

CHAPTER V

CONCLUSION

The various colors of beryl gemstone depend on primary factors such as, ratio of element composition, atomic defection and dislocation, mineral inclusion, distortion of the structure, and crystal pattern grown. Researchers have frequently observed the behavior of iron ions due to their electron activity on d-orbital transition metals, high band gap energy, ease of oxidation, and affinity for forming bonds with oxygen. Although the beryl samples in this study were low in alkali, irons were particularly vulnerable to radiation-induced oxidation. The synthetic sample contained 1.57 wt.% total iron, which was about three times higher than the natural sample, whereas colorless beryl contained just 0.28 wt.% total iron.

The color of irradiated crystal samples changed into intensive yellow (positive b^* value), except for the colorless beryl, which displayed no color change. The UV-Vis spectra of beryl presented the absorbance peak at 375 and 427 nm implied a $d-d$ electron transition of Fe^{3+} , the broad peak at 820 nm indicated the presence of Fe^{2+} , and the shoulder peak at 670-750 nm was interactions of IVCT between Fe^{2+} and Fe^{3+} in octahedral position. Iron oxidation state changed after irradiation by X-ray white beam because the absorption peak position ratio of Fe^{3+} increased and that of Fe^{2+} decreased. The Fe ion oxidation state results of UV-Vis corresponded to X-ray absorption results of pre-edge and multiple scattering regions, especially plane A of crystal sample investigation. The EPR spectra of powdered beryl revealed only a single axial Fe^{3+} center of site symmetry ($g \approx 2$) increased intensity after X-ray irradiation, which is supported by UV-Vis and XANES data.

The EXAFS calculation indicated that Fe ions were situated within a six-coordinated symmetry, consistent with the presence of Fe^{3+} centers in aluminum (Al) sites as confirmed by EPR and the pre-edge fitting of XANES data of powder samples. The simulation of the six-coordinate EXAFS path model suggested that Fe could potentially occupy positions through substitution, such as replacing aluminum (Al), or

interstitial locations like the 6g site. This was supported by the observation of similar bond lengths, approximately ranging from 1.97 to 2.02 Å, in both models. As a result, it was challenging to precisely determine the bond length of the first single scattering (Fe-O₁) or the quantity of Fe-occupied sites within the beryl structure. It appeared that the substitution of Fe for Al sites was more prevalent than for 6g sites, as all the samples could be adequately described using Model-I, which comprised five peaks.

The results of the EXAFS simulation and spectral fitting before and after exposure to X-ray irradiation exhibited remarkably similar characteristics, with only a slight change in the bond length of the first single scattering. However, other analytical techniques such as UV-Vis, XANES, and EPR indicated an increase in the presence of Fe³⁺ ions or a conversion of Fe²⁺ to Fe³⁺. The primary Fe ions were found to be situated within a six-coordinated symmetry according to the EXAFS calculations. Changes in the plane polarization of Fe were observed in the UV-Vis and XANES spectra, particularly in plane A along the c-axis. Additional support for these observations comes from the appearance of a blue color, which was generated by the IVCT between Fe²⁺ and Fe³⁺ ions located at both Al and 6g sites in the beryl structure, suggesting a possible Fe-Fe pair distance of 2.49-2.51 Å. In contrast, in the antiferromagnetic configuration, the nearest Fe-Fe pair distance along the c-axis, considering the nearest Al site, was approximately 4.64 Å (Lin *et al.*, 2013). The shift in beryl coloration towards a more intense yellow hue implied an IVCT Fe²⁺-Fe³⁺ reaction phenomenon induced by X-ray exposure, leading to the conversion of Fe²⁺ ions to Fe³⁺ at both Al and 6g sites. This phenomenon resulted in a decrease in the transfer of electrons between ions with different oxidation states within the crystal lattice and an increase in the transfer of electrons between ions with the same oxidation state (Fe³⁺-Fe³⁺) or between metal ions and oxygen (Fe³⁺-O).

Furthermore, the NIR data revealed a general absence of foreign and water molecules, implying that the impinging X-ray beam could not cause any OH bond breakdown in H₂O. Furthermore, cryogenic cooling of the sample, which is commonly used to reduce free radical mobility, would most likely not help to prevent the observed oxidation effects in beryl induced by synchrotron radiation. The oxidation

process could be attributed to bond cracking and electron release (Eeckhout *et al.*, 2005).

The irradiation treatment requires special care because some irradiated gems, like beryl and spodumene gemstones, tends to have short-lived colors that fade upon exposure to bright light (Weldon, 2023). Irradiation is a less common method for enhancing beryl color. Colorless or light pink beryl gems subjected to neutron and gamma radiation take on a new shade of blue, a "maxixe-type" color (Nassau, Prescott, and Wood, 1976). This color is thought to form due to radiation-induced chemical changes involving carbonate ions in the channels (Edgar and Vance, 1977). However, unlike heat treatment results, the color gradually fades when exposed to light because the maxixe-type color is unstable. As a result, the gem and jewelry industry does not consider radiation treatments as acceptable beryl enhancements. If this color could be stabilized and produced sufficiently, the stone would have great potential as a gem material. Both beryl color samples in this study were treated to an increased yellow shade (*b) by X-ray synchrotron, which tended to be a stable color. In addition, irradiation of beryl by an X-ray synchrotron source did not result in any residual radioactivity being released into the environment. The irradiated beryls are safe to handle and wear, are not brittle as usual. However, care must be taken not to damage pointed faceted corners and edges, like avoiding exposure to high temperatures. The incident X-ray beam size and incident time in a synchrotron source can be adjusted to create two- or three-color shade in one beryl gemstone.