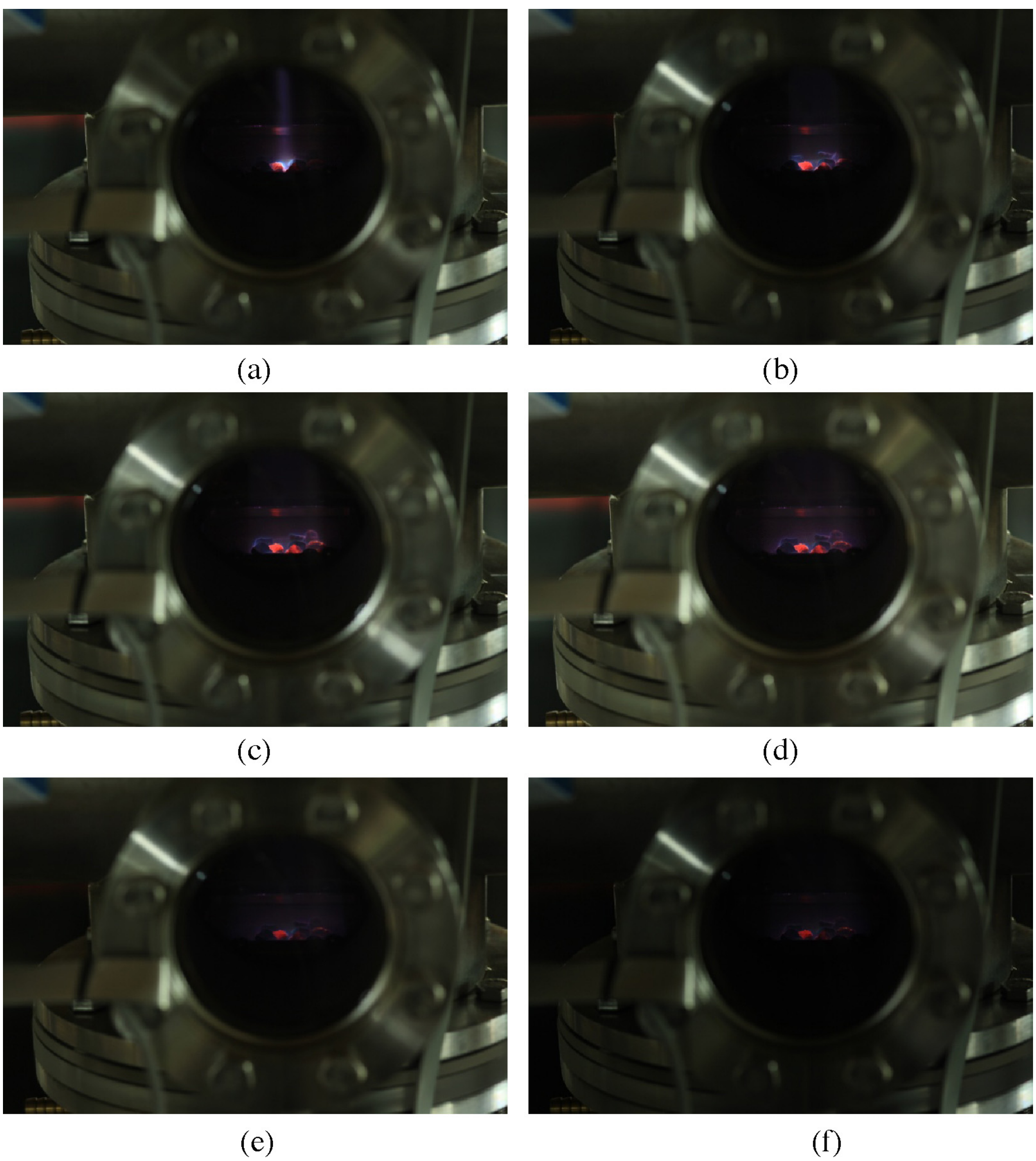

Fig. 3. (a)–(f) Various beam spot sizes can be adjusted for confining the irradiation area,

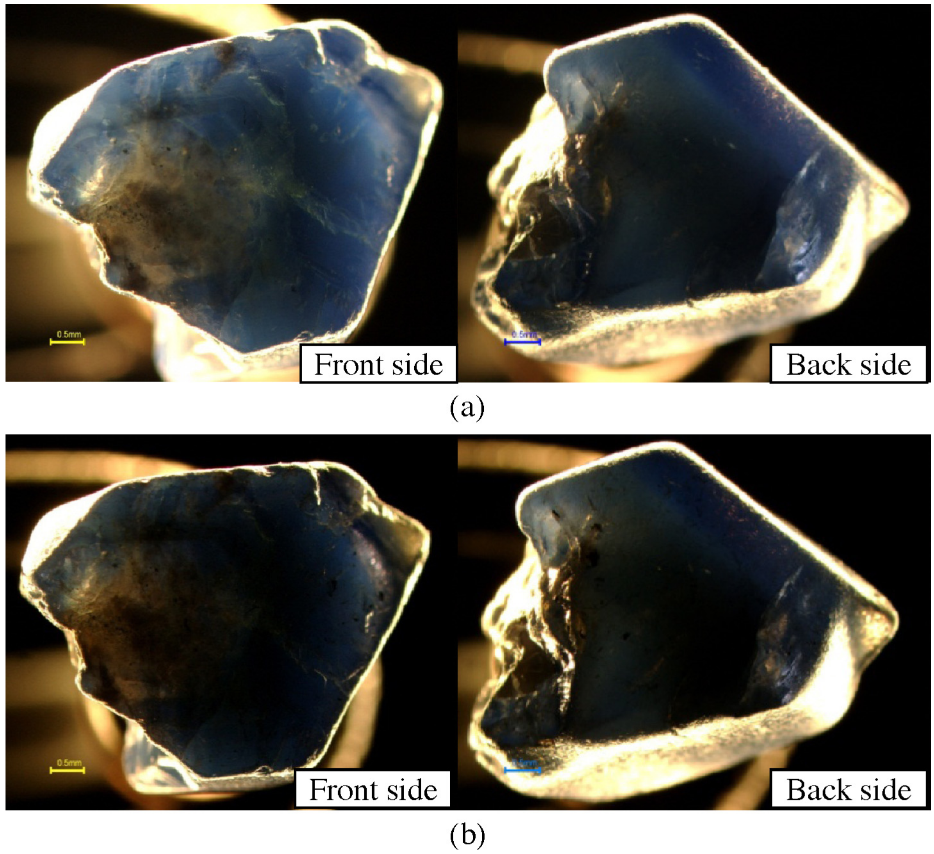

Fig. 4. Original low quality blue sapphire (a) has more intense in blue color after ion implantation (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tray as shown in Fig. 2. The tray is made of stainless steel wire mesh with a 1 cm diameter hole at the center where a Faraday cup is directly mounted behind for ion fluence monitoring.

By varying the electromagnetic field of the ion source, the ion beam spot size at the sample position can be adjusted as shown in Fig. 3. The implanter and all necessary power supplies fit well in a 3 m × 4 m × 3 m normal structure room. In our case the room is equipped with air conditioning in order to reduce the temperature and humidity from the tropical environment.

2.2. Ion beam irradiation on corundum

We have already found that nitrogen ions have potential to enhance color quality of corundum, especially blue sapphire [13]. Therefore, N-ion implantations are reported here. The sample tray contains about 30–50 gems, depending on their sizes. The irradiation area is as large as 50 cm^2 which can cover all gemstones at once. This implanter can offer hundreds of μA of unanalyzed beam of atomic and molecular nitrogen ions in a normal ratio of 1:4. As a N_2^+ ion would be split into two atomic nitrogen ions of half in energy as soon as it hit the target surface, the N-ion implantation thereby delivers a broader ion depth profile in the target material due to the two values of ion energies. In the gem application, the factor/ratio of ion species/charge is less important than ion energy, current and species was not critical. Although without a scanning system, the spatial distribution of the ion beam is Gaussian-like, meaning that the most beam intensity is at the center, we place thicker gems at the central area of the beam while thinner ones away from the beam center. Normally the irradiation time per batch was between 1 and 3 h. A 200 DF5 Varian/Extrion ion implanter was used as a benchmark for this self-developed compact ion implanter. Except for the purity and uniformity of ion beams, the self-developed facility can provide higher ion beam current. The quality and beauty [1] of gemstones were determined using the established grading system followed by gemologists [17]. The success in development of such a low-cost and simple-structured ion implanter provides developing countries with a model of utilizing our limited resources to develop novel accelerator-based technologies and applications.

3. Results and discussions

It amazes us when seeing that several types of corundum were modified by nitrogen ion beams. As in the case of natural blue sapphire with yellow core, blue color can be intensified by N-ion beam as shown in Fig. 4. The other example is on the implantation effects of nitrogen ions on the low quality pink sapphire. After treatment, the sample transformed to violet sapphire as can be seen in Fig. 5. In both cases, the sapphire samples were treated with 40-keV unanalyzed N-ions of ∼100 μA to an average fluence in excess of 1×10^{18} ions/cm^2.

The causes of color in gemstones can be as many as 16 [1,2,18,19]. Among them, transition metal impurities, charge transfer, color centers, and defect electrons mostly are related to the effects of ion implantation. Generally, 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 is the cause of red color, $Fe^{3+} + Ti^{3+}$ in sapphire are the cause of yellow color, $Fe^{2+} + Ti^{4+}$ in sapphire are the cause of blue color, etc. However, in our case, gaseous non-metal ion beams were used in the implantation, and thus the charge transfer of the existing trace elements might be

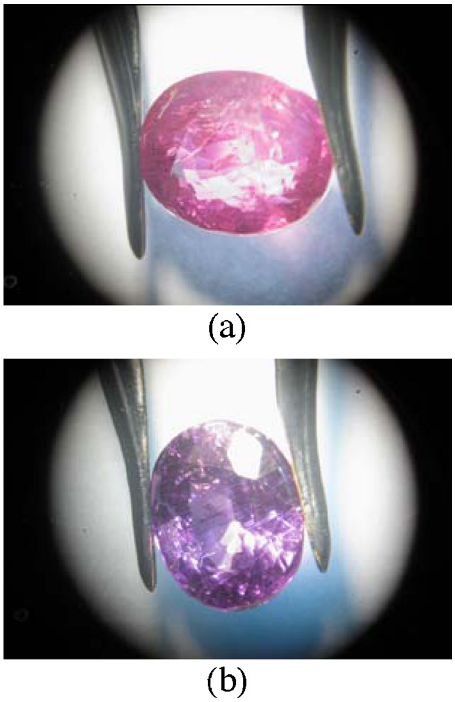

Fig. 5. (a) A low value pink sapphire becomes a higher value violet sapphire after nitrogen ion implantation (b).

the major mechanism. For example, the blue color in sapphire is governed by the intervalence charge transfer (IVCT) [20], as follows:

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (1)$$

$$Ti^{4+} + e^- \rightarrow Ti^{3+} \quad (2)$$

$$Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+}. \quad (3)$$

Nitrogen is non-reactive [21] 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) and the actual colors of corundums are dependent on the concentration fraction of those two species [22]. 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, the color of corundum is possible to be engineered.

The color change in sapphire that is induced by N-ion implantation is probably attributed to the reversed IVCT of $Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+}$ [20], hence more Fe^{2+} enhances blue while less Fe^{3+} reduces yellow. Therefore, in both cases, blue color is intensified, thus paler blue sapphire becomes more blue and pink sapphire becomes violet. Note that the original color of violet or (red + blue) originates from Cr^{3+} (showing red in ruby) and $Fe^{2+} + Ti^{4+}$ (showing blue in sapphire) which after ion implantation turned less yellow but more blue while red not change [23]. Another explanation in the case of pink sapphire is that the energy deposition might stimulate the replacing of $Fe^{2+} + Ti^{4+}$ to the Al^{3+} site in Al_2O_3. Thus blue color is generated in the pink sapphire. This finding supports our previous results [13] that, in case of blue sapphire, if the original color is greenish in core due to the yellow or orange coloration, the original sapphire has turned to be in more pure blue and less green after N-ion implantation.

Ruby is generally known as the most valuable of all color gemstones. However, due to the shortage of naturally good quality raw materials, various treatments have been applied for quality improvement. As mentioned earlier, heat treatment is the most popular method. In Thailand, the method can be classified into two categories, so-called, "Paw Kaw" which refers to the conventional heat treatment process that does not intentionally include any other substance during heating, and "Paw Mai" or new heat treatment method that has also added lead glass in a crucible [24]. Recently, the Thai gems markets are flooded by the latter. Therefore, we applied our ion implanter to these treated gemstones. It is interesting that lead glass filled rubies become more intense in red after ion implantation as shown in Fig. 6. This result seems contradictory to the pink sapphire case in which the N-ion implantation has turned its color to violet. From our measurement [24], the sample becomes dominated by glass (Si_2O_4) and lead (Pb_2O_4) instead of Al_2O_3. The ion beam deposition might generate color centers in glass, thus the color is stronger in red [25]. Details of this mechanism will be discussed elsewhere [26].

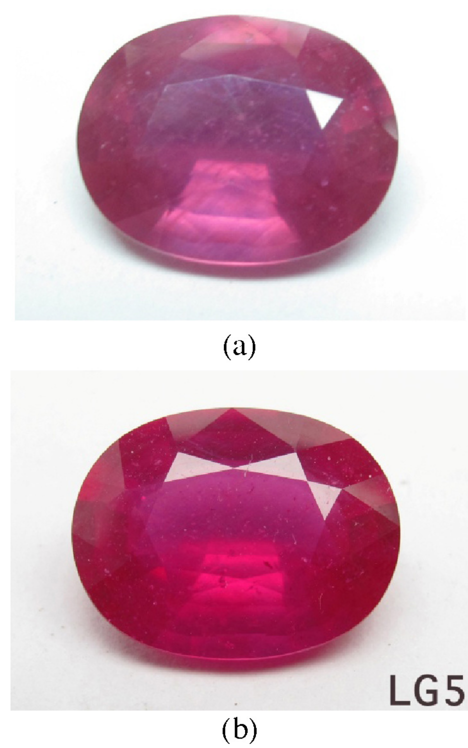

Fig. 6. Comparison of lead glass filled ruby for (a) before and (b) after ion implantation. It is clearly seen that the ruby is redden and clearer after ion implantation.

As discussed above, various phenotype changes in ion beam irradiated gemstones have been observed and confirmed. In all cases, the gems have been judged by gemological professionals who had guaranteed the increase of their values. Actually, a wide variety of corundum from local customers has also been treated by our implanter. This demonstrates that the vertical compact ion implanter development program has accomplished our goal.

4. Conclusions

In developing countries, developing advanced technologies, such as accelerator technology, are not impossible but frequently constrained by limited budgets and the policy to firstly support the projects with social and economic impact. In Thailand gemstone industry has been an important local industry for national revenue. Thus, we have constructed the vertical compact ion implanter for providing service to this particular industry. The machine was featured with simple structure, low cost, and user-friendly operation. The ion implanter has been successfully applied in improving local corundum quality, including; rubies, blue sapphire, pink sapphire, and lead-glass-filled ruby. Dramatic change by ion implantation effects has been noticed. In all cases the gemological professionals judged the gem value and confirmed the significant increase in their values. The success in development of ion implanter provides developing countries with a model of utilizing our limited resources to develop novel accelerator-based technologies and applications.

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