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# Variable range hopping mechanism in band-tail states of feldspars: A time-resolved IRSL study

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ABSTRACT

Time-resolved infra-red stimulated luminescence (TR-IRSL) technique enables an understanding of the dynamics of trapped electrons after IR excitation in the band-tail states of feldspar. This work intends to study the underlying physical mechanism of IRSL production. TR-IRSL studies were carried out on four feldspar mineral specimens of variable chemical composition and structural state. Assuming the IR excited trapped electrons make random walks in the band-tail states and recombine by tunnelling dynamically, hopping time is derived from the OFF time data of TR-IRSL. This analysis indicates that the hopping time decreases with stimulation temperature. Using Einstein diffusion equation, hopping probability is computed and is shown to obey the equation describing variable range hopping mechanism of Mott kind. Mott's parameters (hopping length and hopping energy) are then derived. Hopping length decreases with stimulation temperature whereas hopping energy increases with temperature. The average hopping length and energy are in the range of 11–18 Å and 45–55 meV respectively and the diffusion constant is estimated to be in the range of $10^{-10}$–$10^{-9}$ $cm^2$ $s^{-1}$ for all the feldspar samples.


## 1. Introduction

Feldspar is the potential alternate to quartz in increasing the dynamic datable range of optical dating. Feldspar is very sensitive to radiation and has a large saturation dose compared to quartz. These two factors make feldspar useful to date both young and old samples respectively. A bottle-neck in using feldspar to date older materials is 'anomalous' fading of its luminescence signal. In this phenomenon, the luminescence signals decreases because the tunnelling assisted recombination happens as the wave functions of trapped electron and hole are overlapping. There are considerable efforts put in either to correct for the fading (Huntley and Lamothe, 2001; Kars et al., 2008) or to avoid more prone to fade signals (Thomsen et al., 2008; Buylaert et al., 2009). Even after two decades of research on IRSL in feldspar, the knowledge about the underlying physical mechanism of IRSL in feldspar and the nature of participating electron and hole trapping centres is at minimum. The reason could be that the feldspar is a complex material compared to quartz.

Poolton et al. (2009) reported the existence and participation of the band-tail states in the IRSL process in K-feldspar. They additionally reported that one of the excited states of the electron trapping centre at 1.46 eV is embedded in the band-tail states of the host material. They explained IRSL process as a combination of tunnelling of trapped electrons from both 1) the excited state of electron trapping centre and 2) the band-tail states to the excited state of hole trapping centre which eventually de-excites giving luminescence. At lower measurement temperatures only the former is the recombination route whereas at higher temperatures recombination occurs via both the routes. Jain and Ankjaergaard (2011) explained their TR-OSL (blue, green and IR stimulation) data with the existence of band-tail states and tunnelling from excited state and band-tail state to the hole trapping centre. From both articles it is clear that the electron migration in the band-tail states occurs by hopping.

This study was aimed to understand the underlying physical process responsible for IRSL production, particularly whether the charge transport in the band-tail states is of variable range hopping type of Mott's kind. This work is believed to give a better picture about the IRSL production mechanism which will eventually help the readers to make a way out towards a better solution to anomalous fading. In this article, we analyzed the TR-IRSL OFF (stimulation pulse off) time data from different feldspar samples towards that aim.

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## 2. Sample characteristics

Four mineral specimens of feldspar samples (FL1, FL2_1, FL2_2 and FL3) were used in this study. Mineral assemblages and the structural state of the samples were determined from the XRD data analyses. X-ray diffraction analyses were performed on a PANalyatical Xpert Pro powder X-ray diffractometer using Cu kα radiation at 1.2 kVA (40 kV and 30 mA). The XRD patterns were recorded in the 2θ range of 5–75° with a step size of 0.01° and a counting time of 1 s per step. Xpert Highscore software was used for background correction, $k\alpha_2$ stripping, indexing of the diffraction peaks, and mineral identification by comparison with the International Centre for Diffraction Data files. Triclinicity (or obliquity) was calculated for alkali feldspar samples (FL1, FL2_1 and FL2_2) from the difference between the diffraction lines corresponding to planes 131 and $1\bar{3}1$ and this is a direct measure of Al–Si order in alkali feldspar series. Ideally, for monoclinic, there would not be any splitting between these two lines and hence the triclinicity is 0. For triclinic, the splitting would be highest and this will produce a triclinicity value of 1. Based on these XRD analyses, dominant mineral assemblage in FL3 was found to be andesine and microcline in FL1, FL2_1 and FL2_2 (Table 1). And it was found that all the feldspar samples are in ordered structural state and FL1 is highly ordered among them (Table 1). Elemental concentrations were estimated using ICP-MS of Perkin–Elmer Sciex (Model ELAN DRC II, Toronto, Canada) and followed the procedures outlined by Roy et al. (2007) and Balaram and Gnaneswara Rao (2003). Assuming these feldspars have only K, Na and Ca, the percentage ratio of K:Na:Ca were calculated from the relative contribution and these values place FL1, FL2_1 and FL2_2 in alkali feldspar (mixing of K-feldspars and Na-feldspars) series and FL3 in plagioclase feldspar (mixing of Na-feldspars and Ca-feldspars) series (Table 1).

The width of the band-tail states, $\Delta E$ was estimated from the differences between intensities of IRSL (50 °C) and post IR IRSL ($T$°C) after preheating the samples to temperature $T + 20$ °C for 60 s. Assuming both of these IRSL signals arises from same trap, the differences between these intensities are due, predominantly, to the thermal assistance of the IR excited trapped electrons to the band-tail states (Morthekai et al., in preparation). The results are given in Table 1.

The samples were crushed gently using agate mortar and sieved to get 90–150 μm size fraction. These fraction of grains were used without further chemical treatment. A few mg of samples were mounted on a stainless steel disc using Silkospray silicon oil and three such discs (aliquots) were used from each sample.

## 3. Experimental details

A Risoe TL/OSL Reader DA-20 equipped with pulsing unit and Photon Timer was used for the measurements in this study (Boetter-Jensen et al., 2003; Lapp et al., 2009). The stimulation was achieved by pulsed IR LEDs (870 ± 40 nm) using ON–OFF time of 50–1000 μs. Total stimulation time was 100 s and hence 95 thousand pulses with a pulse period of 1050 μs were used. The stimulated luminescence emission was detected using a photomultiplier tube (EMI 9235QB; 30% QE at ~395 nm) and a combination of optical filters BG-39 (2 mm thickness) and Corning 7-59 (4 mm) which allow the photons of the wavelength of 395 ± 50 nm. The heating rate was 2 °C/s and the heating was done in a pure nitrogen gas atmosphere. Analyses were carried out in R (v. 2.10.1; R Development Core Team, 2009) and Wolfram Mathematica 8.

## 4. Experimental results

The samples were given beta dose of 62 Gy (for FL2_2 it was 12 Gy) and preheated to 280 °C (for FL3 it was 240 °C) for 60 s. The exact preheat temperatures were selected by visual inspection of the TL glow curves. FL1, FL2_1 and FL2_2 had distinctly two main glow peaks at 270 °C and at 330 °C (Supplementary Fig. 1S). FL3 had a high temperature glow peak at 230 °C which apparently arises due to a distribution of trap depths (Sakurai et al., 2001; Correcher et al., 2004). The preheat temperature of FL3 and other samples were selected to be 240 °C and 280 °C respectively. TR-IRSL at $T$°C was measured where the stimulation temperature, $T$ varied from 50 °C to 250 °C at an interval of 25 °C and is shown in Fig. 1. For FL3, the stimulation temperature, $T$ was varied from 25 °C to 225 °C with the same interval. After every TR-IRSL measurement i.e., before measuring at higher temperatures the remnant luminescence signals were washed by illuminating the sample with IR while the samples were at elevated temperatures (225 °C for FL3 and 250 °C for other samples). Further, after every TR-IRSL and thermal-cum-optical wash, a TL (up to 450 °C) measurement was also made. These TL measurements was done to 1) remove any remnant luminescence signals before next stimulation temperature and 2) to check any change in the shape of the glow curve of remnant TL signals. Even after TR-IRSL measurement and thermal-cum-optical wash, considerable remnant TL counts were observed but no changes in the shape of glow curves, irrespective of the stimulation temperature of TR-IRSL measurements, were however observed.

The signal of last 50 μs of the each pulsing period would have been contributed predominantly by 1) slow to relax signal, 2) the Isothermal TL (ITL) signal and 3) the dark counts. The contribution from the ITL to the TR-IRSL was quantified by measuring TR-IRSL without IR stimulation. ITL contribution increased with stimulation temperature and typically for a stimulation temperature of 225 °C the ITL signal for the last 50 μs of the OFF time data was 10% (Supplementary Fig. 2S). The remaining contribution can then be attributed to the slow to relax signal which arises due to tunnelling from the excited state of electron trapping centre. So, an average of TR-IRSL signal from 1000 to 1050 μs was subtracted from each data point of the corresponding data set and normalized by the intensity at the end of ON time (50 μs). This signal is believed to arise predominantly due to electron hopping in band-tail states and eventual tunnelling to and recombination at the hole trapping centre. Only the OFF time data were used for further analyses.

**Table 1**
Sample characteristics.

| Sample | Mineral assemblage[a,b] | Triclinicity[b], $\Delta\ (d_{131} - d_{1\bar{3}1}) \times 12.5$ | Structural state[b] | K:Na:Ca[c] (%) | $\Delta E$[d], eV |
|---|---|---|---|---|---|
| FL1 | Microcline maximum, Albite low, Diopside | 0.88 | Highly ordered | 67:30:3 | 0.52 |
| FL2_1 | Microcline intermediate, Quartz, Oligoclase, Diopside | 0.70 | Intermediate ordered | 68:26:6 | 0.55 |
| FL2_2 | Microcline intermediate, Diopside | 0.53 | Ordered | 79:15:6 | 0.48 |
| FL3 | Andesine, Diopside | – | Ordered | 3:54:43 | 0.56 |

[a] Minerals are listed in order of abundance in each sample.
[b] Obtained from XRD analyses.
[c] Obtained from ICP-MS analyses.
[d] Morthekai et al., in preparation.