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Optical, spectral and thermal properties of natural pumice glass

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HIGHLIGHTS

- Pumice is a natural non-crystalline material with complex luminescence behavior.
- Cathodoluminescence exhibits three main wavebands in the UV, UV-blue and green-IR region.
- Trap structure could be associated with a continuous distribution.

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ABSTRACT

Pumice is a natural Si-rich material displaying a complex cathodo- (CL) and thermoluminescence (TL) glow curves. The UV-IR CL emission consists of (i) a UV waveband in the range of 340–420 nm,(ii) blue band at 450–480 nm and (iii) a broad emission in the green-red region (at 550–650 nm) that could be respectively linked to Non Bridging Oxygen Hole Centers (≡Si–O●), self-trapped excitons and point defects (Mn^{2+} −0.03%- and Fe −1.15%-). Thermal treatments performed on the TL glow curves allowed us to determine that the trap system could be associated with a continuum in the trap distribution, since successive thermal pretreatments in the range of 200–310 °C induce an emission that shifts linearly to higher temperatures when the thermal pretreatment (T_{stop}) is increased, while the intensity of the maxima decreases similarly to the peak area. The evaluation of the Ea values, s value and the trap system calculated by VHR, IR and Glow curve fitting methods considering three possible distribution function for n(E): gaussian, exponential and uniform, has given matching values for the 280 °C TL peak.

1. Introduction

Pumice, exhibiting a non-crystalline structure, has been employed, at least, from Roman times to react with Ca-rich materials (i.e. $Ca(OH)_2$) in presence of water giving rise to a pozzolanic process and leading to compounds with significant cementitious properties. Nowadays, pumice is also employed in exfoliating soaps, dental polishing compounds, filtration of drinking water or removing odor, etc., as well as for building and construction materials. One of its the technological applications is the production of the light-weight structural concrete with pumice aggregate and boron compounds (ulexite or colemanite) to be used for radiation shielding purposes in, for instance, chambers for measuring high-energy photon and electron radiation (Yaltay et al., 2015). Pumice is pH neutral and does not decompose or burn, it is a highly porous fine-grained volcanic rock containing gas bubbles trapped while the lava-flow is solidifying from temperatures close to 800 °C. The silicate component consists of a minor fraction of mineral microcrystals (sanidine, plagioclase, biotite, etc.) distributed in a main glassy groundmass. In the glass, it is assumed that each silicon atom is surrounded by four tetrahedrally coordinated oxygen atoms and adjacent silicon atoms are bridge bonded through a single oxygen atom. Tetrahedrons are linked each other by oxygen bonds and the arrangement of these links between the tetrahedral units determines the classification of the Si-rich compound.

Radiation, pressure, temperature, and the presence of impurities could modify such structure giving rise to different type of defects in this high disordered Si- and Al-rich structure; it can be determined using X-ray diffraction (XRD) that allows to distinguish not only different phases in the sample, but also the degree of crystallinity. Such defects can be, according to their structure and size, point defects (intrinsic or extrinsic), dislocations (linear defects), and planar defects. Intrinsic point defects involve

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vacancies (i.e. Schottky defects or Frenkel pairs) and self-interstitials (additional atoms at an interstitial position). Extrinsic point defects are due to substitutional atoms chemically different from those other intrinsic of the lattice (Stevens Kalceff and Phillips, 1995). Thus, the luminescence properties of silicon oxide, as well as many other physical and chemical features, are dependent on the defect microstructure (that can be characterized by Environmental Scanning Electron Microscope – ESEM-) and determine the presence of both thermoluminescence (TL) and cathodoluminescence (CL) that are luminescence mechanisms based on the trapped charges in lattice defects and a subsequent detrapping process inducing a photon emission at recombination sites.

CL emission is a process whereby light is created from an energetic electron beam. CL supplies data about transient defects after irradiation on the surface of the lattice and is used in the identification of the migration and diffusion of some luminescent centers from the emission bands (Stevens Kalceff and Phillips, 1995). The CL information is of great interest for us in order to establish the more appropriate optical measurement conditions (to select the suitable filters) for the TL measurements. TL is a method based on the emission of light from a solid sample such as insulator or semiconductor when it is heated after being irradiated by some kind of radiation such as X-rays, gamma rays, beam of electrons, cosmic rays, etc. (McKeever, 1985). TL provides information about the trapped charge recombination sites related to metastable defects inside the lattice if the detrapping process is due to heat. All the factors involved in the luminescence phenomena (i.e. lifetime, efficiency, emission spectra, etc.) depend on the crystalline phase which is mainly induced by pressure and temperature. Thus, (i) small variations in the lattice structure due to phase transitions, changes in the chemical composition (dehydration or dehydroxylation processes) that can be detected by means of Differential Thermal Analysis and Thermo-gravimetric Analysis (DTA-TGA) technique to get information about such transformations as well as variation in the water, hydroxyls content and the possible presence of volatile species (usually considered negligible) considering the enthalpy variations in the sample at a specified temperature and at a specified rate, while its change in mass is continuously recorded. (ii) The presence of inclusions, impurities, substituted ions in ppm concentrations or (iii) surface defects reveal changes in the intensity and wavelength position of the emission spectra (Correcher et al., 2004). The TL glow emission is associated with the different trap levels related to the band gap of the material and are characterized by certain physical parameters including the trap depth (E) and the frequency factor (s). The knowledge of these parameters could help us to understand the trap structure and the physical processes inside of the material in addition to improve both accuracy and precision of many TL applications (retrospective dosimetry, dating, environmental dosimetry, etc). The methods to estimate the kinetic parameters of the phosphor is based on the kinetic analysis models (Chen and McKeever, 1997; Kitis et al., 1998; Sakurai and Gartia, 1997; Gomez-Ros et al., 2006a, 2006b), including computerized fitting of the TL glow curves considering a continuous distribution of trapping centers (Sakurai and Gartia, 1997; Gomez-Ros et al., 2006a, 2006b). Some of these methods are based on the (i) analysis of the low temperature interval of peak (initial rise method, IR); (ii) change in the peak position by means of the variable heating rate (VHR method); (iii) evolution of the position of the peak temperature (T_m) when an irradiated sample is linearly preheated up to a maximum temperature (T_{stop}) in the range 200–300 °C.The process is successively repeated at different *Tstop* values.

We herein, have studied the CL (in the UV-IR region) and the blue TL emission of well-characterized Turkish pumice sample by means of ESEM, XRD and DTA-TGA. The TL glow curves were analyzed by IR, $Tm - T_{stop}$ and VHR method to determine the trap system and the E_a values.

2. Materials and methods

Pumice samples collected from the Çardak village surroundings in Nevşehir (Turkey) (Fig. 1a) were analyzed by means of an ESEM, of FEI Company, located in the Spanish National Museum of Natural Sciences (MNCN). It is a low-vacuum ESEM with a large sample chamber wide enough to hold large samples without the sputtered covering onto sample. The chemical composition was determined by XRF using a PHILIPS PW-1404 spectrometer with a Sc-Mo tube, Ge, LIF220, LIF200, PE and TLAP analyzer crystals and Super-Q manager from Panalytical-Spain as analytical software. For the XRF measurements, pumice pellets of 8 g of milled sample with 0.1 g of elbacite were pressed under 20 TM and dried at 40 °C in a climatic chamber. The bulk chemical analysis of the sample is: SiO_2 (71.33%), Al_2O_3 (13.14%), K_2O (4.31%) Fe_2O_3 (1.15%), Na_2O (3.54%), CaO (0.98%), TiO_2 (0.09%), MgO (0.04%), MnO (0.03%), P_2O_5 (0.02%) and loss of ignition (LOI) (5.24%). The XRD analyses were performed using XPOWDER software which also allows a full duplex control of the Philips PW-1710/00 diffractometer (Kent, United Kingdom) using the CuKα radiation with a Ni filter and a setting of 40 kV and 40 mA. The DTA-TGA of 10 mg of grinded white pumice was recorded with a Thermal Analyzer Setaram 100 Set Sys 1750 in N_2 atmosphere. The sample used for this analysis was carefully prepared, crushed in an agate mortar to particle size less than 2 mm discarding the fraction less than 100 mm in order to minimize the effects of absorbed water. Thermal treatment was performed at a heating rate of 10 °C min^{-1} from RT up to 700 °C. 10 mg of powdered pumice glass was held in a platinum crucible with alumina as reference material.

The CL spectra were measured using a Gatan MonoCL3 detector with a PA-3 photomultiplier tube attached to the ESEM model XLS30. The detector covers a spectral range of 250–1000 nm being most sensitive in the blue parts of the spectrum. The samples were placed on polished slabs, at low-vacuum mode without coating to keep open way out to the CL emission. The emission of the samples was collected and amplified using a retractable parabolic diamond mirror and a photomultiplier tube. The distance between the sample and the bottom of the CL mirror assembly was 15 mm. The excitation for CL measurements was provided at 25 kV electron beam.

The stability of TL signal has been studied for natural non-irradiated samples (NTL) using a preheating technique that consists of linear heating of the samples up to a temperature T_{stop} followed by quick cooling to room temperature (RT) and final readout (up to 500 °C) to record the whole remaining TL glow curve, where thermal preheating varies from 250 to 360 °C. The TL measurements were performed using an automated Risø TL reader model TL DA-12 provided with an EMI 9635 QA photomultiplier (Bøtter-Jensen and Duller, 1992). 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 TL reader is also provided with a $^{90}Sr/^{90}Y$ source with a dose rate of 0.012 Gy s^{-1} calibrated against a ^{137}Cs photon source in a secondary standard laboratory (Correcher and Delgado, 1998). The sample was carefully powdered with an agate pestle and mortar to avoid triboluminescence (Garcia-Guinea and Correcher, 2000). All the TL measurements were performed using a linear heating rate of 5 °C s^{-1} from RT up to the corresponding temperature in a N_2 atmosphere. Aliquots of 5.0(1) mg of the sample were used for TL measurements.