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# 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 ~$1 \times 10^{17}$ ions/cm$^2$ 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.



## 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 ($MgO$-$Al_2O_3$) 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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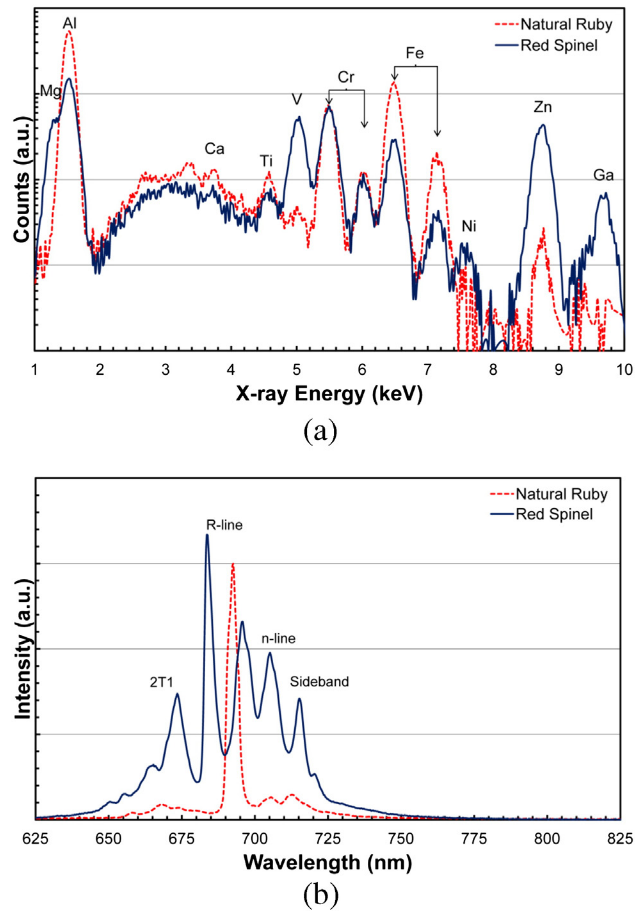


**Fig. 1.** A typical (a) PIXE and (b) IL spectra of the red spinel and ruby from Mogok, Myanmar.

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.

| | Oxide compound (wt%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample | MgO | $Al_2O_3$ | $SiO_2$ | $TiO_2$ | $V_2O_5$ | $Cr_2O_3$ | MnO | $Fe_2O_3$ | ZnO | $Ga_2O_3$ |
| 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 |