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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 N₂⁻ and O-ions. N₂⁻ 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. N₂⁻ 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 Polariscope [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 μm by a 100× 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 N₂⁻ 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 ppm, respectively. The color grading system indicates that the overall color of rubies treated by N₂⁻ 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 ppm. The color grading system indicates that the overall color of rubies treated by O-ions implantation changed from red (R) to orange red (oR).

Fig. 3a and b show the optical absorption spectra for the N₂⁻ 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 N₂⁻ 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 Cr³⁺ and Fe²⁺–Ti⁴⁺ 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 Cr³⁺ absorption features together with a pronounced contribution of Fe³⁺ and Fe³⁺/Fe²⁺ bands at 377/388 nm and 450 nm respectively [25]. More rarely seen was a combination of the Cr³⁺ features with the Fe²⁺–Ti⁴⁺ charge-transfer (IVCT) band of sapphire at around 560 nm [25]. It is unfortunate that, in our measurements, due to strong absorption behavior of Cr³⁺ in ruby, some of these peaks are difficult to identify and compare. Therefore, it

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