Phosphorescence spectra from alkali feldspars as they are cooled

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(Received 23 June 2007; in final form 31 August 2007)

Abstract

We report here phosphorescence spectra over the range 1.55 to 5.5 eV from three alkali feldspars after irradiation as they are cooled from room temperature to 130 K. The dominant emission was at 1.7 eV. With decreasing temperature, the intensity of this band initially decreased, but then increased below 250 K, consistent with the observation of Visocekas and Zink. We confirm their inference that they were measuring the 1.7 eV emission band characteristic of Fe^{3+}. Other emission bands were observed at 2.2, 2.7 and 4.3 eV; their intensities decreased with decreasing temperature.

We were also able to measure the emission spectra of one sample after a 30 minute heating at 120°C; the 1.7 eV band was much reduced and the emission now dominated by the 2.2 eV band, characteristic of Mn^{2+}. The 1.7 eV band now did not show thermal quenching.

Introduction

Phosphorescence emission spanning from IR to UV is detected from irradiated feldspars. Emission occurs when electrons escape from the traps and recombine at the luminescence centres (Aitken 1985). Visocekas et al. (1994), Visocekas and Zink (1995), and Visocekas (2002) reported on phosphorescence emission from feldspars from room temperature to liquid-N_2 temperature. They irradiated feldspars (mostly K-feldspars) with a beta source at room temperature, and phosphorescence emission intensity was measured as a function of time **t**, initially at room temperature. Then measurements were continued with the samples cooled to liquid nitrogen temperature. They found that as the samples were cooled the emission intensity first decreased and then increased, the increase being attributed to thermal quenching. We also note that at low temperature, thermal excitation from shallow traps would not occur, and recombination emission could result only from tunnelling. They also found the emission intensity to be proportional to $\mathbf{t^{-1}}$ and interpreted this as the consequence of tunnelling with a distribution of tunnelling distances (see Huntley, 2006, for recent theory). Visocekas and co-workers also reported that the emission occurred only in the near-IR, with photons of energies less than 2.1 eV (~ 590 nm). They reasoned that this emission was probably the known band at ~ 1.7 eV (~ 730 nm) due to impurity Fe^{3+} substituting for Al^{3+} in the tetrahedra which constitute the frame of the feldspar lattice. However, Visocekas et al. did not show emission spectra during tunnelling in support of this. The object of the present work was to establish this and the temperature dependences of the various emission bands.

In our research we measured several samples belonging to both plagioclase and alkali feldspar groups. Here we give results only for the alkali feldspars; those for the plagioclase feldspars are quite different and have been reported elsewhere (Huntley et al. 2007). Previously, Baril (2002) and Baril and Huntley (2003b) reported phosphorescence spectra of some feldspars at room temperature and above from 1.24 to 5.5 eV (1000 to 225 nm).

Samples

The potassium feldspars studied here are:

K8	-	Microcline, Ward's[1]	45E2941
K12	-	Orthoclase, Ward's[1]	49E5919
K14	-	Microcline, Ward's[1]	49E5918

Aliquots of the samples were prepared by gluing small chips (2 – 3 mm) on aluminum planchets using Crystalbond[2] dissolved in acetone. The planchets were placed in an oven at 50°C for 1 hour to harden the Crystalbond.

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[2] Crystalbond 509: Aremco Products Inc., P.O. Box 517, 707-B Executive Blvd. NY 10989, USA

Emission spectra

Aliquots were given a ~ 800 Gy dose of ^{60}Co gamma radiation and phosphorescence emission spectra were then measured using the spectrometer described by Baril and Huntley (2003b). The CCD-detector was cooled to ~ -60°C using a Peltier cooler and a dry ice/alcohol bath in order to reduce the noise level. Spectra were measured from 1.55 to 5.5 eV (800 nm to 225 nm).

The irradiated aliquots were placed in a cryostat to reduce the sample temperature (minimum 130 K). Light from a sample was guided to the CCD-spectrometer by an optical-fibre bundle. Spectra recorded as the samples were cooled are shown in Fig. 1a to Fig. 1c.

At room temperature sample K8 showed spectral bands at 4.4 eV (280 nm), 2.6 eV (470 nm), 2.2 eV (570 nm) and 1.7 eV (730 nm) (Fig. 1a). At 250 K the intensities of all the bands were reduced, however with further cooling the intensity of the 1.7 eV band increased, while the other bands remained almost unchanged (Fig. 1a). Samples K12 and K14 showed similar behaviour (Figs. 1b and 1c) except they lacked the 2.2 eV and the 4.4 eV bands. The broad feature from 3 – 5.5 eV seen in Figs. 1b and 1c is an artefact, probably due to light scattered within the spectrometer.

To remove the unstable electrons from the shallow traps of irradiated feldspars, we preheated the samples for 30 minutes at 120°C. One hour after the preheat, the samples were measured again. Only the brightest of the three, K8 gave a measurable intensity. The intensity of the 1.7 eV band was much reduced compared to that of the 2.2 eV band by this short preheat. The spectrum is shown in Fig. 2. As this preheat (30 min at 120°C) may not have been sufficient for complete removal of shallow-trap electrons, the samples were heated further at 160°C for 1 hour for their complete removal. The emission intensity was then too weak to measure the spectrum. Fig. 2 also shows the spectra from K8 as it was cooled to 130 K. It is seen that the intensities of both the 1.7 and 2.2 eV bands decreased. There is no indication of the thermal quenching of the 1.7 eV band seen in the non-preheated sample.

Discussion

Phosphorescence spectra from irradiated feldspars at room temperature have been previously reported by Baril and Huntley (2003a) (see also Baril, 2002). In their measurements the same spectrometer was used, but with a different grating, which allowed them to measure spectra from 1.24 to 5.5 eV (1000 – 225 nm). The earlier measurements show that there is also

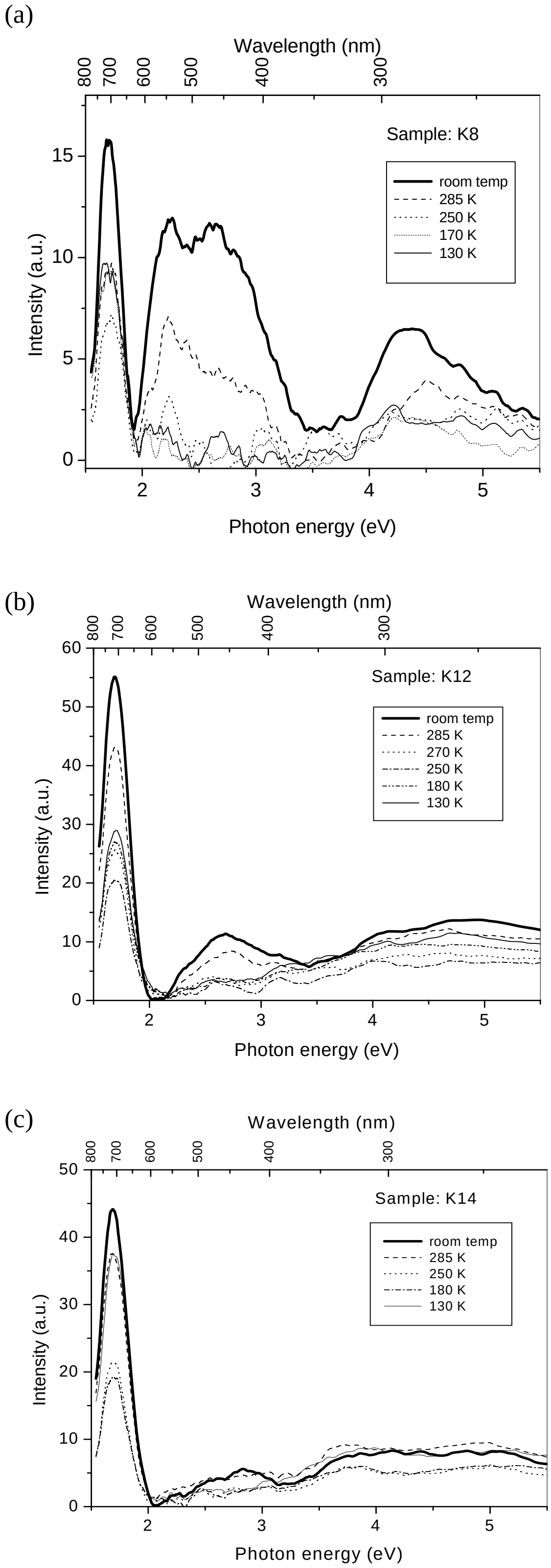

Figure 1: *Phosphorescence spectra of irradiated feldspars K8, K12 and K14 at room temperature and cooler.*

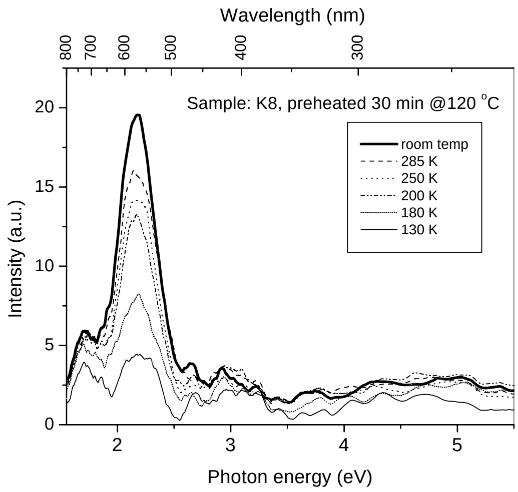

Figure 2: *Phosphorescence spectra of feldspar K8 at room temperature and cooler. The sample was first irradiated and heated 30 minutes at 120°C.*

an emission band at 1.37 eV (900 nm), which is outside the measurement range of the present work. The present measurements showed a band at 4.4 eV, which was seen by Baril and Huntley in other feldspars but not in K8. We presume this is because we used different aliquots, and that K8 is not homogeneous. When the sample K8 was preheated at 120°C for 30 minutes there was a drastic reduction of the bands at 1.7, 2.6 and 4.4 eV. This leads us to think that thermal excitation of, or tunnelling of, shallow-trap electrons leads to the 1.7 eV, 2.6 eV and 4.4 eV emission bands.

The objective of the present work was to test the inference of Visocekas that the phosphorescence emission below 2.1 eV (above 590 nm) was essentially all in the 1.7 eV (red-IR) band due to Fe^{3+}. Our spectra support this, though it is possible that the tail of the 2.2 eV band may make a contribution for some samples as it would for our K8.

As did Visocekas, we found thermal quenching for the 1.7 eV band. White et al. (1986) found an activation energy for thermal quenching of 0.056 eV, and Poolton et al. (1995) found a value of 0.34 eV. However, it was absent for the heated sample (Fig. 2). Thermal quenching depends on the local environment of the center and we thus deduce that the environments are different in the different cases. For us either the heating has changed the environment or the phosphorescence from the heated sample is from a subset of the Fe^{3+} ions that contributed to the phosphorescence of the unheated sample.

Acknowledgements

The research was supported by the Natural Sciences and Engineering Council of Canada. We thank M. X. Chen for the loan of the cryostat.

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Reviewer

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Reviewer's Comments

The results of this study indicate the complexity of luminescence emission from K-feldspars. It is of particular interest that the main emission observed for all three samples is at 1.7 eV and is thus not observed when using conventional bi-alkali photomultiplier tubes. Two of the samples were microclines, K-feldspars that have been shown by others to exhibit anomalous fading. The observation for the microclines in this study that there is emission when the sample is cooled well below the irradiation temperature indicates that considerable release of electrons occurs subsequent to irradiation at room temperature. Although emission at this wavelength, attributed to Fe^{3+}, is drastically reduced by heating for 30 minutes at 120°C, a preheat that is longer than that usually used in dating protocols, phosphorescence at 2.2 eV, attributed to Mn^{2+}, was still observed indicating release of electrons that may manifest itself as anomalous fading.