

A Photoluminescence Study of Dy³⁺ Emissions in Zircon from Central Highlands of Vietnam

Bùi Thị Sinh Vương, Lê Thị Thu Hương*

Faculty of Geology, VNU University of Science, 334 Nguyễn Trãi, Hanoi, Vietnam

Received 21 May 2015

Revised 29 May 2015; Accepted 20 November 2015

Abstract: It has been known that among REEs, Dy³⁺ plays an important role in the structure of Zircon though it just exists as trace elements. The Dy³⁺ is structured in the zircon crystalline lattice and it has a good fluorescence response. From all significant roles of this ion, this paper focused on clarifying the luminescence of Dy³⁺ in Zircon from a mine in Central Highlands of Vietnam (Krong Nang, Dak Lak province) by Photoluminescence (PL) spectroscopy, Energy Dispersive spectrometer (EDS). The analytical results of EDS identified the presence of trace quantities of Dy³⁺ in the bulk of zircon by the typical peaks. The PL spectra showed Dy³⁺ emissions at some characterized band positions with the strongest band at 481nm (near 20790 cm⁻¹) and 581 nm (near 17203 cm⁻¹). The intensity of Dy³⁺ emissions from zircon is related to the concentrations of this ion and its color; the higher the concentration of Dy³⁺, the higher the emission intensity and the brighter the color. The band width of the main peak of Dy³⁺ emissions is narrow indicating that the zircon structure is well crystalline.

Keywords: Zircon, Dy³⁺, Photoluminescence (PL) spectroscopy, Energy Dispersive spectrometer (EDS), Rare earth elements (REEs).

1. Introduction

Zircon, with ideally chemical formula ZrSiO₄, is one of the most studied accessory minerals in geology. Zircon is tetragonal (*I41/amd* and *Z=4*) [1] and REE readily substitutes into the eight coordinate Zr site, which forms triangular dodecahedron. In spite of being resilient to mechanical and chemical weathering, the structure is relatively open with small voids between the SiO₄ and ZrO₈ polyhedra. Such structural voids are potential interstitial sites that could incorporate impurities [2] as illustrated in figure 1.

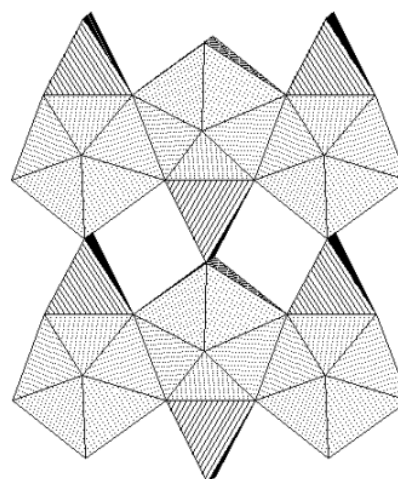


Figure 1. Zircon structure projected on (100); c axis is vertical, b (a₂) axis is horizontal. ZrO₈ dodecahedra are shaded light gray; SiO₄ tetrahedra are striped [2].

* Corresponding author. Tel.: 84-912201167.
Email: letth@vnu.edu.vn

Finch & Hanchar (2003) [2] describe two further possible distorted tetrahedral interstitial sites that may accommodate trace elements such as REE. In natural zircons, 8-coordinated Zr^{4+} is replaced by REEs large, highly charged cations such as Dy^{3+} . Replacement of Zr^{4+} by trivalent cations may occur via coupled substitution involving 4- and 8 coordinates sites: $Zr^{4+} + Si^{4+} = X^{3+} + P^{5+}$ or coupled substitution on the 8-coordinated site alone: $2 Zr^{4+} = X^{3+} + M^{5+}$ where $X^{3+} = REE^{3+}$ (eg. Dy^{3+}) and $M^{5+} = Nb^{5+}, Ta^{5+}$ [3]. Crystallochemically, HREE³⁺ (especially Dy^{3+}) seem to be the most compatible trivalent substituents in the 8-coordinates sites [4]. Zircon containing REEs ions have emitted the characteristic luminescence whose intensities are enhanced in zircon crystal. These luminescence bands are due to the well-known 4f-4f electron transitions within REEs. In particular, the predominance of Dy^{3+} bands in REE³⁺ luminescence spectra of natural zircon has been well documented in some studies [5-7].

Zircon is a representative example indicating implicated optical-properties. These are caused by trace amounts of impurities and crystal defects which could not be detected by ordinary methods, although the physico-chemical nature of the mineral is simple as compared with other silicate minerals. Although defects play an important role in the luminescence of natural zircons, one of the most important groups of activators is the lanthanides. Hence, there is a significant interest in the manner in which lanthanides activate and modify zircon luminescence. Among all, luminescence from Dy^{3+} is one of the most commonly observed lanthanide emissions in natural zircons suggesting that

other lanthanides effectively transfer energy to Dy [8].

2. Sample and method

2.1. Sample Preparation

The majority of the samples used for this study was purchased or collected by the authors during different field trips to the mines in Krong Nang, Dak Lak province. All mines are secondary and zircon can be found together with sapphire. Totally, 36 zircon samples including faceted and rough stones acquired from study area were used for this study. The rough stones were cut and polished on the opposite faces, being parallel to the c-axis. Mostly, they are yellowish orange to reddish-brown in color, with the sample size ranging from 2.7092 to 9.4175 ct. The gemological measurements confirm the weak to distinct purplish brown and brownish yellow pleochroism of these samples. Besides, their specific gravities are within the accepted range for high Zircon which varies from 4.64 to 4.69. Some representative samples are shown in figure 2.

2.2. Energy Dispersive Spectroscopy (EDS)

The surface image and elemental composition of zircon samples are analyzed with an Energy Dispersive Spectroscopy EDS, JEOL JSM-7600F, Oxford ISIS, microanalyser integrated. The accelerating voltage and the realtime used during sample analysis are 20KVA and 21-36, respectively, with the life time of 20 seconds. Each sample was analyzed with 6 points in two different areas of color: yellow and brown (figure 3).



Figure 2. Representative zircon samples showing orange to reddish - brown color.
Photo by B.T.S Vuong.

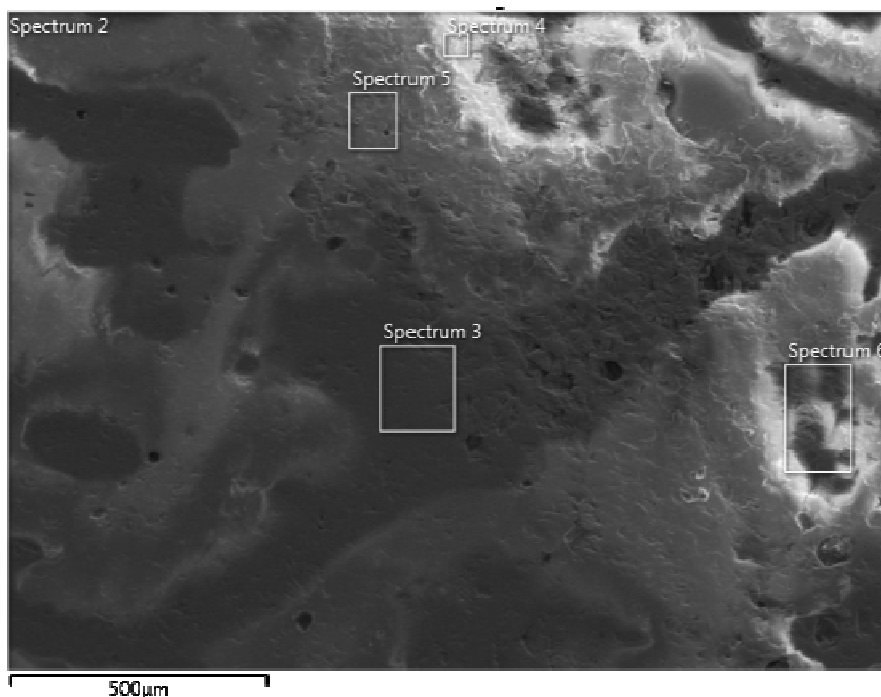


Figure 3. The surface image and point positions for measuring with EDS.
Of which, spectra 2, 3 are in yellow area and spectra 4,5,6 are in brown area.

2.3. Photoluminescence (PL)

Photoluminescence measurements in the visible to near infrared (NIR) range were made using a Horiba LabRAM HR Evolution-dispersive spectrometer. The spectrometer

system was equipped with an Olympus BX41 optical microscope, two diffraction gratings with 600 and 1800 grooves per millimeter, and a Si-based, Peltier-cooled charge-coupled device detector. Photoluminescence was excited

using a 473 nm diode-pumped solid-state laser (9 mW at the sample surface) and the 532 nm emission of a frequency-doubled Nd³⁺:YAG laser (10 mW at the sample surface). An Olympus 100× objective (numerical aperture 0.9) was used. The system was operated in the confocal mode (confocal aperture and entrance slit set at 100 μm); the resulting lateral resolution was ~1 μm, and the depth resolution (with the beam being focused at the sample surface) was ~2–3 μm.

3. Results and discussion

3.1. Energy Dispersive Spectroscopy EDS

The analytical results of EDS show Zr, Si and O as the main components of zircon, especially, the presence of trace quantities of

Dy³⁺ by the typical Dy³⁺ peak (figure 7). The Dy³⁺ is structured in the zircon crystalline lattice and undergoes the same chemical reactions as zircon. The concentration of this ion is so significantly low that it is quite difficult to be able to see its characterized peak. Zooming this peak makes us find easier to prove the presence of this. Furthermore, the Dy peak in spectrum 4 (darker: brown) (figure 4) with intensity value is approximately 70 counts seems to be less distinguishable than that in spectrum 2 (brighter: yellow) with intensity value is almost 80 counts (figure 5). The intensity of the peaks depends on the concentration of the ion. This implied that in the brighter area of the sample the concentration of Dy³⁺ is higher.

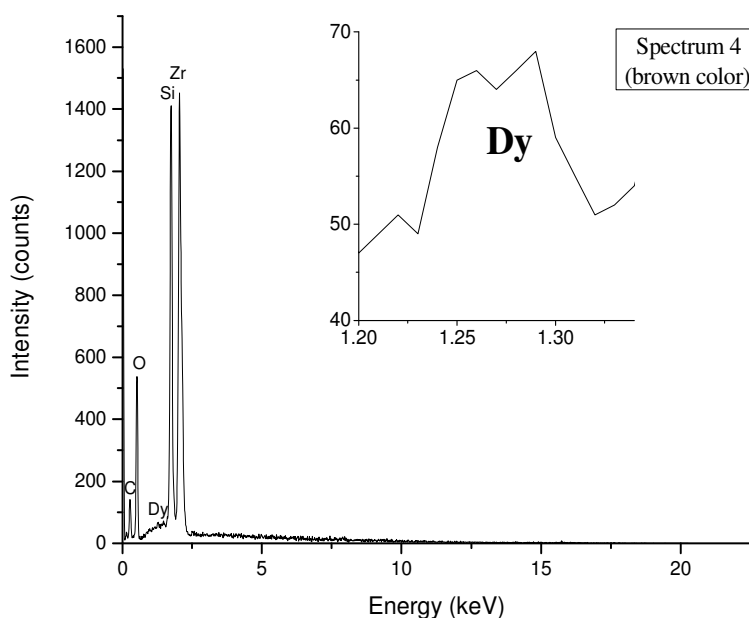


Figure 4. EDS spectrum of Zircon shows the presence of Dy³⁺ in brown area (spectrum 4).

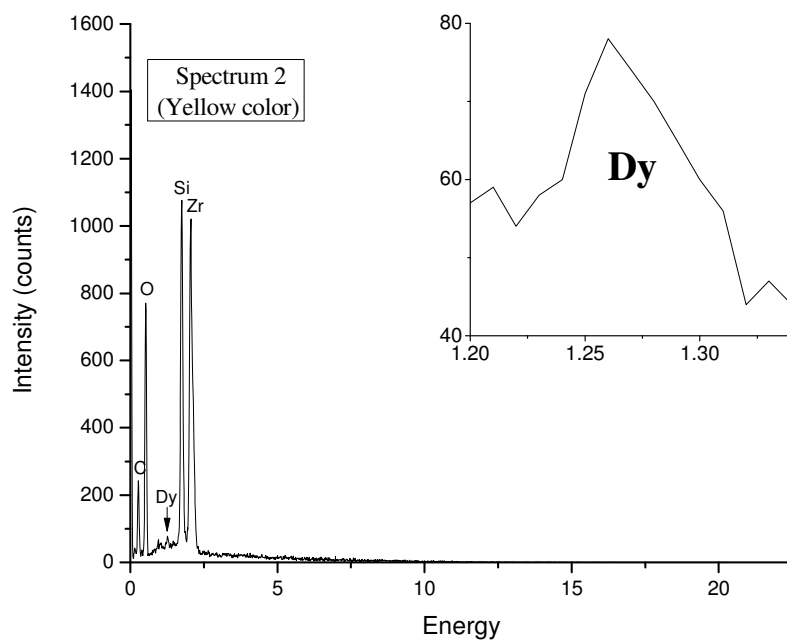


Figure 5. EDS spectrum of Zircon shows the presence of Dy^{3+} in yellow area (spectrum 2).

3.2. Photo-luminescence spectrum

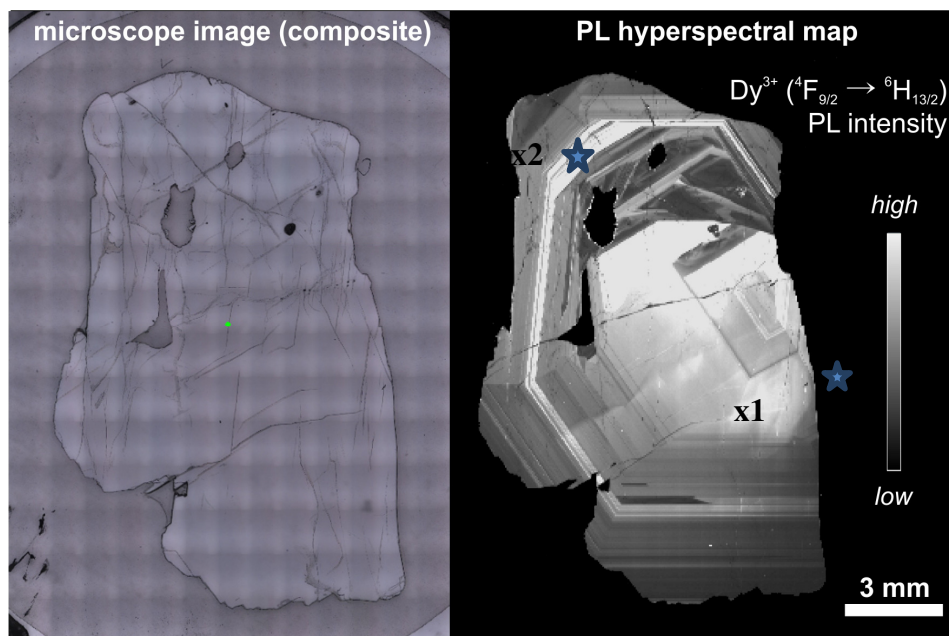


Figure 6. The PL hyperspectral maps show intensity distribution patterns of the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition of Dy^{3+} .

At first, two points including one (x1) in bright area in the center of the crystal and one in dark area (x2) in the rim of the crystal were measured (pointed in the map, figure 6) for studying PL and the results are shown in PL spectra (figure 7). As can be seen in PL spectra from figure 7, the pattern of both spectra is identical, just relative intensities change. The spectra show the strongest Dy³⁺ emissions at 481nm and 581 nm; other band positions (nm)

at 476m, 487s, 496m, 575m, 577m, 579s as natural zircons also commonly do of which m for medium, s: strong, b: broad peak forming background, w: weak. The emission intensity of Dy³⁺ in bright area is higher than that of Dy³⁺ in dark area. This observation, again, confirms the EDS spectra and leads to the understanding that the concentration of Dy³⁺ in bright area of zircon is higher compared to dark area of the sample.

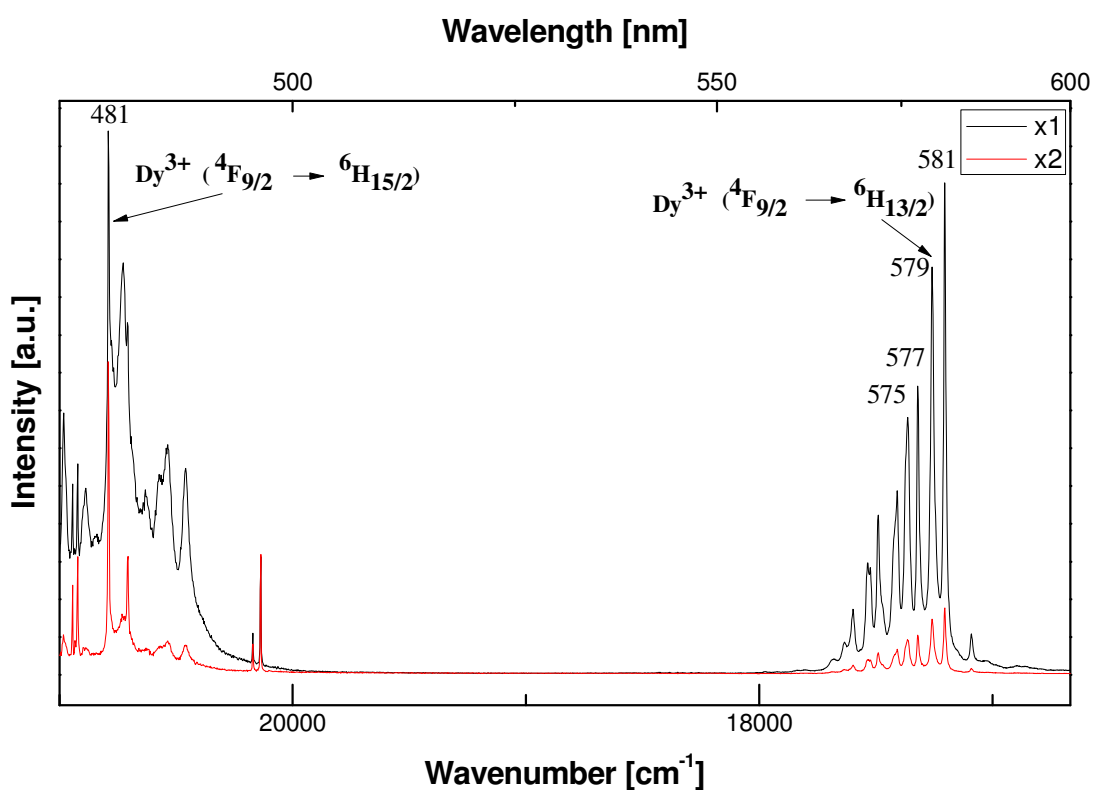


Figure 7. The PL spectra show the emission of trace Dy³⁺ in the bright (x1) and dark (x2) areas of the zircon crystal

The energy level of Dy (III) ion offers the possibility of efficient emissions at 481nm and 581 nm which are due to ⁴F_{9/2} → ⁶H_{15/2} (blue)

(near 20790 cm⁻¹) and ⁴F_{9/2} → ⁶H_{13/2} (yellow) (near 17203cm⁻¹) transitions, respectively, in the spectral region [9, 10].

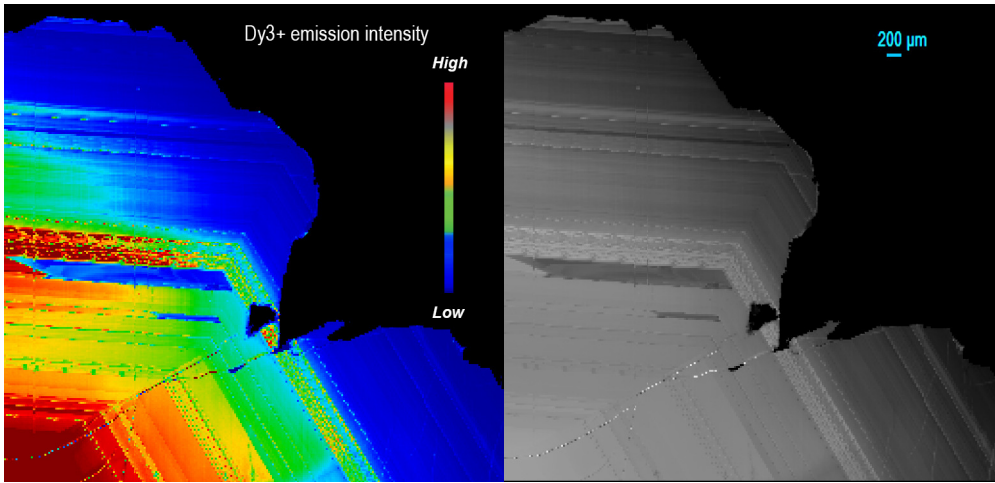


Figure 8. A photoluminescence map with color-coded distribution of Dy³⁺ emission-intensities.

For better understanding and to compare the emission intensity between the bright area and dark area of zircon, we measured the sample with mapping mode (Figure 8). The whole area from bright core to the dark rim is chosen for mapping with color-coded distribution of Dy³⁺ emission-intensities. The red color indicates the high intensity of emission corresponding to the

high Dy³⁺ concentration whilst the blue one indicates the low intensity. A grey-scale coding is also added for better visibility of the growth zoning. It is clearly illustrated that the intensity of Dy³⁺ emissions from zircon is related to the concentrations of this ion, and the fact is the higher the concentration of Dy³⁺, the higher the emission intensity and the brighter the color.

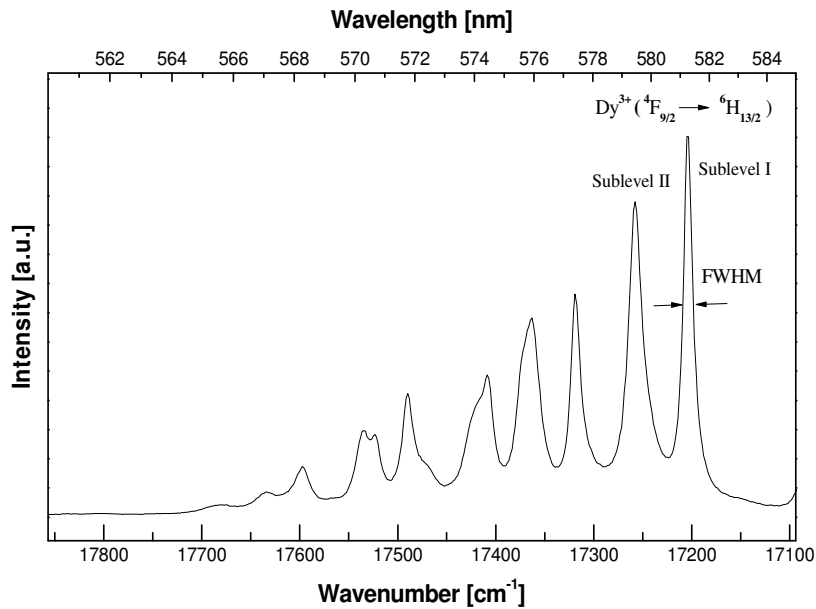


Figure 9. Emission related to the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of trace element Dy³⁺.

Especially, the FWHMs value of two sublevels belonging to the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy^{3+} (labeled I and II in Fig. 9) also contribute to the determination of the metamictization level of zircon. The peaks are relatively sharp and the width of emission bands are narrow (3cm^{-1}). According to a study by Lenz & Nasdala (2015), with the FWHM value in this range, these zircon samples can be evaluated at low metamictization level [11].

4. Conclusions

The result of chemical analysis EDS and photo-luminescence indicate the presence of Dy^{3+} impurity in each Zircon sample. Although the proof of peak that detects this trace element is not easy to distinguish, the EDS result contributed to clarify the aim of this study.

Dy^{3+} luminescence is apparent from natural zircon from Central Highlands of Vietnam. The intensity of Dy^{3+} emissions from zircon is clearly related to the concentrations of this ion and its color by means that the higher the concentration of Dy^{3+} , the higher the emission intensity and the brighter the color. The FWHMs value of two sublevels belonging to the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy^{3+} suggested that the Central Highland zircons can be subjected to the zircon of high type which means the zircon are still very well crystalline. From the above mentioned the use of EDS and photo-luminescence provided excellent information on studying Dy^{3+} impurity in Zircon from Central Highland. Dy^{3+} photoluminescence can be used as an indicator of structural disorder.

Acknowledgement

Many special appreciations go to Dr. Luzt Nasdala and Dr. Christoph Lenz, Institute of

Mineralogy and Crystallography, University of Vienna for the discussion and advices. Special thanks to Dr. Christoph Lenz for PL measurements and to Dr. Nguyen Duc Dung, laboratory of electronic microscope and micro-analysis, University of Science and Technology, Hanoi.

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Nghiên cứu phổ phát quang huỳnh quang của nguyên tố Dy³⁺ trong Zircon vùng Tây Nguyên, Việt Nam

Bùi Thị Sinh Vương, Lê Thị Thu Hương

Khoa Địa chất, Trường Đại học Khoa học Tự nhiên, ĐHQĐHN, 334 Nguyễn Trãi, Hà Nội, Việt Nam

Tóm tắt: Mặc dù là nguyên tố vi lượng, Dy³⁺ đóng một vai trò quan trọng trong cấu trúc của Zircon. Dy³⁺ thay thế cho nguyên tố Zr²⁺ trong cấu trúc và gây nên hiệu ứng phát quang của khoáng vật zircon. Bài viết này tập trung làm rõ hiện tượng phát quang của Dy³⁺ của các mẫu zircon được thu thập từ một mỏ ở Tây Nguyên, Việt Nam (thuộc huyện Krông Năng, tỉnh Đắk Lắk) bằng các phương pháp phổ huỳnh quang (PL) và phổ phân tán năng lượng (EDS). Các đỉnh đặc trưng trong phổ EDS đã chỉ ra sự tồn tại của Dy³⁺ với 1 hàm lượng rất nhỏ ở mức vi lượng. Trong đó, phổ huỳnh quang cho thấy sự phát xạ Dy³⁺ ở một số vị trí đặc trưng với cường độ mạnh nhất là ở vị trí 481 nm (khoảng 20790 cm⁻¹) và 581 nm (khoảng 17203 cm⁻¹). Cường độ phát xạ Dy³⁺ có liên quan đến hàm lượng ion và màu sắc của nó; hàm lượng Dy³⁺ càng cao, cường độ phát xạ càng lớn và các mẫu càng sáng màu. Độ rộng peak phát xạ của Dy³⁺ cho thấy zircon khu vực nghiên cứu có cấu trúc kết tinh cao.

Từ khóa: Zircon, Dy³⁺, quang phổ phát quang (PL), phổ phân tán năng lượng (EDS), các nguyên tố đất hiếm (REEs).