

# Role of ilmenite micro-inclusion on Fe oxidation states of natural sapphires

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**Abstract.** The blue color of the blue sapphire is caused by the Fe-Ti pairs. Recently, the oxidation states of Fe and Ti on high-quality blue sapphire were found as mixed acceptor states of Fe<sup>3+</sup> and Ti<sup>4+</sup>. However, the oxidation states of Fe on natural sapphire with some inclusions were reported as mixing of Fe<sup>2+</sup> and Fe<sup>3+</sup> using the x-ray absorption near edge structure spectroscopy (XANES). Generally, there are mineral inclusions on natural sapphire related to Fe such as hematite (Fe<sub>2</sub>O<sub>3</sub>) and ilmenite (FeTiO<sub>3</sub>). In this study, we investigated the micro-inclusions on natural sapphires by the electron probe micro analyzer (EPMA). The oxidation states of Fe and Fe-O bond length were analyzed by x-ray absorption spectroscopy (XAS). The Fe K-edge extended x-ray absorption fine structure (EXAFS) fitting results focused on the first shell of Fe atoms on high-quality natural sapphires were shown that the Fe-O bond length on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was fitted well with Fe-O bond length of Fe<sub>2</sub>O<sub>3</sub> presenting Fe<sup>3+</sup>. However, the Fe-O bond length on natural sapphires with ilmenite micro-inclusion was fitted with Fe-O bond length of Fe<sub>3</sub>O<sub>4</sub> showing Fe<sup>2+</sup> and Fe<sup>3+</sup>. As the result, the Fe<sup>2+</sup> on natural sapphires was contributed by the ilmenite micro-inclusion.

## 1. Introduction

Sapphire, a gem corundum variety, is a precious inorganic gemstone composing of alpha-alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) and some trace elements causing the coloration. Some Al<sup>3+</sup> ions in sapphire have been replaced by trace elements of transition metal ions and produced the colors. The factors of substitution for Al ion by metal ions are depended on the similarities of ionic radius, atomic size, and electronegativity values. From those factors, it could be indicated that the most important trace elements in sapphire are Fe and Ti [1]. For instance, Fe<sup>3+</sup>-Ti<sup>4+</sup> mixed acceptor states produce blue color [2]; Fe<sup>3+</sup> substitutes Al<sup>3+</sup> showing yellow color [3]; as well as, Al<sup>3+</sup> was replaced with Cr<sup>3+</sup> producing red color also known as ruby, etc [4].

Naturally, sapphires occur in various geological provenances, for example, related to basaltic rocks and metamorphic ones [5]. The chemical structure of sapphire is crystallized in the hexagonal system as hexagonal dipyramids form. The unit-cell of sapphire consists of Al atoms in octahedral coordination bonded to O atoms in hexagonal closest packing [6].

X-ray absorption spectroscopy (XAS) technique is a mighty procedure for studying atomic structure of the absorbing atoms such as oxidation state of investigated atom and bond length between

investigated atom and neighboring atoms. XAS technique consists of two parts including x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) [7].

From previous works, the  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  oxidation state on high-quality blue sapphire were carried out by XANES spectra [2]. Nevertheless, the Fe oxidation state on natural sapphire with some micro-inclusions was reported as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  mixing species [8]. Consistent with other research [9], the Fe oxidation state on ruby samples with some tiny micro-inclusions was changed from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  after improving by ion beam technique and those inclusions were eliminated due to the heat. Generally, the micro-inclusions on sapphire (as well as ruby) related with Fe-bearing mineral were reported as hematite ( $\text{Fe}^{3+}$ :  $\text{Fe}_2\text{O}_3$ ) and ilmenite ( $\text{Fe}^{2+}$ :  $\text{FeTiO}_3$ ) [10]. The crystal habit and crystal symmetry of both mineral inclusions are quite alike as the rhombohedral form in hexagonal system, however, they are classified by chemical analysis using mineral calculation [6]. Therefore, the natural sapphires with ilmenite micro-inclusion will be investigated for the origin of the  $\text{Fe}^{2+}$  oxidation state on natural sapphires.

In this study, the role of ilmenite micro-inclusion on the Fe oxidation states and Fe-O bond length of natural sapphires will be carried out by EXAFS technique.

## 2. Experiment

Natural sapphire samples were collected with different qualities from gem markets based on the existence of ilmenite micro-inclusion as shown in figure 1. The basic gemological properties of the samples were recorded including specific gravity, refractive indices, and internal features to confirm the type of mineral. The samples were prepared by polishing to eliminate the fallibility from the rough surface which effects to the signals to noise ratio from the experiments. The samples were undergone a carbon-coating process to observe the micro-inclusions with an electron probe micro analyzer (EPMA). After that, the samples were cleaned before the XAS measurement. The Fe content of the samples was about  $1000 \text{ mg kg}^{-1}$  detected by laser ablation inductively plasma mass spectrometer (LA-ICP-MS) and it satisfies for XAS measurement.



**Figure 1a.** A representative natural sapphire sample without ilmenite micro-inclusion.



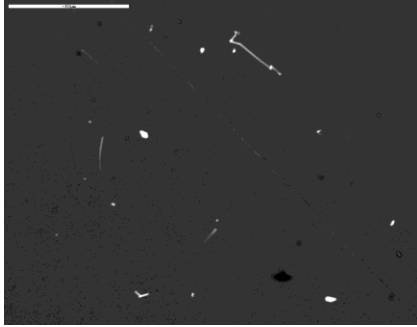
**Figure 1b.** A representative natural sapphire sample with ilmenite micro-inclusion.

In this study, XAS technique was focused on the EXAFS spectra at *K*-edge absorption of Fe atoms. The x-ray beam was utilized from Beamline-8 station, Synchrotron Light Research Institute (Public Organization) [11]. The Ge(220) double crystal monochromator covering the photon energy from 3440 eV to 10000 eV with the 2d spacing around 4.001 Å and the 13-channel array germanium detectors were set for this experiment. The photon energy was calibrated using Fe foil standard for zero oxidation state at 7112 eV. The powder of Fe chemical standards including FeO,  $\text{Fe}_3\text{O}_4$ , and  $\text{Fe}_2\text{O}_3$  were prepared for referencing the oxidation states of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{2+,3+}$  and  $\text{Fe}^{3+}$ , respectively.

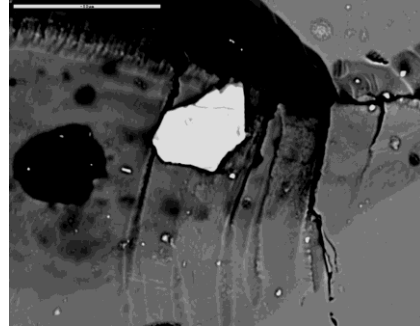
## 3. Results and discussion

The micro-inclusions in natural sapphires were characterized by EPMA (JEOL JSM 6310 model) connected with a wavelength dispersive spectrophotometer (WDS) to analyze the type of micro-mineral inclusions. The micro-mineral inclusions of natural sapphires were analyzed from back scattering electron (BSE) images, for example, an ilmenite micro-inclusion was found in the sample as shown as a white crystal in figure 2b. The WDS results evidencing to the ilmenite micro-inclusion

show high Fe and Ti content as shown in table 1. Nevertheless, this inclusion was not found in high-quality natural sapphires as shown in figure 2a. However, there were micro-inclusions of rutile ( $\text{TiO}_2$ ) shown as white spots spreading on the sample.



**Figure 2a.** BSE image of high-quality natural sapphires without ilmenite micro-inclusion probed by EPMA (scale = 50  $\mu\text{m}$ ).

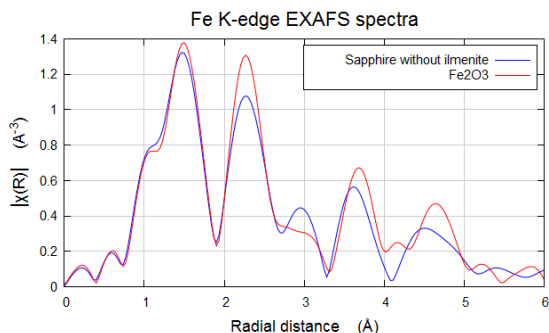


**Figure 2b.** BSE image of natural sapphires with ilmenite micro-inclusion probed by EPMA (scale = 50  $\mu\text{m}$ ).

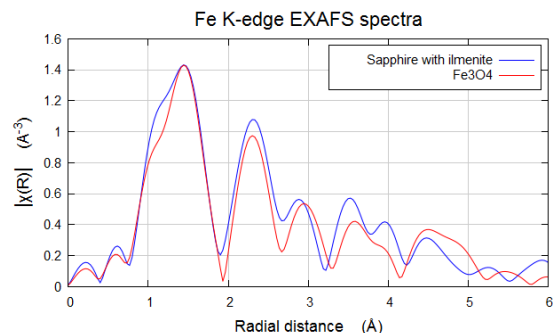
**Table 1.** Normalized semi-quantitative chemical analysis of an ilmenite micro-inclusion on a representative sapphire sample.

Element	Weight %
Ti	31.94
Fe	36.02
O	32.04
Total	100.00

The Fe  $K$ -edge EXAFS spectra of the representative natural sapphires were compared with those of Fe chemical standards. The Athena software was used for the data processing [12]. Focusing on the first shell of Fe atoms, the Fe-O bond length on high-quality natural sapphires without ilmenite micro-inclusion was fitted well with the Fe-O bond length of  $\text{Fe}_2\text{O}_3$  standard presenting as 1.97  $\text{\AA}$ . They resemble in  $R$ -space as shown in figure 3a. Besides, the Fe-O bond length on the representative natural sapphires with ilmenite micro-inclusions was fitted well with the Fe-O bond length of  $\text{Fe}_3\text{O}_4$  standard, a mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species, presenting as 1.94  $\text{\AA}$  as shown in figure 3b. Thus, the  $\text{Fe}^{2+}$  was caused by the ilmenite micro-inclusions while  $\text{Fe}^{3+}$  was originated in the sapphire host corresponded to the previous research [8]. The oxidation state changed from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  by the ion implantation on micro-inclusions on natural ruby by Intarasiri et al. [9] may be interpreted in a similar fashion. The increasing of  $\text{Fe}^{2+}$  content could be affected by the dissolution of ilmenite micro-inclusion during the process.



**Figure 3a.** Fe *K*-edge EXAFS spectra of natural sapphires without ilmenite micro-inclusion plotted in *R*-space.



**Figure 3b.** Fe *K*-edge EXAFS spectra of natural sapphires with ilmenite micro-inclusion plotted in *R*-space.

#### 4. Conclusion

The Fe *K*-edge EXAFS spectra of the representative natural sapphires were not similar between high-quality sapphire without ilmenite micro-inclusion and sapphire with ilmenite micro-inclusion. The Fe<sup>3+</sup> oxidation state was originated on the host structure of natural sapphires. It could be summarized that the Fe<sup>2+</sup> oxidation state on natural sapphires was caused by the ilmenite micro-inclusion.

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