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Towards direct measurement of electrons in metastable states in K-feldspar: Do infrared- photoluminescence and radioluminescence probe the same trap?

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Abstract

Prasad et al. (2017) recently developed a new method of measuring the dosimetric signal in feldspar, based on a Stokes-shifted photoluminescence emission (excitation energy ~ 1.40 eV (885 nm), emission energy ~ 1.30 eV (955 nm)). The new signal, termed as infrared photoluminescence (IRPL), was shown to arise from radiative relaxation of the excited state of the principle trap (dosimetric trap), and allows non-destructive probing of the dosimetric information. Thus, IRPL provides a unique tool to study physical characteristics of these metastable states in feldspar, e.g., number density and spatial distribution, trap depth, photo-ionisation and capture cross-section, excited state lifetime, and tunneling probabilities. The IRPL emission is apparently related to the infrared radioluminescence (IR-RL) in K-feldspar (Trautmann et al., 1998); in the latter, however, the electrons relax after being trapped as a result of exposure to ionising radiation, rather than as a result of excitation within the trap.

In this study, we report the discovery of a second IRPL emission centred at ~ 1.41 eV (880 nm) in a K- feldspar which arises in response to excitation with 1.49 eV photons. Based on the temperature- and dose-dependent behaviour of IRPL and IR-RL, we conclude that the same defect(s) participates in these two emissions. However, IRPL emission is governed by the characteristics of the principle trap (defect) alone, whereas IR-RL depends additionally on thermally assisted transport within the band-tail states. Since IRPL is a site selective technique, it does not, unlike IR-RL, suffer from contamination from higher energy emissions (e.g. from Fe^{3+}). This lack of contamination, and the possibility for thermal/optical pre-treatments and repeated measurements of the same trapped electrons, suggest that IRPL is a robust alternative to IR-RL.

Keywords: Infrared Photoluminescence (IRPL), Infrared-Radioluminescence (IR-RL), Luminescence, Feldspar, Optical Dating, Luminescence Dosimetry, Wide Bandgap Materials.

1. Introduction

Feldspar is a ubiquitous, naturally occurring mineral (band gap, $E_g \sim 7.7$ eV) that is widely used as a geochronometer. In many applications of optical dating (Huntley et al., 1985), it is preferable to use feldspar rather than quartz because of its potential to extend the age range to up to 0.5 Ma; however, it suffers from anomalous fading, an effect that results in age under-estimation (Wintle, 1973), and is more difficult to bleach than the optically stimulated luminescence (OSL) signal from quartz (Godfrey-Smith et al., 1988). Commonly, feldspar is measured using near-infrared

(IR) photons in the range 850-880 nm; the resulting anti-Stokes emission (in UV to red) is called infra-red stimulated luminescence (IRSL; Hütt et al., 1988). In IRSL, the dosimetric trap used in IRSL dating (henceforth, the principle trap) is photo-ionised by a two-step process; (i) IR photons interact with the trapped electrons to convert the occupied trap to its excited state, (ii) electrons in the excited state diffuse out into the band-tail states or the conduction band (depending on the ambient temperature) (Jain and Ankjrgaard, 2011). Eventually, a fraction of these detrapped electrons combines with trapped holes to produce IRSL. The IRSL signal has been subject to rigorous investigation in the last three decades, and promising results have been demonstrated from elevated temperature post IR- IRSL signals (Thomsen et al., 2008; Buylaert et al., 2012; Li and Li,

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2011) and pulsed IRSL (Tsukamoto et al., 2006, 2017; Jain and Ankjrgaard 2011; Jain et al., 2015). However, the stability of the signal and possible artefacts e.g. due to thermally induced transfer are not fully understood (e.g., Jain et al., 2015; Tsukamoto et al. 2017). Based on excitation spectroscopy, Andersen et al., (2012) demonstrated that the different IRSL and post-IR-IRSL signals resulted from the same trap (henceforth, the principle trap).

Trautmann et al. (1998, 1999a,b) proposed an alternative measurement method that seems to use the principle trap but does not rely on optical stimulation. This method, Infrared radioluminescence (IR-RL) or sometimes referred as Infra-red radiofluorescence (IR-RF), is based on the observation that if one exposes the sample to ionising radiation, a dose dependent prompt emission occurs in the near IR. These authors suggested that the IR-RL originates from free electrons produced in the conduction band by ionising radiation; trapping and radiative relaxation of these electrons in the principle trap gives rise to the dose dependent IR-RL. Although the IR-RL signal has not yet been explored as rigorously as the IRSL signals, limited tests suggest that the accuracy of equivalent dose (D_e) estimates may be sample dependent because of possible sensitivity change during measurement (e.g., Buylaert et al., 2012). When used to determine dose, the IR-RL signal may be somewhat inflexible since it is not obvious how one can preferentially select signal components of different stabilities, as is, for instance, possible using thermal treatments and prior stimulation in optical probing methods (e.g. post IR-IRSL; Thomsen et al., 2008).

Recently, Prasad et al. (2017) developed a novel technique for the non-destructive measurement of trapped electrons in the principle trap. The signal they discovered is termed Infrared Photoluminescence (IRPL), where IR refers to the excitation energy and PL refers to the Stokes-shifted photoluminescence arising from radiative relaxation within the principle trap. For dosimetric investigations, these authors used a ~ 1.40 eV (885 nm) laser to excite the trap and recorded emission at ~ 1.30 eV (955 nm). Since IRPL is generated without involving recombination centres, it offers the potential for (i) isolating a non-fading signal using the same techniques that are used with IRSL, and (ii) making precise luminescence measurements at very small trapped electron populations or even very small scales (e.g. sub-micron) because of the ability to repeatedly (i.e. non-destructively) measure the same trapped electrons. In the OSL/IRSL method, one trapped electron can at the most produce one photon in a particular emission, since the measurement is destructive. In contrast, in IRPL,

a single trapped electron can produce a large number of photons, because it can be re-excited many times; this aspect of IRPL allows very high precision measurements, potentially allowing mapping of even single trapping states. Equally importantly, because IRPL directly probes the principle trap, it can be used to improve our physical understanding of feldspar as a dosimetric system, such as e.g., number density and spatial distribution, trap depth, photo-ionisation and capture cross-section, excited state lifetime and tunnelling probabilities relevant to the electron trapping states.

In this study, we explore the relationship between IR-RL and IRPL because it is likely that they both use the same radiative relaxation mechanism within the principle trap. We use low temperature (7 K-295 K) measurements to provide a clearer resolution of the emission peak(s) due to subdued electron-phonon interactions, compared to the room temperature measurements. The purpose of this study is to advance our understanding of the principle trap in feldspar by providing a holistic model combining IRPL, IRSL and IR-RL, so as improve the dating technologies that make use of these signals.

2. Infrared radioluminescence: Previous Studies

Radioluminescence results from transitions of free electrons from the conduction band during trapping or recombination, during interaction of material with ionising radiations such as X-rays, β -rays, etc. (e.g., Schulman et al., 1951). Radioluminescence emissions in feldspar are generally observed in the UV-Red region (e.g., Krbetschek et al., 1997; Prasad et al., 2016). However, in K-feldspar, radioluminescence is also observed in the near infrared region, called Infrared Radio Luminescence (IR-RL). IR-RL in K-feldspar is thought to arise from the trapping of free electrons in the conduction band by the same traps that give rise to IRSL (or trap, according to Andersen et al., 2012), resulting in a broad emission peaking at ~ 865 nm at room temperature (Trautmann et al., 1999a,b; Krbetschek et al. 2000; Trautmann et al. 2000; Varma et al., 2013). Since the number of occupied trapping sites increases with ionising radiation dose, the IR-RL intensity decreases as irradiation progresses, as fewer and fewer sites are available for trapping. On the other hand, UV-Red intensities, presumably resulting from electron-hole recombination, increase with dose; this is possibly due to increasing concentration of holes and decreasing competition from the principle trap (Trautmann et al., 1999b; Erfurt et al. 2003a).

Trautmann et al. (1999a,b) demonstrated that IR-RL emission at ~ 865 nm can be used for dating. Based on the comparison of the IRSL excitation spectrum (peak emission at ~ 1.44 eV) and IR-RL emission spectrum (peak emission at ~ 1.43 eV) at room temperature, they concluded that these two signals originate from the same trap. Erfurt et al. (2003b) inferred two peaks in the near IR region at ~ 910 nm and ~ 865 nm, based on fitting the IR-RL spectrum with a Gaussian distribution function. These authors suggested that the two emissions originate from Pb^+ centers in K-feldspar, by drawing analogy with the spectral response of synthetically grown KCl:Pb sample. Erfurt (2003) reported that IR emission in KCl:Pb crystal at ~ 930 nm and ~ 975 nm correspond to electronic transitions $7^2\text{P}_{1/2} \rightarrow 6^2\text{S}_{1/2}$ and $7^2\text{S}_{1/2} \rightarrow 6^2\text{S}_{1/2}$ respectively, and concluded that the same transitions are responsible for the ~ 865 nm and ~ 910 nm IR-RL emissions in K-feldspar during exposure to ionising radiation. Erfurt (2003) also monitored photoluminescence in the same IR region as the IR-RL, while exciting the sample with UV photons (henceforth, UV-IRPL). This UV-IRPL presumably arises from photo-ionisation of trapped electrons, and subsequent re-trapping of a fraction of the resulting free electron population from the conduction band. Thus, the mechanism generating UV-IRPL is similar to IR-RL, but the emission intensity of UV-IRPL must depend both on a) the concentration of de-trapped electrons in the conduction band due to photo-ionisation of the principle trap as well as from other defects in the crystal that can be stimulated by UV, and b) the concentration of empty sites of the principle trap available for re-trapping and hence able to generate UV-IRPL emission. Erfurt (2003) normalised IR-RL using the UV-IRPL in different geological samples, and demonstrated that the ratio of these two signals (IR-RL/UV-IRPL) decreases monotonically with dose; thus, he concluded that the two phenomena must be interlinked by reduction of the Pb^{2+} to Pb^+ during RL, and vice versa during UV photo-ionisation. However, he did not attempt a quantitative correlation between the dose dependence of UV-IRPL and IR-RL. Furthermore, there appears to be a discrepancy between the relative rate of change of IR-RL and UV-IRPL signals in his bleaching experiments, and the inferred two peaks (~ 910 nm and ~ 865 nm) were never confirmed independently, e.g. by low temperature measurements. It is also important to clarify that the UV-IRPL reported by Erfurt (2003) is not generated by the same mechanism as the IRPL reported by Prasad et al. (2017). Considering a population of trapped electrons; in IRPL, excitation is done with IR photons and the electrons oscillate between the excited

and ground state of the principle trap; because the electrons never leave the trap, the trapped electron population remains unchanged. This is a site selective, non-destructive measurement technique resulting in a steady state signal. In contrast, in UV-IRPL, trapped electrons are photo-ionised by UV light; once in the conduction band these electrons (in addition to returning to the principle trap and so generating UV-IRPL) also have the possibility of recombination with the holes and being re-trapped by the defects other than the principle trap. Thus, UV-IRPL changes the trapped electron population during readout; it is a destructive method. Furthermore, unlike IRPL which selectively targets the excited state of the principle trap, UV stimulation not only excites the principle trap but any electrons in other traps able to be photo-ionised by UV light.

While the proposed mechanism of IR-RL (Erfurt, 2003) is convincing, it has not yet been investigated in detail. There are several unsolved issues, e.g. the absence of a dose-dependent IR-RL signal in Nafeldspar, despite the existence of an IR resonance, the high non-dose dependent background (up to 60% of the signal), sensitivity change, etc., all of which require explanation. The IR-RL model is mainly based on two indirect correlations: (i) the similarity of peak energy of IR-RL emission (~ 1.43 eV) and IRSL resonance (~ 1.44 eV), and (ii) the decrease in IR-RL intensity with ionising radiation dose. In contrast, the IRPL is a site-selective technique, where the signal has been unambiguously tied to radiative relaxation within the principle trap (Prasad et al., 2017). Thus, a detailed comparison of the spectroscopy and dose-dependence of IR-RL and IRPL should provide further insights into the IR-RL mechanism and its link to the principle trap. This comparison is attempted in the following sections.

3. Experimental details

3.1. Samples

We have used well-characterised potassium-rich feldspars for our measurements. Major element analysis was carried out by X-ray fluorescence using the XRF system on the Risø TL/OSL reader. Our first sample R47 (85% K, 12% Na, and 3% Ca by weight) is a feldspar extract from sediment. The second sample R28 (95% K, 5% Na, and 0% Ca) is a museum feldspar specimen. Detailed investigations on these samples are presented in Prasad et al. (2017). The samples were bleached for 48 hours in a solar simulator (Hönlé SOL 2) before undertaking any measurements.

3.2. Instrumentation

All measurements were carried out using the Risø station for Cryogenic Luminescence Research (COLUR) at DTU Nutech, Denmark. It is based on a Horiba Fluorolog-3 spectrofluorometer expanded to include multi-excitation and -detection ports, an X-ray irradiator (40 kV anode voltage, 100 μ A anode current, and 0.06 Gy/s dose rate to quartz), and a temperature-controlled closed-loop He cryostat (7-300 K) (Prasad et al., 2016).

A liquid nitrogen cooled charge coupled device (CCD) was used to record emission spectra following excitation using 1.40 eV (885 nm) and 1.49 eV (830 nm) laser sources. Two long pass interference filters (925 nm, optical density=4) were used to detect emission at $\sim$ 1.30 eV (955 nm), and two 850 nm long pass interference filters (optical density=4) were used to record emissions at $\sim$ 1.41 eV (880 nm) and $\sim$ 1.30 eV (955 nm). IR-RL spectra were recorded with CCD detector during X-ray irradiation. More details on IRPL detection system can be found in Prasad et al. (2017).

All the radio-luminescence measurements reported in this paper were obtained using X-rays. We used a filament-based X-ray tube with a Tungsten (W) anode, operated at 40 kV and 100 μ A. The broad Bremsstrahlung X-ray spectrum was hardened through a 70 μ m aluminium foil and RL measurements were made under low pressure ($\sim 10^{-4}$ mbar) because of security inter-locking issues. The X-rays penetrate the bulk sample (mean energy $\sim$ 13 keV), thus the RL investigations presented here should be comparable to those using a beta source.

4. Results and Discussion

4.1. IRPL emission spectra using 1.49 eV (830 nm) laser at 7 K

Prasad et al. 2017 used a 1.40 eV (885 nm) laser to excite the principle trap. The resulting Stokes-shifted emission peak at $\sim$ 1.30 eV (955 nm) at 7 K must represent the lowest principle-traps excited state detectable with the CCD system. We measured the IRPL following Prasad et al. (2017) in R47 at 7 K (after giving $\sim$ 216 Gy dose using X-rays) by stimulating with a 1.40 eV (885 nm) laser and recording the emission spectrum from 910 nm to 1000 nm through 925 nm long pass (LP) interference detection filters. As expected, the resultant emission (Figure 1, red curve) at $\sim$ 1.30 eV (955 nm) is similar to that reported by Prasad et al. (2017). In order to explore possible higher energy levels in the principle trap, we repeated the measurement

using a $\sim$ 1.49 eV (830 nm) laser and 850 nm LP detection filters. Two emission peaks centred at $\sim$ 1.30 eV (955 nm) and $\sim$ 1.41 eV (880 nm) were observed (Figure 1, black curve; fluctuations possibly due to etalon effect); the peak at $\sim$ 1.30 eV (955 nm) is similar to that reported by Prasad et al. (2017) using 1.40 eV excitation whereas the IRPL peak at $\sim$ 1.41 eV (880 nm) has not been reported before. Given our lack of knowledge of the nature of the principle trap, one may question whether the two emissions using 1.49 eV (830 nm) excitation arise from: (i) the two excited levels of the same defect (two different excited electronic levels, or splitting of the excited level), or (ii) only one excited energy level of the defect but the defect resides in two different sites where the energy is modified by about 0.1 eV because of the difference in the environment (i.e., site dependence). The latter cannot, in principle, be distinguished from the case where the difference in excited energy is linked to two different defect types but this is unlikely given that energy difference is only 0.1 eV.

Figure 1: Infrared Photoluminescence (IRPL) emission spectra measured using two different excitation energies: 1.40 eV (red curve) and 1.49 eV (black curve). The data are measured at low temperature (7 K) on sample R47 (also dosed at 7 K). The spectral regions affected due to filters have been removed.

Interestingly, Erfurt (2003) also reported two IR emissions ($\sim$ 1.36 eV (910 nm) and $\sim$ 1.43 eV (865 nm)) in feldspars by fitting the IR-RL data recorded at the room temperature (RT). If one accepts that the IRPL results from the same trap as IR-RL, the difference in IR-RL peak positions compared to those observed in the IRPL above ($\sim$ 1.30 eV and $\sim$ 1.41 eV) may be related to the measurement temperature (our measurement at 7 K)

or sample dependence. In the next section, we make a detailed comparison of the IR-RL and IRPL emissions to further explore these possibilities.

4.2. IR-RL and IRPL spectra at 7 K and 295 K

We first measured the IR-RL emission spectrum at 7 K on sample R47 after bleaching for 48 hours. Two emissions peaks centred at ~ 1.30 eV (955 nm) and ~ 1.41 eV (880 nm) were observed (Figure 2a); these are similar to the two IRPL peaks observed using the ~ 1.49 eV (830 nm) laser (Figure 2b). However, the relative amplitude of the two peaks is different in IRPL and IR-RL (Figure 2a,b). These IR-RL and IRPL measurements were then repeated at room temperature (295 K); the emissions were found to merge into a single peak (Figure 2a and 2b). Interestingly, when compared to the measurements at 7 K, the peak amplitude was reduced in case of IRPL but increased in IR-RL. Moreover, it appears that thermal quenching is larger for the 1.30 eV IRPL peak than for the 1.41 eV IRPL peak.

We repeated the same experiments using the R28 sample. In this sample only a single broad peak at 1.41 eV (880 nm) is present, in both IR-RL and IRPL (Figure 2c,d). Again, when the temperature was increased from 7 K to 295 K, the IR-RL peak intensity increased but the IRPL intensity decreased.

Several broad inferences follow from the data presented in Figure 2:

1. IRPL and IR-RL show the same emission peaks at ~ 1.30 eV and ~ 1.41 eV at 7 K; however, the exact shape and relative amplitude (e.g. in R47) of these peaks differ in IR-RL and IRPL.
2. While IR-RL shows an apparent thermal assistance, the IRPL shows thermal quenching. Thermal quenching appears to differ between the 1.30 eV and 1.41 eV peaks.
3. Whether there are one or two apparent IRPL emission peaks depends on the sample. Sample R47 (85% K) shows two clear peaks, whereas R28 (95% K) shows only one clear peak. However, two peaks, although not clearly visible, are almost certainly present in R28 spectrum since measurements using ~ 1.40 eV (885 nm) laser excitation demonstrate an emission peak at ~ 1.30 eV (see Prasad et al., 2017, Figure SI-2c)

Our 7 K data provides direct evidence confirming the interpretation of the two RL peaks by Erfurt et al. (2003). However, their peak energies inferred by fitting data measured at room temperature are significantly different to those observed directly in our 7 K data. To examine the role of temperature on peak position, we fitted

our IR-RL data at 295 K (Supplementary Figures SI-1a) with a Gaussian function; this gave peak positions at ~ 1.41 eV and ~ 1.30 eV at 295 K, indistinguishable from the peak positions observed at 7 K. To test whether our room temperature data are nevertheless compatible with those of Erfurt (2003), we refitted our 295 K IR-RL data with the two peak positions fixed at ~ 1.43 eV and ~ 1.36 eV, as reported by him, but this resulted in a significantly poorer fit (Figure SI-1b). Thus, we conclude that the difference between our result and that of Erfurt is not related to the measurement temperature. It may be because he used a different sample. Since the results of fitting at room temperature are consistent with the 7 K data, where the two peaks are resolved experimentally, we can only suggest that further work is necessary to test possible sample dependence of the two RL peak positions.

The difference in the emission characteristics of R28 and R47 suggests that two different defect sites (or defects) might be responsible for the two different emission peaks. Otherwise, the relative amplitude of the two IRPL or IR-RL peaks should have remained constant in different samples (see section 4.1).

4.3. Temperature dependent IR-RL and IRPL

In order to further investigate the temperature dependence of the width of the IR-RL and IRPL peaks observed above, we measured these signals in R47 at temperatures ranging from 7 K to 295 K at intervals of 20 K. The IR-RL spectra were recorded for a sample after 48 hrs of SOL-2 bleaching, while the IRPL spectra were recorded after 1 hour X-ray irradiation (~ 216 Gy) of the bleached sample. Figure 3a shows the temperature-dependent IR-RL spectra observed as the temperature was increased from 7 to 295 K; the X-ray was switched on (for 10 s) only during the RL measurement. Two IR-RL emission peaks (~ 880 nm and ~ 955 nm) are observed, well resolved at 7 K. With an increase in the temperature (7 K to 295 K) the two peaks increasingly overlap, presumably due to phonon-induced broadening; this results in a single broad peak by ~ 220 K. The peak amplitude systematically increases with temperature by about a factor of two; the increase becomes detectable at about 100 K, and it appears that there is no further increase above 250 K. To confirm that our results do not depend upon the exact temperature sequence, we repeated the IR-RL measurements while the temperature was decreased from 295 K to 7 K; the results were indistinguishable from those obtained from the increasing temperature sequence (Figure SI-3).

In contrast to IR-RL, the IRPL emission intensity decreases with an increase in temperature. The two peaks

Figure 2: Left column: Infrared Radioluminescence (IR-RL) spectra at 7 K and 295 K recorded during X-ray irradiation for samples (a) R47 and (c) R28; Right column: Infrared Photoluminescence (IRPL) spectra at 7 K and 295 K recorded using 830 nm (1.49 eV) laser excitation for samples (b) R47 and (d) R28. The red curve shows the data measured at 7 K, whereas, the black curves are the data measured at 295 K.

are well resolved at 7 K, as with IR-RL, but merge into a single peak by ~ 220 K (Figure 3c). Interestingly, the rate of decrease of the 1.41 eV peak intensity with temperature is different from that of the 1.30 eV peak.

In order to evaluate the temperature dependence of the broadening and amplitude of the two emissions, we attempted to deconvolute the data using 2 Gaussian peaks. However, due to temperature-dependent broadening of the spectra, it was difficult to obtain satisfactory fits. Instead, a semi-quantitative analysis was undertaken using two integration windows to separate the two emissions (shown as shaded regions in Figure 3a and 3c). The two peaks in the IR-RL signal (at ~ 1.41 eV (880 nm) and ~ 1.30 eV (955 nm)) show similar behaviour and increase in intensity relatively rapidly between 100 and 250 K. In case of IRPL the signal at ~ 1.30 eV and ~ 1.41 eV appear to be stable up to 200 K. At higher temperatures, emission at ~ 1.30 eV quenches much faster than the emission at ~ 1.41 eV.

Peak broadening is expected due to lattice vibrations at higher temperatures. At low temperature, lattice vibrations are weaker and thus peaks in both PL and RL spectra are better resolved. The increase in IR-RL intensity with temperature suggests that efficient transport of electrons in the band-tail states (Poolton et al., 2002, 2009; Jain and Ankjrgaard, 2011) is important for trapping; this results from phonon-assisted diffusion (PAD) at higher temperatures (band-tail transport ceases at low temperatures because of the lack of PAD). These results suggest that electron trapping during irradiation involves two steps; (i) thermalisation of free electrons from the conduction band, and (ii) subsequent phonon-assisted transport within the band-tail states until trapping into the excited state in the principle trap.

IRPL on the other hand does not involve any band-tail transport at low temperatures; it is produced mainly by intra-defect excitation and emission (Prasad et al., 2017). The decrease in IRPL intensity with temperature is presumably dominated by an increase in non-radiative relaxation, with some leakage to the band-tail states at higher temperatures (e.g., Chithambo, 2007; Prasad et al., 2017). Our data suggest that the defects (or energy levels) giving rise to the ~ 1.30 eV (955 nm) and ~ 1.41 eV (880 nm) have different thermal quenching behaviour. Based on the inter-comparison of the responses of RL and PL to temperature, one may further conclude that IR-RL involves a competition between thermal assistance due to more efficient diffusion of electrons within the band-tail states, and thermal quenching within the defect after trapping. On balance, it appears that PAD is the dominant effect in IR-RL, which results in a similar increase in both the RL peaks. In contrast,

quenching dominates in IRPL.

4.4. X-ray dose dependence of IRPL and IR-RL

The IRPL and IR-RL dose response at 7 K of sample R47 is examined next. To allow a direct comparison between the two techniques, IRPL measurements were carried out without preheating the sample. IRPL spectra were recorded using 850 nm long-pass filters and IR-RL spectra were recorded using a 610 nm long-pass filter. As expected, the IR-RL intensity for both the emission peaks is highest when no prior dose has been given (bleached feldspar) and decreases with X-ray irradiation duration. IRPL shows the opposite behaviour due to an increase in the trapped electron concentration with dose (Figures 4a, b).

As with the temperature-dependence data, we integrated IRPL intensity in the energy range from 1.21-1.24 eV for 1.30 eV emission and 1.41-1.44 eV for 1.41 eV emission and plot the integrated signal as a function of dose. The increase with dose of both the two peaks, and the total IRPL area, is indistinguishable (Figure 4d). Fitting of an exponential function to the dose-response curve (global fit to all the 3 data sets) gave a characteristic dose (D_0) of 641 ± 12 Gy.

The analysis of IR-RL was, however, less straightforward because of the well known large background in the IR-RL signal (Erfurt, 2003); up to 40% of the maximum in our sample) and the possible interference from the ~ 1.72 eV (Fe^{3+} emission) which shows an increase in intensity with dose (Figure, 4c; Figure SI-2 a, b). Interestingly, it was observed that the width of the background IR-RL for the 1.41 eV emission (approximated as IR-RL for our highest dose of 1350 Gy) is wider than that of the IR-RL spectra corresponding to lower doses. This effect gave rise to an anomalous decrease in peak width with an increase in the peak area (Figure SI-2c). However, once the background spectrum was subtracted from the spectrum obtained at each dose, the spectral shapes were approximately similar for different doses (Figure SI-2d). For dose-response analysis, the subtracted spectra in the energy range of 1.21 - 1.46 eV were fitted to a sum of 2 Gaussian peaks (peak 1 at 1.30 eV and peak 2 at 1.41 eV). The responses, as a function of dose, of the normalised areas of peaks 1 and 2, and the net background-subtracted IR-RL signal, are indistinguishable (Figure 4d). Fitting of an exponential decay function to the dose-response curve (global fit to all the 3 data sets) gave a characteristic dose of 561 ± 32 Gy. This value is slightly lower than that obtained using IRPL; however, the considerable background in the IR-RL affects the exact determination of D_0 , and the difference is probably not significant. Certainly, to first or-

Figure 3: (a) Temperature dependent IR-RL spectra, measured from 7 K to 295 K. (b) IR-RL integrals (shaded area in (a)) plotted as a function of dose. (c) Temperature dependent IRPL spectra measured using 1.49 eV laser excitation, measured from 7 K to 295 K. (d) Integrals (shaded area in (c)) plotted as a function of dose. Shaded areas represent integration windows for two emissions ~ 1.30 eV and ~ 1.41 eV. All the measurements were made on sample R47.

Figure 4: (a) X-ray dose response of IR-RL signal at 7 K. The RL data were recorded from 1.2 - 1.85 eV using a 610 nm long pass filter, but they are only plotted here for the IR-RL signal for clarity. Full data can be seen in Figure SI-2a. (b) X-ray dose response of IRPL signal at 7 K. (c) IR-RL spectrum corresponding to 1350 Gy in the spectral range 1.2-1.85 eV; the data are best fitted to a sum of 4 Gaussian peaks. (d) Dose response curves for IRPL and IR-RL. In case of IRPL, two integrated regions (1.21-1.24 eV for 1.30 eV emission and 1.41-1.44 eV for 1.41 eV emission) and total counts under the IRPL spectra were used to create the corresponding DRC. In case of IR-RL peaks were deconvoluted (after subtracting the background spectrum at 1350 Gy). The plot shows normalized areas of peak 1, peak 2, and the net counts under the background subtracted IR-RL spectra. The solid curves are global exponential fits to the data. All the measurements were made on sample R47.

der, the similar characteristic D_0 of the IR-RL and IRPL suggests that the IR-RL signal also arises from the principle trap, and that possible dose-dependent competition effects in IR-RL generation (e.g. trapping or recombination in sites other than the principle trap) are not significant.

It is worth discussing the effect of interference from the ~ 1.72 eV peak (likely Fe^{3+} emission) in IR-RL dating. It can be seen from the data measured at 7 K and the corresponding peak fits (Figure SI-2 a, b) that the Fe^{3+} peak increases rapidly with dose and interferes directly with both the IR-RL signals. While not very significant in our sample, this interference can be important at high doses where the Fe^{3+} emission is relatively much greater than the IR-RL emission. In routine IR-RL dating measurements, one uses a photomultiplier tube with a detection filter and this combination is not able to discriminate against this contamination. One way to resolve this problem may be to preferentially detect the ~ 1.30 eV emission; this is less affected by contamination. In contrast to IR-RF, IRPL is a site-selective technique and thus not affected by such contamination; other centres such as Fe^{3+} are not excited in IRPL.

In summary, our data demonstrate that the same defect very likely participates in both IR-RL and IRPL; the proposed mechanisms are schematically represented in Figure 5. Interestingly, it appears that a ~ 1.72 eV RL peak shows a systematic increase with dose, which may have potential for RL dating (Figure SI-2a).

Figure 5: Band diagram to show the mechanism of IR-RL and IRPL. Both signals arise from the same electron trapping center and their production does not involve recombination centers.

5. Conclusions

We report the discovery of an IRPL emission at ~ 1.41 eV (880 nm), and demonstrate that the ~ 1.30 eV

(955 nm) IRPL emission reported by Prasad et al. (2017) can also be measured using a higher energy 1.49 eV (830 nm) excitation. Both these IRPL emissions show different thermal quenching behaviour but grow similarly with dose. We demonstrate that the IR-RL shows the same two emissions as the IRPL, and that these emissions have the similar dose dependence as IRPL. However, IR-RL can be contaminated from higher-energy emissions (e.g. at ~ 1.72 eV) and contains a large background of unknown origin; these factors affect the shape of the dose response curve. This effect poses real challenges for the IR-RL dating of old samples, especially using a standard photomultiplier and detection filter combination, and may contribute to the sensitivity changes in IR-RL reported earlier. Based on a comparison of the temperature dependence of IR-RL and IRPL we conclude that IR-RL arises from the thermalisation of electrons from the conduction band into band-tail states and subsequent trapping in the principle trap. A final radiative relaxation gives rise to the IR-RL photons. In contrast, IRPL arises from intra-defect excitation and relaxation (Prasad et al., 2017). Thus, IR-RL and IRPL are two complimentary signals from the same defect, the principle trap. Finally, the variation in the relative amplitudes of the IRPL and IR-RL in our two feldspar samples leads to the suggestion that two different sites of the same defect are likely giving rise to the ~ 1.41 eV (880 nm) and ~ 1.30 eV (955 nm) emissions. This interpretation is different from Erfurt (2003) suggestion of two electronic levels in the same defect giving rise to the two IR-RL emissions, and requires further investigations.

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Supplementary Information

Figure SI-1

Model	Gaussian	
Equation	$y = y_0 + A/(w \cdot \sqrt{\pi/(4 \cdot \ln(2))}) \cdot \exp(-4 \cdot \ln(2) \cdot (x - x_c)^2 / w^2)$	
Plot	Peak1(RL)	Peak2(RL)
y0	0.01 ± 0	0.01 ± 0
xc	$1.30161 \pm 9.95727E-4$	$1.41274 \pm 8.0325E-4$
A	4203.14029 ± 74.05796	4290.10973 ± 73.97947
w	0.1431 ± 0.00108	$0.13378 \pm 8.51914E-4$
Reduced Chi-Sqr	244481.75454	
R-Square(COD)	0.99832	
Adj. R-Square	0.99831

Model	Gaussian	
Equation	$y = y_0 + A/(w \cdot \sqrt{\pi/(4 \cdot \ln(2))}) \cdot \exp(-4 \cdot \ln(2) \cdot (x - x_c)^2 / w^2)$	
Plot	Peak1(RL)	Peak2(RL)
y0	0.1 ± 0	0.1 ± 0
xc	1.36 ± 0	1.43 ± 0
A	8568.56838 ± 25.49468	215.59428 ± 14.28052
w	$0.20952 \pm 6.25679E-4$	0.05656 ± 0.00371
Reduced Chi-Sqr	2.30507E6	
R-Square(COD)	0.98416	
Adj. R-Square	0.98411	

Figure SI-1: (a) IR-RL spectrum at 295 K for sample R47. The data are fitted using Gaussian function with all free parameters. The best fit is shown in blue; the two component peaks plotted in red and green (~1.3 eV and ~1.41 eV) have an identical peak position as the directly observed peaks in the 7 K data (see Figure 2a). (b) The same IR-RL data as (a) fitted while fixing the peak values to 1.36 and 1.43 eV, reported by Erfurt 2003. The fitting results are shown in the table on the right. The symbol 'w' signifies FWHM value. A much poorer fit is obtained suggesting that the inferred peak values of Erfurt (2003) do not explain our data.

Figure SI-2

Figure SI-2 : (a) Dose dependent RL spectra (in spectral range 1.2 eV to 1.85 eV) measured at 7 K in sample R47. A 610 nm long pass filter was used to obtain these results. RL spectra were measured intermittently while exposing the prior bleached sample (R47) to X-rays continuously. (b) Fitted RL spectra in (a) with four Gaussian peaks. (c) A plot showing the FWHMs of the individual IR-RL peaks versus the area under these peaks. Peak at 1.41 shows an anomalous behavior, i.e. the FWHM becomes apparently smaller as the area increases. This is due to the effect of the large background (with a wide spectrum) inherent in IR-RL. (d) Normalized IR-RL spectra after subtracting the spectrum at 1350 Gy; the data suggest that the RL spectral shape does not change with dose if the background spectrum has been subtracted.

Figure SI-3

Figure SI-3: (a) Temperature dependent RL spectra measured from 7 K to 295 K. This data is the same data as that plotted in Figure 3a but is shown here again to enable comparison. (b) Temperature dependent RL spectra measured from 295 K to 7 K. (c) Normalised full IR-RL integral (total counts under each spectrum) in sequences (a) and (b) plotted against measurement temperature.