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Premilinary Study in the Cause of Color in Zircon from Krông Năng Mining Area in Đắk Lắk Province

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Abstract: Zircon occurs in many colors including various shades of pink, red, purple, yellow, orange, brown as well as less common shades of green, and blue. Generally, the colors of zircon are caused by the trace element composition (transition metals, lanthanides, actinides and REEs) and radiation damage (radiation induced color centers) [1]. The color centers of zircon are complex and the details surrounding the color-inducing mechanisms are still debated. The authors collected some zircon samples from Krong Nang mining, Central Highlandss, using UV-Vis-NIR and FTIR techniques to determine the causes of their color. The UV-VIS-NIR absorption spectra of these samples show continuous increase absorption from around 600 nm toward the UV region occasionally with shoulder at around 500 nm, which are identified as structural defect color center due to the radiation damage by radioactive elements such as U and Th. The OH- hydrous species was detected in all FTIR absorption spectra confirm a slight radiation damage by radioactive elements of zircon samples.

Keywords: Zircon, UV-Vis-NIR, FTIR.

1. Introduction

Zircon is a zirconium silicate that crystallizes in the tetragonal crystal system: I41/amd and Z=4 [2]. The ideal structure consists of a chain of alternating, edge-sharing SiO_4 tetrahedra and ZrO_8 triangular dodecahedra extending parallel to crystallographic axis. A common empirical formula showing some of the range of substitution in zircon is $(Zr_{1-y}, REE_y)(SiO4)_{1-x}(OH)_{4x-y}$. Zircon comes in a variety of colors and most zircons fall into two general color series of increasing radiation damage: 1/a common pink series that ranges between pink, rose, red, purple (“hyacinth"), and black (highly metamict zircon samples); 2/a less common yellow series that ranges between pale yellow, straw, honey, brown (crystalline to moderately radiation-damaged zircon samples). Normally, the trace element composition (transition metals, lanthanides, actinides and REE) and radiation damage (radiation induced color centers) contribute to the color of this gem. For example, Red zircon has radiation-induced color centers in which Nb^{4+} substitutes for Zr^{4+} [3]. Blue zircon is attributed to the presence of U^{4+} [3]. No spectral features attributed to these color centers have been observed in this study.

The zircon samples from Krong Nang mining area have been studied with a FTIR and UV-Vis-NIR techniques. These techniques are based on different physical phenomena, such as transitions between spin states of nuclei and electrons, energetic transitions of valence electrons, intra-molecular vibrations, or

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vibrations of atoms and molecular units in the lattice. All of the diverse spectroscopic techniques, however, have in common that they probe energy differences between a ground and excited states, mostly upon interaction of the mineral with incident radiation. Such interactions are not only determined by the excited elementary particles or molecules themselves but depend greatly on their local environments. Spectroscopic techniques are thus sensitive to the local structure and provide information on the short-range order.

This study brings a short communication of the applications of spectroscopic analytical techniques to the investigation and characterization of zircon from studied area. The analyzed results state that these zircon from Central Highlands are little bit radiation damage by radioactive elements with the cause of color being structural defect color center due to the radiation damage by radioactive elements such as U and Th.

2. Materials and methods

The majority of the samples used for this study was purchased or collected by the authors during different field trips to the mine (circled area in figure 1).Totally, there are 36 selected samples including cutting samples and rough samples, of which 30 ones used for observing the appearance features and 6 ones (3 cutting and 3 rough)(figure 2) used for studying the spectroscopic characteristics of zircon in study area.

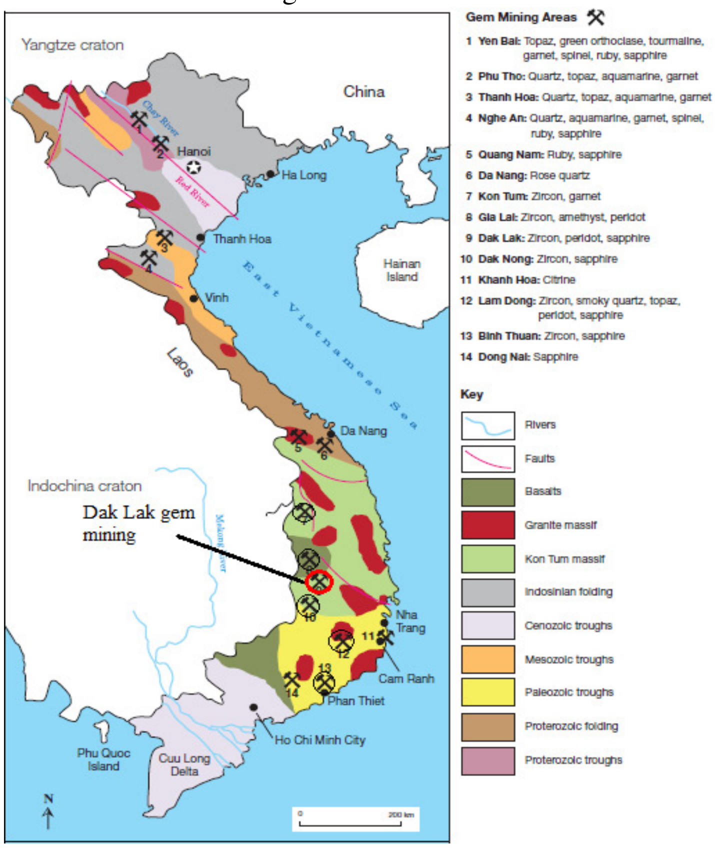

Figure 1. This map shows Vietnam's 14 most important gem provinces and the major geologic environments. The main sources for zircon are also shown in the map in which the studied area Krong Nang in Dak Lak province is pointed out with arrow.

Zr-tn-c 01

Zr-tn-c 02

Zr-tn-c 03

Zr-tn-r 03

Zr-tn-r 06

Zr-tn-r 08

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

The UV-Vis-NIR spectra of zircon were obtained from a Perkin Elmer Lambda 900 spectrophotometer. The absorption spectra were recorded over the range of 200 to 1600 nm in absorbance mode at a scan speed of 300 nm/minutes and a slit width of 2.5 millimeters. The data were complied by Perkin Elmer Spectrum V.5.0.1 program.

The FTIR spectrum were obtained from a Thermo Scientific, Nicolet Model 6700 brands which uses a He-Ne Laser by the study of wave numbers between 400-7000 cm^{-1} in transmittance mode and scan 128 seconds. The standard resolution of the Nicolet 6700 spectrometer is 0.09 cm^{-1}. The data were compiled by OMNIC software program.

3. Results and discussion

3.1 UV-Vis-NIR absorption spectrum

The absorption spectra of 6 natural zircon show similar patterns with a little variation except for the relative intensities of the peaks that can be correlated qualitatively with the depth of the body color and size of the specimens. Each spectrum was recorded from 200-1600 nm. They consist of bands and peaks in four regions:

(1) The appearance of an increasing absorption toward the ultraviolet gives rise to the brown component of the color. This may be considered as a result from a color center that produces a broad absorption band in the

ultraviolet with an absorption "tail" extending into the visible.

(2) A broad region of absorption in the range of 400-600nm with the shoulder at around 500 nm was recorded (figure 3). This absorption pattern is likely to be due to the defect in crystal structure caused by the radiation damage from radioactive elements such as U and Th.

(3) A series of weak but sharp bands such as 590, 652, 689 nm were observed in some darker samples(Zr-tn-r 03, Zr-tn-r 06D and Zr-tn-r 08) that had no influence on the color and were attributed to trace amounts of uranium (as U^{4+}). It can be stated that the darker one contain the higher concentration of Uranium than other brighter.

(4) A weak band centered at 760 nm presented only in the spectrum recorded parallel to the optic axis (Zr-tn-r 06D) [4].

Besides, some spectrum also reveal prominent absorption peaks at 1114 nm and 1505 nm probably due to U^{5+} [5]. The weak sharp bands attributed to uranium were present in each spectrum but with slight variations in intensity. It can be seen from figure 4 that the samples with darker color (Zr-tn-r 08, Zr-tn-r 06 D and Zr-tn-r 03) are characterized with the peaks of higher intensity. The intensity of the peaks depends on the concentration of the ion. This observation, again, confirms the above mention and leads to the understanding that the concentration of U ion in darker zircon is higher as compared to brighter one.

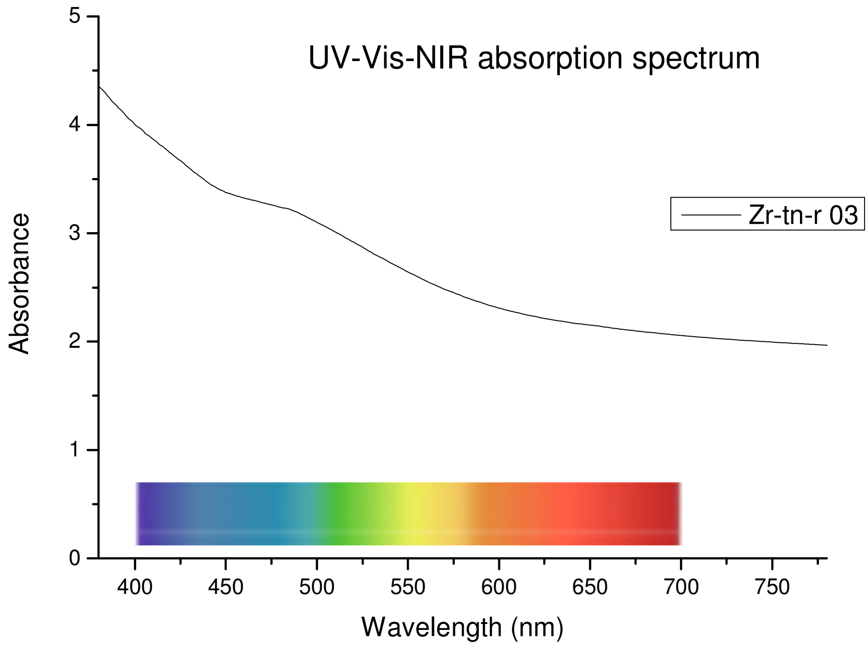

Figure 3. UV-Vis-NIR absorption spectrum of a reprentative zircon sample (Zr-tn-r 03) in the range 400-700 nm

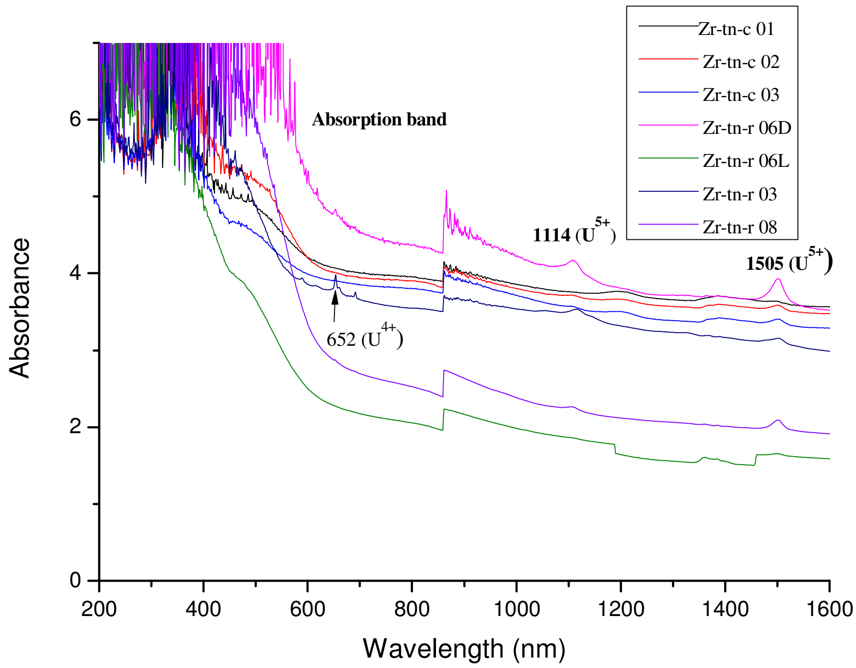

Figure 4. UV-Vis-NIR absorption spectrum of reprentative zircon samples in the full range 200-1600 nm.

3.2. FTIR absorption spectrum

Various bands consistent with those typically seen in Zircon were observed in the FTIR spectra of the Dak Lak zircon (figure 5) such as some strong absorptions bands at 2334, 2501, 2761, 2856, 2918, 3196cm^{-1}. The particular attention is paid to the peak at 3196 cm^{-1} which is the evidence of OH-stretching characteristic. Besides, the presence of peak at 6663 cm^{-1} indicates that a small number of U ions are in the pentavalent state (U^{5+} amorphous) in $ZrSiO_4$ [6]. An absorption band in the 1,400-2,000 cm^{-1} interval is probably related to Si-O stretching which still indicate a well crystalline zircon [6]. Moreover, some spectra indicate two very weak bands located near 4078 and 4268cm^{-1} which may be attributed to the combination of OH stretching and the vibrations of the framework [7].

The details behind the incorporation of OH- and H_2O into various structural sites of zircon remain controversial. Like titanite, an increase in metamictization results in an increase in OH-concentration. Well-crystallized zircon exhibit sharp, anisotropic IR peaks associated with OH, whereas the IR spectra of damaged crystals usually display an additional peak associated with the presence of H_2O molecules [8]. In this study, FTIR spectra confirm the presence of two peaks centered at 3417 cm^{-1} and 3383 cm^{-1} associated with Si occupied tetrahedrons or with OH- defects in crystalline Zircon [9]. All these indicate these samples are crystalline zircon with a little bit radiation damage by radioactive elements [6].

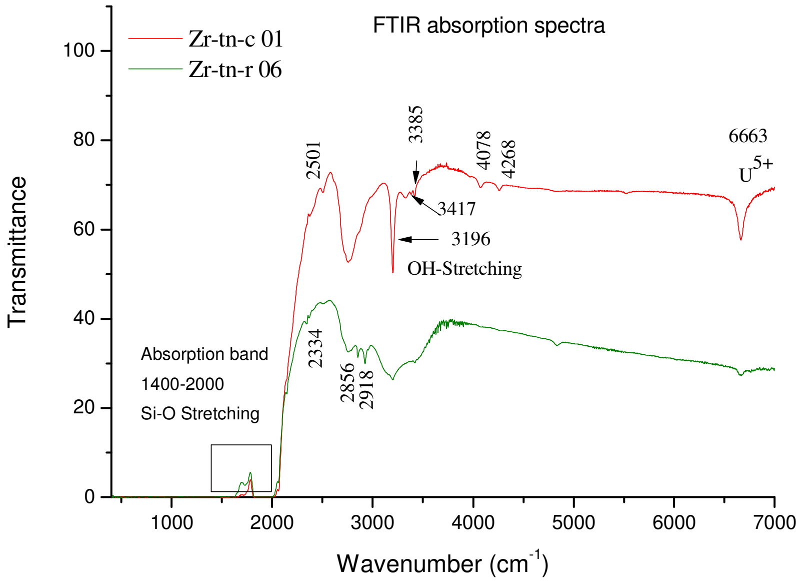

Figure 5. FTIR absorption spectrum of zircon from Dak Lak showed a band at 3196 cm^{-1} that is associated with OH-stretching characteristic and a band at 6663 cm^{-1} that is due to U ion is in the pentavalent state.

4. Conclusions

Study in zircon crystals from Dak Lak province using FTIR and UV-Vis-NIR spectroscopic techniques lead to the understanding of internal structures and the causes of color of the samples. The UV-Vis-NIR absorption spectrum indicates that the causes of orange-brown color components are due to structural defect color center by the radiation damage from radioactive elements such as U and Th. Besides, this also mentioned its color depends on the concentration of U ion, the darker zircon has higher content of this ion than brighter one. In addition, the presence of OH-stretching in zircon structure which is related to structure damage by radioactive elements was indicated by FTIR spectroscopy (peak at 3197 cm^{-1}). They exhibit no evidence of H_2O molecules, thus, these samples can be evaluated at being or becoming metamict and, more importantly, are not detectably radioactive. This locality is likely to be a commercial source of gem zircon as well as other gem materials in the future.

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Nghiên cứu nguyên nhân tạo màu của Zircon huyện Krông Năng, tỉnh Đắk Lắk

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Tóm tắt: Zircon hình thành với nhiều màu sắc bao gồm các sắc thái khác nhau từ hồng, đỏ tới tím, vàng, cam, nâu; ngoài ra còn có màu ít phổ biến hơn như xanh lá cây và xanh dương. Nhìn chung, màu sắc của zircon được gây ra bởi các thành phần nguyên tố vi lượng (kim loại chuyển tiếp, nguyên tố nhóm Lantan, actinides và đất hiếm) và do sự phá hủy phóng xạ (bức xạ gây ra các tâm màu). Tâm màu zircon rất phức tạp và những nghiên cứu chi tiết xung quanh vấn đề cơ chế tạo màu này vẫn còn gây nhiều tranh cãi. Trong nghiên cứu này, tác giả đã thu thập một số mẫu zircon từ mỏ Krông Năng, Đắk Lắk, Tây Nguyên, sử dụng phương pháp phổ hấp thụ UV-Vis-NIR và quang phổ FTIR để xác định nguyên nhân gây màu của chúng. Phổ hấp thụ của các mẫu cho thấy một sự hấp thụ tăng liên tục từ khoảng 600 nm về phía cực tím, với đỉnh hấp thụ vào khoảng 500 nm, điều này được xác định gây bởi sự sai hỏng trong cấu trúc với hiệu ứng tâm màu do sự phá hủy phóng xạ của các nguyên tố phóng xạ như U và Th. Bên cạnh đó, nhóm OH xuất hiện trong tất cả các phổ hấp thụ hồng ngoại trong khi H_2O lại vắng mặt hoàn toàn, điều này chỉ ra rằng zircon vùng Đắk Lắk thuộc loại zircon kết tinh có mức độ metamict thấp.

Từ khóa: Zircon, UV-Vis-NIR, FTIR.