

## Luminescence Properties of Silicate Mineral: Charoite

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Luminescence measurements of charoite are reported which include two main emission bands centred near 380 and 600 nm. There are minor differences in response between cathodoluminescence and radioluminescence and greater differences between light and dark coloured charoite. For a dark sample, there is an additional band near 820 nm which has a discontinuity in intensity near 170 °C. This feature is ascribed to loss of water bonded into the structure. Models for the emission bands in this gem stone are consistent with earlier proposals.

**Key Words:** Luminescence, Charoite, Water bond.

### INTRODUCTION

Charoite;  $(Ca,K,Na)_3Si_4O_{10}(OH,F)H_2O$  is an unusual mineral and of rare occurrence. It formed from alteration of lime stones by the close presence of an alkaline rich nepheline syenite intrusion. The heat pressure and more importantly, the infusion of unique chemicals into the rock is responsible for the transformation into new minerals such as charoite. The colour of charoite is described as a stunning lavender, lilac, violet and/or purple. A dark lilac-violet colour of charoite was attributed to colour centres of  $Mn^{3+}$  by Nikolskaya *et al.*<sup>1</sup> who reported optical, infrared and EPR spectra, indicating that variations on the deep reddish-violet colour are linked with the composition of both manganese and iron. Photoluminescence and X-ray luminescence of charoite shows various bands at 380, 420, 600 and 730 nm<sup>2</sup>. Point defects from impurities and lattice imperfections are responsible for the colour of transparent insulators, such as gem stones and in addition to the optical absorption bands the colour centres are the source of luminescence emission during excitation with UV or ionizing radiation<sup>3,4</sup>.

### EXPERIMENTAL

All measurements reported here were taken using the Sussex University luminescence spectrometer<sup>5</sup>. High sensitivity results from the use of wavelength multiplied detection *via* a pair of spectrometers with gratings blazed for the UV-blue (200-450 nm) and blue-green-red (400-800 nm) parts of the spectrum and a pair of position-

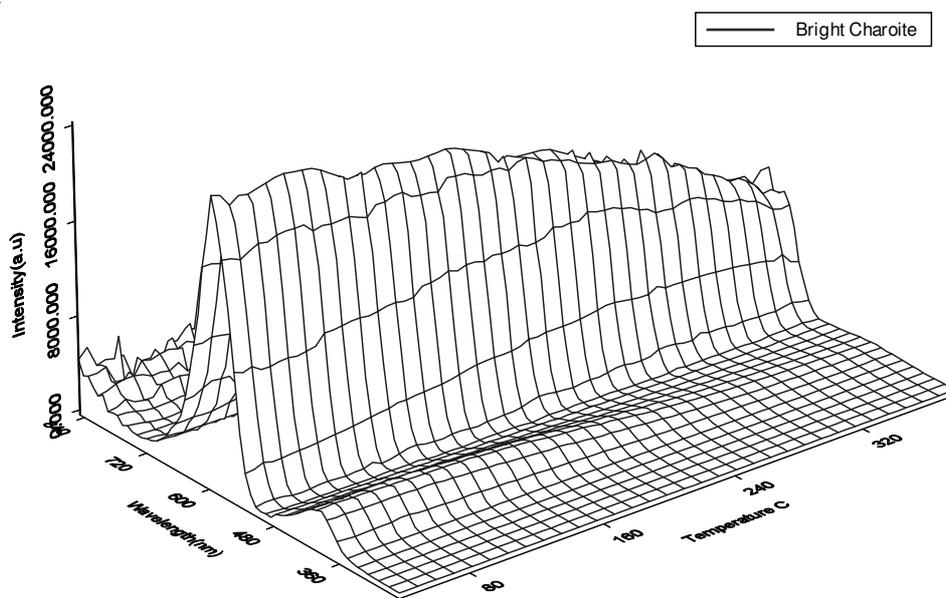
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sensitive photomultiplier tubes. The X-ray unit tube is a Phillips MG MCN 101 X-ray tube and was used with a settings of a 15 mA current and a voltage of 40 KV, which delivers a dose rate of  $15 \text{ GY min}^{-1}$  to the sample. Radioluminescence (RL) was recorded during excitation and simultaneously heating the sample. Cathodo luminescence (CL) measurements was taken by excitation with electron beams of energy up to 14 KeV focused into a spot 2 mm in diameter. A cryophysics model M22 cryostat was programmed with a controller over the low temperature range of 25-300 K at 10 K/min. Above room temperature the heating rate was  $60 \text{ }^\circ\text{C/min}$ . The samples varied slightly in colour, as is typical of charoite minerals.

## RESULTS AND DISCUSSION

**Radioluminescence and cathodoluminescence:** In order to gain some idea of the influence of defect centres in the samples, radioluminescence spectra were recorded at different temperatures from room temperature to  $350 \text{ }^\circ\text{C}$ , for three different samples. For the bright samples (purple and/or violet) there are two broad emission band regions shown in Fig. 1a, namely in the blue (*ca.* 380 nm) and red (*ca.* 590 nm) regions of the spectrum. One notes from the isometric plots of the two cases, that the intensity of light emission for both regions decreases slowly with increasing temperature. However, data plotted for the dark sample (Fig. 1b) show, in addition to the blue emission and to some extent the red band, a second spectacular feature in the infrared region (*ca.* 820 nm) which decays suddenly at about  $175 \text{ }^\circ\text{C}$ . There is also a small rise in signal between the main emission bands.



(a)

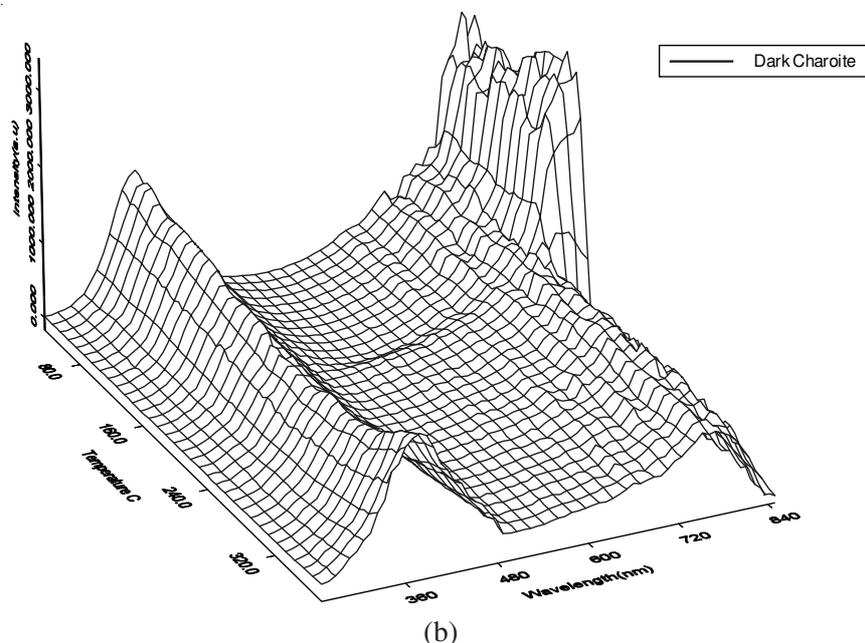


Fig. 1. Isometric plots of radioluminescence (RL) thermoluminescence (TL) for (a) bright and (b) dark charoite

Fig. 2 shows the temperature dependence of two emission bands at 380 and 820 nm, for a dark sample. As is clearly demonstrated here, there is a sudden intensity drop at 175 °C. Whilst samples from various regions, with possible variations in the types and concentrations of impurities, may show different spectra. The addition of the extra 820 nm band is not totally surprising as many bands in this spectral region have been attributed to the presence of iron impurities. Small signal variations can also originate from the position within the sample and possible surface damage introduced during cutting and polishing. Nevertheless, the intensity step in the 820 nm signal must originate from a change taking place in the sample during the heating and measurement. Similar intensity steps above room temperature have been seen<sup>6</sup> in materials which have water bonded into the structure (*e.g.* silica gel and copper sulphate pentahydrate) and the step temperature matches the water release. This can occur over a narrow temperature range, indeed as expected for a phase transition<sup>7</sup>. The implication is that the 820 nm band is linked to an iron and water defect complex.

Detection of signals during X-ray excitation while heating the crystal will reveal a combination of radio-luminescence and thermo-luminescence (TL) signals but these do not normally show an intensity step.

Surface features are studied by the use of cathodo-luminescence (CL) and changes in electron energies offer some information on the depth scale of the changes. Fig. 3 gives a comparison between CL and RL data both collected at room temperature.

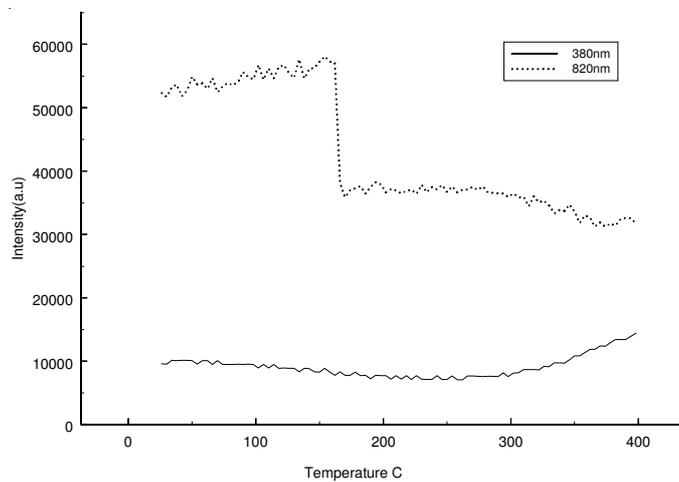


Fig. 2. Temperature dependence of RLTL for dark charoite at two different wavelengths

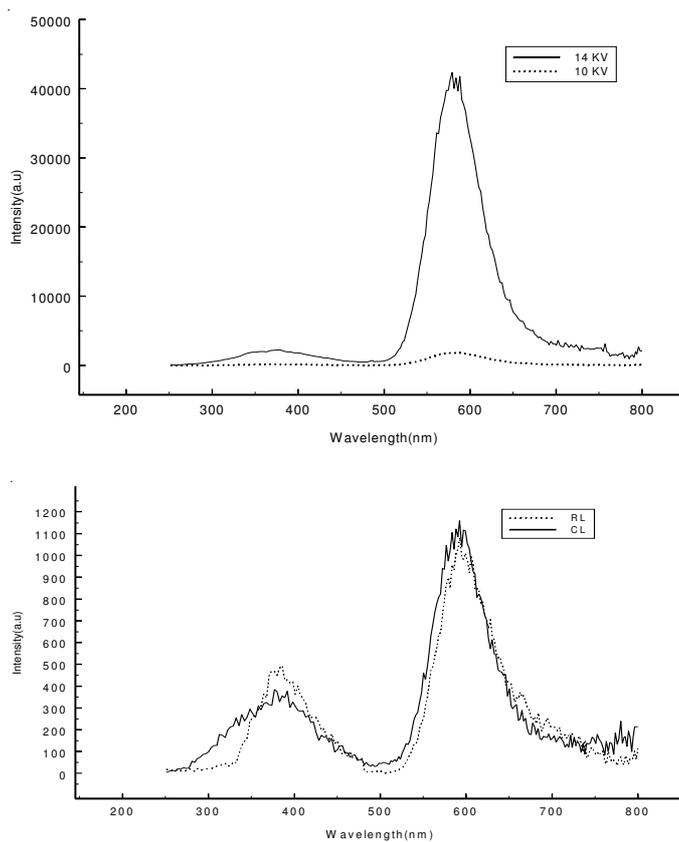


Fig. 3. Comparison between (a) CL spectra for different electron beam energies and (b) CL & RL spectra, both from a bright charoite sample taken at RT

There is a minor shift in wavelength toward blue region of the spectra and a fairly clear indication of appearance of some features around 320 nm. However, one can imagine that the emission in this region is broader for CL signals. Such band broadening is to be expected as there can be variations in site geometry caused by stresses introduced during the cutting process of sample preparation which will have introduced distortions in a damaged surface layer. In continuous excitation during heating, there may be luminescence features which are absent in room temperature CL or RL. Fig. 4 shows cathodoluminescence of a bright violet charoite sample during a temperature ramp (CLTL) from RT to 300 °C. There is, as before, a fairly strong blue luminescence spread over range 350 to 500 nm band which is analogous to the feature of feldspar samples<sup>8</sup>. This feature, plus the broad band around 600 nm are the two significant emissions from RT to *ca.* 130 °C. At this temperature the two mentioned bands mostly decay and some features around 720 nm appear. Emission at this region is also common for luminescence of feldspar. The charoite gemstone is basically a hydrous calcium-potassium silicate with impurities of manganese and iron which produces emission at 600 nm (Mn) and 715 nm (Fe) plus the less intense blue emission. With excitation of the lattice under the electron beam irradiation at higher temperatures the 720 nm peak becomes more evident with respect to the *ca.* 600 nm of manganese. This effect is progressively larger in more heavily damaged charoite lattices as the result of ion beam irradiation<sup>9</sup>. Since CL emission is mostly from the top 100 to 200 nm of the material, it is strongly surface dependent. In CLTL, where there is continuous excitation during heating, there may be a combination of normal CL excited luminescence plus signals from thermoluminescence. However, the surface and bulk dominated signals from the two cases *i.e.* CLTL and RLTL have very distinct features, as contrasted by Figs. 1(b) and 4, for dark or bright samples.

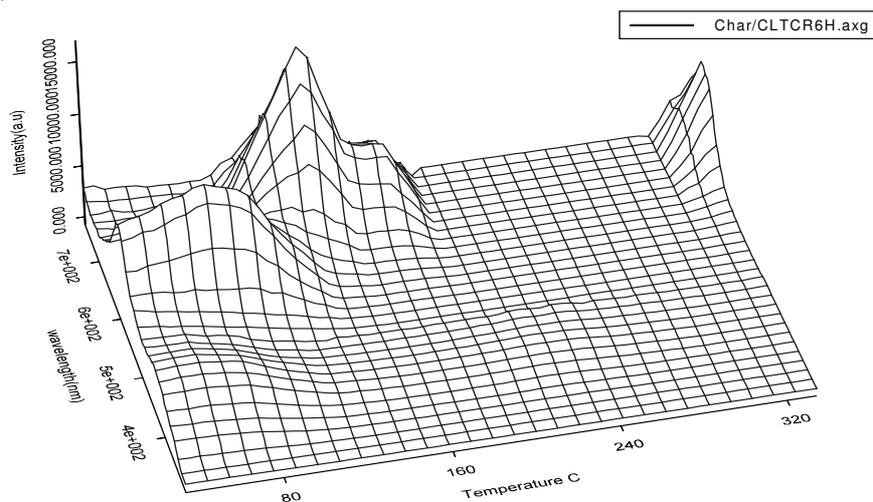
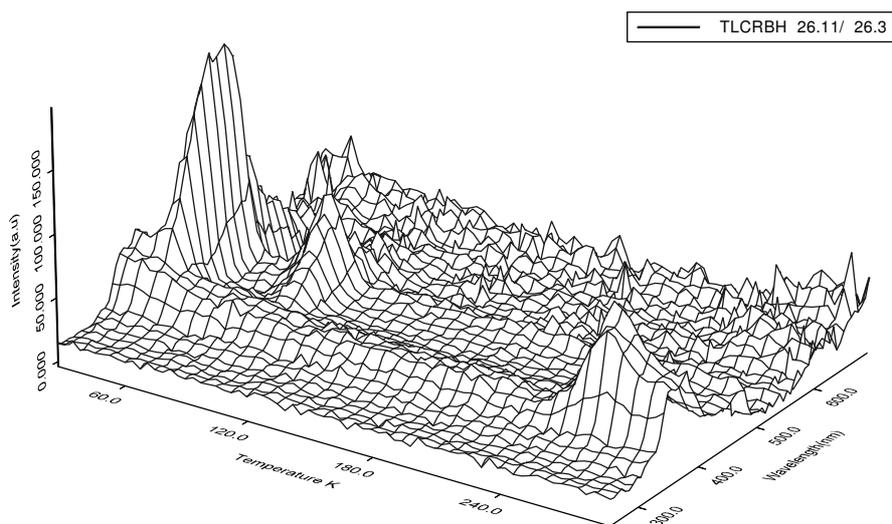


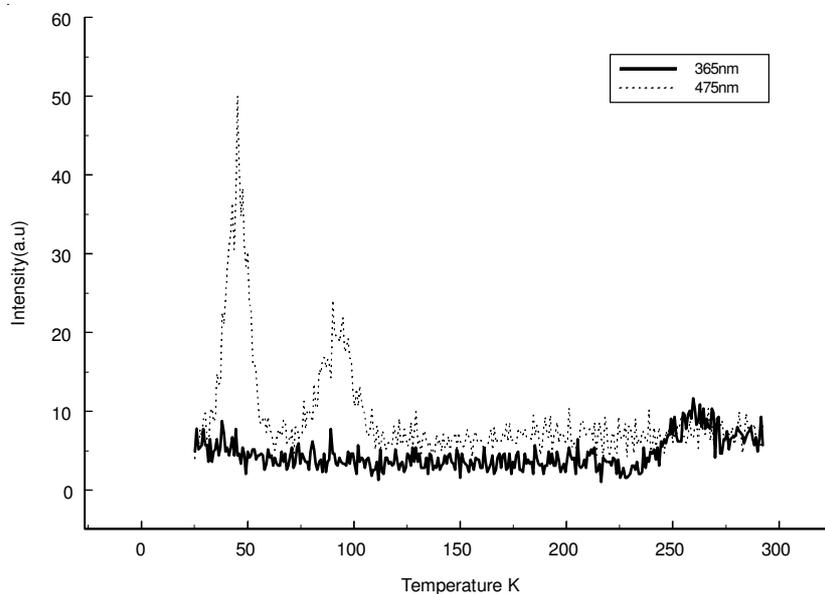
Fig. 4. Isometric plot of CLTL of a bright charoite sample

The unusual feature in both cases is a sharp drop in intensity near 175 °C which, as mentioned, has not the shape associated with a standard TL component (*i.e.* this is not a broad glow peak superposed on a continuous background). One possible reason for such a rapid intensity changes in luminescence intensity is the presence of a phase transition<sup>6,7,10</sup>, since luminescence efficiency significantly changes for different phases. In this case water of crystallization must be considered as a possible impurity. Note the cited 175 °C value is for the heater strip, but at these high heating rates the surface of the sample is somewhat cooler, often by more than 20 degrees<sup>11</sup>.

**Thermoluminescence at low temperature:** TL data of a pre-irradiated bright charoite sample are shown in Fig. 5. The sample was cooled to 25 K and irradiated for 15 min with they X-ray source prior to the TL run. The isometric plot shows the emission of weak signals. There are at least three different emission bands peaks at *ca.* 45, 90 and 250 K with different wavelength maximum near 400, 450 and 360 nm, respectively. This wavelength dependence with temperature suggests the presence of more than one component band. These blue region spectra are common for all our types of experiment, either from bulk (*i.e.* RL) or on near surface (*i.e.* CL). Low temperature measurements of TL give more information about shallower traps related to impurities. Manganese and iron centres emitting at 585-600 and 715-730 nm, respectively, do not establish long-range order luminescence emission centres at low temperatures and they give more intense long wavelength emission centres above RT than blue emissions. The UV-blue emissions become more visible when the lattice is excited under X-ray irradiation at low temperature. They probably derive from strain and/or oxygen defects excited during X-irradiation. From the figure there is also some evidence of a new feature above *ca.* 240 K.



(a)



(b)

Fig. 5. (a) Isometric TL plot after X-irradiation at 25 K; (b) TL glow curves taken from (a) at two different wavelengths in UV-blue region of spectra

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### REFERENCES

1. L.V. Niko,skaya, A.I. Novozhilov and M.I. Samoilovich, *SSSR, Ser. Geol.*, **10**, 116 (1976).
2. P.N. Yarovoi, Y.A. Medvedev and L.A. Ivanova and S.V. Serykh, *Zhurnal Prikladnoi Spektroskopii*, **46**, 938 (1986).
3. V. Correcher and J. Garcia-Guinea, *J. Lumin.*, **93**, 303 (2001).
4. L. Sanchez-Munoz, J. Garcia-Guinea, J. Sanz, V. Correcher and A. Delgado, *Chem Miner.*, **18**, 3336 (2006).
5. B.J. Luff and P.D. Townsend, *Measur. Sci. Technol.*, **4**, 65 (1993).
6. A.P. Rowlands and P.D. Townsend (unpublished).
7. P.D. Townsend, M. Maghrabi and B. Yang, *Nucl. Inst. Methods B*, **191**, 767 (2002).
8. H.M. Rendell, M.R. Khanlary, P.D. Townsend, T. Calderon and B.J. Luff, *Mineralog. Mag.*, **57**, 217 (1993).
9. J. Garcia-Guinea, P.D. Townsend, N. Can, V. Correcher, L. Sanchez-Munoz, A.A. Finch, D. Hole, M. Avella, J. Jimenez and M. Khanlary, *J. Lumin.*, **128**, 403 (2008).
10. P.D. Townsend, A.P. Rowlands and G. Corradi, *Radiat. Meas.*, **27**, 31 (1997).
11. D.S. Betts, L. Couturier, A.H. Khayrat, B.J. Luff and P.D. Townsend, *J. Phys. D*, **26**, 843 (1993).

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