

## Micro-structural defects in ruby samples from Mong Hsu, Myanmar

P. Maneeratanasarn, P. Wathanakul<sup>\*,\*\*</sup>, Y.C. Kim<sup>\*\*\*</sup>, H.M. Choi<sup>\*\*\*</sup>, S.Y. Bang, B.G. Choi and K.B. Shim<sup>†</sup>

*Division of Advanced Material Science and Engineering, Hanyang University, Seoul 133-791, Korea*

*\*Earth Sciences, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand*

*\*\*The Gem and Jewelry Institute of Thailand (GIT), Chulalongkorn University, Bangkok 10330, Thailand*

*\*\*\*Hanmi Gemological Institute (HGI), Laboratory, Seoul 110-390, Korea*

(Received January 12, 2009)

(Accepted February 5, 2009)

**Abstract** Mong Hsu rubies from Myanmar were heat treated in oxidizing (oxygen) atmosphere at 1650°C for 1 hour. The investigations of the micro-structural defects in the samples before and after heat treatment have been carried out by the variety of analysis techniques of FTIR, UV-VIS-NIR and SEM-EDS. It was found that after heat treatment the dark blue cores region were disappeared and turned to orange red color with the presence of the dense cloudy brownish colored tiny particles in and near former blue zoning. As-received ruby samples only revealed the presence of FTIR absorption peaks of diaspore, boehmite and O-H stretching, at 1986, 2115 and 3078/3319 cm<sup>-1</sup>, respectively. The UV-VIS-NIR absorption of as-received and heat treated ruby samples similarly showed peaks at 405, 554 and 693 nm associated with Cr<sup>3+</sup>, but for the same samples, the absorption peak of heat-treated ruby samples at 693 nm was somewhat stronger than that of the untreated ruby samples. Especially the presence of Cr<sup>3+</sup> peaks at 659 and 675 nm was found obviously in as-received ruby samples only. The SEM-EDS investigation disclosed the micro-porous defect structures commonly related to the core regions of the untreated ruby samples, which after heat treatment in an oxidizing environment those defect features have been dissolved into the host phase resulting in the lightening or disappearance of the dark coloration of ruby core.

**Key words** Ruby, Heat treatment, SEM-EDS

### 1. Introduction

Ruby is mainly composed of aluminium (Al) and oxygen (O) forming the corundum structure ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) and contains small amounts of other elements such as 0.03~0.1% chromium ions (Cr<sup>3+</sup>), trace elements or impurities, which substitute for the octahedral site of aluminium ions (Al<sup>3+</sup>), resulting in the cause of red color in ruby [1, 2].

Myanmar has been traditionally very important source of the gemstones, especially Mogok and Mong Hsu district in which the gem stones of rubies and sapphires have been abundantly found. The as-mined rough rubies from Mong Hsu occur in the marble-type metamorphic deposits and have typical characteristics of a distinct color zoning with transparent red rims and dark-blue to almost black cores [3-5]. These features are unique among the rubies in other sources; however, the existence of core regions decreases their values in the gem market. There are some reports that the dark blue core region in Mong Hsu rubies could be removed by the

heat-treatment in an oxidizing or reducing atmosphere, resulting in the enhancement of color saturation, lucidity and trading value [6, 7]. Achiwawanich *et al.* reported that the annealing heat-treatment of Mong Hsu rubies in the inert (reducing) atmosphere does not exhibit the presence of an orange region or whitish particles but the heat-treatment in air or oxidizing atmosphere shows the occurrence of dense tiny particles or an orange area [6, 7]. Most of the previous work has been mainly focused on the chemical effect on the origin of the coloration of dark core and/or blue zoning in those rubies and therefore more comprehensive investigation in terms of both the chemical and structural effects are needed.

This work is aimed to investigating the microstructural behaviors of the defects in Mong Hsu rubies during the heat-treatment in oxidizing atmosphere in order to clearly elucidate the micro-structural change of the ruby samples.

### 2. Experimental

As-received ruby samples are listed in the Table 1 with their registrations. As-received ruby samples were cut into 2 pieces and then polished using diamond paste.

<sup>†</sup>Corresponding author  
Tel: +82-2-2220-0501  
Fax: +82-2-2291-7395  
E-mail: kbshim@hanyang.ac.kr

Table 1  
The registrations of as-researched ruby samples

Pictures of as-received samples (before cutting)	Sample code	Carats	Description
	M1	1.2760	Red color with dark blue core
	M2	0.9405	Red color with dark blue core

The polished specimens were then cleaned in an ultrasonic bath with the sequence of acetone and DI-water in order to remove adventitious hydrocarbon components on the surface. Subsequent to the initial surface examinations, the specimens were subjected to heat-treatment using an electric furnace with an oxygen flow rate of approximately 30 ml/min at 1650°C for one hour.

Both samples, as-received and heat-treated, were examined by a transmission optical microscope (OM, Olympus, Japan) equipped with CCD camera in order to observe the surface feature and mineral inclusions. Fourier transform infrared spectrophotometer (FTIR, Nexus 470, USA) and ultra violet-visible-near infrared spectrophotometer (UV-Vis-Nir, UV-3101PC, Japan) were employed for the optical characteristics analysis before and after heat treatment. The microstructural defect and chemical composition of the specimens were evaluated using scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDS, JSM-6330F, Japan).

### 3. Results and Discussions

Figure 1 shows the color change of the dark core region after the heat-treatment at 1650°C in oxidizing atmosphere for one hour. It is seen that the dark blue cores region in as-received specimens turned to orange red color and some parts of core region were changed to pinkish red color. The blue bands existing in the bottom-left of the core region were completely faded and then turned to orange red color with the appearance of the alignment of dense tiny particles along these bands.

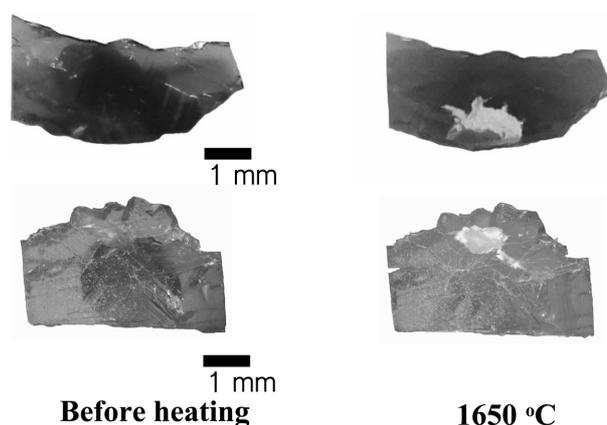


Fig. 1. Color change in the dark blue core regions of Mong Hsu rubies after heat treatment in oxidizing atmosphere at 1650°C for 1 hour.

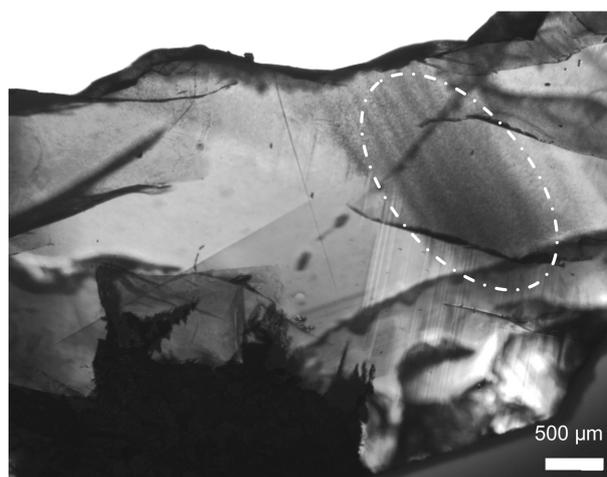


Fig. 2. The presence of the dense cloudy brownish tiny particles near the former dark blue core region.

The dense cloudy particles and cross-silk were also observed in some areas near to core region as shown in Fig. 2. These features made the ruby specimen appear semi-translucent and lessen its market value [6].

The FTIR analysis shows that the as-received specimens disclosed the absorption peaks of diaspore at 1986  $\text{cm}^{-1}$ , boehmite at 2115  $\text{cm}^{-1}$  and O-H stretching at 3078  $\text{cm}^{-1}$  and 3319  $\text{cm}^{-1}$  (Fig. 3a). After heat-treatment in an oxygen-rich atmosphere, all these FTIR absorption peaks disappeared, resulting from the combination of OH from diaspore and H from O-H stretching.

The UV-VIS-NIR absorption spectra of as-received specimens showed the peaks at 405, 554 and 693 nm assigned for  $\text{Cr}^{3+}$ , but the heat-treated ruby samples showed the absorption peak at 693 nm which was somewhat stronger than that of the as-received samples (Fig. 3b). It is very interesting that as-received specimens with

quite dark blue core showed obviously the absorption peaks in the well-known  $\text{Cr}^{3+}$  lines at 659 and 675 nm, however after heat treatment these absorption peaks became weaker. It is noted that these absorption peaks at 659 and 675 nm are responsible for the coloration in core region.

Fig. 4 shows the surface morphology of the as-received ruby specimens. Many cracks and fissures called the

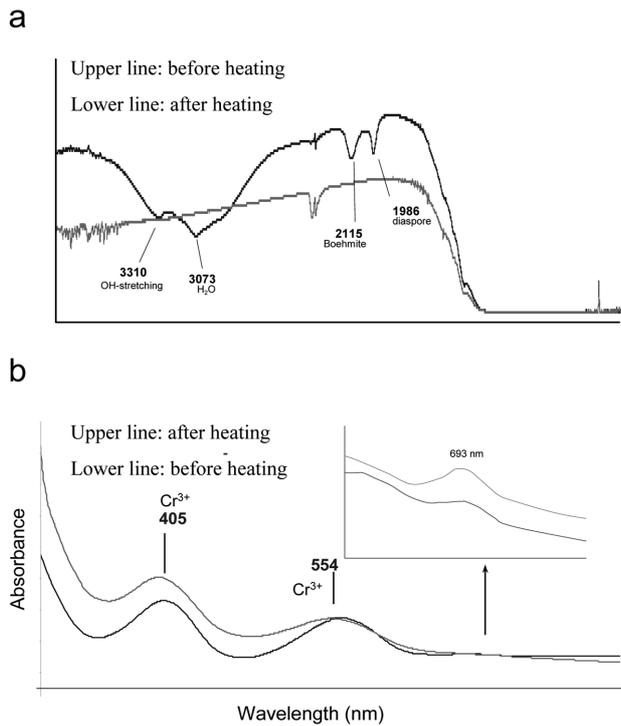


Fig. 3. FTIR and UV-VIS-NIR absorption spectra of Mong Hsu ruby specimens investigated.

healing fractures, the alignment of the angular cavities with remained growth solution fluid were seen more noticeably and particularly found at the dark blue cores region than red rim region. The healing fractures were originated from the fracture developing and flowing growth solution during or after the crystal growth [5]. There are also the mineral region like blade and shave on the surface of as-received samples. The mineral was confirmed to be phlogopite ( $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ ) by EDS analysis. Elemental mapping of the EDS analysis revealed the distribution of possible trace elements on the surface of specimens (Fig. 5a). It is noted that the distribution of Zr that was often seen at the edge of holes or fissures (Fig. 6). After heat-treatment, there is

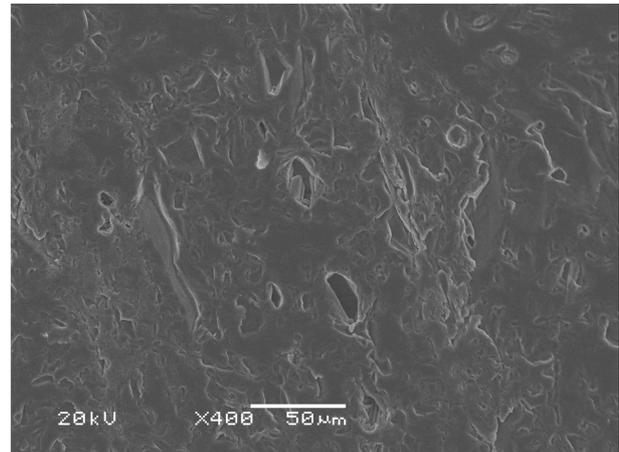
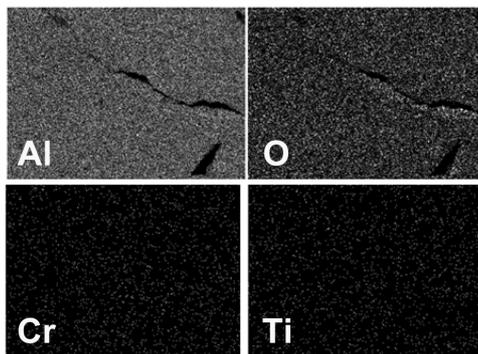


Fig. 4. Microstructural defects such as cracks, fissures and holes in the surface of ruby sample.

(a) Before heat treatment



(b) After heat treatment

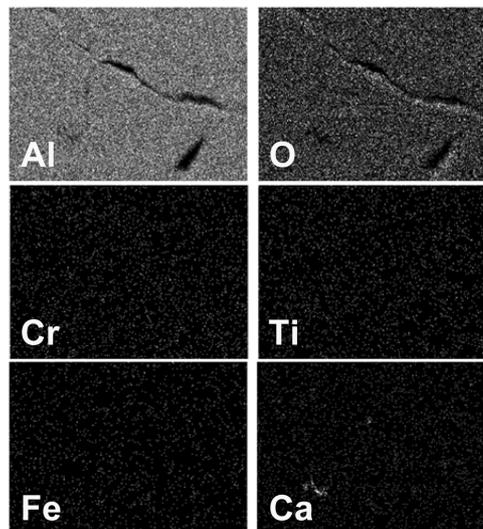


Fig. 5. The distribution of possible elements on the sample surface in fixed area before and after heat treatment in oxygen environment  $1650^\circ\text{C}$  for 1 hour.

change in surface morphology and microstructural defects. The surface melting is also observed from the heat-treated specimen as shown in Fig. 7. These phenomena is thought to be caused by the compositional reaction among Al-, Fe-, or other elements-based phases during

heat treatment in oxygen environment at 1650°C. These specimens also showed the wave and step lines in the surface melting areas. Investigations of the specimens using SEM-EDS revealed the micro-porous defects commonly related to the core regions of the as-received

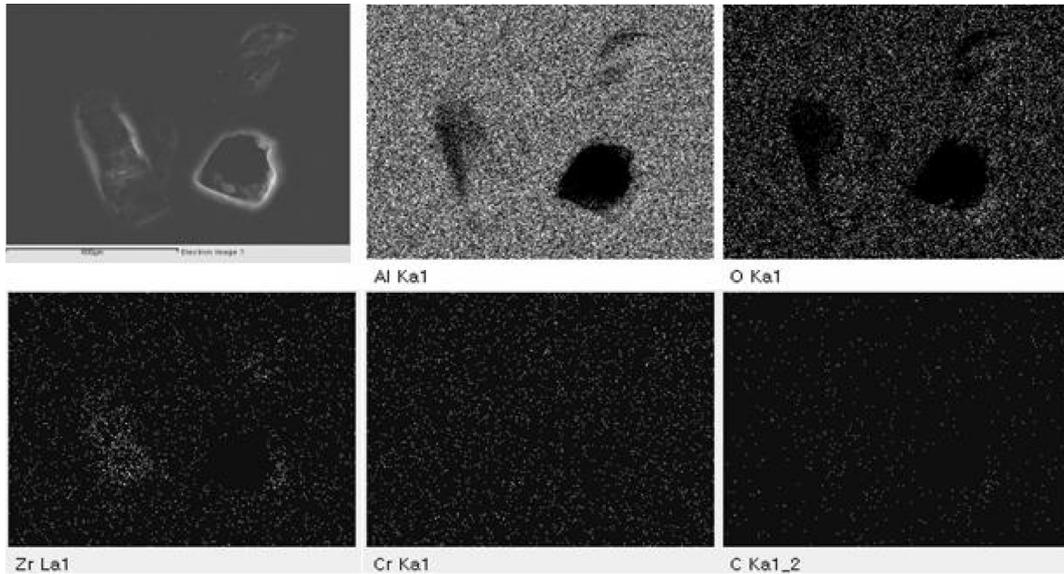


Fig. 6. The distribution of possible elements on the as-received sample surface in fixed area.

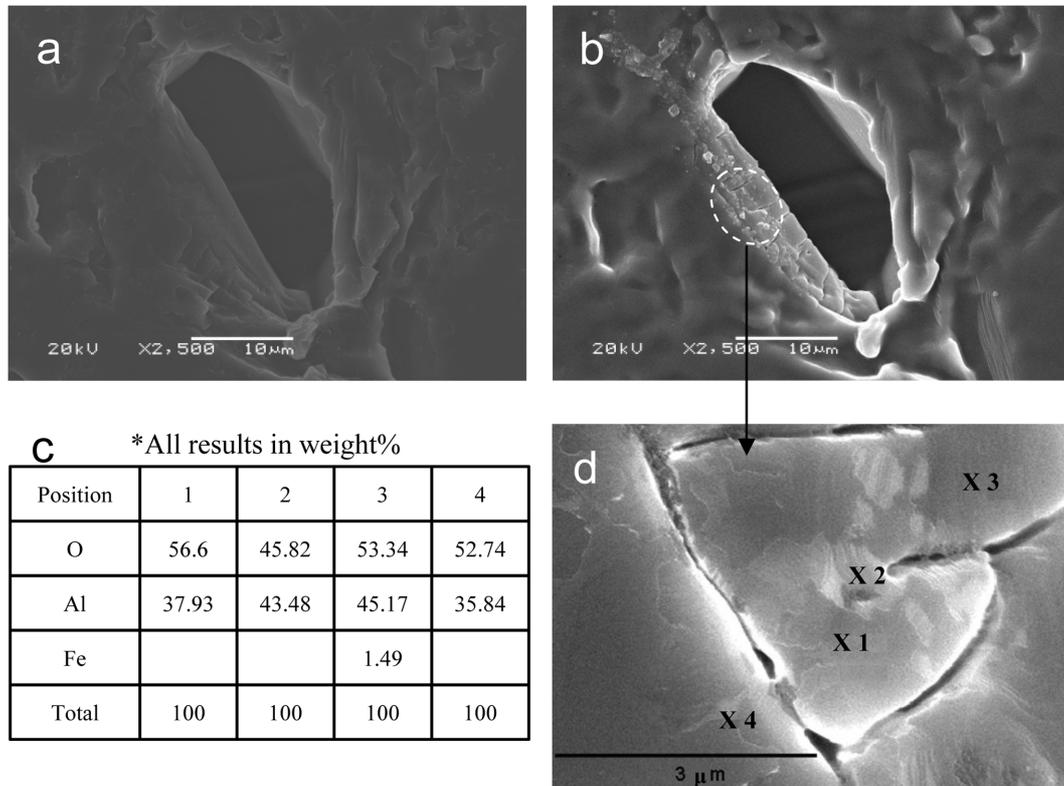


Fig. 7. Change in the surface morphology of a ruby specimen after heat treatment (a) as-received ruby specimen.(b) surface melting of heat-treated ruby specimen. (c) and (d) The surface melting was caused by the compositional reaction among Al-, Fe-, or other elements-based phases during heat treatment in oxygen environment at 1650°C confirmed by EDS analysis.

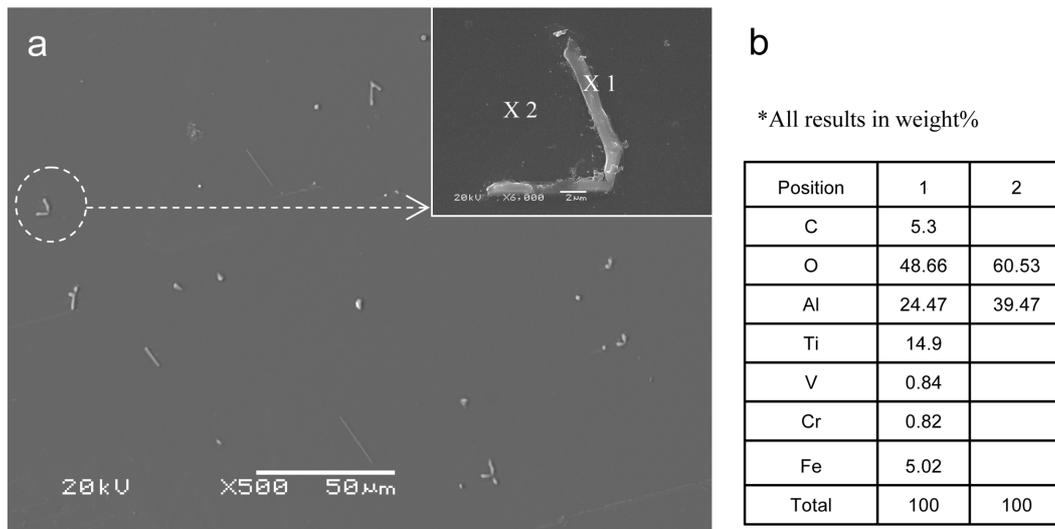


Fig. 8. (a) SEM image shows the precipitated tiny particles on the ruby sample surface after heat treatment. (b) Chemical composition of the tiny particles analyzed by EDS method.

ruby sample. However, after heat treatment in an oxidizing environment those defects have been dissolved into the host crystal, resulting in lightening or disappearance of the dark coloration of the ruby cores. According to the appearance of the dense cloud small particles in the specimens after heat-treatment, those tiny particles of which the chemical composition consisted of Ti, Fe, Cr, V, Al, O (Fig. 8) and therefore those tiny particles are thought to be  $\text{TiO}_2$  and the precipitates resulted from the precipitation of transition elements during heat treatment. Fig. 5b shows the distribution of Fe exposed to the surface of the specimens after heat treatment in the contact area between former dark blue core region and red rim area was found, which before heating it was not detected on the surface of the specimens. This may be attributed by the bond breaking of  $\text{Fe}^{2+}\text{-O-Ti}^{4+}$  charge transferring, resulting in the cause of blue color in corundum, and then free Fe ions move to the specimen surface.

#### 4. Conclusions

The micro-porous defect structures commonly related to the dark blue color in core regions of the ruby samples before heat treatment. After heat treatment in an oxidizing environment those defect features have been dissolved into the host phase, resulting in lightening or disappearance of the dark coloration of the ruby cores. This features indicated that the dark cores of Mong Hsu rubies from Myanmar are responsible by not only the chemical effect but also the physical effect, the micro-structural defects.

#### Acknowledgements

We wish to acknowledge the financial support of the Fusion Material Program of Hanyang University (HFM) and Hanmi Gemological Institute (HGI) Laboratory, Seoul, Korea.

#### References

- [ 1 ] T. Themelis, "The heat treat of ruby and sapphire", 1st ed., Gemlab Inc. Publ. (Word Graphics, Inc., USA, 1992) p.1.
- [ 2 ] T. Osipowicz, *et al.*, "Nuclear microscopy of rubies, analysis of trace elements and inclusions", Nucl. Instr. Meth. B104 (1995) 590.
- [ 3 ] A. Peretti, *et al.*, "Rubies from Mong Hsu.", *Gems & Gemology* 31(1) (1995) 2.
- [ 4 ] J.L. Sanchez, *et al.*, "Micro-PIXE analysis of trace element concentrations of natural rubies from different locations in Myanmar", Nucl Instr and Meths. B130 (1997) 682.
- [ 5 ] R.W. Hughes, "Ruby & Sapphire", RWH Publishing, (Boulder, Colorado, 1997) p. 60.
- [ 6 ] S. Achiwawanich, *et al.*, "XPS and ToF-SIMS analysis of natural rubies and sapphires heated in an inert ( $\text{N}_2$ ) atmosphere", *Appl. Surf. Sci.* 252 (2006) 8646.
- [ 7 ] S. Achiwawanich, *et al.*, "XPS and ToF-SIMS analysis of natural rubies and sapphires heat-treated in a reducing (5 mol%  $\text{H}_2/\text{Ar}$ ) atmosphere", *Appl. Surf. Sci.* 253 (2007) 6883.
- [ 8 ] K. Nassau, "The physics and chemistry of color: The fifteen causes of color", Wiley-Interscience (John Wiley and Sons, New York, 2001) p. 317.