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# Ion beam analysis of rubies and their simulants

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#### ABSTRACT

Ion beam analysis (IBA) is a set of well known powerful analytical techniques which use energetic particle beam as a probe. Among them, two techniques are suitable for gemological analysis, i.e., Particle Induced X-rays Emission (PIXE) and Ionoluminescence (IL). We combine these two techniques for the investigations of rubies and their simulants. The main objective is to find a reference fingerprint of these gemstones. The data are collected from several natural rubies, synthetic rubies, red spinels, almandine garnets and rubellite which very much resemble and are difficult to distinguish with the gemologist loupe. From our measurements, due to their different crystal structures and compositions, can be clearly distinguished by the IL and PIXE techniques. The results show that the PIXE spectra consist of a few dominant lines of the host matrix elements of each gemstone and some weaker lines due to trace elements of transition metals. PIXE can easily differentiate rubies from other stones by evaluating their chemical compositions. It is noticed that synthetic rubies generally contain fewer impurities, lower iron and higher chromium than the natural ones. Moreover, the IL spectrum of ruby is unique and different from those of others stones. The typical spectrum of ruby is centered at 694 nm, with small sidebands that can be ascribed to a Cr<sup>3+</sup> emission spectrum which is dominated by an R-line at the extreme red end of the visible part of the electromagnetic spectrum. Although the spectrum of synthetic ruby is centered at the same wavelength, the peak is stronger due to higher concentration of Cr and lower concentration of Fe than for natural rubies. For spinel, the IL spectrum shows strong deformation where the R-line is split due to the presence of MgO. For rubellite, the peak center is shifted to 692 nm which might be caused by the replacement of Mn<sup>3+</sup> at the Al<sup>3+</sup> site of the host structure. It is noticed that almandine garnet is not luminescent due to the idiochromatic nature of the stone.

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## 1. Introduction

A natural gemstone, a crystalline form of mineral, is desired for its beauty, valuable in its rarity and durable enough to be enjoyed for generations. Gemologists may face two problems in the identification of gemstone. The first is the determination of whether it is natural or synthetic and real or substitute. Synthetic ones are much less valuable, but may not distinguished by conventional tests. Also there are several natural gemstones very much resemble to ruby and are difficult to identify with the gemologist loupe. The second problem is the determination of the source of gems that can have a profound impact on their market value. Therefore, it is important to strengthen the conclusions of the gemologist observations with the chemical composition of the gemstones. Among a wide variety of analytical methods applied to gemstones, such as Raman microspectroscopy, neutron activation analysis, and energy dispersive X-ray fluorescence spectrometry, ion beam analysis (IBA) techniques have several extra advantages in addition to the generally known non-destructiveness and good spatial resolution.

Ion beam analysis (IBA) technique has just been introduced for the non-destructive elemental analysis in Thailand [1]. They constitute a set of powerful analytical techniques of which at least two techniques are suitable for gemologists; i.e. Particle Induced X-rays Emission (PIXE) and Ionoluminescence (IL). These techniques are potential sensitive tools for both qualitative and quantitative analysis of minerals [2]. The emitted X-rays, in the case of PIXE, originate from the de-excitations between inner atomic

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levels, induced by the MeV proton beam and therefore, are only related to the nature of the chemical element. On the other hand, in the case of IL, the near IR to UV radiations corresponds to outer energy levels of atoms or molecules that are affected by the chemical environment of the atoms. Accordingly, the IL spectrum also depends on the host of the trace elements. Therefore, the results from these measurements can provide a useful fingerprint pattern for a large number of gemstones.

Ruby is generally known as the most valuable of all color gemstones. It is the mineral corundum (Al<sub>2</sub>O<sub>3</sub>) that has apparent color from a pink to blood-red. Corundum is allochromatic, which means that the chemistry of their basic formula does not cause any selective absorption so that they are clear or colorless in the pure state. In these types of gems, it is the traces of impurities that act as chromophores. As for rubies, the red color is caused mainly by the presence of a few percent of the element chromium (Cr). Prices of rubies are primarily determined by their color. The brightest and most valuable red color called "pigeon's blood" color prevails over other rubies of similar quality. However, some stones appear very similar to rubies and are hard to distinguish with the gemologist loupe. Such stones are, for examples, red spinel, almandine garnet and rubellite. Therefore, PIXE and IL were applied for investigations of various red gemstones in the present study with the main objective to distinguish the natural rubies from their imitations and substitutes.

## 2. Experimental details

Both cut and uncut of  $\sim$ 100 rubies from various deposits, 30 red spinels, 1 rubellite and 10 almandine garnets were investigated. PIXE and IL electromagnetic radiation were induced by a proton beam accelerated to 2 MeV by a 1.7-MV tandem accelerator of Chiang Mai University. The proton ions were generated from titanium hydride (TiH<sub>2</sub>) powder in a negative ion Cs-sputter source. The beam was collimated with a diameter of  $\sim 1$  mm, and the beam current on the sample was less than 10 nA. Base pressure in the vacuum chamber was about  $6 \times 10^{-6}$  mbar. Each gem was mounted on the head of a small bolt with super epoxy adhesive and was screwed into a sample holder which can hold as many as 50 gems. By this way the top surface of each stone can easily be adjusted to the same level. For PIXE, X-rays were detected by a Si(Li) detector located at 120° to the beam direction. Multichannel analyzer card, connected to a computer, was used for data accumulation. In the experiment, a 74-µm mylar foil thickness, with a hole of 0.38% of the active area of the detector, was placed in front of the beryllium window of the detector as an absorber in order to reduce the count rate caused by elements of low atomic numbers. A flood of electrons from an electron gun was used in order to reduce the bremsstrahlung continuum background from due to the charging of insulator sample like these gemstones. Each measurement took around 10 min and the spectra were analysed by the GUPIXWIN software [3]. For IL, the emitted light was recorded by the Fiber Optics spectrometer (Model S2000, Ocean Optics, Inc.) placed outside the analysis chamber. The configuration featured a 600 lines/mm grating (set for 300–950 nm), 2014-element linear silicon CCD array detector, and a 1000  $\mu$ m diameter optical fiber for signal collection. Optical resolution of the system is ~1.3 nm FWHM. The spectra were displayed by OOIBase32–32 bit Spectrometer operating software [4]. In order to collect a satisfying emission peak, each spectrum was recorded at about five seconds.

# 3. Results and discussions

Fig. 1 displays a collection of five PIXE spectra from natural and synthetic rubies and various others red gemstones. The results show that the spectra consist of a dominant line of the host matrix elements of each gemstone and a few weak lines due to the trace elements of transition metals. PIXE can easily differentiate rubies from other stones on the basic of their chemical compositions. The oxide compositions of rubies from various origins and of rubies imitations and substitutes are summarized in Tables 1 and 2, respectively. Fig. 2 displays the IL spectra of these gemstones, in the wavelength region between 600 and 800 nm. It is clear that IL spectrum of rubies are different from others stones.

## 3.1. Rubies and synthetic rubies

Ruby crystal is in hexagonal and rhombohedral system and has hardness of 9.0 on the Mohs Hardness Scale. The chemical formula of rubies is  $Al_2O_3$  with  $Al \sim 53$  wt.% and  $O \sim 47$  wt.% [5]. From our PIXE measurement, the strong X-ray peak of Al is clearly seen and the peaks of Cr and Fe and other trace elements, e.g. Ti, V, and Ga are also observed. We have analysed natural rubies from four origins and found that they exhibit similar levels of Ti, V, and Ga but a markedly different Cr and Fe concentrations (Table 1). The wide variations in Cr and Fe contents are reflected in the range of color, from paler to stronger in red. It is useful to relate between two concentrations of any couple of key trace elements in a *x*-*y* plot to see if any population field appears. Examples of such plots are shown



Fig. 1. PIXE spectra of a natural ruby with synthetic ruby and resembling gemstones.

#### Table 1

Chemical composition in trace elements of natural rubies	s collected from various deposits (in ppms)
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Deposits/Elements	Fe			Cr			Ti			V			Ga		
	Ave.	Std	LOD	Ave.	Std	LOD	Ave.	Std	LOD	Ave.	Std	LOD	Ave.	Std	LOD
Bo Rai (Thailand)	4520	1229	30	1989	529	23	143	74	19	<	-	22	<	-	38
Mozambique (Africa)	1850	842	8	3185	1623	8	61	20	12	<	-	60	29	17	9
Mogok (Myanmar)	56	46	6	2712	1349	14	828	595	9	182	59	24	43	9	13
Mong Hsu (Myanmar)	2615	2172	29	2178	1150	35	140	112	34	450	23	122	101	26	28

Note: Ave. = average value concentration; Std = standard deviation; LOD = Limit of detection; < = below limit of detection.

#### Table 2

Chemical compositions in oxides of ruby imitations and ruby substitutes (in wt.%).

Oxide compound	Natural ruby (Thailand)	Synthetic ruby	Red spinel	Rubellite	Garnet (Almandine)
MgO	<	<	17.81 ± 1.99	<	0
Al <sub>2</sub> O <sub>3</sub>	99.19 ± 0.44	97.32	80.48 ± 7.36	39.95	20.60 ± 0.63
SiO <sub>2</sub>	0	1.08	<	57.06	43.59 ± 5.22
CaO	$0.03 \pm 0.02$	0	<	0.61	$0.68 \pm 0.11$
TiO <sub>2</sub>	0.02	0.01	$0.05 \pm 0.03$	0.02	0.03 ± 0.01
Cr <sub>2</sub> O <sub>3</sub>	$0.23 \pm 0.04$	1.58	$0.46 \pm 0.26$	0	$0.01 \pm 0.01$
MnO	0	0	<	2.33	$0.63 \pm 0.24$
Fe <sub>2</sub> O <sub>3</sub>	$0.50 \pm 0.07$	0.01	$0.40 \pm 0.12$	0.02	34.47 ± 4.51
ZnO	0.01 ± 0.01	0	$0.60 \pm 0.37$	0	0
V <sub>2</sub> O <sub>3</sub>	0	0	$0.17 \pm 0.08$	0	0
$Ga_2O_3$	$0.01 \pm 0.01$	0	$0.02 \pm 0.01$	0	0

Note: < = below limit of detection.



Fig. 2. IL spectra of a natural ruby with synthetic ruby and resembling gemstones.

in Fig. 3. Together, they show the capability of origin separation for natural rubies. This is in agreement with other papers [6,7].

The typical IL spectrum of ruby is centered at ~693 nm, with small sidebands that can be ascribed to a  $Cr^{3+}$  emission spectrum at the extreme red end of the visible part of the electromagnetic spectrum. Basically, the major impurities in natural rubies are Cr and Fe. For rubies, chromium is responsible for the red coloration of them, due to the presence of  $Cr^{3+}$ -ions which replaces  $Al^{3+}$  in the  $Al_2O_3$  lattice. Details of IL spectrum of ruby is be detailed in Fig. 4. The strongest peak, at ~693 nm, namely R-line, is for the transition of excited electron from <sup>2</sup>E to ground state (<sup>4</sup>A<sup>2</sup>) [8]. From literature, there are two possibilities of such transition [8], thus, they should have 2 peaks at ~692 and ~694 nm, respectively [1]. However, the limited energy resolution of our detector, of ~3.5 nm, is too poor to separate these two peaks. The peaks at ~659 and ~668 nm are assigned to be the transition of excited

electron from 2 bands of  ${}^{2}T_{1}$  to ground state, respectively. On the right side of the main peak, there are two other peaks. The peak at ~705 nm is named n-line [9] and the one at the far end is called Sideband [10]. Sideband and n-line do not belong to the electronics transition of Octahedral–d<sup>3</sup> system of ruby, but they can be assigned to be something else, such as atomic or molecular vibration. Note that we have reported that the Cr<sup>3+</sup> luminescence is strongly affected by the quenching by iron [11].

By comparing the trace elements of natural ruby and its imitation, one can readily conclude that synthetic ruby contains fewer impurities than natural one. In comparison of their luminescence, although the shapes of the luminescent spectra are almost similar but the peak intensity of the former is relatively higher than the latter. As mentioned above, intensity of the main  $Cr^{3+}$  luminescence is simply related to the chromium and iron contents and our PIXE measurement has found that the synthetic one contains



Fig. 3. Trace elements and ratio of trace elements in natural rubies.



Fig. 4. IL spectrum of ruby.

higher concentration of chromium but lower concentration of iron than the natural one.

# 3.2. Spinels

Spinel has just recently been recognized for its own value since in those days people had believed that spinel was sapphire. However, with increasing knowledge in gemology, people realized that spinel was gemstone whose hardness is only one order lower than the sapphire in the Mohs scale. Spinels can be found in a variety of colors such as red, pink, red-pink, orange, red-orange, red-brown, blue, purple, green, yellow and even white or black, but the most expensive and popular one is "red spinel". Spinel crystal is in octahedral isometric system, the chemical formula is MgAl<sub>2</sub>O<sub>4</sub> (MgO + Al<sub>2</sub>O<sub>3</sub>) with MgO ~ 28 wt.% and Al<sub>2</sub>O<sub>3</sub> ~ 72 wt.% [5]. The origin of the color of red spinel is believed to be similar to rubies, i.e. the replacement of Cr<sup>3+</sup> in Al<sub>2</sub>O<sub>3</sub> matrix. As seen from Fig. 1, PIXE spectrum of spinel shows the existing of Mg in addition to other elements similar to rubies. The principal peak on IL spectrum is also observed at the same wavelength to that of rubies. However the main peak or the R-line (683–695 nm) of their luminescence is lower and the sidebands are higher than that of rubies. Note that the IL spectrum of red spinel shows more peaks than that of ruby. It seems that there is 2 times more splitting of <sup>2</sup>T<sub>1</sub> energy level of



Fig. 5. IL spectrum of red spinels.

spinel than of rubies (see Fig. 5 for details). Also, there are extra peaks at sideband in the spinel spectrum. We have examined for the case thoroughly and we have attributed the difference to the existing of MgO in the stones structure [12].

## 3.3. Almandine garnet

Garnets are a group of silicate minerals. They possess similar physical properties and crystal forms but have different chemical compositions. Almandine, an iron alumina garnet, of deep red color, inclining to purple, is one of the most commonly used for jewelry making production. Historical studies indicate that almandine garnet was a popular gem but its value is low because it can be found in great abundance worldwide. The crystal formula is  $Fe_3Al_2(SiO_4)_3$  with  $SiO_2 \sim 36$  wt.% and  $Al_2O_3 \sim 20$  wt.% [5]. Garnet crystal is in cubic system and has a hardness of 6.5-7.5 on the Mohs Hardness Scale. The cause of red color in almandine garnet belongs to FeO, one of the three major compound elements in the stone, of about 43 wt.% [5]. Therefore, in Fig. 1, the existing of Fe-peak is very clear. PIXE can also easily identify the species of garnets by calculating the chemical compositions of the stones. On the contrary, the almandine garnet does not produce luminescence under the bombardment of ion beam. This might be due to because the idiochromatic nature of the stones, in which their apparent color derive simply from the chemistry of their basic formula, in opposite to the allochromatic nature of rubies and spinels, the absence of luminescent centres and the quenching effect of the strong iron concentration.

## 3.4. Rubellite

The rubellite is the most valuable form of the colorful family of the tourmalines. Its color shines in the most beautiful nuances from red to pink. The color of most other pink or red tourmalines displays a more or less clearly visible tinge of brown in artificial light, but a true rubellite shines just as intensely in artificial light as it does in daylight. The chemical formula of rubellite is Na(Mg,Fe,Mn,Li,Al)<sub>3</sub>Al<sub>6</sub>(BO<sub>3</sub>)Si<sub>6</sub>O1<sub>8</sub>(OH,F)<sub>4</sub> and a crystal is in trigonal system. Its hardness is of 7–7.5 on the Mohs Hardness Scale. Natural red color is created by traces of manganese in its (Mn<sup>43</sup>) valence state [13]. Therefore, in the PIXE measurement, one can easily observed Al, Si and Mn for they are the major components of rubellite structure. For IL spectrum, the strong peak located in the red region spectrum, similar to that of ruby, is clearly observed. However, the peak centre appeared at 691.65 nm. It should be ascribed to a Mn<sup>3+</sup> emission of rubellite structure [13].

## 4. Conclusions

We have proposed a new procedure to sort natural rubies from their imitations and substitutes. While PIXE appears as an effective and relatively simple analytical technique that can be used to identify and quantify trace elements, IL is potentially a highly sensitive method for measuring optically active impurities and defects in gemological samples. Our measurements show that the PIXE spectra consist of a dominant line of the host matrix elements of each gemstone and a few weak lines due to the trace elements of transition metals. It is noticed that synthetic rubies generally contain fewer impurities and contain lower iron but higher chromium than the natural ones. Therefore, PIXE can easily differentiate rubies from other stones by comparing their chemical compositions. We have also found that IL spectrum of ruby is unique and different from other stones. The typical spectrum of ruby peaks at  $\sim$ 694 nm, with small sidebands that can be ascribed to a Cr<sup>3+</sup> emission spectrum which is dominated by an R-line at the extreme red end of the visible part of the electromagnetic spectrum. The spectrum of synthetic ruby is centered at the same wavelength but the peak is stronger due to higher concentration of Cr and lower concentration of Fe than the natural ones. For spinels, the spectrum shows strong deformation and the R-line is split due to the existing of MgO. For rubellite, the peak is centered at  $\sim$ 692 nm. This peak should be ascribed to Mn<sup>3+</sup> emission of its structure. It is worth noticing that almandine garnet does not luminesce due to its idiochromatic nature. In conclusion, these two ion beam analytical techniques, i.e., PIXE and IL, is of great interest to gemologists for the identification of gemstones as well as to physicists for the study of atomic and molecular behaviour of trace elements in the gemstone systems.

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## References

- T. Kamwanna, Developments of ion beam analysis techniques for micro and nanoscale materials, (Ph.D. thesis), Graduate School Chiang Mai University, Chiang Mai, 2008.
- [2] H. Calvo del Castilo, J.L. Ravalcaba, T. Calderon, Anal. Bioanal. Chem. 387 (2007) 869.
- [3] J.L. Campbell, J.A. Maxwell, S.M. Andrushenko, S.M. Taylor, B.N. Jones, W. Brown-Bury, Nucl. Instrum. Meth. B. 269 (2011) 57.
- [4] OOIBase 32TM Spectrometer Operating Software. n.p.: Ocean Optics Inc., 1989.

- [5] D. Barthelmy, Mineralogy Database, Available from: <<u>http://www.webmineral</u>.
- com>.
  [6] T. Calligaro, J.-P. Poirot, G. Querre, Nucl. Instrum. Meth. B 150 (1999) 628.
  [7] K. Thirangoon, Ruby and Pink Sapphire from Aappaluttog, Greenland: Status of [7] K. Thirangoon, Ruby and Pink Sapphire form Aappaluttog, Greenland: Status of [7] K. Thirangoon, Ruby and Pink Sapphire form Aappaluttog. Ongoing Research. Available from: <a href="http://www.gia.edu/gia-news-research-">http://www.gia.edu/gia-news-research-</a> nr32309>.

- [8] D.F. Nelson, M.D. Sturge, Phys. Rev. 137 (1965) A1117.
  [9] R.C. Powell, Phys. Rev. 155 (1967) 296.
  [10] U. Rothamel, J. Heber, W. Grill, J. Phys. B Condens. Mater. 50 (1983) 297.
- [11] U. Juncomma, S. Intarasiri, D. Bootkul, U. Tippawan, S. Singkarat, "Ionoluminescence Characteristics of Rubies and Red Spinel [in Thai]", Proceedings May 29–30, 2012, Srinakharinwirot University VICHAKARN 6, Bangkok, Thailand.
- [12] B. Srisataporn, D. Bootkul, A. Kiratisin, B. Phichaikamjornwut, S. Intarasiri, S. Singkarat, "Ion Beam Analysis of Spinel", Proceedings: The 3rd International Gem and Jewelry Conference (GIT 2012), December 12–16, 2012, pp. 220–223.
- [13] C.S. Hurlbut, R.C. Kammerling, Gemology, 2nd ed., Jonh Wiley & Son, New York, 1991.