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Characterization of dark core and blue patch in Mong Hsu ruby

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Abstract Mong Hsu rubies from Myanmar include typically the dark core and blue patch but most of the previous research has merely focused on the dark core. This work is aimed to understanding clearly the characteristic of the dark core and blue patch of Mong Hsu rubies. It was found from the FTIR analysis that the dark core and blue patch region showed the absorption peaks of boehmite (1986 cm^{-1}), diaspore (2115 cm^{-1}) and water (3400~3900 cm^{-1}) but the absorption peaks of O-H stretching (3309 cm^{-1} and 3078 cm^{-1}) were found only in blue patch region. The UV-VIS-NIR analysis of the dark core region revealed the stronger absorption of Cr^{3+} at 405 and 554 nm compared to the blue patch region. In range of 600~800 nm, the UV absorption characteristic at 659, 675 and 693 nm assigned to Cr^{3+} of core group samples is distinct from that of blue patch. The SEM-EDS examinations disclosed the existence of lots of micro-cracks and pores in the core regions compared to blue patch region.

Key words Mong Hsu ruby, Dark core, Blue patch

1. Introduction

Myanmar has been very plentiful and well-known source of the high grade gemstones, particularly Mong Hsu and Mogok district where mine of rubies and sapphires have been numerously found [1]. Initially rubies and sapphires form Myanmar had been widely researched on their trace element concentrations and inclusions [2, 3]. Later many researchers have been interested in rubies from Mong Hsu because of their typical characteristics such as separated color zoning with dark cores, blue patch and transparent red rims. The dark core and blue patch can be easily eliminated by the heat treatment under reducing or oxidizing atmosphere [4, 5]. Peretti et al. reported the characteristics of the violet core and red rim in untreated ruby by the UV-VIS-NIR spectroscopic analysis, showing the difference in the intensities of absorption band in range of 550~800 nm, without mentioning on the blue patch characteristic [6]. Most of previous works have been focused on various heat treatment methods to remove them for increasing their value in gem-trade and dealt with only the decoloration mechanism of core region without any explanation on the characteristics of blue patch. However, more inclusive and detailed understanding of the characteristic of core and blue patch are required. This work is aimed to examining the characteristics of core and blue patch in Mong Hsu ruby, Myanmar.

2. Experimental

9 raw ruby samples were collected and chosen for this work. 5 samples of them were cut and polished using diamond paste followed by cleaning in an ultra-sonic bath with the sequence of acetone and DI-water in order to remove adventitious hydrocarbon components on the surface. All samples were classified into 4 groups; 1) core, 2) blue patch, 3) red rim, and 4) core and red rim. Their surface feature and internal inclusions were examined by a transmission optical microscope (OM, Olympus, Japan) equipped with CCD camera. 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. The surface morphology and chemical composition of specimens were analyzed using a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDS, JSM-6330F, Japan).

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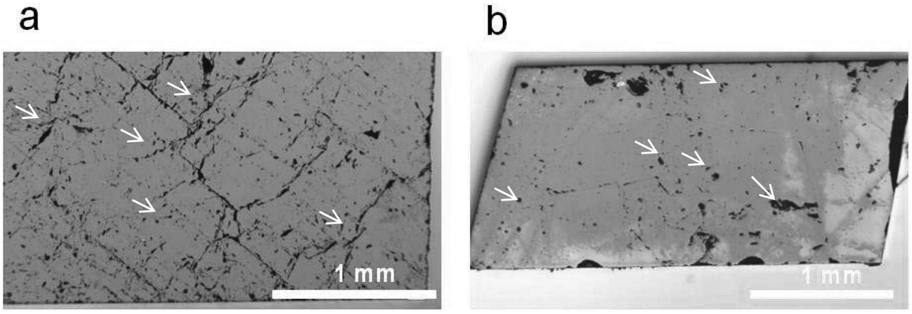


Fig. 1. Optical micrographs of the surface of (a) core region and (b) blue patch region.

3. Results and Discussions

Figure 1 shows surface morphology of core region and blue patch region. The surface of the core specimens exhibits many micro cracks and pores but the surface of blue patch area shows only a few micro cracks and pores. The core region usually exists in the middle area of analyzed samples with dark color and typical hexagonal or rectangular features. The blue patch region exists in the surrounding area between core and red rim.

Figure 2 shows comparison of FTIR absorption spectra of each group samples by graph merging. All groups showed the presence of absorption peaks of boehmite (1986 cm^{-1}), diaspore (2115 cm^{-1}), C-H stretching (2924 and 2850 cm^{-1}), carbon dioxide (2340~2360 cm^{-1}) and water (3400~3900 cm^{-1}) but the presence of absorption peaks at 3309 and 3078 cm^{-1}, assigned for O-H stretching, was found only in blue patch group and core and red rim group. Considering only blue patch and core group, it was clearly seen that core group shows distinctively low absorption peak at 1986 (boehmite) and 2115 cm^{-1} (diaspore) and not show absorption peak at 3309 and 3078 cm^{-1} (O-H stretching) compared with blue patch group as shown in Fig. 2. Thus it was noted that the absence of absorption peak at 3309 and 3078 cm^{-1} of core group would be able to distinguish core from blue patch group.

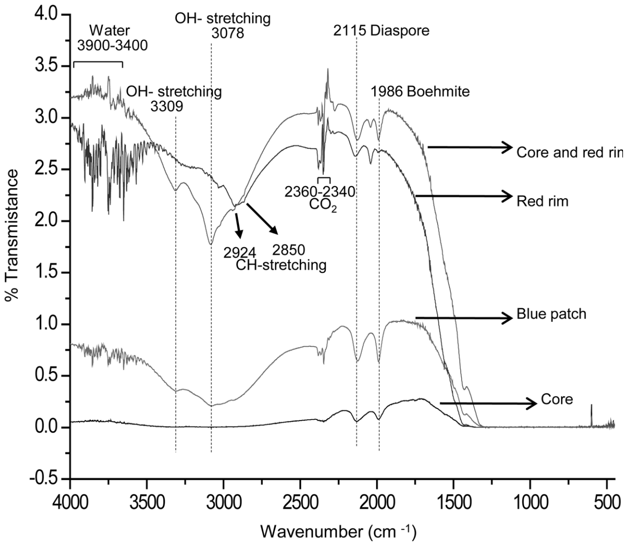


Fig. 2. Comparison of FTIR absorption spectra of all specimen groups in the range of 4000~450 cm^{-1}.

Figure 3 shows the UV-VIS-NIR absorption character-

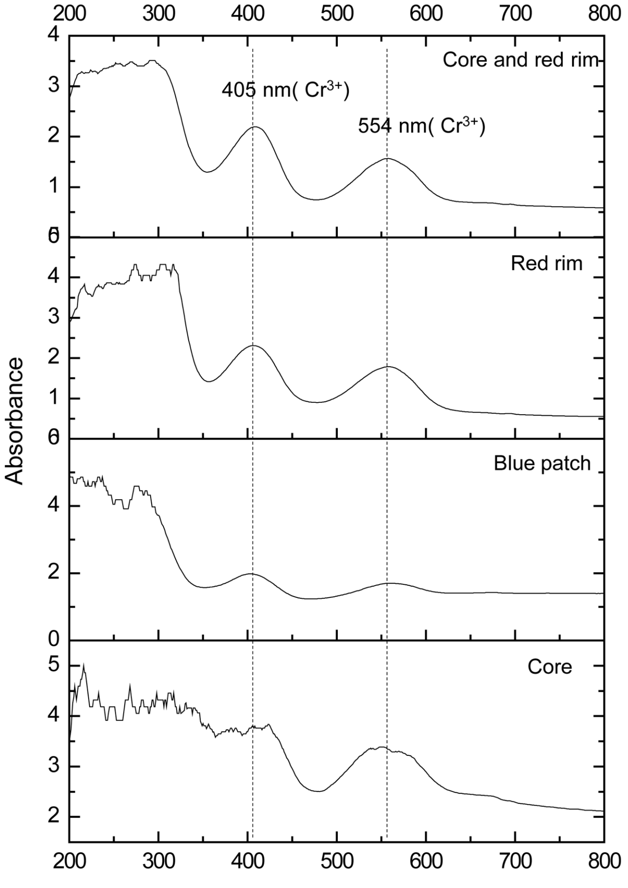


Fig. 3. The UV-VIS-NIR absorption spectra of as-received specimens, representing those of core group, blue patch group, red rim group and core and red rim group in range of 200~800 nm.

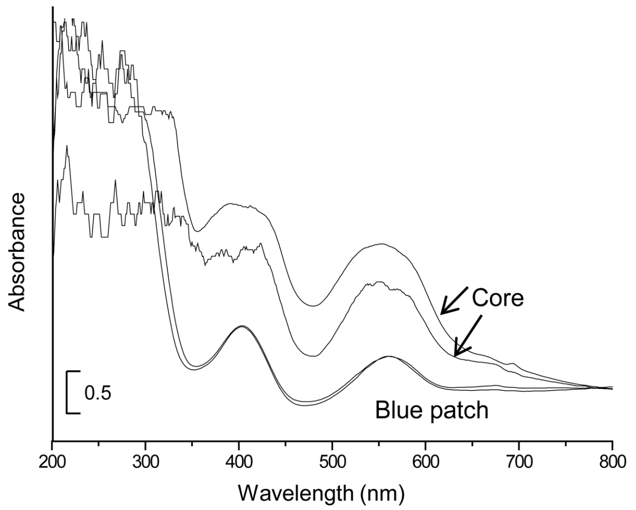


Fig. 4. Comparison between the UV-VIS-NIR absorption spectra of blue patch and those of core group in range of 200~800 nm.

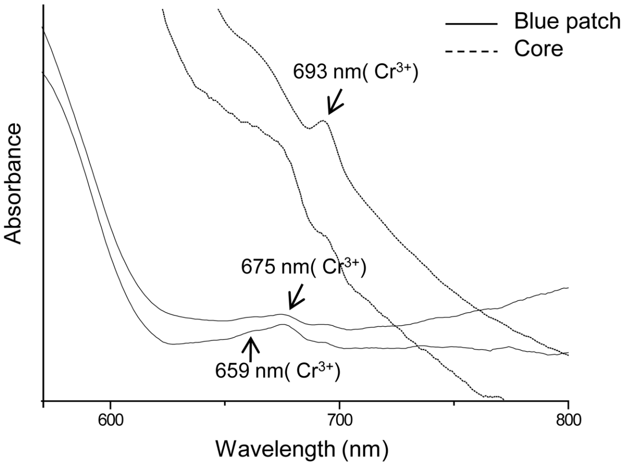


Fig. 5. Comparison between the UV-VIS-NIR absorption spectra of blue patch and those of core group in range of 600~800 nm.

istic of as-received specimens, representing those in all 4 groups as previously mentioned in the range of 200~800 nm. The UV absorption at 405 and 554 nm that are attributed to the presence of Cr^{3+} were found in all groups of specimen. Considering only specimens in blue patch and core group, the curves for core group sample noticeably show stronger UV absorption than blue patch sample as shown in Fig. 4. This indicates that the amount of Cr^{3+} in core group samples is higher than that in blue patch group samples, which is later confirmed by EDS method. In range of 600~800 nm, the UV absorption characteristic at 659, 675 and 693 nm of core group samples is distinct from that of blue patch samples as shown in Fig. 5. These well-known peaks at 659, 675 and 693 nm are attributed to Cr^{3+} [6]. It was noticed that the curve for core group shows dominant peak at 693 nm while the curve for blue patch group shows dominant peak at 675 nm (Fig. 5). Therefore the difference of UV absorption features in range of 600~800 nm between core group and blue patch group samples would be the mean to distinguish core from blue patch group.

The SEM-EDS investigation reveals the surface morphology of the as-analyzed ruby specimens in core and blue patch group (Fig. 6). It can be noted that many micro-cracks and pores distinctively exist in core region more than in blue patch region. Elemental mapping of the EDS analysis exhibits the distribution of trace elements on the surface of specimens in core and blue patch groups as shown in Fig. 7a (left) and 7b (left). Al, O, Cr and Ti elements were found in both core region and blue patch region. Although the results of elemental analysis of specimens in core region and blue patch analyzed by the X-ray mapping mode showed no difference, by means of EDS quantitative analysis as shown in Fig. 7a (right) and 7b (right), the amount of chromium in core group samples is higher than that in blue patch group samples. Meanwhile the amount of titanium in core samples is slightly different from that in blue patch samples.

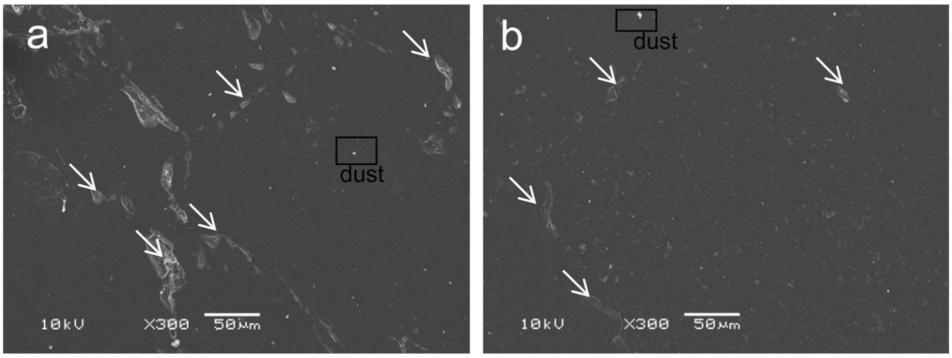
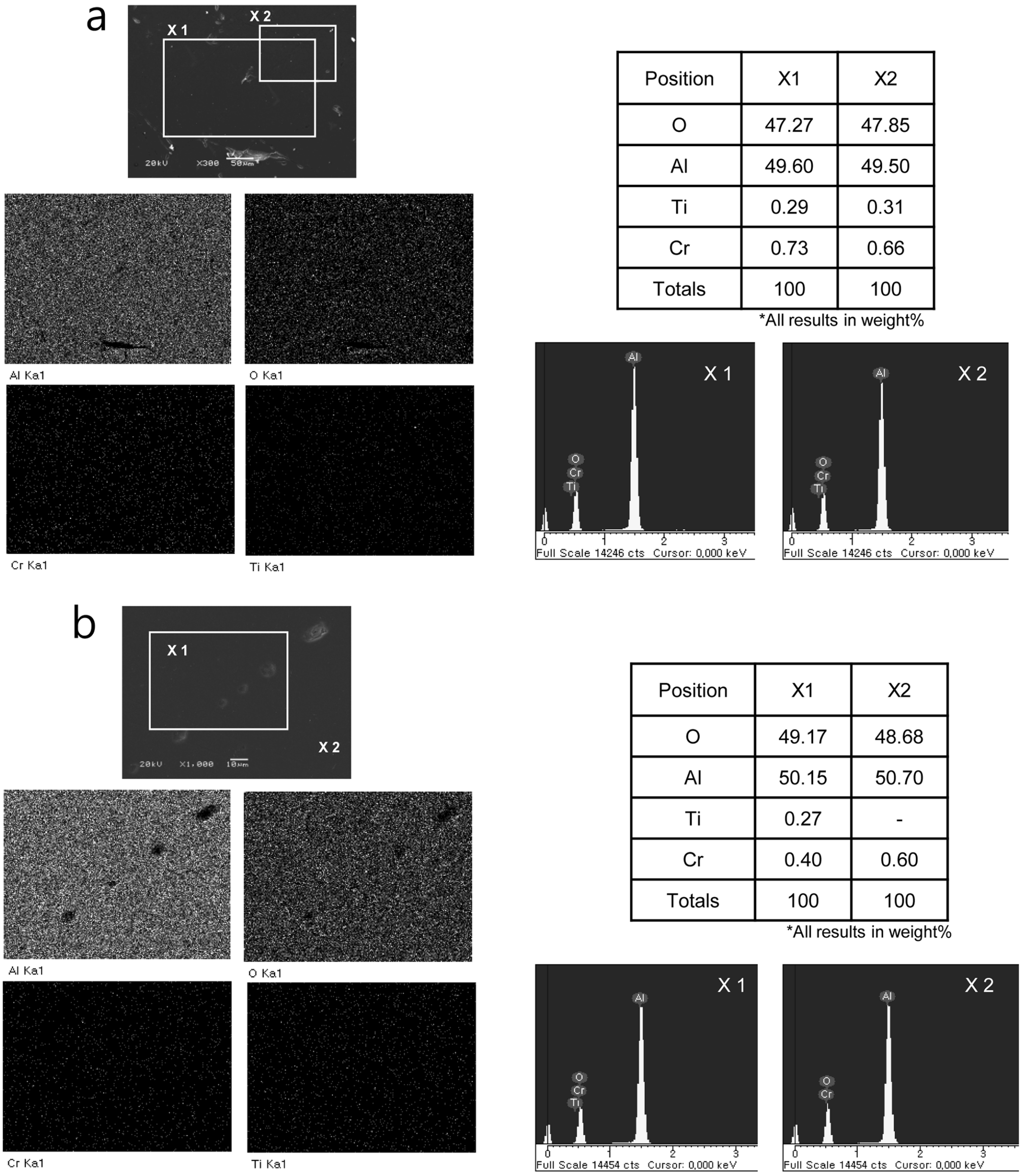


Fig. 6. SEM micrographs of the surface of the as-analyzed ruby specimens in (a) core and (b) blue patch group.



Position	X1	X2
O	47.27	47.85
Al	49.60	49.50
Ti	0.29	0.31
Cr	0.73	0.66
Totals	100	100

*All results in weight%

Position	X1	X2
O	49.17	48.68
Al	50.15	50.70
Ti	0.27	-
Cr	0.40	0.60
Totals	100	100

*All results in weight%

Fig. 7. The elemental distribution of the surface of specimen in (a) core group (left) and (b) blue patch group (left) and the amount of detected trace elements in (a) core group (right) and (b) blue patch group (right) analyzed by EDS method.

4. Conclusions

It was found that the characteristics of core and blue patch, nevertheless of their similarity, can be clearly distinguished by spectroscopic techniques; FTIR, UV-VIS-NIR analysis, and SEM-ESD. In particular, the presence of strong UV-VIS-NIR absorption of Cr^{3+} at 405 and 554 nm and UV-VIS-NIR absorption feature in range of 600~800 nm was obviously seen in core specimens compared to blue patch specimens. The absence of FTIR absorption peak at 3309 and 3078 cm^{-1} of core specimen, which was caused by the lack of O-H stretching bond, would be the indicator to distinguish core characteristic from blue patch characteristic. Moreover core specimens have characteristic of the existence of many micro-cracks and pores in core region compared to blue patch specimens. However the trace elements and their quantities in core and blue patch specimens would be able detected by EDS method and showed slightly the different quantity of trace element, further experiment on chemical composition by using other methods would be needed for more accurate and quantitative measurement.

Acknowledgements

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