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CATHODOLUMINESCENCE PROPERTIES OF TURQUOISE

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Abstract: The present work deals with the optical properties of turquoise mineral as 'odontolite' or bone turquoise by cathodoluminescence (CL). Therefore CL measurements made on the turquoise mineral are reported at low and room temperature with different modulation frequencies. A Mn^{2+} band at about 550nm in Ca^{2+} sites is present as a sharp band. Mn^{2+} is a transition metal ion that has an electron configuration of $3d^5$ and interacts strongly with the crystal field (d → d) transition.

Keywords: *Turquoise, Cathodoluminescence, Rare Earth*

TURKUAZ MİNERALİNİN KATODOLUMİNESANS ÖZELLİKLERİ

Özet: Bu çalışmada 'odontolite' veya kemik turkuaz olarak da bilinen turkuaz mineralinin optiksel özellikleri ele alınmıştır. Bu nedenle turkuaz minerali üzerine yapılan CL çalışmaları farkı modülasyon frekanslarında oda ve düşük sıcaklıklarda verilmiştir. Ca^{2+} merkezinde yaklaşık 550 nm de yer alan Mn^{2+} bandı keskin bir şekilde görünmektedir. Mn^{2+} metalinin elektron konfigürasyonu $3d^5$ olup bir geçiş metalidir ve krsital alan ile güçlü bir şekilde etkileşim gösterir.

Anahtar Kelimeler: *Turkuaz, Kathodolüminesans, Nadir toprak elementi*

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1. Introduction

'Odontolite' was used during the Middle Ages to decorate metallic art and religous objects such as reliquary crosses. It was recognized since the 19th Century as a mineral different from the precious stone turquoise. The turquoise group of minerals are hydrated basic phosphates based upon the formula $AB_6(PO4)_xPO_3(OH)_{2-x}(OH)_8.4H_2O$ where A is Ca, Cu^{2+} , Fe^{2+} , Zn and B is al, Fe^{3+} or Cr^{3+} [1]. It is then called turquoise of new rock, occidental turquoise, bone turquoise or 'odontolite'. All these different designations are derived from turquoise because of its very similar colorations [2]. The properties, above all the colour, of turquoise minerals and 'odontolite' are also very similar but the latter is slightly less hard than turquoise (hardness 5 Mohs compared with 5-6 Mohs for turquoise). Cid-Dresdner showed the crystal structure of turquoise, $CuAl6(PO4)4(OH)_8.4H_2O$, consists of zig-zag chains of Al octahedral running in the direction of the b axis and sharing corners with each other and with P tetrahedral. The Cu is in distorded octahedral coordination, sharing four edges with four Al octahedral. Turquoise is the Al end member and Fe the end member is chalcosiderite. As far as we are concerned there is no literature on luminescence of turquoise but the amount of published data on the Raman spectra of mineral phosphates is limited [3-4].

Luminescence is light emission when energy is deposited into a material. The means of delivering energy can be divided into 2 broad types: stimulation, where the magnitude of the incident energy is less than that of the emitted light, and excitation, when the incident energy is greater. Forms of stimulation include heat (thermoluminescence, TL) and laser light (optically stimulated luminescence, OSL); excitation includes electron beam irradiation (cathodoluminescence, CL) or X-irradiation (radioluminescence, RL). Whatever the nature of the incident energy, the energy cascades associated with the subsequent luminescence are often similar, and hence different forms of excitation/stimulation explore subtly different aspects of luminescence center within materials.

CL spectroscopy is a promising technique for the analyses of trace element concentrations and distributions in minerals; in many cases, it also provides additional data, which cannot be obtained from backscattered electron image (BSE) or observing under the optical miscoscope [5]. The CL spectroscopy can also be used as microprobe studying activators in minerals; hence, it is important to note some inherent problems associated with the collection of the signals. These considerations are particularly relevant for mineralogical and geological applications, since for historical reasons the CL in these scientific areas often involves unfortunate practices such as earlier simplistic inter-comparisons of signals. A serious experimental problem is that diffraction gratings and photomultipliers vary considerably in efficiency as a function of wavelength. This system response implies modifications of the spectra in intensity and the shape of the bands [6]. Since these variations are strongly dependent on the impurity content of the samples, they will differ between specimens of the same material and the between different zones of the same sample [7]. Luminescence research on aluminosilicate phases have successfully linked to manganese and iron point defect with the 560 and 720 nm emissions in accordance with band theory models [8].

The spectral measurement of the turquoise indicates luminescence emission. Here we report the luminescence property of the turquoise. To our knowledge, this is the first such work using luminescence in turquoise.

2. Experimental

Cathodoluminescence time resolved spectroscopy was performed on a apparatus designed and built at the University of Sussex, UK but at now in our luminescence lab in Celal Bayar University . The acceleration potential was 10 kV and the current was 20 nA, corresponding to an incident power density of 0.8 mWcm^{-2}. The primary electron beam was pulsed using a Thandor TG501 5 MHz function generator as a sine function with a frequency of 90 Hz, except for the lifetime measurement. The CL response was gated using an EgandG Ortholoc-SC 9505 2-phase lock-in amplifier. Spectra were measured in the temperature range 40 to 300 K using an *f*/4 scanning monochromator and a cooled red-sensitive photomultiplier tube. It is worth noting that the broad diameter of the beam significantly reduces any instability due to secondary electrom emission. Two different measurements were performed namely alternative current (AC) and direct current (DC). In AC measurement, an Ortholo-SC9505 two phase lock-in amplifier was employed. This instrument was used in normal mode where it performs in exactly the same way as an ordinary lock-in amplifier, i.e. only one channel is needed. Output from PM tube is first fed into a Brook-deal 5002 current pre-amplifier mounted near to the tube. This pre-amplifier provides a more suitable input to lock-in, being able to sink a considerable DC current. Its output can be varied to provide the optimum amount of AC gain against DC reduction. All spectra were recorded from the lower to higher wavelengths. All spectra shown here have been corrected for the system response. The electron beam was chopped at frequencies from 9 to 9kHz and the photomultiplier output was measured on a lock-in amplifier. In DC measurement, relatively high light intensities of the signals generated by the sample examined in this study made the more sophisticated techniques for detecting weak dc signals. In most cases, a dc signal was desirable, e.g., when there were strong lifetime effects at low-chopping rates, the signals were such that the background noise from the PM tube was negligible. Of greater importance for DC measurements proved to be the background due to the reflection at the sample of light from the gun filament. The CL response was studied as a function of intensities and wavelength or energy in both AC and DC measurements.

3. Results and Discussion

Spectra CL of turquoise (AC measurement) display large difference between room and low temperatures and two different spectra regions at short wavelengths between 200 and 370 nm, i.e. UV-blue and long wavelengths between 380 and 800 nm, i.e., green-red-IR with a boundary at 370 nm (Fig1 a).

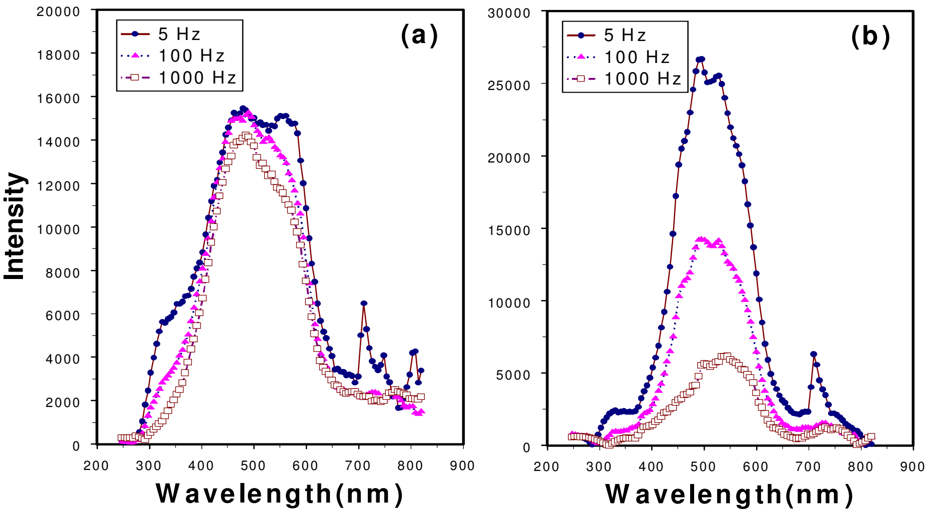

Figure 1. A comparision of CL spectra from turquoise at room and low temperature for AC measurements. The lock-in amplifier modulation frequencies were 5, 100 and 1000 Hz. Although in arbitrary units, the scales are consistent.

The thermal behavior of both regions is dissimilar, as follows: (i) in the UV-blue region, at room temperature, turquoise just displays a shoulder at about 300 nm.; conversely at cryogenic temperatures, this UV-blue emission grows up to 328nm and 2500 a.u. (ii) in the green-IR region, at room temperature turquoise shows a large isolated peak circa 471 nm and 555 nm of about 15300a.u. while under the cryostat goes up about 27000 a.u. and shifts 493 nm and 529 nm (see fig 1). A Mn^{2+} band at about 550nm in M sites (most probably Ca^{2+} sites) is present as broad band that overlaps with some rare earth bands. Mn^{2+} is a transition metal ion that has an electron configuration of $3d^5$ and interacts strongly with the crystal field (d → d) transition [9]. Luminescence emission of trivalent rare earth elements can also take place in the 5d electron shell that interacts strongly with the crystal field, i.e. Gd^{3+} arising from the $^6P_{7/2}$ state (328 nm) and Tb^{3+} arising from the $^5D_3$ state (493 nm). Mn^{2+} is the mostly probable luminescence center suitable for substitution for Mn^{2+} in the natural process of crystallization because of their close ionic radii and charges. The next possible candidates are Cr^{3+} replacing Mn^{2+} and Cr^{4+} replacing Si^{4+}. The ionic radius of aluminum in octahedral coordination is of 0.67 A. The main substituting luminescence centers are Cr^{3+} with an ionic radius of 0.75 A in octahedral coordination, $Mn^{2+}$and Mn^{4+} with ionic radii of 0.81 and 0.67 A in octahedral coordination. As can be seen from the figure 1 the emission at about 710 nm seen at room and low temperature can be ascribed to Cr impurities.

As can bee seen from the figure 2, spectra CL of turquoise (DC measurements displays similar results with strong growing of circa two times of the UV-blue spectra band in cold conditions of sample in respect to the RT recordings.

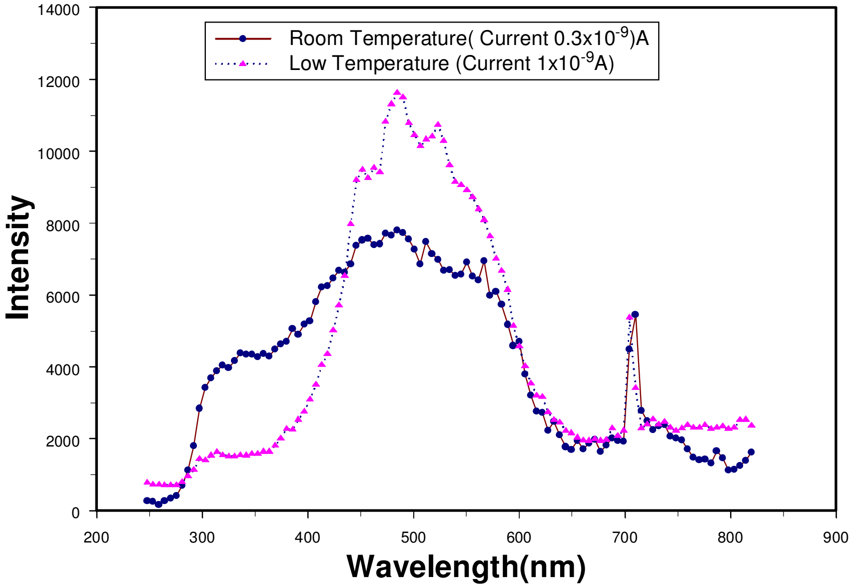

Figure 2. CL spectra of turquoise recorded at room and low temperatures for DC measurements

4. Conclusion

The phenomenon of minerals luminescence has been known for a long time. Current works on luminescence of minerals with their spectroscopic characteristics and interpretation have revealed potentialities for luminescence in mineralogy. In this work, turquoise, $CuAl_6(PO_4)_4(OH)_8.4H_2O$ displays a natural great luminescence, which takes place in the 5d electron shell that interacts strongly with the crystal field. The observed bands can be assigned as follows: Gd^{3+} (328 nm) and Tb^{3+} (493 nm). Mn^{2+} is a transition metal ion that has an electron configuration of $3d^5$ and interacts strongly with the crystal field (d → d) transition.

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