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Study of paramagnetic and luminescence centers of microcline feldspar

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Abstract

Microcline feldspar crystal has been analyzed in order to determine the centers suitable for use in ESR and luminescence dating. ESR measurements at RT showed the Fe^{3+} line, and at 77 K the Si–O$^-$..X signal with $g = 2.0052$, 2.0098 and 2.0128. TL glow peak at 157 and 300 °C in UV interval were observed and in the VIS range we noted peaks at 150, 280 and 340 °C. TL growth curve of the 340 °C peak could be fitted by a saturating exponential equation and can be used in TL dating. Emission curves showed band widths 1.95 ± 0.09, 2.73 ± 0.08 and 4.94 ± 0.50 eV. Transitions from $^4T_1 \rightarrow {}^6A_1$ of Fe^{3+} can be associated with the 1.95 eV band and the transition from $^4A_1\ {}^4E(G) \rightarrow {}^6A_1(S)$ with 2.73 eV band.

Keywords: ESR; Thermoluminescence; Emission spectrum; Feldspar; Microcline

1. Introduction

Feldspar crystal is in the aluminum silicate series, which may be classified chemically as members of the ternary system $NaAlSi_3O_8$ (albite)–$KAlSi_3O_8$ (orthoclase)–$CaAl_2Si_2O_8$ (anorthite). Therefore, the general composition of feldspar can be expressed by the formula MT4O8, in which T sites are filled by Si, Al and eventually by Fe^{3+}; the M sites are occupied by alkaline metals (K^+ and Na^+) or alkaline-earth metals (in general, Ca^{2+}, Sr^{2+} and Ba^{2+}). They compose 60% of the Earth's crust and can be found in igneous rocks. Although the feldspars are susceptible to alteration and weathering, they are second in abundance to quartz among the arenaceous sediments.

Brazil has more than 50×10^6 ton of feldspar reserves, and granitic pegmatite rocks are the main production source, located in the southern and northeastern parts of the country. Therefore, it will be very interesting if the feldspar can be used routinely in ESR and TL dating methods.

Many efforts have been made to identify and analyze the feldspar centers. Speit and Lehmann (1982) investigated EPR spectra of 15 feldspar samples with widely different compositions and showed Al–O$^-$–Al, O$^-$…Al, Si–O$^-$…X (X is a divalent metal ion, Mg^{2+} or Be^{2+}) and Pb–O$^-$…X (X is Pb^{2+} and Mg^{2+}) hole centers, detected after X-ray irradiation, and one electron center, Ti^{3+}.

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TL of feldspars has also been studied by many authors (Visocekas, 2000; Hütt et al., 1999; Correcher and García-Guinea, 2001). Kirsh et al. (1987) reported a very complex monochromatic TL glow curve for albite ($NaAlSi_3O_8$) exhibiting eight TL peaks and for microcline ($KAlSi_3O_8$) five. They compared ESR measurements with TL emission spectra and discussed several possibilities to explain the emissions. They associated emissions at 450–480 and at 500–560 nm with radiative recombination between thermally released electrons with Al–O^-–Al and Al–O^- ... M^{2+} (M = Zn, Mg, Mn), respectively. Finally, the emissions at 580–660 nm were explained as relaxation of Eu^{3+} ions excited by the blue photons.

Mittani et al. (1999) investigated ESR and TL results after various thermal treatments and γ-ray irradiation experiments on K-feldspar (orthoclase). They suggested a model to explain the emission of the 310 °C TL peak as follows: during irradiation the electron is released from an Al–O^{2-}–Al center, and is trapped in Fe^{3+} ion and Fe^{2+} is formed; subsequently during the reading of the TL the electron is thermally released from Fe^{2+} and recombines with the Al–O^-–Al center emitting TL.

In OSL dating the infrared stimulation (800–900 nm) can be used for most of the feldspar crystals and emissions can occur in a wider wavelength range spanning 250–650 nm. Hütt et al. (1988) proposed a model to explain this emission. They suggested a thermal assistance mechanism, in which photons of the infrared raise electrons from the ground state to the excited state. Then some of them rise thermally into the conduction band and OSL is emitted by recombination of the electron with a hole trapped in a luminescence center.

In the present work, results of measurements of ESR, TL, OSL and emission spectra of microcline feldspar will be presented. Annealing and irradiations experiments were performed in order to verify correlations between the ESR signals and the luminescence centers. TL, OSL and ESR growth curves were analyzed in order to identify the centers suitable for use in dating method.

2. Experimental procedure

The specimen investigated in this work is a microcline with few albite trace contents, verified by X-ray diffraction. The sample was collected from the natural reserve located in Paraná state, Brazil. Impurity contents were determined by neutron activation analysis (NAA). About 100 mg of two portions of the sample and two standards, Buffalo River Sediment (NIST-SRM-2704) and Coal Fly Ash (ICHTJ-CTA-FFA-1), were irradiated in the swimming pool research reactor, IEA-R1 m, at a thermal neutron flux about $5 \times 10^{12}\,ncm^{-2}\,s^{-1}$ for 8 h. γ-radiation spectra were obtained after 7 and 15 days decay time using a Ge-hyperpure detector, model GX 2020, Canberra, FWHM 1.9 keV gamma peak of ^{60}Co and an 8192 channel S-100

Table 1
Chemical composition of microcline feldspar sample obtained by NAA and X-ray fluorescence technique

Element	Sample 1—(NAA) (ng/g)	Sample 2—(NAA) (ng/g)	Sample 3—(XRF) (ng/g)
Sm	41.8 ± 4.2	52.9 ± 4.2	
Lu	14.5 ± 5.0	32.0 ± 5.7	
Yb	196.3 ± 43.6	113.6 ± 38.2	
La	279.6 ± 56.5	232.1 ± 47.1	
Sb	846.2 ± 35.8	931.9 ± 35.7	
Ce	327.4 ± 155.8		
Cr		566.2 ± 269.5	
Sc	52.4 ± 3.6	65.0 ± 3.7	
Na	$(37.0 \pm 0.1) \times 10^6$	$(48.8 \pm 0.2) \times 10^6$	$(16.0 \pm 0.5) \times 10^6$
Ba	$(230.7 \pm 23.2) \times 10^3$	$(316.8 \pm 27.3) \times 10^3$	
Cs	$(59.5 \pm 1.6) \times 10^3$	$(69.3 \pm 1.9) \times 10^3$	
Rb	$(2.03 \pm 0.06) \times 10^6$	$(1.94 \pm 0.06) \times 10^6$	$(3.6 \pm 0.1) \times 10^6$
Fe	$(181.7 \pm 16.0) \times 10^3$	$(123.1 \pm 16.4) \times 10^3$	$(528 \pm 53) \times 10^3$
K	$(19.5 \pm 0.8) \times 10^3$	$(30.6 \pm 1.1) \times 10^3$	$(159 \pm 5) \times 10^6$
O			$(380 \pm 11.4) \times 10^6$
S			$(139 \pm 14) \times 10^3$
Al			$(87 \pm 3) \times 10^6$
Ca			$(370 \pm 37) \times 10^3$
P			$(338 \pm 34) \times 10^3$
Sr			$(130 \pm 13) \times 10^3$
Pb			$(102 \pm 10) \times 10^3$
Ga			$(82 \pm 8) \times 10^3$
Si			$(352 \pm 11) \times 10^6$