

MECHANISMS OF LUMINESCENT RESPONSES IN THERMAL AND OPTICAL STIMULATION OF POTASSIUM FELDSPARS

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We propose a model describing the mechanism for generation of an optically stimulated luminescence signal in potassium feldspars when irradiated in an IR absorption band (IR OSL). The model assumes that this type of stimulated luminescence is intercenter by nature, arising in tightly bound deep trap/ionized luminescence center pairs. At the same time, the thermoluminescence (TL) signal and the optically stimulated afterglow (OSA) signal arise in a recombination process with participation of the conduction band. We describe the results of an experimental test of the proposed model.

Keywords: *potassium feldspars, stimulated luminescence, complex centers, luminescence dating.*

Introduction. Potassium feldspars have found wide application as paleodosimeters in various methods (IR OSL, TL, OSA, etc.) for luminescence dating of geological and archeological objects. However, to date the detailed mechanism of the processes leading to the appearance of luminescence in potassium feldspars remains undetermined. The goal of this work was to develop and rationalize a model describing the mechanism for the appearance of luminescence in potassium feldspars and taking into account the different interactions between lattice defects in this group of minerals. We performed a series of experiments to test the proposed model.

Objects of Investigation and Experimental Procedure. The object of investigation was microcline crystals (which could contain up to 5% albite), orthoclase crystals, and grains of feldspars extracted from samples from deposits of the Voka outcrop in northeastern Estonia (approximate composition of extracts: orthoclase 50%, microcline 30%, albite 5%, the rest was quartz).

The spectral luminescence characteristics of the minerals were recorded on a general purpose computer-controlled apparatus [1]. The luminescence detector was a Hamamatsu H8259 photon counter; the source of stimulating radiation was a DKsSh-1000 xenon lamp with Karl Zeiss SPM-2 monochromator (in some cases, a PRK-100 mercury lamp through light filters). Laboratory irradiation of the samples was carried out with a URS-2 x-ray apparatus (tube with tungsten anode, accelerating voltage 35 kV).

Basic Characteristics of Dosimetric Trapping Centers. The basic characteristics of dosimetric trapping centers, i.e., deep centers in which the lifetime of electrons is a few million years and which are used for dating geological and archeological objects, have been known for a long time. A summary of these data can be found in review [2]. These characteristics may vary slightly depending on the specific crystal modification of the feldspar.

The appearance of dosimetric luminescence signals from feldspars is usually interpreted based on a simple band scheme where, for example, the TL signal arises due to ionization of deep trapping centers, followed by transition of electrons to the conduction band, while optical liberation of electrons is a two-step process: on stimulation by IR light, the electron transfers from the ground state to the excited state, from which, as a result of thermal activation, it then ends up in the conduction band. In both cases, luminescence is believed to arise in recombination of free electrons with ionized luminescence centers. Optical stimulation in the shorter wavelength band (350–400 nm) leads to direct optical ionization of the dosimetric centers.

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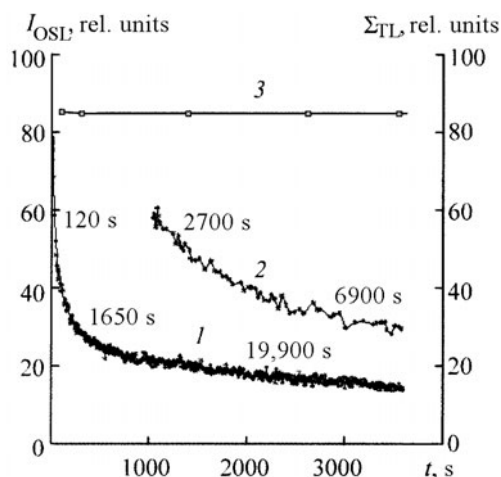


Fig. 1. Effect of IR irradiation on optically stimulated and thermoluminescence signals in feldspars irradiated in the laboratory: time variation of the IR OSL intensity with optical emission at room temperature (1) and 140°C (2), the numbers on the curves indicate the values of the time constant τ assuming that the curves are described by the sum of exponentials of the form $I_n = I_0 n \exp(-t/\tau_n)$; 3) effect of optical emission on the light sum of the thermoluminescence.

In detailed study of phenomena associated with thermally and optically stimulated luminescence of feldspars, a number of contradictions have been observed that cannot be explained within a simple band model. Optical emission in the IR band (at least to a residual IR OSL signal on the order of 2%–3% of the initial level) does not cause an appreciable decrease in the TL light sum (Σ_{TL}) (Fig. 1) (compare with the data in [3]). The temperature-dependent optical emission (TOE) curves, i.e., the temperature dependence of the OSL on a TL background, do not decay in the region of the low-temperature (100°C–200°C) TL peaks (Fig. 2), which after laboratory irradiation of the feldspars are luminescent, although judging from literature data (see, for example, [2, 4]), most of the ionized luminescence centers disappear in the region of these peaks. The time dependence of the IR OSL decay $I(t)$ for exposure to IR radiation of constant intensity consists of at least two components: a fast component and a slow component. Consequently, there are non-identical luminescent centers that luminesce either readily or with difficulty. There are possibly some intermediate types of centers. In contrast to IR OSL, for optically stimulated afterglow (OSA), the stimulation spectrum of which contains, besides a long-wavelength IR region, a number of even shorter-wavelength bands (for example, 350 nm), and decay of the TOE curves is already observed in the region of the low-temperature TL peaks (Fig. 2) (the size of the OSA signal was defined as the number of photons measured per second after a 10 ms pause when stimulation was stopped [5]).

Model for Stimulated Luminescence of Feldspars. It seems to us that the characteristic features described above for processes leading to the appearance of TL, IR OSL, and OSA signals are consistently explained by a model having the following properties.

1) The model is described by a band scheme in which, compared with the conventional scheme, levels and transitions are added that are associated with complexes of deep trap/recombination center pairs. Along with the complexes, there are single trapping centers and luminescence centers. Since a complex consisting of an ionized luminescence center and a deep trap with a localized electron is electrically neutral, the probability of its interaction with "foreign" electrons and holes is negligibly small [6]. This explains why the TOE curves do not decay in the region of the low-temperature TL peaks.

2) TL arises upon thermal ionization of only single centers. Thermal ionization of complexes is not accompanied by TL (probably due to thermal quenching).

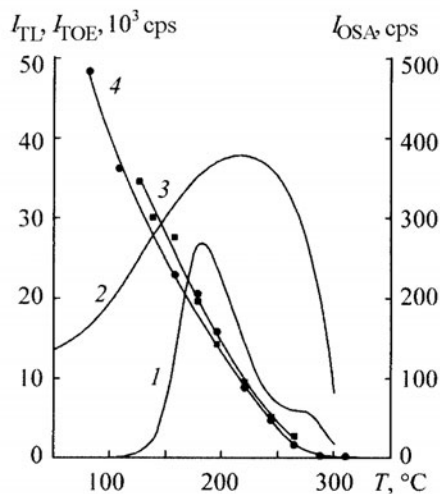


Fig. 2. Thermoluminescence curves (1), optical stimulation of luminescence (2), and optical stimulation of afterglow (3, 4) in a sample exposed to x-rays at room temperature; 2) IR stimulation, 3) stimulation by light at $\lambda = 350$ nm, 4) IR stimulation; curves 3 and 4 were obtained for the blue luminescence band in the sawtooth heating mode; the OSL signals were recorded at room temperature after an appropriate heating cycle.

3) Stimulation in the IR band can cause the appearance of only a small number of free electrons in the conduction band (usually no more than 2% of the total number of electrons trapped in the dosimetric levels).

4) The luminescence signal observed with IR stimulation arises either when some potential barrier is overcome in this complex or when a tunneling transition occurs for an electron going from an excited trapping center to an excited level of the ionized luminescence center. The tunneling transition mechanism corresponds to our model. Such a mechanism is valid both for "blue" and other luminescence centers. If this mechanism is realized, then we should observe a dependence of the tunneling probability not only on the distance between partners in the complex, which should form some discrete series of distances associated with the lattice constant, but also on temperature, since the dimensions of the electron cloud (the wave function) increase as the vibrational energy increases.

5) Higher excited states of the trapping center overlap with band states. They are clearly apparent as short-wavelength bands in the OSA stimulation spectrum. Irradiation of feldspars in these bands is accompanied by ionization (depletion) of the trapping centers and appearance of electrons in the conduction band.

Experimental Test of Some Consequences of the Model and Discussion of Results. We have established that during emission of feldspar [stimulated] by IR light, the probability of a tunneling transition of an electron from an excited trapping center to an excited level of an ionized luminescence center sharply falls off (see Table 1) in our objects as the energy of the vibrational level ΔE_{OSL} increases, where accordingly the brightness of IR OSL also decreases (in our case, by more than a factor of 20). We associate this effect with the fact that in the initial step, tunneling recombination occurs mainly with nearby partners, which does not require finding an excited trapping center in a high vibrational level. The IR OSL decay curves $I(t)$ over the course of emission also indicate the presence of several kinds of complexes.

An attempt to approximate the decay curve for the IR OSL signal with optical emission by a Becquerel function $I(t) = I_0/(1 + \alpha t)^\omega$ (where α is a constant characterizing the probability of the recombination process; I and I_0 are the instantaneous and initial intensities of the IR OSL signal; ω is a constant describing the nature of the recombination process (usually the value of ω is in the range 1–2); t is the emission time) gives a value of $\omega = 0.5$ – 0.8 , i.e., <1 , for the studied samples, which is not acceptable since in this case the light sum emitted upon IR stimulation

TABLE 1. Change in ΔE_{OSL} as a Result of Optical Emission of Feldspars Exposed to X-Rays

| Sample | ΔE_{OSL} , eV | |
|-----------------------------|-----------------------|-------|
| | initial | final |
| Polymorphous (Voka outcrop) | 0.16 | 0.35 |
| Microcline crystal | 0.10 | 0.21 |
| Orthoclase crystal | 0.13 | 0.23 |

Note. Emission time is 1 h.

$\Sigma_{opt} = \int_0^{\infty} I(t)dt$ tends toward infinity. This provides a basis for assuming that $I(t)$ must be written as the sum of exponentials, in this case $I(t) = \sum_k I_{0n} e^{-t/\tau_n}$, in which for $n \neq \infty$, we obtain the final result for Σ_{opt} .

The behavior described above is observed both for single-phase microcline and orthoclase crystals and also for samples with a diverse phase composition, as we find in most feldspars extracted from deposits (including the test samples from deposits of the Voka outcrop).

Conclusion. We have constructed a model for the generation of IR-stimulated luminescence in potassium feldspars used for dating geological and archeological objects. The model is described by a band scheme in which, compared with the conventional scheme, we introduce electrically neutral complexes in which the main IR-stimulated luminescence flux arises on recombination of electrons in tightly bound complexes of trapping level/luminescence center pairs, without involving free electrons from the conduction band. The observed luminescence arises due to an intracomplex tunneling transition of electrons from excited trapping centers to excited levels of ionized luminescence centers.

From the data discussed above, it also follows that intracenter localization of excited states ΔE_{OSL} , in addition to a possible effect from the crystal modification of the feldspar, also depends on temperature, on the isolated region of the luminescence spectrum, on the emission capability of the studied sample, whether or not the sample was subjected to preliminary heating before the measurement, etc. Thus the proposed model, when we take into account the thermal quenching process, explains the large scatter in literature data on the value of ΔE_{OSL} .

Although the proposed model explains a broad range of phenomena associated with stimulated luminescence in potassium feldspars, it needs refinement and requires some more detail and further experimental testing. More detail is especially required concerning the microstructure of the complexes, including the actual distance between their components.

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