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UV effect on the cathodo- and thermoluminescence properties of a gem-quality Cr-rich diaspore (α-AlOOH)

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HIGHLIGHTS

- CL and TL properties of gem-quality diaspore samples were determined after 100 h of UVC exposure.
- The UVC exposure induces significant changes in the intensity of the CL.
- The 100 h UVC-irradiated and as received samples display three maxima.
- The physical trapping parameters were estimated by using GCA program.

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ABSTRACT

This work reports on the cathodoluminescence (CL) and thermoluminescence (TL) properties of gem-quality diaspore samples from Milas/Muğla (Turkey) after 100 h of ultraviolet-C (UVC) exposure. The UVC exposure induces significant changes in the intensity of the CL emission in the range of 400–800 nm that would be mainly associated with photo-oxidation processes of the impurities (Cr^{3+}, Ti^{3+}, Fe^{2+}) that substitute for Al^{3+} in the diaspore (α-AlOOH) lattice. The UVC effect on the 400 nm-TL behavior of beta irradiated samples in the range of 0.1–8 Gy modifies the TL glow curves probably due to both photo-transfer process where electrons release from deeper to shallower traps and redox reactions involving, also, breakages-linkages of chemical bonds. Meanwhile, the 'as received' samples consist of three maxima centered at about 120, 180, and 234 °C, the 100 h UVC-irradiated samples display three maxima at 122, 220 and 270 °C. The physical trapping parameters (intensity and peak position, trap depth and pre-exponential factor) for each TL curve were estimated by using a computerized glow curve analysis program.

1. Introduction

Thermoluminescence (TL) emission of natural, ceramic and synthetic materials including silicates, phosphates, carbonates or oxides, usually displays well-defined glow peaks that are employed in the fields of archaeological and geological dating (Burbidge, 2012), detection of irradiated foodstuffs (Beneitez et al., 1994) or retrospective dosimetry (Bailiff et al., 2004) etc. Among these materials, natural alumina (Al_2O_3) and diaspore (α-AlOOH) appear as useful phosphor materials for personnel dosimetry since they are ubiquitous and can be found as brightly colored gemstones (ruby with a minor amount of Cr^{3+}; sapphire with Fe^{3+} and Ti^{3+} chromophore). Additionally, they are chemical and physically stable due to rely on highly refractory features (melting point in the range of 2000–2050 °C) and highly corrosive (Mohs hardness 9) (Garcia-Guinea et al., 2001). Specifically, α-AlOOH has a crystalline structure based on layers of oxygen atoms in hexagonal close packing, hydroxyl anions are placed in the corners of the octahedral and the aluminum ions in 50% of the octahedral interstices of each successive layer giving rise to several point and structural defects which play an essential role in the luminescence processes (Smith et al., 2001). In addition, the thermal expansion of diaspore is anisotropic where the a-axis increases approximately double than b and c-axis (Xu et al., 1994). Although this is a relatively common mineral in metamorphic bauxite deposits, gem-quality green diaspore (herein reported) is worldly scarce and is only located in the İlbir Mountains area (SW Turkey) (Hatipoğlu et al., 2010a, 2010b, 2010c). The Al^{3+} cations are the responsible of the green-colored gemstone that is formed due to large changes in the local electrical field of lattices when substituted by

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homovalent chromophores. Such impurities, giving rise to structural and point defects, are associated with excitation-de-excitation processes when exposed to UV or ionizing radiation (Garcia-Guinea et al., 2001; Correcher et al., 2003). According to Garcia-Guinea et al. (2001), the spectral luminescence emission of Goian diaspore is due to Ti^{4+} (670 nm red band), Cr^{3+} (700 nm red-infrared emission) and Fe^{3+} (720 nm infrared waveband). In addition, they also analyzed the TL glow curve of the diaspore and found as a low temperature maximum, peaked at 180 °C and the TL glow curves present a wide broad above 220–250 °C (Correcher et al., 2003). TL emission provides also information about the trap structure where, using different methods (Initial Rise, Peak Shape, Glow Curve Deconvolution, etc.), one can determine the trap structure namely the activation energy, Ea (in eV), the frequency factor, s (in s^{-1}), and the kinetic order, b, attending to the shape and intensity of the glow peaks. One of the most useful method is based on Levenberg–Marquardt algorithm that assumes first order kinetic processes (b = 1) to assess the trapping–emitting centers values within the forbidden gap (Kitis et al., 2000). This method allowed Correcher et al. (2003) the estimation of trap parameters for the of 180 °C TL peak of irradiated Spanish blue diaspore mineral where E_a = 0.95–1.12 eV and s = 3.67E + 10–1.82 E + 12 s^{-1} depending on the given dose in the range of 0.1–100 Gy at 5 °C s^{-1}. They could observe how the peak does not change the position as the dose increases, therefore can be assumed that the trap parameters fits to a first order kinetics process. There are quite few studies on the TL characteristics of beta irradiated diaspore minerals however, there is no evaluation on UVC-exposed beta irradiated ones. UVC can cause bond breaking with sufficient energy to induce TL emission as a partially ionizing radiation. Therefore, this kind of excitation energy seems to induce the activation of traps due to the breakages-linkages of the chemical bonds involving, among others, hydroxyl groups (Garcia-Guinea et al., 2018). This fact might be to take into account to determine the potential feasibility of this material for UV dosimetry purposes (Fencl, 2007). In general, UV-irradiation may cause photo-transfer (PTTL) (electron release from deeper to shallower traps) and bleaching effect on the TL signal. To examine the effects of the UV-irradiation on trap parameters of natural materials, there are several studies related to calcite samples (Dubey et al., 2017; Kalita and Wary, 2014), but no reports have been performed concerning such effect on AlOOH. Kalita and Wary (2014) evaluated UV irradiated natural calcite to investigate its trap properties. They argued if the dosimetric peak shifts towards low temperatures under UV irradiation, this mechanism is generally called “photo-transfer” and the intensity of new peak of UV irradiated sample should decrease. Topaksu et al. (2015) have discussed TL properties of UV-irradiated Turkish ulexite to consider the material whether it could be potentially used as a UV dosimeter because it reveals reasonable luminescence sensitivity to 253.7 nm illumination. (Topaksu et al., 2015). CL appears as a very effective method to (i) characterize the surface of the materials since the emission can be linked to intrinsic (lattice defects) and extrinsic (impurities) defects in the lattice and (ii) to determine the chemical composition from a qualitative viewpoint. The electron beam induces an excitation up to 2–3·10^{-3} mm in depth (for energies of 25 kV), and usually provides information in the UV-infrared spectral region including, among others, luminescence parameters (i.e. lifetime, efficiency, emission spectra, etc.).

This study mainly focuses on the CL and TL properties of a natural diaspore sample collected from Küçükçamlık Hills of İlbir Mountains in Milas/Muğla considering (i) the relationship between the luminescence emissions and point and structural defects, (ii) characterization of the TL trap parameters assuming first-order kinetic processes and (iii) evaluation of the UVC effect on the TL and CL emission.

2. Materials and methods

Diaspore samples were obtained from diasporite deposit at İlbir Mountains in the Milas/Muğla (southwest of Turkey). The CL

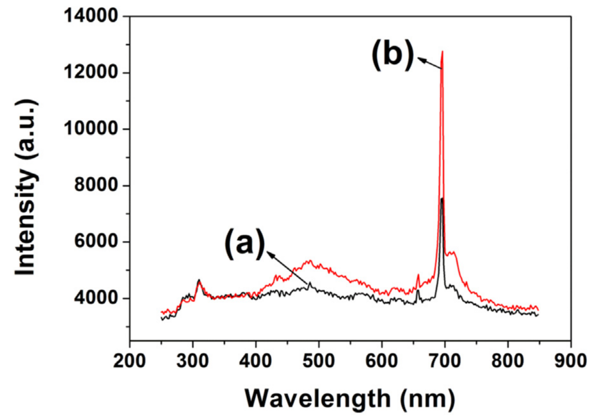

Fig. 1. Cathodoluminescence spectral emission of (a) ‘as received’ and (b) 100 h UVC-exposed diaspore measured at RT.

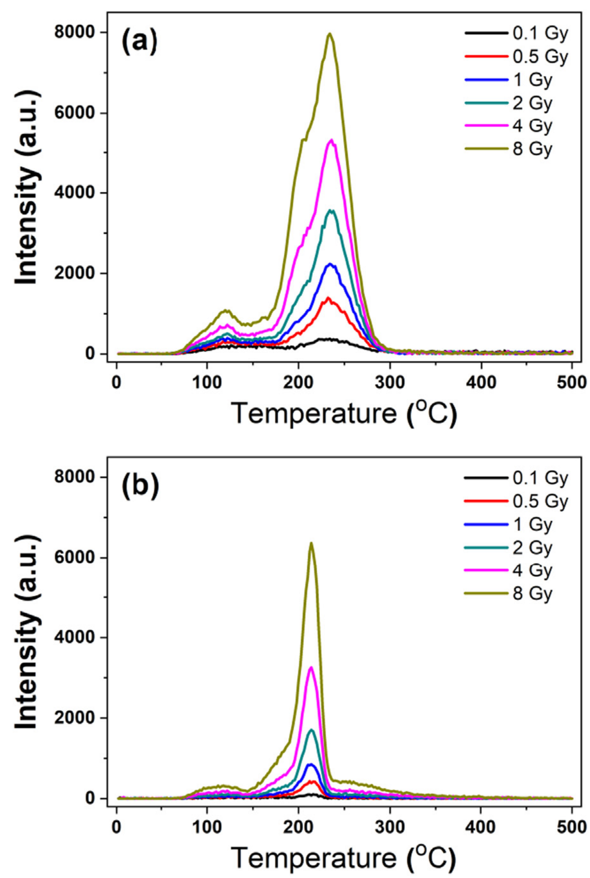

Fig. 2. TL glow curve of beta irradiated diaspore (a) ‘as received’ and (b) after 100 h UVC-exposed.

measurements were performed in the range of 250–850 nm using a Gatan MonoCL3 detector with a PA-3 photomultiplier tube; model XLS30 of the FEI Company (1.8–2.0 A and 25 kV). The sample was put on the polish surface, at low-vacuum mode without coating. The distance between the sample and the bottom of the CL mirror arrangement was 16.7 mm. The TL measurements were carried out using an automated Riso TL system model TL DA-12 reader with an EMI 9635 QA photomultiplier. The emission was observed through a blue filter (a FIB002 of the Melles-Griot Company) where the wavelength is peaked at 320–480 nm; FWHM is 80(16) nm and peak transmittance (minimum) is 60%. The system has a $^{90}Sr/^{90}Y$ source with a dose rate of 0.012 Gy s^{-1} calibrated against a ^{60}Co photon source in a secondary