

Luminescence characterization of a sodium rich feldspar

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We herein report on the radioluminescence and thermoluminescence properties of a Sodium rich feldspar ((Na,K)[AlSi₃O₈]) with a mean molecular composition of orthoclase (Or) and Albite (Ab) of Or₁Ab₉₉. Despite the complexity of the luminescence emissions of the sample, it is possible to determine six different emission bands at about 300, 380, 420, 460, 550 and 680 nm. The 300 nm emission can be associated to structural defects related to the recombination process in which the diffusion of Na ions is involved. The UV-blue emission bands have the following features: (i) the 380 nm, typical of mineral phases containing SiO₄ groups, is related to intrinsic defects in the lattice; (ii) the 420 nm band is associated to the presence of Cu (II) ions close to the hole traps or the recombination on a centre formed from a hole-Oxygen atom adjacent to two Aluminium atoms (Al-O-Al) and (iii) the 460 nm waveband is due to the presence of Ti⁴⁺. The green and red emissions are respectively associated to the presence of Mn²⁺ and Fe³⁺ ions. The ratio between the relative intensities, peaked at 290 (the more intense waveband) and 550 nm is about 10 for both TL and RL, which implies that the efficiency of recombination centres does not change regardless of the type of the process.

Keywords: Radioluminescence, Thermoluminescence, Na-rich feldspar, spectral emission.

1. Introduction

Both radioluminescence (RL) and thermoluminescence (TL) emissions from mineral phases are usually employed in luminescence dating [1,2], retrospective dosimetry [3], material characterization [4] and detection of irradiated food [5]. Among them, quartz and feldspars are suitable materials since they exhibit (i) sensitivity to radiation, (ii) high reproducibility of the luminescence response, (iii) good dose-luminescence linearity in the ranges of interest (up to 100 Gy) and (iv) high stability of the luminescence signal after long time of storage [3]. In addition, they are ubiquitous not only in nature, but also as a part of man-made objects (e.g. electrode coatings [6]) and appear as a reasonable alternative to the conventional dosimetric systems, if necessary. Basically, TL provides information about the trapped charge recombination sites related to metastable defects inside the lattice that depend on the trapping-detrapping processes during the heating readout. For this purpose, one assumes that the lattice structure and the luminescence spectrum do not change significantly in the temperature range where the charge is released from a particular deep trapping level [1]. RL with x-rays is a sensitive method for obtaining information about the efficiency of recombination centres rather than shallow traps [7]. All the properties involved in the luminescence phenomena (i.e. lifetime, efficiency, emission spectra, etc.) depend directly on the crystalline phase, which is mainly influenced by pressure and temperature. Thus, small changes in the lattice structure due to the presence of inclusions, impurities, substituted ions or surface defects in ppm concentrations reveal changes in the intensity and wavelength position of the emission spectra.

This research focuses on the study of the RL and TL spectra of a well-characterised Sodium rich feldspar in the range of 200-800 nm.

2. Materials and Methods

a) Sample characterization

Measurements were carried out on a natural Albite sample collected in Minas Gerais, Brazil (Fig 1). The sample, a Sodium rich feldspar ((Na,K)[AlSi₃O₈]) with a mean molecular composition of Orthoclase (Or) and Albite (Ab) of Or₁Ab₉₉, has been elementary analysed by x-ray fluorescence (XRF) using a PHILIPS PW-1404 with an Sc-Mo tube with analyser crystals of Ge, LIF220, LIF200, PE and TLAP. A Super-Q manager (Panalytical-Spain) was used as the analytical software (Table 1). Three pellets of 8 g of milled sample with 0.1 g of an acryl type resin (Elbacite 2045, produced by E.I. Dupont de Nemours Co., Ltd.) were pressed under $2 \cdot 10^4$ kg (about 2000 kg/cm²) and dried at 40°C in an atmospheric chamber. Trace elements were analyzed by a Finnigan MAT SOLA (Finnigan MAT, Bremen, Germany) plasma source mass spectrometer (ICP-MS). Each sample was introduced into 27.12 MHz argon plasma using a Meinhard concentric nebulizer and a Gilson Minipuls 2 peristaltic pump. The instrument was calibrated using pure NIST traceable single-element stock solutions, supplied by Alfa Products Ltd., (Karlsruhe, Germany) (Table 2).

b) Luminescence measurements

Luminescence spectra were obtained from cleaved chips of 3x3x2 mm³ (~5 mg) of eight aliquots of the Albite sample mounted with silicone oil onto Aluminium discs using the spectrometer of Sussex University. The samples were not mechanically treated to avoid triboluminescence processes [8]. Signals were recorded over the 200-800 nm wavelength range, with a resolution of 5 nm for 100 channel spectra, and 3 nm for 200 channel spectra. All signals were corrected for the spectral response of the system. The RL was obtained during excitation of the samples with 50Gy of x-rays employing a Phillips MG MCN 101 x-ray tube with a current of 15 mA and a voltage of 25 kV delivering a dose rate of 10 Gy·min⁻¹ to the sample. TL measurements of mineral coatings were made in the Sussex (UK) TL

spectrometer. High sensitivity results from the use of wavelength multiplied detection via a pair of spectrometers, with gratings blazed for the UV-blue (200nm-450nm) and blue-green-red (400nm-800nm) parts of the spectrum, and a pair of position-sensitive photomultiplier tubes [9]. Signals were recorded over the wavelength range 200nm to 800nm, with a resolution of 5nm for 100 channel spectra, and 3nm for 200 channel spectra, and all signals were corrected for the spectral response of the system. Because of second order diffraction, signals beyond 780nm are artifacts of the apparatus if there are also strong signals near 390nm. Sample processing and measurements were made under red light to avoid the transfer of the trapped electrons from the semi-stable sites into hole centres (including luminescence centres) due to light sensitivity. The experimental spectral data of the RL and TL analyses were fitted with six multiparameter gaussian functions using the Peak Fit program (supplied by Jandel Scientific Software).

3. Results and Discussion

As illustrated in Fig 2 and 3, the TL and RL spectra obtained from the Albite samples in the range of UV-IR exhibits a very complex structure that can be deconvoluted into six overlapping Gaussian peaks. The number of peaks has been chosen based on the following three criteria: (i) the first derivatives of the intensity with respect to the wavelength ($dI/d\lambda$) are zero, (ii) the value of the correlation coefficient that mathematically indicates the quality of fitting (Table 3) is a maximum, and (iii) it is possible to assign to a given emission a physical meaning. In this sense, it is possible to identify six emission bands peaked at 300, 380, 420, 460, 550 and 680 nm in both TL and RL, which indicate that regardless of the luminescence process involved, they have a common origin.

The TL and RL spectra of all the analysed samples (four spectra each) displays a similar behaviour, namely the emission peaked at 300 nm is the more intense waveband. The intensity of this maximum is ten times higher than that of the green emission, the second waveband in intensity and is more than 80% of the relative intensity. This fact can be appreciated in Table 3, where the parameters for the fitting procedure, peak numbers, energy values (in eV) and the corresponding standard deviations 1σ (SD) are shown. The uncertainties represent the precision (1σ) of the mean value of the luminescence response of four replicates each and all the analysed parameters (i.e. position, width, integrated area and relative intensity of the peaks) were refined to a confidence limit of 95% accuracy using an iterative process. This UV band is related to defect-sites associated with the presence of the Sodium atoms in the Potassium aluminosilicate lattice [10, 11]. This maximum is the most important signal in Na-rich feldspars and is potentially useful for retrospective dosimetry [12]. The 380nm UV emission band is characteristic of mineral phases containing SiO_4 groups (quartz and silicates) and can be related to intrinsic defects in the lattice [10,13]. This waveband is a well-studied emission and is observed when interstitial alkalis lay in adjacent positions to aluminium ions; it can be also employed in the fields of UV-dosimetry [14,15] and retrospective dosimetry [12]. The 430nm emission (common to several feldspars with different chemical compositions and variable Al/Si order) can be due to either to the recombination on a centre formed from a hole-oxygen atom adjacent to two Al atoms (Al-O-Al) [16] or to the presence of Cu (II) ions placed next to the hole traps [17], detected in this sample in amounts of ppm (6 ppm). Finally, the 480nm band can be assigned to the presence of Ti^{4+} [13] (0.09% in this sample). In the first case, the minor changes detected can be mainly associated with the modifications in other peaks, rather than to structural changes (displacements of the atoms due to the presence of vacancies or impurities) in recombination centres (Al-O-Al). The green band at 550nm is quite common in all strain-free alkali K-

aluminosilicates; being attributed to Mn^{2+} substitutions in Calcium sites in the lattice, both in natural and synthesized feldspars. This band seems to be characteristic of a d^5 electronic configuration [18]. According to the chemical analysis, the content of Mn^{2+} is 0.02% in the sample here studied. The 680nm waveband is produced when the irradiation reduces some Fe^{3+} into Fe^{2+} impurities [19]. In the aluminosilicate lattice, some Si (tetrahedrally coordinated) or Al sites can be substituted for Fe^{3+} , acting as recombination sites either for holes or electrons. When Fe^{3+} is placed on the T_1 site (in ordered feldspars) the emission is produced in the visible red region, but if it is included in a disordered lattice the emission is in the IR region [20]. T_1 is one of the four-membered rings of tetrahedra parallel to the (100) plane in an Albite structure. For this reason, it should be possible to associate the position of this emission band with the structural state of feldspar.

4. Conclusions

Similarly as in other alkali feldspars, the emission spectra bands of a well-characterised Na-rich feldspar here studied exhibit emission bands at 300, 380, 420, 460, 550 and 680 nm that can be attributed to structural and point defects. Thus, the emission peaked at lower wavelengths (290nm) is associated to structural defects located in the twin-domain boundaries related to the recombination process in which the diffusion of Na ions is involved. The UV-blue emission waveband have these properties: (i) the 380 nm is characteristic of mineral phases containing SiO_4 tetrahedral and is related to intrinsic defects in the lattice; (ii) the 420 nm band is linked to the presence of Cu (II) ions placed next to the hole traps or the recombination on a centre formed from a hole-Oxygen atom adjacent to two Al atoms (Al-O-Al) and (iii) the 460 nm waveband is due to the presence of Ti^{4+} . The low intensity green and red emissions are associated, respectively, to the presence of Mn^{2+} and Fe^{3+} ions. The

multiple emission spectra described by six dominant wavebands for Albite show that the same recombination centers are active independently of the applied process: TL or RL.

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6. References

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Table 1. Chemical composition of the analysed albite by x-ray fluorescence. Measurement is expressed in terms of oxide since the sample is prepared in oxidizing atmosphere.

SiO ₂	TiO ₂	Al ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Fe ₂ O _{3t}	Lost Ignition
67.63	0.09	19.52	0.02	>0.01	0.17	11.38	0.30	0.14	0.06	0.48

Table 2. Concentration of the impurities (in ppm) in the albite sample measured by ICP-MS.

Rb	Ba	Sr	La	Ce	Y	Th	Cu	Cr	Mn	Ni
258	22	---	5	2	11	8	6	---	19	---

Table 3. Physical parameters estimated from TL and RL spectra obtained from the analyzed Na-rich feldspar. The curves were fitted by a sum of six Gaussian curves.

		Peak Number						
TL	1	2	3	4	5	6	r	
Position (nm)	295±6	371±8	417±9	460±9	556±5	693±10		
E (eV)	4.21±0.09	3.34±0.07	2.97±0.05	2.70±0.04	2.23±0.03	1.79±0.03		
Intensity (a.u.)	466±21	19±2	12±3	6±2	24±3	8±2		
Intensity (%)	87±2	3.6±0.3	2.2±0.5	1.1±0.2	4.5±0.3	1.5±0.2	0.992	
Area	17822±685	1277±91	532±69	237±43	1937±160	1040±113		
Area (%)	78±3	5.6±0.4	2.3±0.3	1.1±0.2	8.5±0.7	4.6±0.5		
FWHM*	36±3	62±4	41±6	36±4	75±9	125±10		
RL								
Position (nm)	297±8	372±9	419±9	459±16	552±6	681±10		
E (eV)	4.18±0.11	3.33±0.08	2.96±0.06	2.71±0.10	2.25±0.03	1.82±0.03		
Intensity (a.u.)	353±11	24±3	16±3	9±3	30±3	7±3		
Intensity (%)	80±2	5.5±0.7	3.7±0.5	2.1±0.6	6.7±0.7	1.7±0.6	0.995	
Area	13819±584	1318±188	761±190	369±117	2317±193	842±98		
Area(%)	71±3	7±1	4±1	1.9±0.6	12±1	4.3±0.5		
FWHM*	37±2	51±4	44±6	37±5	74±10	104±10		

* FWHM means Full Width at Half Maximum and r is the correlation coefficient of fitting of the sum of six Gaussian curves.

Figure 1.- Natural albite ((Na,K)[AlSi₃O₈]) sample.

Figure 2.- TL emission of albite fitted with six multiparameter gaussian functions. The dashed lines correspond to the calculated fitted gaussian peaks, which make up the calculated fitted solid line. The encircling line is directly compared with the experimental dotted line that corresponds to the mean value of the experimental results.

Figure 3.- RL of the analysed Na-rich feldspar fitted with six multiparameter gaussian functions. The dashed lines correspond to the calculated fitted gaussian peaks, which make up the calculated fitted solid line. The encircling line is directly compared with the experimental dotted line that corresponds to the mean value of the experimental results.



3 cm



Intensity (a.u.)



