Oxidation state of Fe in irradiated sapphire samples by XAS technique

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Abstract. Corundum (ruby & sapphire) consists of Al₂O₃ and trace elements relating to the cause of color such as Cr, Fe, and Ti. Irradiation is one of gemstone enhancements for improving their color. The aim of this study is focused on the oxidation state of Fe ions that concern with the cause of yellow color in irradiated sapphire by XAS technique. In this study, natural sapphire samples from Sri Lanka were collected. The samples were irradiated with high energy electron beam at 40,000 kGy, 60,000 kGy, and 80,000 kGy. XAS technique was emphasized on Fe K-edge XANES spectra. The Fe-chemical standard includes FeO and Fe₂O₃ referred to Fe²⁺ and Fe³⁺ oxidation states, respectively. According to the results, the absorption edge position of the Fe K-edge XANES spectra detected from the samples is similar to the position from Fe₂O₃. Moreover, the linear combination fitting of Fe ions in the samples compared with the Fe-chemical standard shows that the cause of yellow color on irradiated sapphire samples could be affected by Fe³⁺ concerning with the UV-Vis-NIR spectra. Hence, it could be summarized that the increasing of yellow color in irradiated sapphires is due to the increasing of high energy electron doses and the ratio of Fe³⁺ oxidation state on the sample surface.

1. Introduction
Natural corundum, i.e. ruby and sapphire, mainly comprises of Al₂O₃ and trace elements such as Cr, Fe, Ti, V, etc [1]. The cause of colors in natural corundum is due to trace elements or color center, for example, the yellow color caused by Fe³⁺ replacing Al³⁺. Nowadays, the natural corundum with high quality is very rare, thus, there are many methods for improving its quality such as heat treatment, diffusion, and irradiation by; for example; gamma, electron, and neutron. Typically, the milky sapphire could be turned to yellow sapphire after irradiation. However, there is no evidence to explain the cause of yellow color in irradiated sapphire. Previously, it still slightly mentioned that the oxidation state of sapphire whether or not irradiation is Fe³⁺ proved by x-ray absorption spectroscopy (XAS) focusing on Fe K-edge x-ray absorption near edge structure (XANES) spectra [2-4].

Naturally, Fe²⁺ and Fe³⁺ ions are commonly found in sapphire. In this study, we want to know which Fe oxidation state concerning to the yellow coloration of irradiated sapphires. Therefore, it need to measure the XANES spectra of FeO (Fe²⁺) and Fe₂O₃ (Fe³⁺) standard to compare with those of the samples by XAS technique. The purpose of this study is to clarify the mechanism of yellow color causing in irradiated sapphire.

2. Experiments
For this experiments, the natural milky sapphire samples were collected from Sri Lanka. The samples were polished on 2 sides. Then, the samples were irradiated with high energy electron beam accelerated...
by the high energy electron accelerator at 40,000 kGy, 60,000 kGy, and 80,000 kGy doses. The irradiation method was performed at Thailand Institute of Nuclear Technology (Public Organization). The samples were compared their colors before and after irradiation as well as after fading of irradiation by the naked eyes (figure 1) combined with UV-Vis-NIR spectrophotometer for measuring the absorption of trace elements of the samples. In this study, we focused on the Fe K-edge XANES spectra to verify the Fe oxidation state of the samples at Beamline-8 station, Synchrotron Light Research Institute (SLRI), Thailand. The powder of Fe chemical standard consisting of FeO and Fe2O3 was used for measuring the actual Fe oxidation state as shown in figure 2. The parameters of XAS experiment includes 13-array Ge detector, Ge (220) double crystal monochromator, energy range from 7075 eV to 7275 eV, and energy calibration at 7112 eV.

3. Results and Discussion
UV-Vis-NIR absorption spectra of the samples showing the higher Fe3+/Fe3+ intensity at 450 nm of irradiated sapphires comparing with non-irradiation ones and the decreased Fe3+/Fe3+ intensity of the samples after fading irradiation are illustrated in the figures 3, 4, and 5. As the results, it could be suggested that the sputtering and evaporation of high energy electron beam [5-6] may bring Fe3+ ions in the sapphire structure to the surface with Van der Waals forces producing the increasing of yellow color after irradiation. Then, the high energy electron particles are faded and the Fe3+ ions are removed from the sample surface due to the elimination of Van der Waals forces affecting to the decreasing of yellow color.
Figure 3. UV-Vis-NIR spectra of sapphire samples before irradiation, after irradiation at 40,000 kGy and after fading of irradiation.

Figure 4. UV-Vis-NIR spectra of sapphire samples before irradiation, after irradiation at 60,000 kGy and after fading of irradiation.

Figure 5. UV-Vis-NIR spectra of sapphire samples before irradiation, after irradiation at 80,000 kGy and after fading of irradiation.

According to Fe K-edge XANES spectra (figures 6, 7, and 8), the binding energy ($E_0$) of both sapphire samples before and after irradiation shows the Fe$^{3+}$ oxidation state nearby 7126 eV comparing with the Fe$_2$O$_3$ chemical standard [2]. However, the $E_0$ positions of both samples are slightly different, besides, the $E_0$ position of irradiated samples is more approached to Fe$^{3+}$ behavior than the $E_0$ position of non-irradiated ones. It could be connected to the Fe$^{3+}$ proportion of the sample surface after irradiation is more than those of the samples before irradiation confirmed by linear combination fitting (LCF) results in the table 1. LCF is a statistical method applied to compare the possible proportion of FeO (Fe$^{2+}$) and Fe$_2$O$_3$ (Fe$^{3+}$) of the samples before and after irradiation at different doses. The various doses of irradiation affected the Fe$^{3+}$ proportion of the sample surface. The sapphire sample after irradiation at 40,000 kGy is slightly changed of delta Fe$^{3+}$ and yellow coloration. The irradiated samples at 60,000 kGy are gradually changed more than the irradiated samples at 40,000 kGy. The highest different delta of irradiated samples at 80,000 kGy shows clearly changed of highly intense yellow coloration more than 40,000 kGy and 60,000 kGy as shown in table 1 and concerning with XANES results. Thus, the physics mechanism of yellow coloration in irradiated sapphire samples is based on the different doses of irradiation.
Figure 6. Fe K-edge XANES spectra of Fe chemical standard comparing with sapphires before and after irradiation at 40,000 kGy.

Figure 7. Fe K-edge XANES spectra of Fe chemical standard comparing with sapphires before and after irradiation at 60,000 kGy.

Figure 8. Fe K-edge XANES spectra of Fe chemical standard comparing with sapphires before and after irradiation at 80,000 kGy.

Table 1. Linear combination fitting results showing the ratio of FeO and Fe$_2$O$_3$ in sapphire samples with Δ value$^a$.

| Chemical standard | 40,000 kGy Before irradiation | 40,000 kGy After irradiation | 60,000 kGy Before irradiation | 60,000 kGy After irradiation | 80,000 kGy Before irradiation | 80,000 kGy After irradiation |
|-------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| FeO (Fe$^{3+}$)   | 0.000 ± 0.055                 | 0.000 ± 0.055                 | 0.000 ± 0.063                 | 0.000 ± 0.057                 | 0.000 ± 0.061                 | 0.000 ± 0.051                 |
| Δ                 | 0.000                          | 0.006                          | 0.010                          |                               |                               |                               |
| Fe$_2$O$_3$ (Fe$^{2+}$) | 0.956 ± 0.155                 | 0.956 ± 0.156                 | 0.956 ± 0.179                   | 0.956 ± 0.174                 | 0.956 ± 0.143                 |
| Δ                 | 0.001                          | 0.017                          | 0.031                          |                               |                               |                               |

$^a$ Δ is the different value of Fe$^{2+}$ and Fe$^{3+}$ oxidation states on the samples before and after irradiation.

4. Conclusion
From Fe-K edge XANES spectra of the sapphire samples, the Fe oxidation state of both before and after irradiated sapphires is Fe$^{3+}$. However, it could be found that the Fe$^{3+}$ proportion of irradiated sapphires...
is higher than the samples before irradiation. It could be consistent with the UV-Vis-NIR absorption spectra. Therefore, it could be summarized that the Fe$^{3+}$ ions were sputtered and evaporated on the sample surface caused by high energy electron beam, moreover, the Fe$^{3+}$ ions were gradually removed from the surface after fading of irradiation. This mechanism relates to the increasing of yellow color after irradiation as well as the decreasing of yellow color after fading of irradiation involved with doses of irradiation.

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