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The optical characteristic of electron irradiated beryl by UV-Visible and mid-IR spectroscopic analyses

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Abstract

Optical properties of crystal are the most important aspects in evaluating the beauty and the value of heliodor. The color of some yellow heliodor can be improved by irradiation. In this work, electron irradiation was performed on heliodors to characterize of changed in their optical properties. The specimens were irradiated with 20 MeV electrons to fluences in range of 4.46×10^{15}-2.65×10^{16} cm^{-2}. Their characteristic spectra were investigated by UV-Vis, FTIR and EDXRF spectroscopy for comparison to pristine samples. The absorption bands in the 500-800 nm region of natural heliodor crystals caused by electron irradiation belong to a complex center, which consists of Fe^{3+} ions and radiation defect. The behaviors of water in the specimens were detected in the region of 4,000 – 4,800 cm^{-1}. The releases of water from channels in specimen crystals were appeared after electron irradiation.

Keywords: beryl; electron irradiation; UV-Vis; Mid-IR

1. Introduction

Heliodor is a yellow, greenish yellow, or golden-yellow member of the beryl family of cyclosilicate minerals, which also includes goshenite, aquamarine, emerald and morganite. Like other beryls, heliodor is a mineral composed of beryllium aluminum silicate with ideal formula $Be_3Al_2(SiO_3)_6$. The structure consists of 6-membered rings (Si_60_{18}) and cell data: P6/mcc, a = 9.21 Å, c = 9.18 Å [1]. The Si_60_{18} rings stacked upon each other created the channels parallel to the *c* axis. The channels in the structure are contained admixtures of alkali elements such as Na^+, K^+ and Li^+. Each 6-membered ring of the channel is linked by aluminum and beryllium ions in the distorted octahedral and tetrahedral coordination, respectively.

Pure beryl is colorless, but impurities within the crystal structure cause beryl to occur in a variety of colors. The yellowish colors of heliodor come from trace amounts of iron (Fe^{3+}) impurities within the mineral's crystal structure

[2]. The iron contained in heliodor can be altered by radiation treatment. There are many data on methods for enhancement of beryl by gamma and neutron irradiation in the literature [3 – 5]. In contrast, the effect of electron irradiation has never been reported on any type of beryl. The effect of an electron beam (e-beam) on beryl needs to be studied urgently.

The paper presents the effects of electron irradiation on the optical properties of natural heliodor. Energy Dispersive X-ray Fluorescence (EDXRF), including Ultraviolet–visible spectroscopy (UV-Vis) and Fourier transform infrared spectroscopy (FTIR) were used to study the chemical behaviors and the optical spectra of the specimens with a different electron fluences to understand the color change mechanism. The combination of these techniques revealed the correlation between the type and concentration of admixtures and color centers of natural heliodor to support the initial point of the jewellery manufacturing process.

2. Materials and methods

Natural pale heliodor crystal from field in Nigeria was investigated. The samples were cut in half perpendicular to the crystallographic c-axis in to 7 pieces with dimensions for each piece of about (8x8x2) mm^3. Subsequently, all specimens were polished by using silicon- carbide abrasive paper. The optical properties of the polished heliodor samples after the e-beam irradiation were studied by comparison with the natural polished one specimen.

The third generation Eagle micro-Probe EDXRF spectrometer from Edax Inc. was used for analyzing major oxides and trace elements in the remaining specimen after cutting. The spectrometer was installed at the Gem and Jewelry Institute of Thailand (Public Organization), Thailand. The sample was excited by X-rays (Rh tube) with the power of 40 kW and the current of 250 μA.

The polished natural specimens were irradiated by the electron accelerator which located at the Gems Irradiation Center, Thailand Institute of Nuclear Technology (TINT), Thailand. The accelerators power was 10 kW which can produced high-energy ionizing electron at 20 MeV. All specimens were subjected to e-beam at fluences ranging from 4.46×10^{15} – 2.65×10^{16} cm^{-2}.

The optical absorption spectra were measured on the platelets oriented perpendicular to the c-axis before and after irradiation by using the PerkinElmer lambda 750 UV/Vis/NIR spectrophotometer located at the Gems Irradiation Center, Ongkharak Branch, TINT. The wavelength for the optical spectra collected was recorded from 200 to 1,400 nm by setting a spectral resolution of 2 nm with a scan speed of 250 nm min^{-1}. All of the measurements were done in room temperature.

The Bruker ALPHA Spectrometer was used for measured the mid-infrared spectra of the heliodor samples. The spectra were recorded in the region of 400 – 5,000 cm^{-1} with a resolution of 4 cm^{-1} at the Department of Mineral Resources under the Ministry of Natural Resources and Environment, Thailand.

3. Results and Discussion

The natural pale heliodor change to yellow color after e-beam irradiation. The intensity of color were gradually increased when the level of electron fluences rising up to 2.65x10^{16} cm^{-2}. However, it seems that the intensity of the color is saturated at around 1.76x10^{16} cm^{-2} of electron fluences level.

The analytical data of a given sample obtained by EDXRF were summarized in Table 1. The EDXRF analysis indicated that the heliodor sample was Cs rich with cesium weight fractions of 3.72%. The results for heliodor samples investigated in comparison to the other locality beryl which both samples, Yellow beryl [6] and CAM1 [7], originated from Aracuai, Minas Gerais, Brazil. Consistent with the chemical formula of beryl ($Be_3Al_2(SiO_3)_6$), all the compared samples contained SiO_2, Al_2O_3 and BeO as major elements. The studied sample contain minor quantities of transition metal ions, in total 0.01 wt% MnO and 0.78 wt% FeO. The FeO content in the heliodor and the yellow beryl showed higher than in CAM1 which is morganite (pink beryl) as reporting in [7]. The minor contents of Na_2O, MgO and TiO_2 also were recorded. The trace contents of Br_2O and Rb_2O only presence in heliodor sample.

Table 1 EDXRF analysis of heliodor in comparison with other beryl originated from Aracuai, Minas Gerais, Brazil Data are given in wt% and nd means not detection.

	Heliodor	Yellow beryl [6]	CAM1 [7]
SiO_2	62.73	66.85	63.61
Al_2O_3	17.62	18.65	17.89
BeO	12.38	13.42	nd
Na_2O	0.65	0.06	1.12
K_2O	nd	0.02	0.03
CaO	nd	nd	0.02
FeO	0.78	0.40	0.04
MgO	0.55	nd	nd
MnO	nd	0.01	0.02
TiO_2	0.08	nd	nd
Cs_2O	3.72	0.60	3.31
Li_2O	nd	nd	nd
Br_2O	0.01	nd	nd
Rb_2O	0.03	nd	nd
Total	98.55	100.01	86.04

The UV–Vis-NIR absorption spectra (E⊥c) of the natural and e-beam irradiated heliodor are presented in Fig. 1. The natural specimen showed distinctive absorption peaks, one around 813 and the other around 1,402 nm. After irradiation with 1.34x10^{16} cm^{-2} electron fluence, the intensities of the absorption band at 813 nm have decreased.

When increase the electron fluence to 2.65x10^{16} cm^{-2}, this peaks disappeared. On the other hand, the absorption band at 1,402 nm did not showed any changes in their intensity even receiving the maximum of electron fluence.

After specimens were irradiated, the color change from pale to yellow is due to the disappearance of the absorption band at around 813 nm. The previous studies have suggested that the yellow color of beryl related to charge-transfer between Fe^{3+} ions substituting for octahedral Al^{3+} ions in the crystal and the surrounding oxygen ions [8]. Upon e-beam irradiation, the electrons that are removed from the Fe^{2+} ions are trapped at an unidentified site in the heliodor structure. Fe^{2+} ions at tetrahedral and octahedral sites in the heliodor crystal donate one electron to an electron trap and are converted to Fe^{3+} ions responding to disappeared of the peak at 813 nm. The absorption intensities of the distinctive peaks (813 nm) in the spectra quickly decrease with increasing electron fluences. The intensity of this peak appears to saturate at about 1.76x10^{16} cm^{-2} of electron fluence level, as shown in Fig. 2.

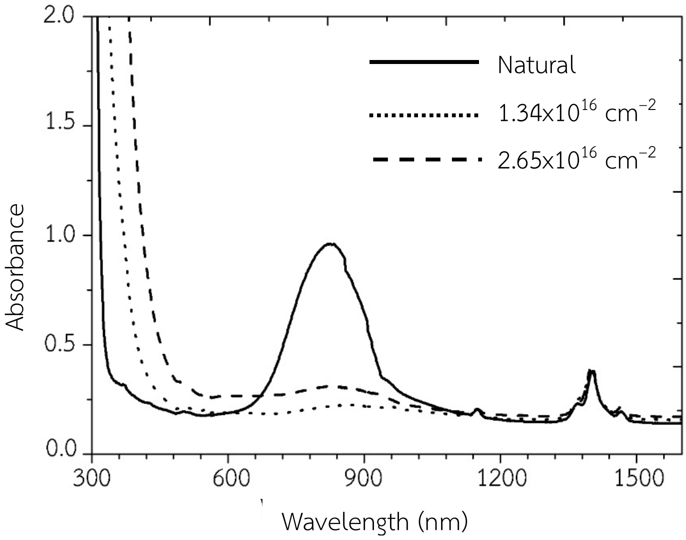

Fig. 1 UV-Vis-NIR spectra of heliodor sample: natural state (solid line), after e-beam irradiations at 1.34x10^{16} cm^{-2} (dashed line) and 2.65x10^{16} cm^{-2} (dotted line).

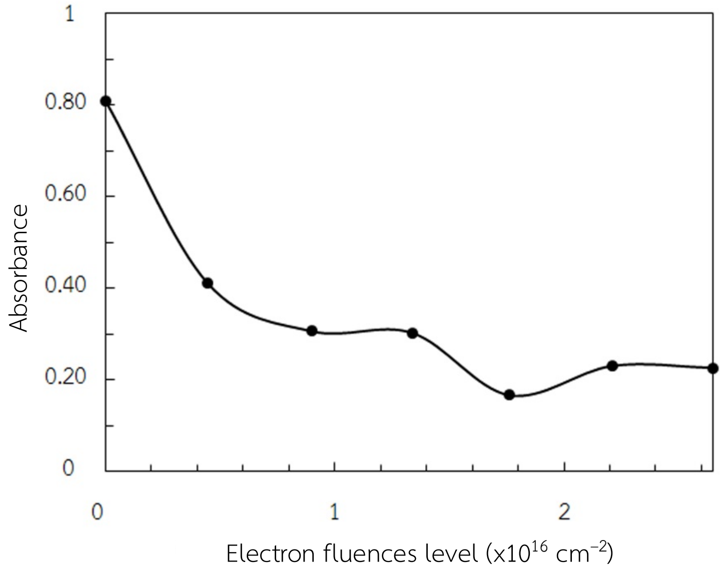

Fig. 2 Intensity changes of the 813-nm absorption peaks with electron fluences level.

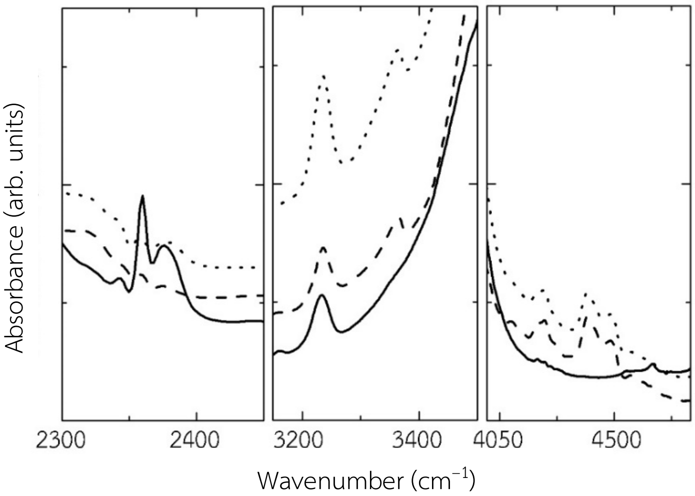

Fig. 3 Mid-infrared spectra of heliodor sample: natural state (solid line), after e-beam irradiations at 1.34x10^{16} cm^{-2} (dashed line) and 2.65x10^{16} cm^{-2} (dotted line).

The mid-infrared spectra before and after e-beam irradiation measured at room temperature are shown in Fig. 2. Mid-infrared absorption measurements in the different electron fluence level samples indicate the presence of type-I and type-II water together with OH^-. The spectrum can be divided in three spectral regions at about 2,300 – 2,450, 2,600 – 3,500 and 4,000 – 4,800 cm^{-1} as shown in Fig. 3. The first region was reduced the intensity after e-beam irradiation which corresponding to the modes of the crystal structure SiO_2 BeO and Al_2O_3. The second region indicates the presence of foreign molecules in heliodor which increasing the intensity after e-beam irradiation. The final region corresponds to the stretching modes of OH^- and is used to analyses water and OH^- molecules in the channels. After e-beam irradiation the mid-infrared spectra in this region change significantly. The intensity of both type-I and type-II water is increased.

4. Conclusion

The present work gives an overview about knowledge and controversial discussions of color change by electron in heliodors. UV-VIS spectroscopy provided a basic understanding of the mechanism of the color change in heliodor caused by e-beam irradiation. The color change from pale to yellow is due to the disappearance of absorption band at 813 nm related to charge-transfer between Fe^{3+} ions substituting for octahedral Al^{3+} ions. In addition, this absorption band are useful guides for estimating optimal electron fluences. Mid-IR analysis showed that heliodor accommodates many different molecules in its channels and that their microscopic structures and their role to produce color are still open questions.

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6. References

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