Laser excitation spectroscopy of beryllium heat treatment in synthetic ruby

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Abstract. Ruby is a gem variety of corundum (\(\alpha\)-Al\(_2\)O\(_3\)) that is colored red by trivalent chromium (Cr\(^{3+}\)) substituting for Al\(^{3+}\) in the corundum structure. Recently, the beryllium (Be) heat treatment has been practiced as a technique to enhance the color of ruby. The ruby will turn orange to be an orange sapphire as a result of the enhancement. Some advanced technics to identify the Be heat-treated orange sapphire have been developed such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), secondary ion mass spectrometry (SIMS) and laser-induced breakdown spectroscopy (LIBS). We studied the effect of Be atoms in the corundum structure using the red, green, blue and purple laser excitation spectroscopy with the wavelengths of 634 nm, 545 nm, 452 nm and 408 nm respectively. The fluorescence spectra were analyzed for unheated, normal heat treatment and Be heat treatment synthetic ruby samples. The fluorescence intensity of the Be-heated samples was lowest compared to the unheated and normal treated ones for both high and low Cr content.

1. Introduction
As a gemstone, corundum (\(\alpha\)-Al\(_2\)O\(_3\)) is a well-known material with various colors such as red, blue, yellow etc. The colors in corundum mostly relate to impurities in the crystal structure. For an instant, blue sapphire is caused by Fe and Ti elements \([1]\). The blue color has been proposed to be caused by mixed acceptor states of Fe\(^{3+}\)-Ti\(^{4+}\) \([2]\). Ruby is the red color of corundum that is composed of Al\(_2\)O\(_3\) with a chromium (Cr\(^{3+}\)) impurity \([3]\). The color of ruby can be enhanced by traditional heat treatment \([4]\) and beryllium (Be) heat treatment \([5]\). The orange color resulted from Be heat treatment has been proposed to be caused by the Be\(^{2+}\) donor state at 475 nm \([6]\).

To differentiate between a natural sapphire and the Be heat-treated corundum, some advance technics have been developed such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) \([7]\), secondary ion mass spectrometry (SIMS) \([5]\) and laser-induced breakdown spectroscopy (LIBS) \([8]\). Unfortunately, there is not every testing laboratory can afford such instruments.

In this work, we investigate unheated, normal heated and Be heated synthetic ruby samples using the laser excitation spectroscopy with the wavelength of 634 nm, 545 nm, 452 nm and 408 nm respectively.
2. Experiment
The synthetic ruby (SR) samples were collected with different Cr contents. The samples were labeled as SR1 and SR2, and represented Cr contents of approximately 3000 mg/kg and 6000 mg/kg, respectively, which were determined by LA-ICP-MS. Each sample was cut into three pieces: one piece was stored as an unheated sample and the others were either normal heat-treated or Be heat treated, as shown in figure 1.

![Figure 1. Synthetic ruby samples with different contents and treatments.](image)

In our previous work [6], we found that fluorescence properties of the synthetic ruby for unheated and normal heated samples showed strong fluorescence under UV shortwave (254 nm) and UV longwave (365 nm) excitation light, whereas the Be-heated samples exhibited weak to inert fluorescence in the shortwave region and moderate to weak fluorescence in the longwave region. In this work, we carried out the laser excitation spectroscopy with the color of red (634 nm), green (545 nm), blue (452 nm) and purple (408 nm) to measure the relative fluorescence intensities of the ruby at 694 nm.

The fluorescence excitation spectra of the synthetic ruby samples were obtained in reflectance mode using a portable spectrometer with an integrating sphere. We measure the samples with each laser color for the samples SR1 and SR2 respectively.

3. Results and discussion
Figure 2 shows the spectra of SR1 and SR2 with unheated, normal heated and Be-heated samples. The fluorescence of the red laser excitation shows similar spectra of SR1 for unheated, normal heated and Be-heated samples (figure 2a) while the fluorescence spectra of SR2 show higher intensity for normal heated and lower intensity for Be-heated sample comparing to the unheated sample (figure 2b). The fluorescence of the green laser excitation spectra of SR1 shows higher intensity for normal heated and lower intensity for the Be-heated sample comparing to the unheated sample (figure 2c) while the fluorescence spectra of SR2 shows similar spectra for unheated and normal heated but lower intensity for Be-heated sample (figure 2d). The fluorescence of the blue laser excitation spectra of SR1 shows higher intensity for normal heated and lower intensity for the Be-heated sample comparing to the unheated sample (figure 2e) while the fluorescence spectra of SR2 shows lower intensities for both normal heated and Be-heated samples comparing to the unheated sample (figure 2f). The fluorescence of the purple laser excitation spectra of SR1 shows higher intensity for normal heated and lower intensity for the Be-heated sample comparing to the unheated sample (figure 2g) while the fluorescence spectra of SR2 show lower intensities for both normal heated and Be-heated samples comparing to the unheated sample (figure 2h).

The normal heat-treated sample shows a higher fluorescence intensity while the Be-heated sample shows the lower fluorescence intensity comparing to the unheated sample for SR1. The normal heat-treated sample and Be-heated samples trend to show lower fluorescence intensities comparing to the unheated sample for SR2.
Figure 2. The spectra of SR1 and SR2 with unheated, normal heated and Be-heated samples excited by red (a, b), green (c, d), blue (e, f) and purple (g, h) lasers.
4. Conclusion
The laser excitation spectroscopy could be used to identify the Be-heated synthetic ruby sample out of the unheated and normal treated synthetic ruby samples. The fluorescence intensity of the Be-heated samples was lowest compared to the unheated and normal treated samples for both high and low content of Cr.

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