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## Effect of heat treatment on the luminescence properties of natural apatite

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### ABSTRACT

Regarding gemstone identification, the effect of heat treatment under reduction condition to optical and luminescence properties of natural green apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , F, Cl) from Madagascar has been investigated. Although electron microprobe analysis (EPMA) shows a luminescence defect of rare earth element such as Ce (0.47%), Pr (0.22%) and Nd (0.15%), however original sample does not show luminescence properties. With consecutive heating process, the color alteration from green to colorless of samples, and also the enhancement of luminescence properties of  $\text{Ce}^{3+}$  in natural apatite was observed. Mechanism of fluorescence enhancement and color changes during heating process were discussed using optical spectra and emission spectra. Optical spectra of heated apatite point out that green and blue color assigned to the existence of a photochromic center of  $\text{Ce}^{3+}$ - $\text{SiO}_3^-$  radical and  $\text{SO}_3^-$ , respectively. Consequently, the vanishing of these both bands resulted in the colorless heated apatite at 800 °C. Heated apatite showed emission band at 365 nm because of the deactivation of electron from 4f of  $\text{Ce}^{3+}$  to 5d. Optical spectra reveal that the correlation of luminescence enhancement and the fading of yellow tint of heated apatite by means of the descending of  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$  charge transfer process. The ultimate contribution of this work is the finding of the difference of luminescence properties between non-heated and heated apatite which can be used as an effective tool for gem identification. This identification tool is remarkable because it is rapid and non-destructive.

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### 1. Introduction

Natural apatite, a phosphorus mineral with general formula  $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$  [1], is known as a semi-precious gemstone due to variety of colors such as blue, green, and yellow.

In addition, it is renowned that natural apatite is a luminescence mineral according to constitution of luminescence intrinsic defect of rare earth elements [1]. Therefore, apatite structure has been widely used as common framework for luminescence material in many applications such as white light emitting diode, cathode ray tube and field emitting displays. [2–5]. Similar to natural apatite, the synthetic can be luminesced by the deactivation of electron from 4f to 5d of rare earth elements doping such as  $\text{Ce}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Th}^{3+}$  [1]. In the sense of gemstone, blue natural apatite is the most popular among others in gemstone market. Therefore natural green apatite is usually heated in order to change to blue color. With a proper heat treatment, green color of natural apatite can be changed to neon like bluish-green color which similar to the blue color of the most valuable and precious gemstone, Paraiba tourmaline. Since blue apatite is an imitation of Paraiba tourmaline, it has been named as Paraiba apatite [6]. Due to this reason, distinguishability between heated blue apatite and Paraiba tourmaline

with naked eyes is troublesome. Additionally, reflective index and specific gravity of Paraiba tourmaline and natural apatite are in the same range, leading to confusing to distinguish heated blue apatite from Paraiba tourmaline using basic parameters. Indeed, the cause of blue color of natural Paraiba tourmaline and natural apatite is different. Blue color of Paraiba tourmaline are originated by exclusively  $\text{Cu}^{2+}$  while blue color of natural apatite is conducted to two causes including  $\text{SO}_3^-$  center and  $\text{MnO}_3^-$  [7, 8]. In addition, previous studies showed that various color of synthetic apatite can be accomplished using Co, Ni and Nd as a doping for violet, yellow-green and pale green, respectively [9].

Nowadays, luminescence spectroscopy has been considered as an effective tool for gemstone identification by means of rapid and non-destructive technique. For diamond identification, luminescence spectroscopy is a routine technique used for discriminated treated and synthetic diamond from their natural [10]. Although, luminescence spectroscopy is a promising technique for gemstone identification, there are a few studies related to other gemstones [1]. In the case of apatite, a number of reports are available on luminescence properties of natural apatite but there are no report for the use of luminescence properties in the application of identification [1, 11–13]. Moreover, the luminescence properties of heated natural apatite have not been reported yet. Regarding gemologist perspective, the aim of this work focused on the effect of heat treatment process on the luminescence properties of natural

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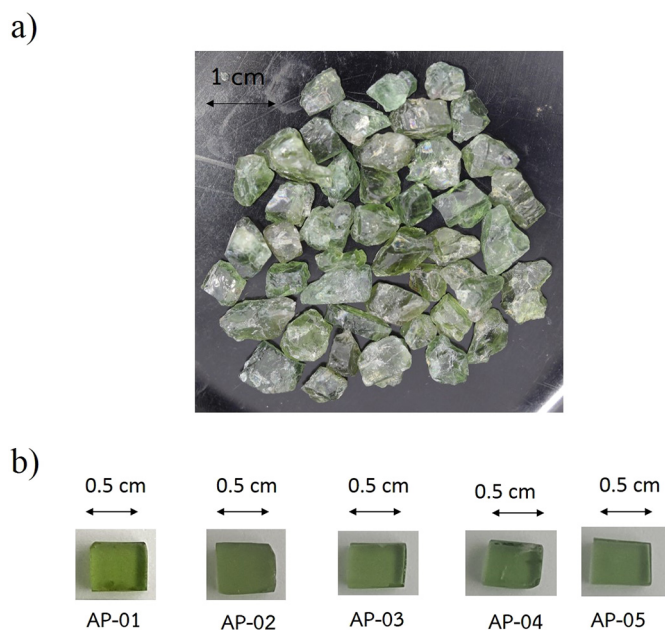
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apatite from Madagascar in order to apply luminescence technique for gemstone identification. In order to explore the correlation of color alteration and luminescence properties, optical and emission spectra of natural green apatite were carried out during heat treatment process. Major phase and elemental constitution of natural green apatite were studied using X-ray diffraction and electron microprobe analysis (EPMA), respectively. Moreover, the structure alteration during heating process was preliminary explored by DTA curve under the  $N_2$  atmosphere.

## 2. Material and Methods

The natural green apatite in this study was sold in Chanthaburi gemstone market, Thailand and assumed to originate in Madagascar (Fig. 1a). Original sample structure was analyzed by means of X-ray powder diffraction (XRD) pattern, elemental analysis and thermal analysis. The crystal structure was carried out using X-ray diffractometer, Rigaku TTRAX III with Cu K $\alpha$  radiation ( $\lambda = 1.540 \text{ \AA}$ ). XRD pattern was obtained by step scanning from  $2$  to  $80^\circ 2\theta$  with speed as  $3$  degree per minute. Structure of apatite was identified by comparing with the XRD PDF card files of the Joint Committee of Powder Diffraction Standards. Elemental analysis was analyzed by Electron Probe Micro Analyzer (EPMA) (JEOL model JXA 8100 super probe). Sample was carried out at acceleration voltage of  $15.0 \text{ kV}$ , probe current of  $2.184 \times 10^{-8} \text{ A}$  and beam diameter of  $1\text{--}5 \text{ \mu m}$ . The results were automatically corrected by JEOL software. Differential thermal analysis (DTA) of the original sample was accomplished by Netzschsta 449C thermal analyzer under  $N_2$  atmosphere with heating step  $10^\circ \text{C}/\text{min}$ .

The effect of heat treatment process was studied using five samples which were cut and polished to all parallel faces in a  $0.5 \times 0.5 \times 0.2 \text{ cm}$  dimensions (Fig. 1b). Heating treatment was carried out under reducing atmosphere with heating temperature between  $300$  to  $800^\circ \text{C}$  and in the step of  $100^\circ \text{C}$ . Reducing atmosphere was prepared by introducing carbon powder to enclose samples in alumina crucible. The filled and covered crucible was heated using electric furnace at determined temperatures for  $1 \text{ h}$ . After turning off the furnace, heated samples were left to cool down without specific cooling rate, then luminescence and optical spectra were recorded.



**Fig. 1.** a) Original natural green apatites from Madagascar and b) five samples in a size of  $0.5 \times 0.5 \times 0.2 \text{ cm}$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Luminescence spectra were carried out by scan method of Agilent Cary Eclipse Fluorescence Spectrophotometer using  $600 \text{ V}$  of photomultiplier tube as a detector and xenon flash lamp as an excitation source. All emission spectra were recorded at  $300$  to  $800 \text{ nm}$  using  $275 \text{ nm}$  as excitation wavelength.

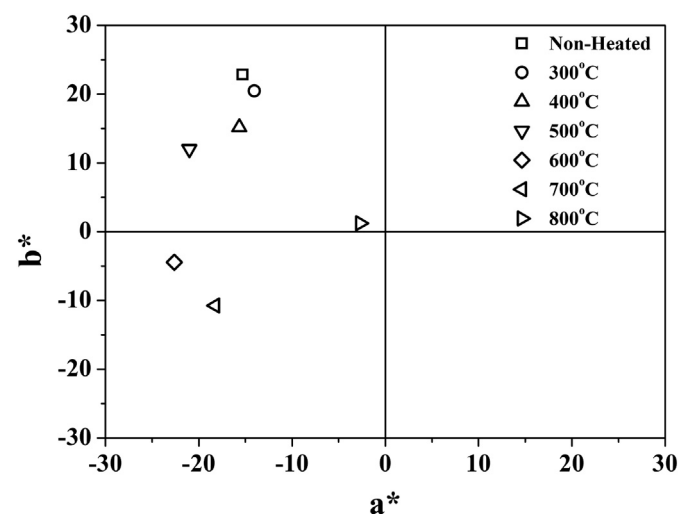
UV–visible absorption spectra and color measurement were accomplished by Agilent Cary 60 UV–Vis Spectrophotometer with xenon pulse lamp source as a light source and photomultiplier tube as a detector. Color quality of samples was calculated by means of CIE  $L^*a^*b^*$  color index using with D65 light source and  $2^\circ$  detection angle.

## 3. Results and Discussion

### 3.1. Sample Characterizations

As shown in Fig. 1a, original color of apatite samples from Madagascar was green. Exact colors of five sample specimens were identified using CIE  $L^*a^*b^*$  color index. As shown in Fig. 2, chromaticity coordinate of non-heated samples agrees well with green color by negative of  $a^*$  and positive of  $b^*$ .

To determine major phase of the original sample, X-ray powder diffraction (XRD) was carried out in the range of  $20$  to  $80^\circ 2\theta$ . As shown in Fig. 3, most peaks in XRD pattern of sample allow us to indicate the sample to a pure phase of apatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  (PDF No. 01-083-8012). Apatite sample has a hexagonal structure with space group of  $P6_3/m$  as a typical apatite phase and lattice parameters value are  $9.398 \times 9.389 \times 6.886 \text{ \AA}$ . EPMA result shows major composition of natural apatite as a typical apatite (Table 1) including Ca, P, and F. In detail, elemental analysis data present significant amounts of impurity elements including non-metals and metals. Major interference nonmetals of sample are  $\text{SiO}_2$  and  $\text{SO}_3$  in the percentage of  $0.92\%$  and  $0.88\%$ , respectively. Major interference metals are rare earth elements including Ce, Pr and Nd in the percentage of  $0.47\%$ ,  $0.22\%$  and  $0.15\%$ , respectively. The presence of point defects could be associated with optical properties and luminescence properties of natural green apatite. As reported previously, green and blue color of natural apatite related to the presence of  $\text{SiO}_2$  and  $\text{SO}_3$ , respectively [7] and the presence of rare earth elements corresponded to luminescence property of natural apatite. However, in this study the presence of rare earth elements does not generate luminescence in non-heated apatite. Thus, it is pointed that the quenching process of rare earth elements could be caused by other point defects.



**Fig. 2.** CIE chromaticity coordinates in two dimension of  $a^*$  and  $b^*$  values plot of original and heated samples.

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