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Luminescence and ESR properties of Brazilian feldspars

J.F.S. Bitencourt[a,*], D.M. Silva[a], P.H. Silva[a], A. Kinoshita[b,c], C.S. Munita[d], S.H. Tatumi[a]

[a] *Faculdade de Tecnologia de São Paulo, CEETEPS/UNESP, Praça Cel.Fernando Prestes, 30, 01124-060 São Paulo, SP, Brazil*
[b] *Universidade do Sagrado Coração, R. Irmã Arminda 10-50, 17011-160 Ribeirão Preto, SP, Brazil*
[c] *Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, USP, Av. Bandeirantes, 3900, 14040-901 Ribeirão Preto, SP, Brazil*
[d] *Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear, c.p. 11049, 05422-970 São Paulo, SP, Brazil*

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Abstract

The IRSL and TL responses of three different feldspar crystals have been analysed. TL measurements were taken in the ultraviolet UV (290–370 nm) and the visible VIS (340–610 nm) regions of the spectrum. For the UV region and for a natural sample, peaks were observed at 283, 287 and 310 °C for grey, white and pink crystals, respectively. For samples irradiated after prior preheating, it was noted that TL peaks occurred at about 200 °C for all the samples; irradiation with high doses above 500 Gy induced the formation of one additional peak at 170 °C. The VIS region results were similar to those for the UV. ESR experiments have been developed to verify the influence of radiation and heat treatments on the centres and preliminary results showed great variation in the intensities of $[TiO_4]^-$, Al–O^-–Al and Fe^{3+} centres.

1. Introduction

Infrared-stimulated luminescence (IRSL) signals of feldspar crystals have been used extensively in the dating of geological events helping geologists reconstruct palaeoenvironment (Hashimoto et al., 2005; Argyilan et al., 2005). One of the advantages of using IRSL of feldspar is that this signal is effectively bleached at deposition.

Hütt et al. (1988) proposed a mechanism for IRSL of feldspar. In this model, the incidence of infrared photons on feldspar can raise electrons from the ground state into an excited state and from the latter some of them are raised thermally into the conduction band. Afterwards, some electrons reach the luminescence centres, when recombination takes place and a strong signal is seen from 300 to 600 nm, depending on the sample characteristics.

Early work on the TL of feldspar showed anomalous fading at room temperature (RT); e.g. Wintle (1977) mentioned a labradorite with a TL peak at 300 °C, for which the initial decay at RT was about 20% in 2 h. Guérin and Valladas (1980) observed serious fading in the 300–400 °C region of the TL glow curve in volcanic feldspar. Kirsh et al. (1987) reported a very complex monochromatic TL glow curve for albite exhibiting eight TL peaks and for microcline five peaks. Due to the complexity of feldspar TL emission many authors (Correcher et al., 1999; Correcher and García-Guinea, 2001; Benoit et al., 2001; Tatumi et al., 2005) continue to determine the centres and kinetics of the charges related to the luminescence signals.

In the present work, the TL response of three different samples irradiated to high doses with γ-rays and the correlation with their EPR signals are presented.

2. Experimental procedures

The three specimens investigated in this work were verified by X-ray diffraction. One sample with white (FELW) colouration is an orthoclase rich with barium, and another with grey (FELG) colour is a microcline; both were collected from the natural reserve located in Rio Grande do Norte state, northeastern region of the country. The last sample is pink (FELP) and was from Santa Catarina state, in the southern part of Brazil; it is a microcline.

Neutron activation analysis was applied to the three feldspar. The samples were prepared by manually grinding, in an agate mortar and pestle, in order to pass through a 100–200 μm mesh

* Corresponding author. Fax: +55 1133267611.
E-mail address: tatumi@fatecsp.br (S.H. Tatumi).

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Table 1
Chemical composition of feldspar samples obtained by NAA, FELP = pink feldspar, FELW = white feldspar and FELG = grey feldspar

Element (ppm)	FELP	FELW	FELG
Na	$(24.4 \pm 0.5) \times 10^3$	$(27.3 \pm 0.5) \times 10^3$	$(24.7 \pm 0.5) \times 10^3$
K	$(99 \pm 9) \times 10^3$	$(111 \pm 10) \times 10^3$	$(103 \pm 9) \times 10^3$
La	4.8 ± 0.1	1.5 ± 0.1	-0-
Th	0.4 ± 0.1	-0-	0.02 ± 0.07
Cr	50 ± 2	8 ± 1	-0-
Cs	0.40 ± 0.04	76 ± 2	112 ± 3
Sc	0.140 ± 0.004	0.06 ± 0.006	0.0130 ± 0.004
Fe	$(1.30 \pm 0.06) \times 10^3$	$(0.39 \pm 0.04) \times 10^3$	$(0.08 \pm 0.03) \times 10^3$
Eu	0.30 ± 0.02	0.060 ± 0.009	0.06 ± 0.01
Ce	5.0 ± 0.3	1.8 ± 0.1	-0-
Hf	0.60 ± 0.04	-0-	-0-
Ta	-0-	-0-	0.20 ± 0.04
Co	0.4 ± 0.03	0.14 ± 0.01	0.4 ± 0.04

Table 2
Chemical composition of major elements found in feldspar samples obtained by X-ray fluorescence for FELP = pink feldspar, FELW = white feldspar and FELG = grey feldspar

Element (mol%)	FELP	FELW	FELG
SiO_2	66.18	65.5	66.42
Al_2O_3	18.96	19.29	18.6
MnO	<0.002	0.004	0.022
MgO	<0.01	<0.01	<0.01
CaO	0.78	<0.01	0.01
Na_2O	3.29	2.98	2.73
K_2O	10.19	11.75	11.41
TiO_2	0.023	0.001	0.009
P_2O_5	0.003	0.513	0.542
Fe_2O_3	0.16	0.01	0.09
Loss ignition	0.26	0.3	0.28

Table 3
Chemical composition of trace elements found in feldspar samples obtained by X-ray fluorescence for FELP = pink feldspar, FELW = white feldspar and FELG = grey feldspar

Element (ppm)	FELP	FELW	FELG
Ba	5611	81	294
Ce	<35	<35	<35
Cl	553	<50	<50
Co	<6	<6	<6
Cr	<13	<13	<13
Cu	6	5	11
F	<550	<550	<550
Ga	16	23	22
La	<28	<28	<28
Nb	<9	<9	<9
Nd	<14	<14	<14
Ni	<5	<5	8
Pb	48	11	10
Rb	141	3213	4679
S	<300	<300	<300
Sc	<14	<14	<14
Sr	1500	8	11
Th	4	44	61
U	<3	<3	<3
V	<9	<9	<9
Y	<2	6	<2
Zn	2	2	3
Zr	13	<2	<2

sieve. After this treatment the material became more homogenous, so that it could be used in trace-element analysis. Contamination from agate mortar is not a serious problem, since silicon was not determined. Constituent elements in coal fly ash, NIST-SRM-1633b, was used as a standard, and IAEA - Soil 7 trace elements in Soil were used as check samples in all the analyses. The samples and the standard were dried in an oven at 100 °C for 24 h and stored in desiccator until weighing. About 100 mg of the samples, and the standards, were weighed into polyethylene bags and covered with aluminium foil. Groups of the samples and the reference material were packed in aluminium foil and irradiated in the swimming pool research reactor, IEA-R1m, from the IPEN-CNEN/SP, at a thermal neutron flux of about 5×10^{12} n cm^{-2} s^{-1} for 8 h. The spectra of γ-rays were obtained after 7 and 25 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 Canberra MCA (Munita et al., 2001). The results for the three feldspars are summarized in Table 1.

X-ray fluorescence (XRF) analysis was carried out on one portion of each sample, using a Philips FRX spectrometer, model PN 2.400 with Rh anode and 3 kVA of power; the standard material used was JG-1a. The mean molecular compositions of orthoclase, albite and anorthite in terms of percentage were calculated using the chemical analysis results shown in Table 2. We obtained the following compositions: $Or_{86.99}Ab_{12.97}An_{0.04}$ for FELW, $Or_{87.63}Ab_{12.33}An_{0.04}$ for FELG and $Or_{81.36}Ab_{15.45}An_{3.19}$ for FELP.

All the ESR spectra were taken at RT and 77 K, below saturation, by means of the homodyne X-band VARIAN E-4 spectrometer with 100 kHz magnetic field modulation, a microwave power of 20 mW and a TE_{011} mode cavity. The modulation amplitude used was 2.5 G peak-to-peak and the scan speed was 4000 G in 480 s for RT measurements and at 77 K it was 2.0 and 100 G in 60 s, respectively.

TL glow curves were measured in an oxygen-free nitrogen atmosphere using a Daybreak Nuclear and Medical Systems Inc., Model 1100-series and the heating rate used was 10 °C/s. TL measurements were taken in the UV (290–370 nm) and the VIS (340–610 nm), using optical filters Schott U-340 and Schott BG-39, respectively.

For ESR, TL and IRSL the specimens were carefully ground with a mortar and pestle, and the fraction between 88 and 180 μm was selected. The selected grains were treated with 10% HCl for 10 min, in order to reduce spurious TL. Then they were washed extensively with distilled water and subsequently with acetone. All the γ-ray irradiation was performed at RT with a ^{60}Co source and the distance of the sample from the source was changed depending on the required dose, for low doses from 5 to 10 Gy the dose rate was 0.0546 kGy/h, for the dose range of 20 to 1 kGy it was 0.3906 kGy/h and for the range 4–10 kGy, 4.1 kGy/h.

3. Results and discussion

From Table 1 we note that rare-earth elements such as La, Ce and Eu, were able to be detected by NAA. These elements can improve the luminescence intensity by replacing Al and Ca in the crystalline lattice. Some transition metals, such as Fe and Co, were also found; these substitute Si or Al. It was also observed that FELP has a high concentration of iron compared to FELW and FELG. Complementary results for trace elements as Ba, Ca, Ga, etc. are shown in Table 3. It was noted that the differences between the concentrations of some elements as detected by NAA and XRF could be the result of sample inhomogeneities. The chemical results obtained are similar to those reported by Kirsh et al. (1987) and Tatumi et al. (2005).

Fig. 1(a) shows typical natural TL glow curves obtained in the UV, showing peaks at 283, 290 and 293 °C for FELG, FELW and FELP, respectively. For the VIS region measurements, the TL peak temperatures were displaced a few degrees (Fig. 1(b)). We could identify peaks at 293 and 285 °C for FELG and FELW, respectively; for FELP two TL peaks were observed at 298 and 389 °C (see Figs. 1(b) and (d)). The occurrence of two peaks in natural TL glow curves, in the VIS region, has been seen for another microcline feldspar sample, that contained a high iron concentration (about 182×10^3 ng/g) (Tatumi et al., 2005). A relatively high Fe_2O_3 concentration was found in FELP (Table 2), indicating that iron may be related to the emission of the 389 °C TL peak.

The TL emitted in the UV region by samples irradiated after previous heat treatment at 480 °C for 10 min showed only one peak at around 194 °C (Fig. 1(c)). This peak increased with increasing doses up to 1 kGy; above this dose, the saturation of the photomultiplier tube occurred in normal measurements. However it was noted that TL intensity continued to increase after 1 kGy, when detecting the TL with an additional neutral density filter between the sample and the PMT. The TL emitted in the VIS region showed a similar response to those for UV (e.g. Fig. 1(d)).

Fig. 2 shows the IRSL response for γ-irradiated samples after previous heat treatment (480 °C for 10 min), FELG (Fig. 2(c)) and FELP (Fig. 2(b)) gave a linear growth over the given dose range (5–10^3 Gy). FELW showed a linear increase in the low-dose interval and supralinearity in the dose range of 20 to 10^3 Gy, approximately (Fig. 2(a)).

The ESR results showed two prominent signals with g values about 1.95–2.05 and 3.6–4.0, (Fig. 3). Speit and Lehmann (1982) cited these signals as Ti^{3+}, Al^-–O^-–Al and Fe^{3+} centre (FeO_2^{2-} model, orthorhombic crystalline field), respectively. The Ti^{3+} centre is the only electron centre that we could verify in this work.

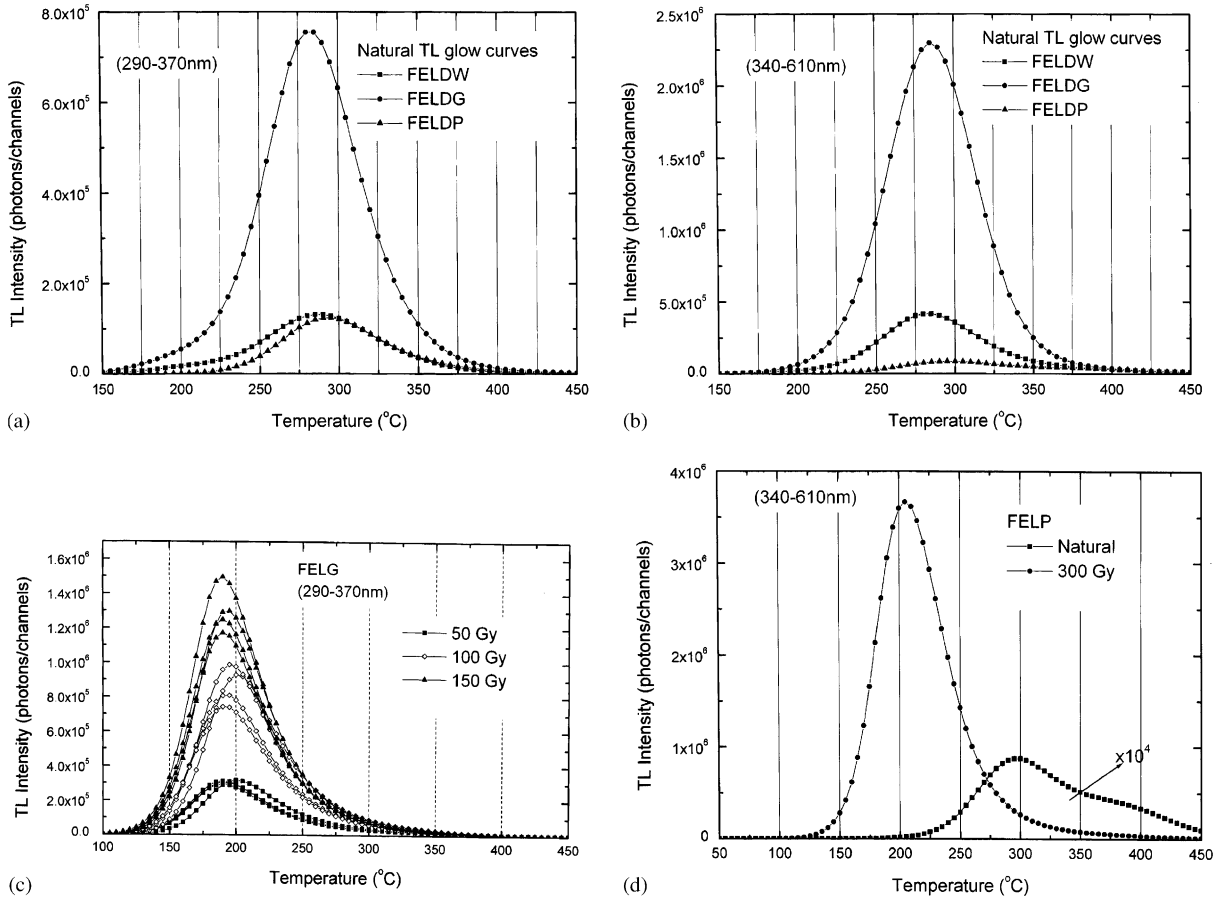

Fig. 1. Examples of TL glow curves of feldspar: (a) natural samples of FELP, FELW and FELG measured in the UV; (b) natural samples of FELP, FELW and FELG measured in the VIS; (c) irradiated samples of FELG in the UV; and (d) natural and irradiated samples of FELP in the VIS.

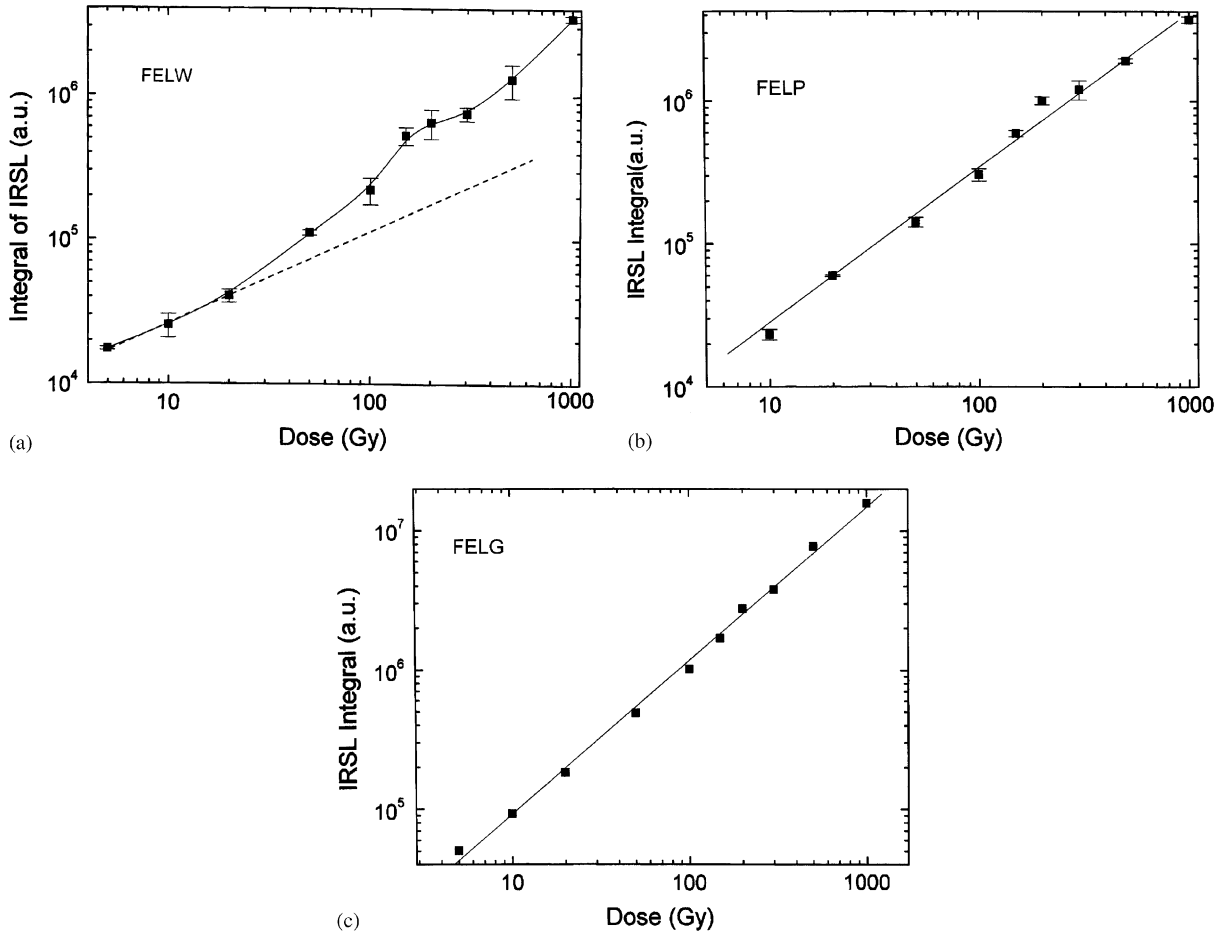

Fig. 2. IRSL growth curves for: (a) FELW, supralinear growth after 20 Gy approximately; (b) FELP, linear growth; and (c) FELG, linear growth.

From Fig. 3 we observed a decrease in all the Fe^{3+} signals when the samples are irradiated with high doses (200–10 × 10^3 Gy). For FELW the Al centre was detected in greater detail scanning slowly from 3.180 to 3300 G (Fig. 3(a)) and an increase in the Al-centre intensity with dose was noted. FELP gave very weak Al-centre signals that become almost constant with the dose. However, FELG gave Al centres with additional signals, may be due to Ti^{3+}; these signals increased up to 300 Gy and decreased for higher doses (Fig. 3(c)).

Only for FELP we noted a new signal with $g = 2.5$, when the sample was irradiated with doses higher than 10^3 Gy, approximately. This signal can be related to the Fe^{3+} centre, in the FeO_4^{5-} model found in a cubic crystalline field (Speit and Lehmann, 1982; Ikeya, 1993), indicating a distortion in the crystalline field due to exposure to high doses of radiation.

It was observed that Al-centre intensities decayed slowly when the samples were heated at high temperatures (100–400 °C), whereas the Fe^{3+}-centre intensities remained almost constant for FELW and increased for FELP. The last sample has a high Fe concentration and exhibits a broad Fe^{3+} signal at $g = 4.049$, suggesting that the heating improved the formation of the clusters of magnetically interacting Fe^{3+} ions.

4. Conclusions

TL measurements were taken in the UV (290–370 nm) and the VIS (340–610 nm) regions of the spectrum. The UV region showed the following peaks: for natural samples TL peaks at 283, 290 and 293 °C for the grey, white and pink crystals, respectively; for samples irradiated after prior heat treatment, a TL peak around 200 °C was found for all the samples. The VIS region results were similar to those in the UV.

ESR measurements showed Fe^{3+}, Al–O^-–Al and Ti^{3+} centres in our samples. The Fe^{3+} centres decreased with the irradiation. For FELP we observed the formation of another signal with $g = 2.579$ related to Fe^{3+}, with FeO_4^{5-} model found in cubic crystalline field; this sample contains a high concentration of iron.

The Al–O^-–Al centre increased with the irradiation in the case of the FELW, became almost constant for FELP, and for FELG the signals increased up to 300 Gy and decreased for higher doses.

The samples showed similar TL behaviour, suggesting that the centres related to TL emission should be associated with ions that compose the crystalline lattice; following this as-

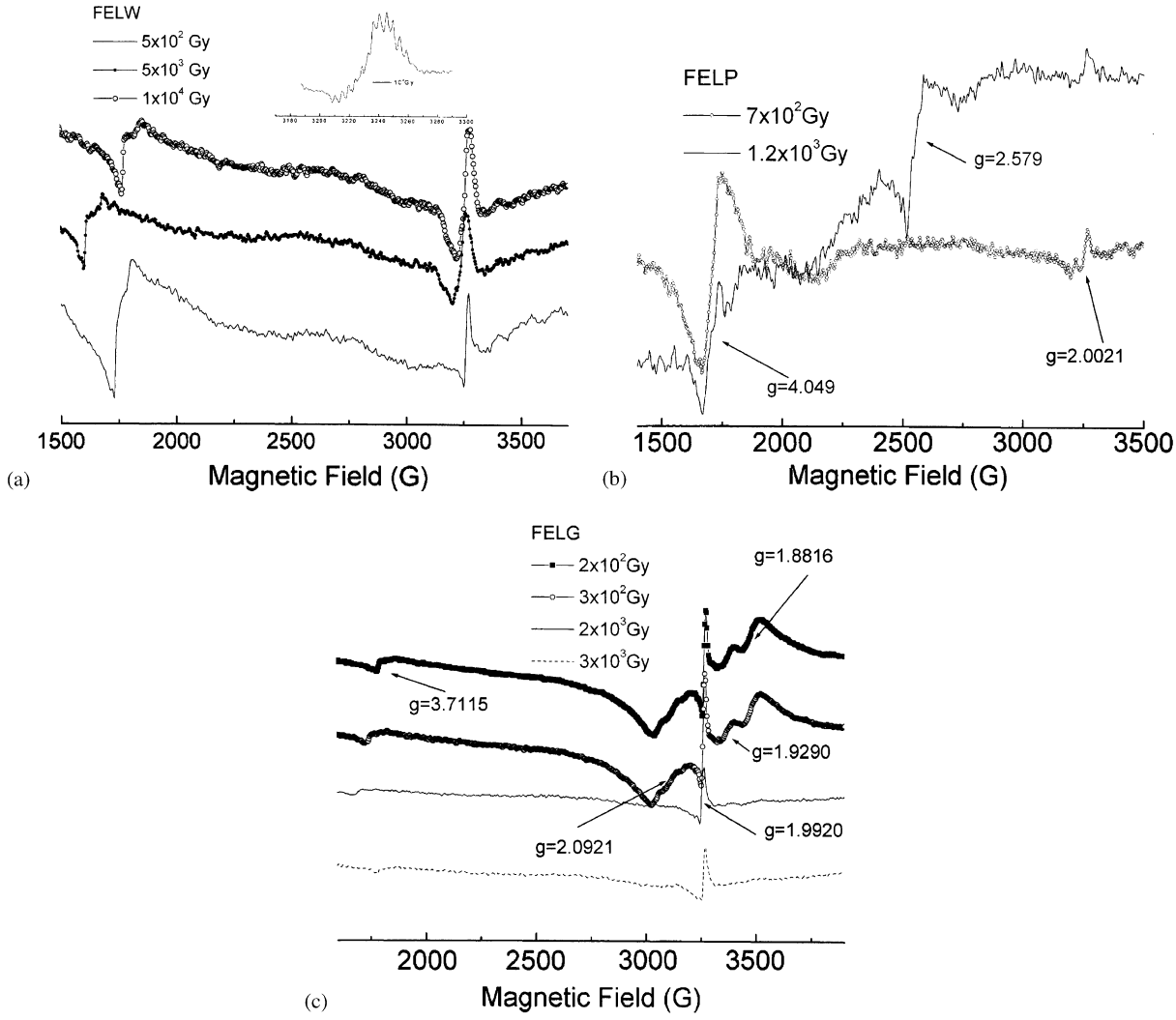

Fig. 3. ESR spectra of (a) orthoclase sample with Fe^{3+} and Al–O^-–Al centers; (b) microcline feldspar with Fe^{3+} and Al–O^-–Al and (c) microcline sample with Ti^{3+} center.

sumption, we can select the Al centres. Kirsh et al. (1987) associated emissions at 450–480 nm and at 500–560 nm with radiative recombination between thermally released electrons with Al–O^-–Al and Al–$O^- \ldots M^{2+}$ (M = Zn, Mg, Mn), respectively. Another model that used the Al centre was proposed by Mittani et al. (1999), they explained the emission of the 310 °C TL peak as follows: during irradiation the electron is released from an Al–O^{2-}–Al centre, and is trapped in Fe^{3+}, forming Fe^{2+} ion; subsequently during the reading of the TL the electron is thermally released from Fe^{2+} and recombines with the Al–O^-–Al centre emitting TL. We believe that this model cannot explain all the TL emission of our feldspar samples, particularly those that do not contain high Fe concentration; additional TL and emission spectra experiments needs to done.

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