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On the spectra luminescence properties of charoite silicate

J. Garcia-Guinea[a,*], P.D. Townsend[b], N. Can[c], V. Correcher[d], L. Sanchez-Muñoz[d], A.A. Finch[e], D. Hole[b], M. Avella[f], J. Jimenez[f], M. Khanlary[b,g]

[a] Museo Nacional Ciencias Naturales, Geology, Calle Jose Gutierrez Abascal 2 Madrid 28006, Spain
[b] School of Engineering & Information Technology, University of Sussex, Brighton BN1 9QH, E Sussex, UK
[c] Faculty of Arts and Sciences, Physics Department, Celal Bayar University, Manisa, Turkey
[d] CIEMAT, Department of Radiation Dosimetry, Avenue Complutense 22, Madrid 28040, Spain
[e] Centre for Advanced Materials, University of St Andrews, Irvine Building, St Andrews, Fife KY16 9AL, UK
[f] Department of Fisica Materia Condensada, ETSI Industriales, University of Valladolid, Valladolid 47011, Spain
[g] Physics Department, Imam Khomeini International University, Qazvin, Iran

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Abstract

Charoite is a hydrous alkali calcium silicate mineral [$K_4NaCa_7Ba_{0.75}Mn_{0.2}Fe_{0.05}(Si_6O_{15})_2(Si_2O_7)Si_4O_9(OH)\cdot 3(H_2O)$] exhibiting an intense lilac colour related to Mn^{2+} and Fe^{3+} colour centres. These ions also contribute to a strong luminescence at ~585 and 705 nm. This work studies the thermal dependence of these luminescent centres by (i) thermoluminescence (TL) of pre-heated and pre-irradiated charoite aliquots, (ii) by time-resolved cathodoluminescence (TRS-CL) at room and cryogenic temperatures (RT and CT), (iii) by spatially resolved spectra CL under scanning electron microscopy (SRS–CL–SEM) and (iv) by ion beam spectra luminescence (IBL) with H^+, H_2^+ and $^4He^+$ ions at RT and LT. The main peak, ~585 nm, is linked to a transition $^4T_{1,2}\,(G)\rightarrow {}^6A_7(S)$ in Mn^{2+} ions in distorted six-fold coordination and the emission at ~705 nm with $Fe^{2+}\rightarrow Fe^{3+}$ oxidation in Si^{4+} lattice sites. Less intense UV–blue emissions at 340 and 390 nm show multi-order kinetic TL glow curves involving continuous processes of electron trapping and de-trapping along with an irreversible phase transition of charoite by de-hydroxylation and lattice shortening of $\Delta a = 0.219$ Å, $\Delta b = 0.182$ Å; $\Delta c = 0.739$ Å. The Si–O stressed lattice of charoite has non-bridging oxygen or silicon vacancy–hole centres, and Si–O bonding defects which seem to be responsible for the 340 nm emission. Extrinsic defects such as the alkali (or hydrogen)—compensated [AlO_4/M^+] centres could be linked with the 390 nm emission. Large variations in 585 and 705 nm intensities are strongly temperature dependent, modifying local Fe–O and Mn–O bond distances, short-range-order luminescence centres being very resistant under the action of the heavy ion beam of $^4He^+$. The SRS–CL demonstrates strong spatial heterogeneity in the luminescence of the charoite.

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1. Introduction

Charoite is a rare gem mineral from the Russian Sakha Republic. Its name was approved as a new mineral by the International Mineralogical Association in 1978 with the formula $K_5Ca_8(Si_6O_{15})(Si_2O_7)(Si_4O_9)(OH)\cdot 3H_2O$. It is included in the Dana classification class 70.1.2.3 as chain-silicate column or tube structures with columnar silicate units of double crankshaft chains, i.e., Monoclinic $P^*/4$ (pseudo orthorhombic) $2/m$. Charoite samples outcrop in the Murun geological massif located in the Chara River area, SW Yakutia, which was formed by evolution from alkaline ultrabasic to alkaline granite melts by differentiation and layering of a potassic alkaline magma [1]. Charoite shows an intense dark lilac–violet colour attributed to Mn^{3+} colour centres as determined by optical, infrared and EPR methods, which indicate that colour variations are linked with Mn contents at 1000 ppm and iron at 100 ppm levels [2]. Differential thermo-gravimetric

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*Corresponding author. Tel.: +34 91 4111328; fax: +34 91 5644740.
E-mail address: guinea@mncn.csic.es (J. Garcia-Guinea).

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analyses of charoite show that dehydration occurs in two main steps at ~290 and 430 °C [3]. Photoluminescence and X-ray luminescence measurements of charoite in various redox conditions exhibit luminescence maxima at 380, 420, 600 and 730 nm [4]. Those authors proposed the following centres: (i) 380 nm due to radiative transitions $^2d_{3/2} \rightarrow {}^5f_{7/2}$ in Ce^{3+} substituting for Ca^{2+}, (ii) 420 nm associated with electron-vibrational transitions $4F^6 5d^1 \rightarrow 4F^7$ in Eu^{2+} ions, (iii) 600 nm as a result of the transition $^4T_{1,2}$ (G)$\rightarrow 6A_7$(S) in Mn^{2+} ions in distorted six-fold coordination, (iv) Fe^{3+} ions substituting for Si^{4+}. In oxygen, charoite turns to a greyish-brown colour and the intensity of the 600 nm peak drops. In a hydrogen atmosphere, charoite turns white and a more intense 600 nm luminescence peak is enhanced by the reductive reaction $Mn^{2+} \rightarrow Mn^{3+}$. The colour changes from white to grey, i.e., the concentration of the emitting Mn^{2+} centres increases, while the concentration of colouring ions Mn^{3+} decreases. The absence of an emission at 730 nm is linked with the $Fe^{3+} \rightarrow Fe^{2+}$ reduction [4].

Charoite has useful chemical characteristics akin to defect–emission relationships in more common rock-forming silicates such as feldspar or pyroxene. However, unlike those minerals, charoite has (i) very little aluminium (0.01%), (ii) little sodium (2%), (iii) hydroxyl groups, (iv) coexistence of large amounts of potassium (9.5%) and calcium (22%), (iv) purple colour attributed to MnO and Fe_2O_3 allowing comparisons with other spectra at 40 K in silicates to determine the manganese and iron emissions [5–7]. For the UV–blue region, luminescence from the published defect assignments for charoite (i.e., Ce^{3+} and Eu^{2+} [4]) may be supplemented by structural defects on the charoite lattice, such as $[AlO_4/M^+]$, Si–O breaking bonds or E′ centres in SiO_2 tetrahedral [8–14].

The main aims of the present study are (i) to record high-sensitivity spectra of the charoite silicate from 40 to 773 K by thermoluminesence (TL) of pre-heated and pre-irradiated charoite aliquots; time and spatially resolved cathodoluminescence (TRS–CL and SRS–CL–SEM), and IBL with H^+, H^{2+} and $^4He^+$ ions; (ii) to understand further the emission-defect assignments of the luminescence peaks in agreement with their observed kinetic evolution under different physical conditions.

2. Experimental

Charoite samples studied here were previously characterized by X-ray diffraction (XRD), electron probe microanalyses (EPMA) and simultaneous thermo-differential thermal analysis and thermogravimetry (DTA–TG). Under the optical lens, single-phase grains of purple charoite portions were carefully selected avoiding mineral inclusions such as aegirine, tinaksite, K-feldspar barium-rich; ohmilite, digenite, galena and rilandite. TL measurements of natural and pre-heated charoite aliquots were carried out using a Risø TL system model TL DA-12 [15]. This reader has an EMI 9635 QA photomultiplier and the emission was observed through a blue filter (a FIB002 of the Melles–Griot Company), whose wavelength range is 320–480 nm; FWHM is 80 ± 16 nm and peak transmittance is 60%. The instrument is also provided with a $^{90}Sr/^{90}Y$ source providing β-irradiation with a dose rate of 0.020 Gy s^{-1} calibrated against a ^{60}Co photon source in a secondary standards laboratory [16]. All TL measurements were performed using a linear heating rate of 5 °C s^{-1} from room temperature (RT) up to 550 °C in a N_2 atmosphere. Four aliquots of 5.0 ± 0.1 mg powdered charoite were used for each measurement. The incandescent background was subtracted from the TL data.

Ion beam luminescence measurements (IBL) were performed under vacuum using the 3.0 MeV Van der Graff accelerator facility at the University of Sussex generating a spot size of ~0.25 cm^2. For investigations of temperature dependence, a proton beam accelerated at 0.95 MeV with a current of ~100 nA generated the luminescence. The beam had an incident power density of ~2 kW m^{-2}. H^+ ions were used to minimize the collision damage caused to the sample. Experimental IBL conditions are shown in Table 1. IBL data were collected every 10 K from 40 to 300 K. Cryogenic temperatures (CT) were achieved using an 8 W close-cycle helium refrigerator, and thermal contact between the compressor head and the sample was maintained using Ag dag. The sample was irradiated only while data were being acquired to reduce the exposure. A typical ion dose during an experimental run was $\sim 5 \times 10^{15}$ H^+ ions. Repeat analyses of the same samples show excellent reproducibility in the luminescence profiles, although differences in the positioning and size of different samples cause some variation in absolute intensity. IBL analysis was performed on charoite-polished slices. The sample was oriented such that the ion beam encounters the surface of the sample at an angle of ~22° from the normal to the face sample and the light is collected 22° from the perpendicular in the opposite direction. The incident beam and the emitted light vary by 45°. Using a standard modelling package (SRIM), this geometry gives an estimated penetration range of the H^+ ions into silica as ~10 μm. Light emissions were collected by a quartz fibre optic coupled to a f/4 SpectroPro 300I monochromator. The detector used was a Roper Scientific image intensified CCD camera operated using the WinSpec software package. The system operates in the range 200–1100 nm by performing two separate spectral analyses between 200 and 600, and 500 and 1100 nm, respectively, and then matching the spectra in the 500–600 nm region. Raw intensity counts were typically integrated to ~200 counts. The intensity data were corrected for system response against a W lamp by assuming a black body radiation profile. Wavelength was calibrated against the emissions of an Hg lamp and the resolution at the analytical conditions applied corresponded to ~2 nm.

Sample degradation experiments were performed on the charoite slice at RT, using 2 MeV $^4He^+$ ions. Beam currents were ramped between 50, 1000 and 2500 nA to allow a range of ion doses between 10^3 and 10^{17} ions over