Causes of color in purple- and yellow- quartz

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Abstract. Quartz is a variety of gemstone consisting of SiO₂. The various colors of quartz are caused by Fe as a trace element. This study focused on the investigation of Fe oxidation states affecting colorations of purple- and yellow- quartz by X-ray absorption spectroscopy (XAS) and UV-Vis-NIR spectroscopy. The amethyst (purple- quartz) and citrine (yellow- quartz) were collected as the samples. As the XAS results, there was only Fe³⁺ oxidation state on both purple- and yellow- quartz considering with the absorption energy position at the Fe K-edge compared to the Fe-oxide chemical standards i.e., FeO and Fe₂O₃. However, the UV-Vis-NIR absorption spectra of the purple- and yellow- quartz were different. Therefore, we propose that the coloration of purple- and yellow- quartz was caused by Fe³⁺ oxidation states as the donor states at 3.59 eV and 2.28 eV with the different energy band gaps of the purple- and yellow- quartz that were 4.13 eV and 4.88 eV respectively derived from Tauc Plot method.

1. Introduction
Quartz is a semi-precious inorganic gemstone consisting of silica (SiO₂). Naturally, the quartz structure is crystallized in the trigonal system in the tectosilicate group of minerals with commonly prismatic crystal habit [1]. Pure quartz without impurities is colorless, however, it could be found in various colors caused by some trace elements such as amethyst (purple- quartz), citrine (yellow- quartz), rose- quartz (pink- quartz), etc. Previously, the purple and yellow colors of quartz were proposed with unclear species of Fe color centers. For example, the Fe oxidation state in purple- quartz was questioned between Fe³⁺ probed by electron paramagnetic technique [2] as well as Mössbauer spectroscopy [3] and Fe⁴⁺ derived by geochemical calculation [4].

X-ray absorption spectroscopy (XAS) especially a region of x-ray absorption near edge structure (XANES) is a powerful technique for studying the oxidation state of the absorbing atom [5]. Besides, the UV-Vis-NIR spectroscopy is a technique for finding the energy state of the ionic absorption relating to the color of the minerals. The combination of the oxidation state and the energy state has been applied to describe the color mechanism of gemstones such as Fe³⁺-Ti⁴⁺ mixed acceptor states in blue sapphire [6] and Be²⁺ donor state in synthetic ruby [7].
In this study, the investigation of Fe oxidation states of purple- and yellow- quartz will be carried out by the XAS technique and UV-Vis-NIR spectroscopy. Moreover, the role of the Fe oxidation state will be described as the color mechanism of purple- and yellow- quartz.

2. Experiments
Natural quartz samples with different colors were collected from gem markets including amethyst and citrine as shown in figure 1. The basic gemological properties of the samples were recorded such as specific gravity, refractive indices, and internal features to confirm the type of gemstone. The Fe content of the samples was sufficient to be detected by the synchrotron fluorescence detector for XAS measurement.

![Figure 1. A set of the samples including amethyst and citrine, respectively.](image)

In this study, the XAS technique was focused on the Fe K-edge XANES spectra using 19-element germanium detectors for fluorescence mode at Beamline-1.1W, Synchrotron Light Research Institute (Public Organization). The photon energy was calibrated using the Fe foil standard for zero oxidation state at 7112 eV. The Fe chemical standards including FeO and Fe$_2$O$_3$ were prepared as the Fe$^{2+}$ and Fe$^{3+}$ referencing oxidation states, respectively. For UV-Vis-NIR measurement, the absorption spectra of the samples were carried out by transmission mode using Lambda$^\text{TM}$ 650 with an integrating sphere.

3. Results and Discussion
The Fe K-edge XANES spectra of the natural quartz samples with various colors were compared with those of Fe chemical standards. The data processing was analyzed by Athena [8]. To verify the Fe oxidation state, the Fe K-edge photon energy positions and the corresponding uncertainties were summarized by the first derivative calculation according to table 1. Focusing on the edge position ($E_0$), the Fe foil, FeO and Fe$_2$O$_3$ spectra were classified at 7111.8 eV, 7119.0 eV and 7123.5 eV representing to Fe$^0$, Fe$^{2+}$ and Fe$^{3+}$ respectively. Besides, both amethyst and citrine were shown as the presence of Fe$^{3+}$ oxidation states with the edge positions at 7124.2 eV and 7124.6 eV respectively. Although the edge positions were not exactly at the same energy position due to uncertainty of measurements as shown in table 1 and figure 2, we could confirm the Fe$^{3+}$ oxidation states by the pre-edge peak positions that were aligned at 7114.9 eV. Therefore, we could not find the Fe$^{2+}$ oxidation state in both purple- and yellow- quartz.

| Sample     | Oxidation state | $E_0$ / eV |
|------------|-----------------|------------|
| Fe foil    | Fe$^0$          | 7111.8 ± 0.6 |
| FeO standard | Fe$^{2+}$ | 7119.0 ± 0.6 |
| Fe$_2$O$_3$ standard | Fe$^{3+}$ | 7123.5 ± 0.6 |
| Amethyst   | Fe$^{3+}$       | 7124.2 ± 0.6 |
| Citrine    | Fe$^{3+}$       | 7124.6 ± 0.6 |
Figure 2. Fe K-edge XANES spectra of Fe standards, amethyst and citrine samples.

The UV-Vis-NIR spectra of purple- quartz and yellow- quartz were different absorption patterns corresponded to the previous research [9]. The optical absorption spectra and the energy bandgap ($E_g$) were determined based on the Tauc Plot method for a direct allowed transition [10]. The purple- quartz showed the absorption peaks at 345 nm and 545 nm (figure 3(a)) and the energy bandgap ($E_g$) was 4.13 eV from the Tauc Plot (inset) whereas the yellow- quartz showed only the absorption peak at 345 nm (figure 3(b)) and the bandgap energy ($E_g$) was 4.88 eV from the Tauc Plot (inset). Based on the study of Fe oxidation states by XAS results, it could be interpreted that the purple- quartz showed the absorption peaks of Fe$^{3+}$ at 345 nm (3.59 eV) and 545 nm (2.28 eV), otherwise, the yellow- quartz showed the absorption energy state of Fe$^{3+}$ at 345 nm (3.59 eV) as well as the absence of the absorption signal at 545 nm (2.28 eV).

Figure 3. UV-Vis-NIR spectra of amethyst (a) and citrine (b) with Tauc plots (inset).

The cause of the purple and yellow color in the purple- quartz and yellow- quartz could be described by the color center illustrated as the energy band model. Both colors showed the Fe$^{3+}$ donor state at 3.59 eV and 2.28 eV, however, the different colors could be caused by the different energy bandgap which was related to the absorption pattern. The energy bandgap of purple- quartz ($E_g = 4.13$ eV) was smaller than yellow- quartz ($E_g = 4.88$ eV). For purple- quartz (figure 4(a)), the Fe$^{3+}$ donor state at 3.59 eV was located near the conduction band; the Fe$^{3+}$ donor state at 2.28 eV was a shallow donor level with respect to the conduction band, then, the electron from these states could be donated to the conduction band and these empty states were filled by electrons from the valence band relating to the absorption at 345 nm
and 545 nm. For yellow- quartz (figure 4(b)), the Fe$^{3+}$ donor state at 3.59 eV has presented the donation of electrons to the conduction band, then, the electron from the valence band was transitioned to the empty state as shown the absorption at 345 nm; the Fe$^{3+}$ donor state at 2.28 eV was a deep donor level with respect to the conduction band, then, the electron from this state could not be donated to the conduction band and this state was not empty. Therefore, it could not present the absorption at 545 nm.

![Figure 4](image-url)

**Figure 4.** An energy band model of Fe$^{3+}$ donor states in amethyst (a) and citrine (b).

4. **Conclusion**

The cause of color in both purple- and yellow- quartz was affected by the Fe$^{3+}$ donor states probed by the XAS technique. Moreover, the different energy band gap was related to the variable absorption energy states of purple- and yellow- quartz shown in the UV-Vis-NIR region.

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