Spectroscopic characteristics of natural fluorite induced by electron-beam irradiation

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Naturally synthesized fluorite crystals were investigated in terms of their spectroscopic characteristics to indentify the origin of their colors and dynamics of color variation induced by electron-beam irradiation. Specimens with various colors and shades categorized into four groups were irradiated by an electron beam with two different power densities and subsequently heat-treated at various temperatures and times to investigate the kinetics of the color change process. Various aspects of spectroscopic characteristics before/after e-beam irradiation and heat treatment were analyzed by comparative studies by a UV-V is spectrophotometer, a Fourier transforminfrared spectrometer, an X-ray fluorescence spectrometer, X-ray diffraction, and a photoluminescence spectrometer. The variety of color groups of natural fluorite samples were confirmed to be caused by various defects and F-centers generated by e-beam irradiation.

Key words: Natural fluorite, Electron-beam irradiation, F-center.

Introduction

The nature of the fluorite structure makes it accessible to a wide variety of defects, including many that have the potential to cause color [1]. These include certain impurities of specific oxidation states, structural vacancies, and combinations of the two.

Fluorite, CaF₂, with a pure chemical composition is generally colorless, but also presents green, blue, yellow, and purple. There are four groups of models to explain the color; 1) inclusions of organic compounds, 2) some type of impurity defects such as Mn²⁺, REE³⁺ (rare earth element)⁵⁺, or REE²⁺, 3) colloids of metallic Ca formed under radioactive irradiation, 4) some type of hole or electron center with the charge trapped somewhere in the lattice.

First of all, the analyses of rare-earth impurities in natural fluorites have been reported by several investigators [2-5]. The fluorite structure readily incorporates many impurity ions, some of which have been purported to cause color. REEs are very common impurities in fluorite, along with certain transition elements, because they are similar in terms of ionic size and charge state to calcium. Electronic transitions involving electrons from the d and f orbitals of these elements are a major cause of color in minerals including fluorite [6]. Under the conditions found in most natural environments, the majority of the REEs will exist in the trivalent oxidation state. Thus, if they are incorporated into fluorite it will most likely be as REE³⁺, necessitating a coupled substitution to retain charge neutrality. Only Sm, Eu, and Yb are easily incorporated into fluorite in the divalent state [7]. Trivalent REEs either do not absorb in the visible, or are not strong enough absorbers to have an effect on the color [5]. However, several divalent REEs, including Sm²⁺ and Eu²⁺, are purported to absorb strongly in the visible, and cause color in fluorite [6, 8, 9, 10]. For example, Sm²⁺, Dy²⁺ and Tm²⁺ are the cause of a green color in fluorite [10]. Divalent samarium has been implicated in the cause of color in light to emerald green fluorite [6]. A colorless to green color change fluorite by X-ray irradiation, with absorption peaks at 680, 610, 440, 422, 396, 355, 305, 281, 255, 240 and 218 nm were attributed to divalent samarium. Furthermore, this color is bleached by heating at temperatures of about 300 °C, and this explained as the divalent samarium reverting back to trivalent [9]. Also the other spectrum of green fluorite contains bands at 580 and 400 nm, which are attributed to F-centers in the presence of trivalent yttrium, and a band at 714 nm caused by F-centers near Ce ions [11]. Moreover, the cause of yellowish-green color in fluorite bands at 230, 335 and 400 nm are similar to those in other fluorite studies, with the addition of a band at 306 nm, probably due to the 4f → 5d transition of trivalent cerium [12]. The Ce- and Y-associated F-center can be bleached upon heating [13].

The most well-defined defect center in fluorite that gives rise to color is the F-center, which is an electron trapped in a fluorine ion vacancy. It is the most popular theory for a purple color in fluorite primarily because F-centers produce similar color in other alkali halides, with a broadband absorption around 560 nm and it is relatively easy to produce by irradiation or additive
coloration [14]. Dark blue or black fluorite results from F-center and color centers change to light blue by heat treatment. This color is mostly brighter by 100-150 °C of proper heat treatment, and bleached at 200-300 °C. The location of the absorption bands of an F-center in fluorite are at 375, 525 and 560 nm. Calcium colloids also exhibit an absorption band at 560 nm [1, 15, 16]. If both F-centers and calcium colloids produce purple color and have similar optical absorption spectra, the idea that it is not actually the Ca colloids that produce the color, but the F-centers present, is reinforced.

Based upon numerous references, higher energy irradiation is well known to produce color centers and color center aggregation. Although there are some studies on high energy electron irradiation and the optical properties of fluorite induced by this irradiation, there is no report about the annealing effect on optical properties in various electron irradiated fluorite. Also the fact that electron-beam irradiation energy and the probability of infiltration have a very intimate connection has been confirmed. It has been also confirmed that if the depth of electron penetration is insufficient, the defects (as vacancies) that havea direct effect on the crystal color does not occur. On the basis of these confirmations, we used higher electron-beam than in previous studies, and focused on producing F-centers and impurity defects as electronic transitions of rare-earth elements. The dynamics of color bleaching was also investigated to improve the controllability of defect type and concentration.

**Experimental methods**

Fluorite samples in this study were faceted and all of a natural very light color. Natural CaF$_2$ with various colors of green, yellowish-green, pink, and colorless were used. 2.5 MeV and 10 MeV electron-beam equipment were used in the study, and the electron-beam current was 1 mA, the average generation capacity of the electron-beam was 10 kW, and the test range was 800 mm × 20 mm below the beam gun. Also, the distance from the beam gun to the sample was fixed and 20 cm, and tests ran under 2 × 10$^{17}$ e/cm$^2$.

We have selected and sorted the samples with relevant results into four groups, which brought color changes to the fluorite after electron-beam irradiation. With the selected samples, under an oxidation condition, the temperature changes from 200, 250, 300, 350 and 400 °C, and a heating rate was controlled at 5 K·min$^{-1}$, a hold time at 1 h. After the heat treatment, the samples were slowly cooled. Also, under the same environment, the hold time was varied to 1-12 h, and after the heat treatment, the samples were cooled down to room temperature.

The optical properties of before/after electron-beam irradiation and heat treatment were investigated using a UV-V is spectrophotometer (SHIMADZU UV-3600, JAPAN), and a Fourier transform infrared (FT-IR) spectrometer (SHIMADZU IRAffinity-1, JAPAN). The quantitative analyses was carried out by an X-ray fluorescence spectrometer (ED-XRF) (SHIMADZU XRF-1700, JAPAN) with 4 kV-95 mA conditions. The structure of the fluorite samples were confirmed by XRD measurements using a Rigaku ULTIMA IV diffractometer with 40 kV, 100 mA and CuKα radiation in the scan range 10-90 ° at a low speed of ~5 °·min$^{-1}$.

Resulting from the electron, vacancies, and impurities due to the distinct optical absorption of the specimens, when the structure starts a transition from a low energy level to a high energy level, and then back to a low energy level, part or the whole energy generated from a luminous body is emitted in the form of light. To collect information on the electron state of impurities or the material structure of the specimen via a spectrum, we have measured the photoluminescence (PL) spectrum of the fluorite after exposing to the electron-beam and heat treatment. The PL spectra of before and after electron-beam irradiation/after heat treatment in color changed natural fluorite was recorded at room temperature using a DARSA PRO-5000 SYSTEM photoluminescence spectrometer with a 500 mW Xenon lamp as the excitation source.

**Results and discussion**

Figure 1 is the UV-Vis absorption spectra of the fluorite samples with various colors investigated in this study. The first solid line represents colorless fluorite, in which no clear absorption peak was observed. The second dashed line is for pink fluorite. The broad absorption peak shown at around 560 nm is the peak related to F-centers, which is the cause of the most famous pink or purple color, and at the same location also shows calcium colloids which act as a reinforcement of the color. These peaks were easily produced by irradiation, and it was also relatively easily bleached by heat treatment as described later. The third dotted line is the yellowish-green fluorite; the absorption features of 335 and 400 nm are similar to those in other fluorite studies, and the location of most

![Fig. 1. Absorption spectra of natural fluorite samples.](image-url)
peaks are similar to the green fluorite and only an intensity difference was detected. The last shown dashed dot line is the green fluorite; the peaks were observed at 600, 400, and 350 nm and these peaks coincide with the absorption peak (610, 422, 396, 355, 305, 281, 255, and 240 nm) of green samples changed from colorless due to X-ray irradiation.

ED-XRF analysis revealed that each fluorite contains an appreciable amount of impurities as summarized in Table 1. First of all, Mn is assumed to be one of the elements that causes the color of the fluorite in numerous literature [1]. Yttrium is known to associate with Y and F-centers within many fluorites and produce various colors. Co is not reported to possess special characteristics in the literature, but the fact that it is contained only in the pink fluorite leads to the assumption that this element is a cause of the pink color. From XRF chemical composition analysis, we have found that major color elements contained in most fluorites such as rare-earth elements were not detected except yttrium due to their untraceable amount.

In the previous literature [9], specimens were irradiated with different beam intensity and it was reported that the color was not very clear when irradiated at 1.4 MeV. To produce stronger and better colors and to find out the difference between studies done in the previous literature which used low level irradiation, the specimens in this study were irradiated at 2.5 MeV and 10 MeV. As shown in the Fig. 2, the specimens changed their color from colorless and the characteristic absorption peaks were grown when irradiated at 2.5 MeV and 10 MeV. The absorbance of each peak was far greater when irradiated at 10 MeV.

After irradiation, the absorption peaks at 400 nm and 590 nm grew while the absorption peak at 712 nm grew slightly. Absorption peaks shown at 400 nm and 590 nm indicate the existence of F-centers and Y\(^{2+}\). An F-center is produced when an electron is trapped in the vacancy of a fluorine ion. Aggregation of yttrium and F-centers is known to be a cause of a blue color, and the absorption peak shown at 590 nm appears to be a cause of the purple color when shifted to 560 nm. Also, the absorption peaks at 590 nm and 712 nm represent a defect center in which yttrium and cerium are coupled and this defect turns out to be easily bleached by heat as described later.

As shown in Fig. 3, the absorption peaks caused by the F-center, Y\(^{2+}\) or Ce shown at 400, 590, and 712 nm after electron-beam radiation can be bleached and the color produced returned to the original color by heat treatment.

![Fig. 2](image2.png)

![Fig. 3](image3.png)

<table>
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<th>Sample</th>
<th>FC1</th>
<th>FC2</th>
<th>FC3</th>
<th>FG1</th>
<th>FG2</th>
<th>FG3</th>
<th>FYG1</th>
<th>FYG2</th>
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<td></td>
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<td>Pink</td>
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Table 1. Chemical composition data of fluorite samples by ED-XRF. (Unit: wt%)
However the dark color was nearly recovered to its original color by heat treatment at $300^\circ$C, $350^\circ$C, and $400^\circ$C within a reasonable time span. This bleaching is caused by electronic transition for which the electron at unstable status returns to stable status by external energy.

The dynamics of color bleaching can be described by Arrhenian thermally activated behavior. The activation energy, $E$, necessary to recover the original color by the heat treatment is calculated by the Arrhenius equation;

$$t = t_0 \exp(-\Delta E/RT) \text{ or } \ln(t) = \ln(t_0) - \Delta E/RT$$  \hspace{1cm} (1)

Here, $t$ refers to the time necessary for color recovery at a given temperature, $t_0$ is the pre-exponential factor, $R$ the gas constant, and $T$ the absolute temperature. When this equation is fitted to the experimental data as shown in Fig. 6, the activation energy was calculated to 84.58 kJ/mol.

Fig. 7 shows the Fourier transformed infrared (FT-IR) spectra of the specimens before and after electron-beam irradiation and these spectra are compared to that of the heat-treated specimen. The spectra show that four absorption bands at 364 cm$^{-1}$, 1550 cm$^{-1}$, 2357 cm$^{-1}$ and around 3500 cm$^{-1}$, which result from the characteristic vibration of hindered rotations of the hydroxyl ions, H-O-H bending of the H$_2$O molecules, CO$_2$ or KBr pellets, and OH stretching vibration band, respectively. However, there was no significant difference between the FT-IR spectra of the specimens even after electron-beam irradiation and heat treatment.

Since a strong level of electron-beam irradiation at 2.5 MeV and 10 MeV may affect the crystal structure not only producing defect centers, the crystallinity was checked by X-ray diffraction. As shown in Fig. 8, the diffraction patterns obtained were matched to that of the crystal structure of CaF$_2$ of JCPDS file no. 35-816. Therefore, one can conclude that the fluorite specimens did not experience a structural change by electron-beam irradiation. However, it is noteworthy that the diffraction intensity reduced noticeably in the irradiated specimen and this is attributed to an increased defect center concentration and, hence, X-ray absorption by this defect centers.

Photoluminescence spectra in Fig. 9 contain two distinctive peaks. The strong peak at 370 nm can be assigned to F-centers, and the even stronger peak at 423 nm is caused by Eu$^{2+}$ located at the surface of the specimen [10]. These strong peaks exhibited an appreciable increase in intensity after electron-beam irradiation, but after heat treatment the peak intensity...
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was reduced dramatically than for the original specimen. From these intensity changes of the peaks, one can conclude that F-centers or Eu$^{2+}$ surface defects were extensively generated by electron-beam irradiation and these defects were eventually annihilated by heat treatment.

Conclusions

In this study, high energy electron beams of 2.5 MeV and 10 MeV were employed as a means to control the color of natural fluorite crystals, and the produced alteration in color was controlled precisely by subsequent heat treatment at various temperatures and times. Natural fluorite crystals with various colors showed noticeable color changes when irradiated by an electron-beam, and it was found that electron-beam generated color centers and other defects (vacancies) within fluorite crystals and trapped electrons produced color variations.

We can estimate from the spectroscopic analysis that even with untraceable amount as analyzed by XRF, detectable color changes were produced by rare-earth elements, especially Y and Eu, and it is necessary to measure precisely the concentration of rare-earth elements in ppm units to identify a quantitative relationship between a rare-earth element and color. From various spectroscopic analyses, we can conclude that electron-beam irradiation creates defects in fluorite such as F-centers, which seriously affect the color of the crystal. Also, it was confirmed that a higher density of defects was produced by a higher energy electron beam and heat treatment at a higher temperature was needed to bleach these F-centers and other defects. This is due to not only the concentration of defects but also numerous defect formations by electron-beam irradiation of higher energy above 2.5 MeV.

The past research on the mechanism of color in fluorite have revealed its complexity compared to other simpler crystal systems such as alkali halides. It is apparent that each color may have more than one possible cause. An additional study on the basic property of CaF$_2$ might be necessary to clarify the mechanisms of the color.

References