



Analysis and modification of natural red spinel by ion beam techniques for jewelry applications



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ABSTRACT

Natural spinel (MgAl_2O_4) can be found in several colors resembling corundum, i.e. rubies and sapphires. In particular, spinels with saturated red appearance, called spinel-rubies or balas rubies, are the most appreciated. However, the beautiful rich red spinels are very rare, they can be found in a range of pastel shades blended with either brown, orange or purple. Therefore, the objectives of the present studies are to investigate the origins of the color blending and to improve the optical property of this gemstone by ion beam techniques. Two non-destructive ion beam analysis techniques, i.e., particle induced X-ray emission (PIXE) and iono-luminescence (IL), have been employed for geochemical analysis of the gems. As an alternative method, ion beam treatment using N_2 -ion was applied for improving optical appearance and color enhancement of the red Burmese (Myanmar) spinel. For each run, samples were implanted at ion energy of 70 keV to a fluence of $\sim 1 \times 10^{17}$ ions/cm² and subsequently surface cleaning. UV-Vis spectroscopy, Raman spectroscopy and photoluminescence spectroscopy were selected for sample characterization. As for comparison, the spinel samples from the same origin were heated in air and undergone the same measurement. We have found that the color appearance of spinel can be engineered by both techniques. However, the heating has transformed the normal or the ordered spinel to the inverse or the disordered one, and thus disorder might be used as criteria to determine if the stone has been heated. On the other hand, the crystalline structure of the spinel remains almost the same or slightly disordered after ion implantation. This finding leads to future applications for jewelry.

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1. Introduction

It was estimated that till the 1800s, the spinel gemstone crystal was thought to belong to the corundum family. However, the chemical formula of the spinel is a magnesium aluminum oxide ($\text{MgO-Al}_2\text{O}_3$) in which the ratio of MgO to Al_2O_3 is 1:1 [1]. Its specific gravity is 3.58 to 3.61 and the refractive index ranges between 1.712 and 1.740 [1]. The hardness of this gemstone on Mohs scale is 8 [1]. Spinel are mined in Myanmar (Burma), India, Sri Lanka (Ceylon), Afghanistan, Thailand, Sweden, Brazil, Australia and The United States [2]. Spinel is found in many colors ranging from red, pink, violet, purple, green and indigo to blue. The most valuable amongst the spinel is the red one [3]. It is often mistaken for an actual natural ruby and only on close inspection could one tell the difference. The pure red spinel is very rare, most of them can be found in a range of pastel shades blended with either brown, orange or purple. Mineralogists state that the red and natural pink spinel derive its color from the trace element and mineral

chromium, while the orange to purplish one owe their color to the trace elements and minerals like iron and chromium [4].

The method for enhancing the optical property of spinel is by heat treating at successively high temperatures to ~ 1200 °C for 24–30 h [5]. At such temperatures not only the second color is removed, thermal damage for a large percentage often results from the heating process. Moreover, the crystal structure is also changed thus the sample is completely clarified [5]. Spinel with the general chemical formula AB_2O_4 , have a unit cell capable of holding a large number of cations occupying octahedral and tetrahedral sites in different ways. The cation distribution is said to be “normal” if all the A cations (Mg, Fe^{2+} , Zn, Mn) are on tetrahedral sites with all B cations (Al, Cr, Fe^{3+}) on octahedral sites or “inverse” if it is characterized by occupation of one of B-sites by a divalent cation with one trivalent cation taking its place on the A-site [6]. The MgAl_2O_4 spinel formed in nature is assumed to have a strong preference for the normal structure, since simple radius ratio arguments suggest that smaller cations would prefer to occupy tetrahedral sites and Mg^{+2} is the smallest ($r = 0.66$ Å) [6]. Heating the natural spinel to high temperatures, aluminum and magnesium ions start to change sites, giving rise to more random distributions of the cations leading to different degrees of inversion [6]. This change in the

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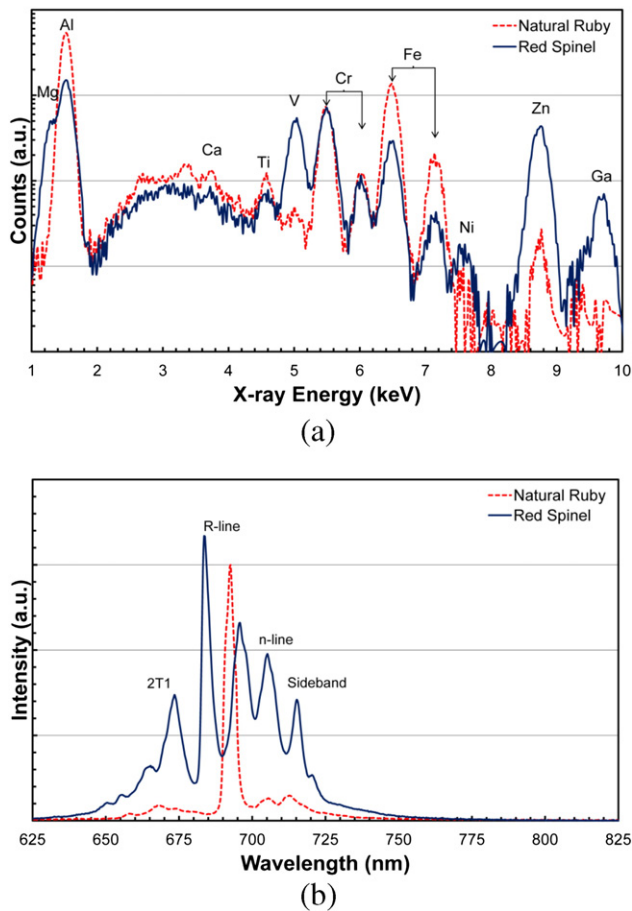


Fig. 1. A typical (a) PIXE and (b) IL spectra of the red spinel and ruby from Mogok, Myanmar.

distribution of the cations are accompanied by changes in the thermodynamic properties of the spinel and can be retained depending on the temperature of the heat treatment and cooling rate [7,8,9].

Raman and photoluminescence (PL) techniques are good tools to examine the normal or inverse of structure spinel phases. Raman spectroscopy has been applied to test the distribution of the cations in the spinel structure. PL analyses the light emitted by a material when irradiated with a light beam. In gemstones, luminescent ions can occur as intrinsic impurities or they may be introduced as intentional dopants. PL and Raman spectroscopic techniques allow the investigation of disorder phenomena related to natural or treatment formation conditions. Both techniques have shown themselves attractive for applications in the gemstone characterization, being totally non-destructive and applicable to even large, odd shaped objects. Moreover, they are of help in solving problems concerning the provenance of an unknown gems, both through inclusion determination and information about disorder phenomena depending on the mineral genesis [10,11].

We have previously reported that ion implantation has potential for application in the natural corundum [12,13]. The appearance of samples, especially ruby, became more transparent, preferable color increasing and less percentage of impurity [12,13]. The method appears to be new and repeatable for improving gemstones properties. Therefore, the ion beam treatment might be a new alteration of the inclusion scene and color enhancement of spinel. This work focused on two main parts; i.e., ion beam analysis and ion beam treatment of spinel. The former is aimed for characterizing the natural spinel by using nondestructive characteristic of ion beam techniques. Understanding its property is crucial for setting up a standard technique to distinguish red spinel from ruby and also for setting up the treatment conditions. On the other hand, the latter is applying basic principles of ion implantation for enhancing the optical properties of red spinel from Myanmar. Some samples from the same origin had undergone heat treatment in air between 600–1000 °C for informative comparison. Information provided by UV-Vis spectroscopy, Raman spectroscopy and PL spectroscopy was used to draw conclusions.

Table 1
Geochemical analysis of the red spinel originated from Mogok, Myanmar.

Sample	Oxide compound (wt%)									
	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	MnO	Fe ₂ O ₃	ZnO	Ga ₂ O ₃
rP1	24.126	72.996	2.308	0.002	0.004	0.085	0.107	0.118	0.203	0.052
rP2	23.954	73.310	2.310	0.024	0.091	0.072	0.006	0.122	0.084	0.029
rP3	23.612	73.812	0.308	0.005	0.203	0.268	0.009	0.443	1.320	0.020
rP4	25.523	73.256	0.535	0.014	0.036	0.265	0.004	0.237	0.082	0.048
rP5	24.989	72.988	0.867	0.011	0.031	0.393	0.000	0.583	0.116	0.022
rP6	24.977	72.109	1.381	0.016	0.079	0.565	0.000	0.111	0.720	0.044
rP7	24.288	72.844	1.635	0.011	0.111	0.444	0.000	0.141	0.463	0.063
rP8	24.185	70.773	4.355	0.093	0.130	0.061	0.013	0.223	0.101	0.067
rP9	24.747	72.457	1.262	0.013	0.088	0.269	0.088	0.174	0.866	0.038
rP10	24.775	72.638	1.558	0.024	0.124	0.305	0.008	0.095	0.431	0.043
rP11	25.114	72.850	0.980	0.050	0.212	0.292	0.011	0.080	0.368	0.043
rP12	23.667	71.049	3.934	0.036	0.220	0.219	0.015	0.169	0.618	0.074
rP13	25.225	73.920	0.214	0.022	0.101	0.058	0.009	0.153	0.270	0.029
rP14	24.883	73.341	0.805	0.022	0.058	0.136	0.004	0.149	0.567	0.036
rP15	24.288	72.844	1.635	0.011	0.111	0.444	0.000	0.141	0.463	0.063
rP16	23.496	71.690	2.653	0.027	0.068	0.516	0.017	0.495	0.980	0.057
rP17	23.672	71.318	3.272	0.033	0.099	0.461	0.000	0.248	0.829	0.069
rP18	25.138	72.731	0.650	0.028	0.192	0.281	0.005	0.173	0.735	0.069
rP19	23.986	73.913	0.478	0.030	0.051	0.277	0.006	0.409	0.824	0.026
rP20	24.846	73.605	0.903	0.016	0.073	0.045	0.007	0.270	0.215	0.019
rP21	22.708	65.167	11.183	0.062	0.141	0.155	0.102	0.193	0.257	0.033
rP22	24.383	73.425	1.086	0.058	0.109	0.135	0.040	0.193	0.555	0.016
rP23	24.068	72.172	2.188	0.021	0.123	0.316	0.005	0.172	0.887	0.047
oP1	24.185	70.773	4.355	0.093	0.130	0.061	0.013	0.223	0.101	0.067
oP2	24.846	73.605	0.903	0.016	0.073	0.045	0.007	0.270	0.215	0.019
oP3	24.390	72.660	2.388	0.030	0.152	0.116	0.003	0.089	0.143	0.029
oP4	24.263	72.144	2.872	0.024	0.112	0.040	0.000	0.218	0.307	0.019
oP5	25.386	73.491	0.081	0.014	0.127	0.086	0.028	0.137	0.620	0.030

Table 2

Color grading using GIA system of spinel samples for before and after heat-treated at 800 and 1000 °C in furnace. Note that R = Red; SlpR = Slightly purplish Red; StpR = Strongly purplish Red; RP/PR = Red Purple or Purple Red.

Sample	As received	Heat treated 800 °C	Heat treated 1000 °C
rP-1	 SlpR2/3	 SlpR3/3	 StpR3/3
rP-4	 SlpR3/3	 StpR2/3	 StpR3/3
rP-6	 R3/2	 R5/3	 R6/3
rP-8	 SlpR3/3	 SlpR3/3	 StpR3/3
rP-9	 SlpR3/3	 RP/PR2/3	 RP/PR3/3

2. Experimental details

2.1. Gem materials

Gem materials were red spinel coming from local occurrences of Myanmar (Burma). 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 diameter.

2.2. Ion beam analysis

The elemental compositions of the spinel samples were analyzed using PIXE and IL based on a 2-MeV proton beam produced by a 1.7 MV tandem Tandetron accelerator. The proton beam was collimated with a diameter ~1 mm, and the beam current on the sample was ~10 nA. For PIXE, the Si(Li) detector, set up at 120° to the beam direction, connected to an amplifier and a digital multichannel analyzer (MCA), detected X-rays at 87 mm from the sample. An ORTEC multichannel analyzer card, connected to a personal computer, was used for data acquisition. A 74- μm mylar foil was placed in front of the detector as an absorber in order to reduce the count rate caused by impurities of low atomic numbers. An electron cluster produced by an electron gun was applied to degrade the bremsstrahlung effect caused by the charging up phenomena. Base pressure in the vacuum chamber was $\sim 6 \times 10^{-6}$ Torr. Quantitative analysis of PIXE spectra, the elemental composition ($Z \geq 13$) in the samples, was achieved using the GUPIXWIN code [14]. For IL analysis, emitted light was transmitted by a fiber optic light guide placed at $\sim 160^\circ$ to the beam direction and connected to the Ocean Optics S2000 spectrometer outside the analysis chamber. This spectrometer was connected to a personal computer running the OOBBase32 software [15] to acquire the spectra.

2.3. Ion implantation

N_2 ions were applied for ion beam modification of natural spinel. The ion was generated by a Freeman ion source, using a 200 KV Varian ion implanter. The beam was scanned on both horizontal and vertical directions, to be a rectangular cross section beam with $10 \times 10 \text{ cm}^2$ size, following by measuring the beam current at four corners to adjust the uniform distribution. Consequently, the remaining ion beam was collimated to a circular cross section with radius ~ 10 inch diameter for transporting to a target section. The target holders were designed with special considerations, aiming at avoiding sputtering contamination on the gem surface as much as possible. Each gemstone was fixed on carbon tape which attached to the sample holder directly, avoiding a colliding of ion beam to the carbon tape. The operating pressures in the target chambers were $\sim 10^{-6}$ Torr. For each run, samples were implanted at ion energy of 70 keV to a fluence of $\sim 1 \times 10^{17}$ ions/ cm^2 and subsequently surface cleaning.

2.4. Heat treatment

A conventional furnace was used for heating the samples. The heating rate, from room temperature to 600 °C, was 60 °C/min, with a 600 °C holding time for 30 min and from 600 °C to the maximum firing temperature of 800 °C and 1000 °C respectively the heating rate was 20 °C/min; soaking time was 5 h. The specimens were removed to rapid cool outside the furnace until room temperature was reached.

2.5. Sample characterization

The optical absorption spectroscopic study was carried out by a Perkin Elmer Lambda 950 UV/VIS Spectrometer which recorded over the range from 300 to 800 nm. The Raman and PL measurements were carried out by a Renishaw InVia Raman microscope, using an

argon laser (wavelength 532 nm) as an excitation source. The Raman spectrum recorded over the range of 250 to 2500 cm^{-1} and the PL spectrum recorded over the range of 550–750 nm.

2.6. Justification

In order to investigate the color characteristics of the spinel, the Gem Dialogue system [16] was used for describing and grading the samples. Color in gemstones breaks down into three components: hue, saturation, and tone. “Hue” is most commonly understood as the color of the gemstone. “Saturation”, ranging between 0 and 6, refers to the brightness or vividness of the “hue”, and “tone”, ranging between 0 and 10, is the lightness to darkness of the “hue” [17]. The grades of the gemstones were judged by authorized gemological professionals.

3. Results and discussion

3.1. Ion beam analysis

Fig. 1 demonstrates the ion beam analysis results of the red spinel originating from Mogok, Myanmar compared with its cousin, i.e. ruby. The PIXE spectrum consists of dominant Al and Mg lines, due to the host matrix light elements, and few weak lines due to the trace elements of transition metals. Spinel is allochromatic, meaning that the chemistry of their basic formula does not cause any selective absorption so in the pure state, they are white or colorless. It is tiny, trace amounts

of impurities that act as the chromophores. Table 1 summarizes the chemical concentration of all investigated samples. As for IL, spectrum of red spinel, peaks were observed at the same wave length to that of rubies [18], but the spectrum, belonging to Cr^{3+} [19] in spinel, is complex as it is comprised of a strong zero phonon line near 685 nm as well as vibronic sidebands of that line, and other lines associated with Cr^{3+} pairs [18]. Note that IL spectrum of red spinel has a number of peaks more than that of ruby and there are extra peaks at sidebands in the spinel's spectrum. It seems that there is a splitting of energy level in the transition energy of spinel, in such that 4 of $2T_1$ energy levels instead of 2 in the case of rubies [20].

3.2. Heat treatment

Table 2 displays spinel samples before and after heat treated in the furnace. We have found that their color tone became darker after the treatment. For example sample rP-6 with original red color with light tone (3) and saturation level 2, said [R3/2] became medium tone (5) and saturation level 3, said [R5/3] after heated with 800 °C and medium dark tone (6) and saturation level 3, said [R6/3] with 1000 °C respectively. Moreover, samples rP-1, rP-4 and rP-8 of original color “Slightly purplish Red (SlpR)” became “Strongly purplish Red (StpR)” and sample rP-9 of original color “Slightly purplish Red (SlpR)” became “Red Purple or Purple Red (RP/PR)” after heated with 1000 °C. For understanding of the process, sample rP-6 was selected for fully characterization and the results can be summarized as follow.

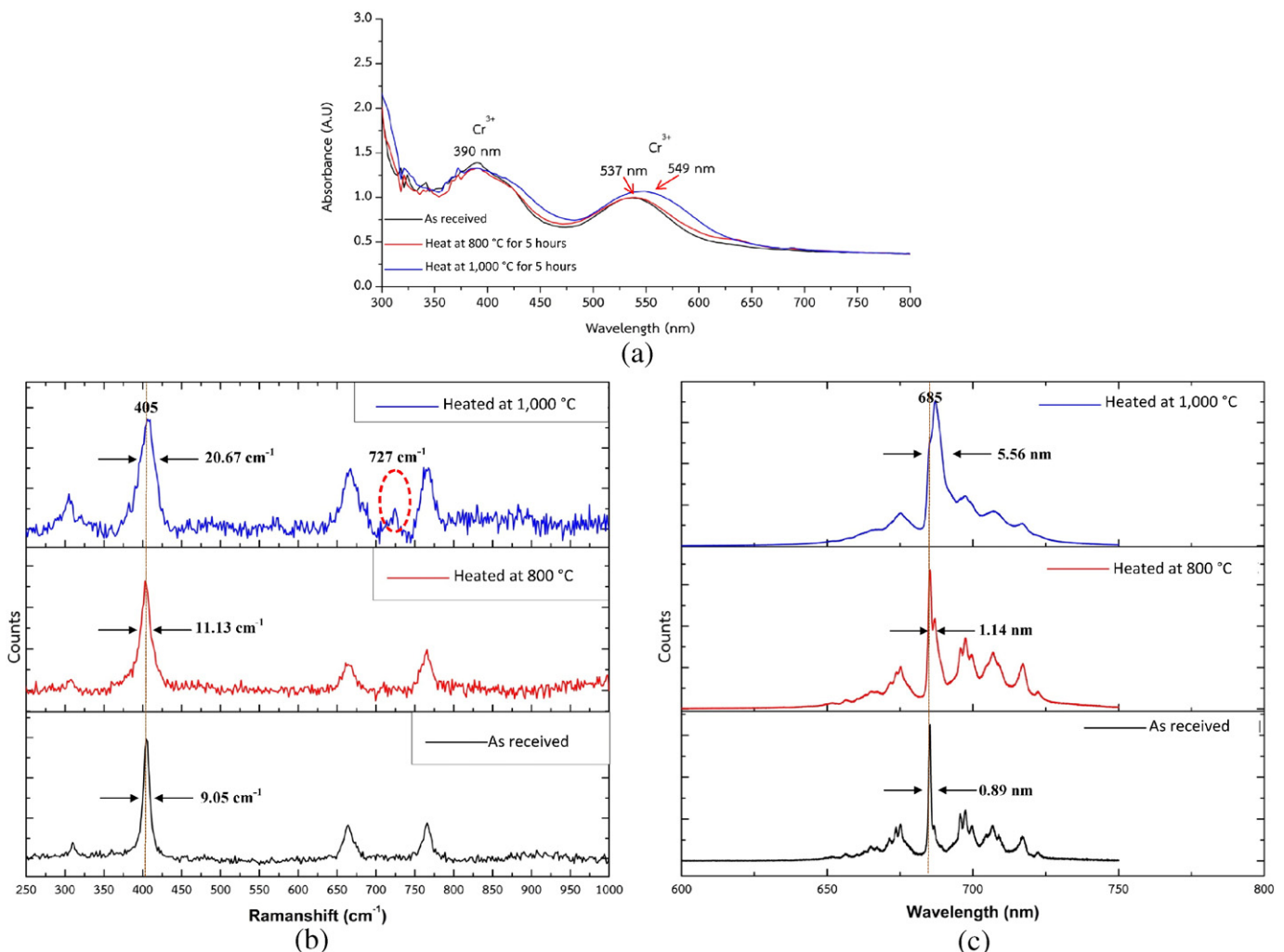






















Fig. 2. Comparison of (a) UV-absorption spectra (b) Raman spectra and (c) luminescence spectra of spinel sample rP-6 for before and after heat-treated at 800 and 1000 °C.

Table 3

Color grading using GIA system of spinel samples for before and after N_2 -ion implantation. Note that R = Red; SlpR = Slightly purplish Red; StpR = Strongly purplish Red; oR = orangey Red; RO/OR = Red Orange or Orange Red.

Sample	As received	1st implanted	2nd implanted	3rd implanted
rP-15	 StpR3/3	 StpR3/3	 RO/OR3/2	 RO/OR3/2
rP-16	 StpR3/3	 StpR3/3	 R2/2	 R3/2
rP-26	 SlpR3/3	 StpR2/3	 StpR3/3	 StpR3/3
rP-14	 SlpR3/3	 SlpR3/3	 StpR2/3	 StpR3/3
oP-2	 SlpR3/3	 StpR3/3	 oR3/2	 RO/OR3/2

3.2.1. UV-Vis spectroscopy

Optical absorption in the UV–visible region for the received spinel and heat-treated spinel, sample rP-6, recorded at room temperature, are shown in Fig. 2(a). For the received sample, in the visible region, there are two large absorption peaks near 390 and 537 nm which are assigned to the transition associated with Cr impurity. These two bands correspond to the spin-allowed $4A_{2g} \rightarrow 4T_{1g}$ and $4A_{2g} \rightarrow 4T_{2g}$ transitions, respectively [21]. After heating, these bands are broadened depending on the temperature. Moreover, after heating to 1000 °C, the second band peak shifts to a higher wavelength, as for overall measurements, the band ranges from 536 to 539 nm shifts to 546 to 549 nm. The maximum absorption is moving to longer wavelengths as the amount of delocalisation increases, and thus the “ordered” spinels are disordered by heating.

3.2.2. Raman spectroscopy

Raman spectra of received and heat treated sample rP-6 are shown in Fig. 2(b) with major peaks at ~ 405 , 665, and 767 cm^{-1} . With increasing heating temperature, all Raman bands widen, which is confirmed by measuring the full-width at half-maximum (FWHM) values of the main peak near 405 cm^{-1} . During heating, a small peak near 314 cm^{-1} continuously shifts toward lower frequencies. In the spectrum of the samples heated at 1000 °C, a new weak peak appears near 727 cm^{-1} . Our results is in excellent agreement with previous studies [22] that the Raman spectrum of the natural red Burma spinel consists of four bands: 313 cm^{-1} ($T_{2g}(1)$), 408 cm^{-1} (E_g), 667 cm^{-1} ($T_{2g}(2)$), and 767 cm^{-1} (A_{1g}). These bands represent octahedral Al and tetrahedral Mg stretching and deformation modes. The broadening on the low wave number tail of the 408 cm^{-1} (E_g) band, which becomes evident after heating to 800 °C and above, was assigned to a bending mode of Al in tetrahedral coordination [23]. The additional band near 727 cm^{-1} occurring at 1000 °C of the heated sample has been assigned to a fundamental Raman active AlO_4 vibration [23]. The evolution of Raman spectra

with increasing heating temperature probes the Al coordination showing tetrahedral modes only at high temperature [23].

3.2.3. Photoluminescence spectroscopy

Fig. 2(c) displays the typical PL spectra of spinel sample rP-6 before and after heat-treated. The spectrum of an untreated spinel consists of a strong line near 685 nm and accompanied by several lower peaks on both sides. The strong line, namely R line, actually represents a multiplet of lines which are not resolved (separation is $\sim 6.5\text{ cm}^{-1}$ or $\sim 0.3\text{ nm}$). Sharp zero-phonon R bands originate from the $2E \rightarrow 4A_2$ transition of octahedrally coordinated Cr^{3+} and are accompanied by phonon-sidebands (R-PSB) mirror symmetric to R lines [24,25]. In our case, an overlapping of a small peak to a main peak at $\sim 688\text{ nm}$ was observed. Luminescence lines, which are neither component of R nor R-PSB lines, are called “N” lines [24]. In a completely ordered $MgAl_2O_4$ spinel (normal spinel) with all Mg in tetrahedral (T) and all Al in octahedral (M) coordination, the PL spectrum would only consist of the R and the associated R-PSB lines. The observed N lines represent these different Mg, Al disordered Cr surroundings (Al partially occupies T sites and Mg M sites), and their intensities correspond to the probability of a specific Cr environment [25]. The dominance of the R line accompanied by N lines in our measurement indicates that the untreated Burma spinel is a normal spinel with some defects. After heating, the relative intensities of the luminescence spectra changed. With increasing temperature, the N lines become more dominant and the R line decreases in intensity. The spectra show a remarkable change from rather well-defined peaks of the unheated sample to broadened and poorly defined humps after treatment with increasing temperature. Thus, with increasing temperature, the level of inversion of Al partially occupies T sites and Mg M sites, namely “inverse spinel”, increase [6].

3.3. Ion beam treatment of red spinel

Table 3 displays spinel samples before and after ion implantation. It is interesting that their color can be modified similar to heat-treated

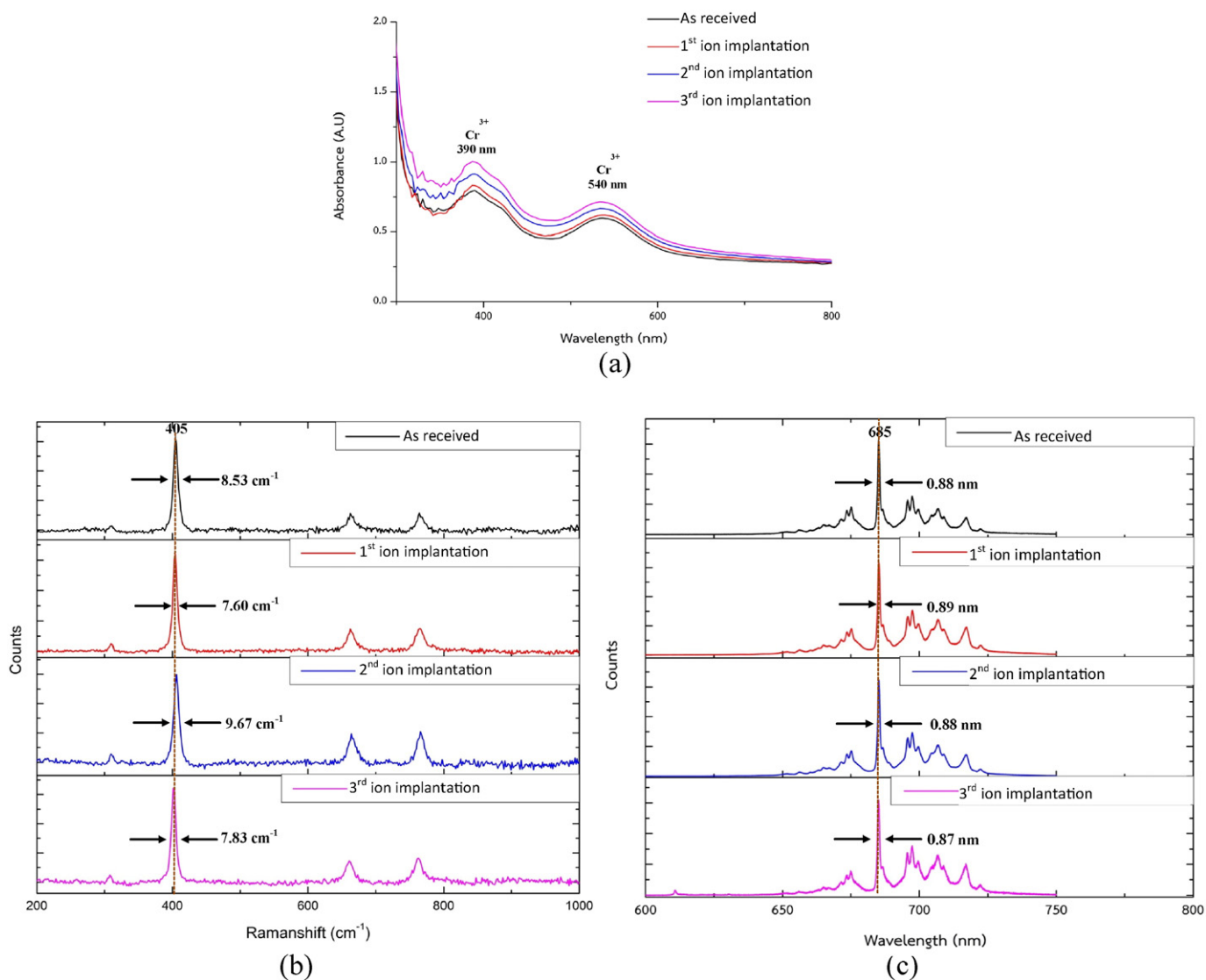


Fig. 3. Comparison of (a) UV-absorption spectra (b) Raman spectra and (c) luminescence spectra of spinel sample rP-15 for before and after ion implanted. For each run, samples were implanted at ion energy of 70 keV to a fluence of $\sim 1 \times 10^{17}$ ions/cm² and subsequently surface cleaning.

spinel at high temperature. For example sample rP-26 and rP-14 of original color “Slightly purplish Red (SlpR)” became “Strongly purplish Red (StpR)”; sample oP-2 of original color “Slightly purplish Red (SlpR)” became “Red-Orange or Orange-Red (RO/OR)”; and sample rP-15 of original color “Strongly purplish Red (StpR)” became “Red-Orange or Orange-Red (RO/OR)” after ion implantation. The most interesting example is the sample rP-16 of original color “Strongly purplish Red (StpR)” became pure Red (R) after ion implantation. For further understanding, sample rP-15 was selected for full characterization and the results can be summarized as follow.

3.3.1. UV-Vis spectroscopy

Example of ion beam treatment of exclusive red spinel, sample rP-15, in term of UV-Vis measurement is demonstrated in Fig. 3(a). UV-Vis spectra of the sample, both before and after ion beam treatment, show the crystal field transition (d-d) for Cr³⁺ (in octahedral coordination) bands centered at approximately 390 and 540 nm [21], dominating the absorption. UV-Vis spectrogram can be used to study the mechanisms of coloration caused by transition metal in gemstones [26]. Color in red spinel is related to the contents of chromium and iron in individual samples. High chromium content causes dominant red color, while iron content causes brown color, correlates with the

absorption spectrum [26]. When both chromium and iron are present, the absorption spectra are intermediate between the mixed colors, and the dominant color shows higher absorption by the corresponding element. In our case, the ion implantation does not alter shape of these bands. However, the absorption spectra in each color band increases after ion implantation, indication of color increasing.

3.3.2. Raman spectroscopy

The Raman spectra of red spinel, sample rP-15, both before and after ion beam treatment, are shown in Fig. 3(b). The most prominent feature is the narrow line ~ 405 cm⁻¹. The FWHM (full width at half maximum) of this line is 8.53 cm⁻¹. In natural unheated gem spinel, the FWHM width of the 405 cm⁻¹ line ranges from ~ 6.8 to 10.6 cm⁻¹ depending on origin [27]. As seen above heat-treated spinel can be identified by reference to a broadening of the Raman line width at 405 cm⁻¹. However, ion implantation does not alter shape of this line. The width of this peak remains approximately the same. Measurements of other samples show the same trends that the peak width remain approximately the same or reduce slightly, e.g. changing from 7.65 to 7.27, and 8.56 to 8.06, respectively. This is evident that the crystalline structure of the specimen remains almost the same or slightly disordered after ion implantation.

3.3.3. Photoluminescence spectroscopy

Fig. 3(c) displays the typical PL spectra of spinel sample rP-15 before and after ion implantation. It is well known that the red spinels contain Cr^{3+} , from trace levels to even more than 1 at.%, because it can easily substitute for Al^{3+} in octahedral sites. Since Cr^{3+} is very often luminescent, its presence allows spinels to be investigated by means of PL spectroscopy, which is able to evidence disorder phenomena in the spinel structure. In fact, Cr^{3+} can occupy different crystalline sites in the spinel structure and the different occupancies clearly influence the PL behavior of the materials [25]. In our case, focusing only on the zero phonon line near 685 nm which is the strongest, we find that its FWHM remain approximately the same or increase slightly after ion implantation. This confirms that the crystalline structure of the gems remains almost the same or slightly disordered after ion implantation.

4. Discussions

The present study demonstrated that the color appearance of spinel has been modified by ion beams as similar as by heat-treated at high temperature. For heat treatment, it was believed that the spinel color was modified by the oxidizing or reducing atmosphere during the treatment [28]. As for ion implantation, many causes of color in gemstones including transition metal impurities, charge transfer, color centers and defect electrons may mostly positively affected by the treatment. Various metallic elements at certain oxidation states give rise to different colors in different gems. The reason for color changing may be because the ion implantation treatment created unbalanced positive charge in the structure. Subsequently, 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) \rightarrow Fe^{3+} (in cation site 1) + Fe^{2+} (in cation site 2) and the actual colors of spinel might be dependent on the concentration fraction of those 2 species. Thus, the color of red spinel is possible to be engineered as similar to the ion implantation of natural ruby [28]. However, with the ion energy in the present study, the ion range is pretty shallow. It is known that the heat treatment affects the entire crystal; but ion implantation should only affect the area where the ion is injected. We do not have a definitive answer at this time that how deep the color appearance is modified by ion beams. Further studies are necessary in order to conclude the color depth profile of the ion implanted samples.

5. Conclusions

We have successfully applied ion beam technology to gemological analysis and treatment of spinel. Ion beam analysis, i.e. PIXE and IL were applied for non-destructive characterization of spinel for data base set up. As a new modification technique, ion beam treatment was applied for improving optical appearance and color enhancement of the red Burmese spinel. It was found that the color appearance of spinel has been modified by ion beam as similar as by heat-treated at high temperature. The results from UV-Vis spectroscopy, Raman spectroscopy and PL spectroscopy measurements can be effective tools for drawing up the explanation of these findings. On one hand, the heating has transformed the normal or the ordered spinel to the inverse or the disordered one, and thus disorder might be used as criteria to determine if the stone has been heated. On the other hand, the crystalline structure

of the spinel remains almost the same or slightly disordered after ion implantation. This finding leads to future applications for jewelry.

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