Luminescence Spectra of Alkali Feldspars: Influence of Crushing on the Ultraviolet Emission Band

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LUMINESCENCE SPECTRA OF ALKALI FELDSPARS: INFLUENCE OF CRUSHING ON THE ULTRAVIOLET EMISSION BAND

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ABSTRACT

Grinding and milling processes lower the intensity of the ultraviolet emission band of alkali feldspars. The luminescence spectra of aliquots of natural transparent adularia from Saint Gothard, Switzerland, that were crushed at different energies, show the irreversible collapse of the UV 290 nm peak. Simultaneously, the 390 nm blue emission increases in accordance with the milling treatment, which reduces the presence of ionic charge compensators (Na$^+$) and sensitizes the structure (producing [AlO$_4$]$^\circ$ centers).

The annihilation of the 290 nm UV peak by crushing could be linked with cracks-strain-exsolution features of the lattice of adularia. For this reason, the use

of this 290 nm peak and energetic milling treatments in dating and dosimetric routines, should be rejected.

INTRODUCTION

The introduction of intrinsic defects by mechanical grinding and milling in natural minerals, such as natural calcite, produces new TL peaks or selectively enhances some glow peaks[1-2]. Spectroscopic techniques linked to luminescent methods have been used to study synthetic materials such as salicylate, chloride salts and europium beta-diketonates.[3-5] Luminescence techniques are commonly used in retrospective and environmental dosimetry, archaeological and geological dating and detection of irradiated foodstuffs. Feldspar minerals are essential in these luminescence techniques because they make up approximately 70% of the Continental Earth's Crust, alkali feldspars are almost always present in plutonic, metamorphic and detritic rocks. The standard thermoluminescence (TL) method is based on the emission of light from a solid when it is heated after being irradiated under alpha, beta and gamma irradiations.

The luminescence signal is detected by photomultiplier tubes and is recorded as a function of temperature and/or wavelength. The luminescent intensity and the shape of the glow curve depend on the trapping parameters associated with the impurities and defects involved in addition to the radiation dose and the heating rate. Radioluminescence (RL) is a method based on the luminescence emitted from a material at the same time as an irradiation process using nuclear radiation (γ-rays, β-particles, X-rays, etc)[6]. The grinding and milling of samples alters the temperature position and intensities of the UV-blue spectra emissions of alkali feldspars. Adularias ($KAlSi_3O_8$) at different degrees of grinding and milling (block, mortar, mill) have been characterized here by TL and RL to match changes in the spectral emissions.

EXPERIMENTAL

Measurements were carried out using natural white and clean adularia samples (K-feldspar) from Saint Gothard Switzerland. The sample of adularia (ASGS) was selected from a set of well-characterised adularias from the mineral collection of the Museo Nacional de Ciencias Naturales (Madrid, Spain). Different chips sliced in blocks (3x3x2.1 mm), carefully powdered aliquots in agate pestle and mortar (50-75 μm) and milled mechanically up to less than 10μm were prepared. The ASGS lattice at room temperature was studied under X-ray diffraction using a Siemens D-5000 automated diffractometer with CuK_α radiation. The patterns were obtained by step scanning from 2° to 64° 2θ in steps of 0.020°, with a count of 6 s per step. Spectral measurements of natural ASGS samples were made using the Sussex 3D TL spectrometer[7]. Signals were recorded over the 200nm-800nm wavelength range, with a resolution of 5nm for 100 point spectra, and 3nm for 200 point spectra, and all signals were corrected for the spectral response of the system. The X-ray unit tube was a Phillips MG MCN 101 X-ray tube with a current of 5mA and a voltage of 5kV delivering a dose rate of 10 Gy min^{-1} to the sample. RL was recorded during excitation and then the samples were heated to 400°C at 2.5°C s^{-1} while the TL spectra were recorded in N_2 atmosphere. Aliquots of 5.0±0.1 mg each of adularia were used for each measurement. Sample processing and measurements were made under red light.

RESULTS AND DISCUSSION

The chemical composition (by atomic absorption) of the studied adularia sample is SiO_2 64.00%, Al_2O_3 18.03%, Fe_2O_3total 0.04%, CaO 0.12%, Na_2O 1.18%, K_2O 15.80%, P_2O_5 0.01% and ignition loss 0.61%. This K rich feldspar by XRD displays a Al/Si order of 0.829 and S_2 (~triclinicity) of 0.011. The small

content of Na_2O agrees with the exsolved Na phase detected under electron microprobe. It is well known that the luminescent properties of some materials can be altered under pressure (i.e. crushing or grinding). In fact, in grains subjected to frictional effects a tribo-thermoluminescence effect can appear. Therefore, to erase the luminescence contribution of charges on the surface of the grain that could be created as a consequence of the grinding and milling processes, powdered samples were placed in ethanol solution for 5 minutes.

Figure 1a shows isometric plots (TL intensity in a.u. -arbitrary units- vs. temperature in °C vs. wavelength in nm) of natural TL glow curves (signal recorded from non-irradiated samples) for distinct crushed ASGS samples. The three ASGS samples display no differences in spite of the mechanical pretreatment. In all the cases, one broad band from 600 - 700 nm could be observed (Fe^{3+} point defects) which is in agreement with the 0.04% Fe_2O_3 total from the chemical analysis. However, when these three samples were exposed to 50 Gy of beta radiation, some changes in the luminescent response could be appreciated (Fig 1b). ASGS adularia, in concordance with its X-ray diffraction report (structure of sanidine) shows a characteristic spectra TL emission of volcanic sanidine which includes a broad band around 400nm. In addition, the 3D TL plot of the X-irradiated adularia (50 Gy) displays a weak UV 300nm emission band, typical of alkali feldspars in which sodium is present as $NaAlSi_3O_8$ phase or containing interfaces between $KAlSi_3O_8$ and $NaAlSi_3O_8$ phases.

In contrast with the ASGS block signals, a decrease in intensity of the TL signal of over 30% in powdered samples, in the 300-350nm spectral region, (31% for the 50-75μm portion and 39% for the lower than 10μm samples) can be observed (Fig 2a). Similar results were obtained for RL measurements, although the decrease of the signal is less significant, about 20% and 30% for the 50-75μm portion and <10 μm portion respectively, in comparison with the block signal (Fig 2b). This reduction in TL intensity is probably linked with the absorbed dose which decreases along with the grain size during the irradiation process. The
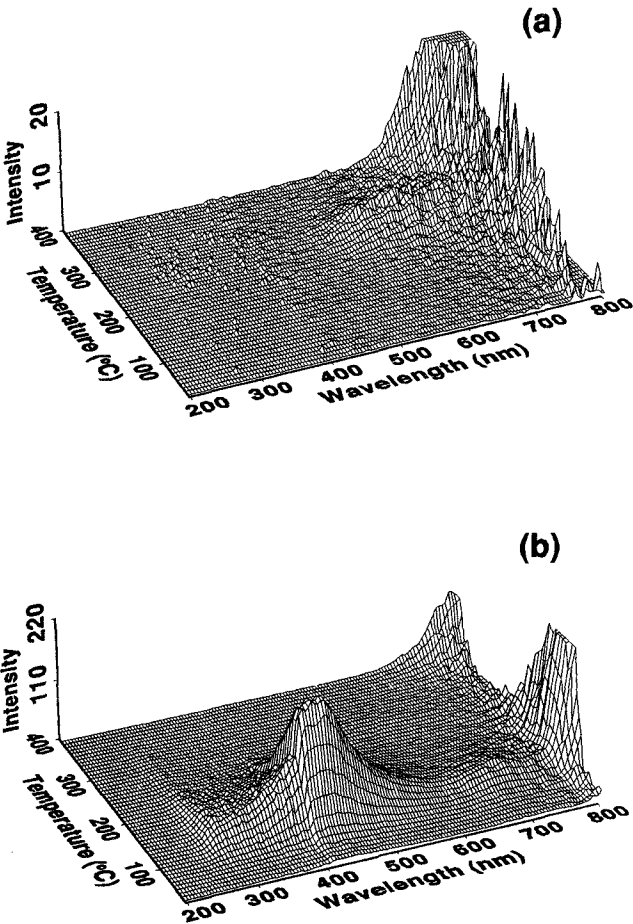
FIG 1.- Thermoluminescence spectra (TL intensity in a.u. -arbitrary units- vs. temperature in °C vs. wavelength in nm) analysis of a transparent adularia from Saint Gothard (Switzerland). a) The three different samples (mortar, mill, block) only display a weak signal around 600-700 nm (Fe^{3+} defects) natural thermoluminescence. b) The three different samples (mortar, mill, block) display very similar 3D TL signals after being X-irradiated with 50Gy.

(a)
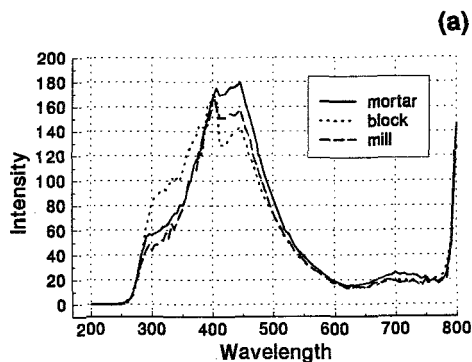
FIG 2a.- Slice at 150°C of the spectra thermoluminescence plot of the adularia after 50 Gy of X-irradiation. Curves have been normalised at 401nm to compare the UV and Blue spectra regions. The decrease of the UV emission band is linked with the increase of the crushing energy.

(b)

FIG 2b.- Radioluminescence at 10 Gy/minute at room temperature of adularia (188 acquisition data). Curves have been normalised at 401nm to compare the UV and Blue spectra regions. The decrease of the UV emission band is also linked with the increase of the grinding and milling energy. However the blue band shows a different behavior.

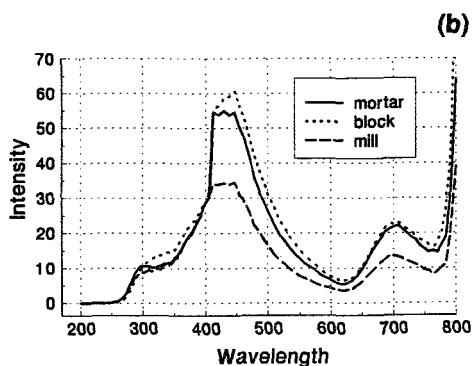electron-hole mechanisms which explain the UV-blue luminescence emissions (380 nm) from alkali aluminosilicate structures (e.g., quartz) have been studied by Martini et al. (1995). Martini's theory says that prolonged high-temperature annealing reduces the presence of ionic charge compensators (in adularia Na^+ and less K^+) and sensitizes the structure which increases its blue emissions during radioluminescence and thermoluminescence after short irradiations. The Al^{3+} ion is commonly present substituting Si^{4+}. For local charge compensation, a positive charge is needed; an alkali$^+$ ion, a H^+ ion or a trapped hole are therefore present. The resulting centers are $[AlO_4/alkali^+]$, $[AlO_4/H^+]$ and $[AlO_4]^°$. Martini et al. (1995) attribute the blue emissions to 380 nm centers because electrodiffusion in hydrogen atmosphere eliminates this 380 nm band (H^+ recombines with the $[AlO_4]^°$ holes). In the case of the feldspars studied here, the $[AlO_4/alkali^+]$ and $[AlO_4]^°$ centers are coupled during the thermal self-diffusion processes through the bulk and interfaces; a specific number of electron-holes are necessary for the atomic transport of alkalis. The production-annihilation of luminescent $[AlO_4]^°$ centers can be analyzed in terms of ionic self-diffusion.

In the other part of the spectral region of the curve, from 350nm to the infrared region (over 800nm) and in the UV region (under 300nm), some changes of behavior of the TL and RL measurements are detected for block and ground and milled ASGS. However, a large difference (~45%) in the RL intensity over 400nm has been found for the milled sample. This behavior is probably due to the hard crushing treatment. In addition, the dispersion of the TL responses does not change significantly when the grain size varies. This result allows the use of powdered alkali feldspars in studies involving luminescence emissions from the 390 nm emission band. This is common to many feldspars species[8]. and its easier handling makes the cutting of chips unnecessary.

The geological hydrothermal origin of this adularia provides a double structural character. On the one hand, by XRD they can be defined as sanidine or annealed strain-free feldspars, however, the weak 290nm spectra emission

denotes a configuration of strained coherent exsolved feldspar characteristic of microcline, orthoclase, albite, perthite, etc. The subsolidus exsolution in alkali feldspars (at around 600°C) separates Na and K phases and produces perthites. In cryptoperthite textures, the structures are continuous throughout the lamellar interface and the coherent exsolution involves elastic stresses and strains in the phases. In accordance with a previous paper[9] , the 290nm UV emission has been linked with the presence of $NaAlSi_3O_8$ phases in the sample and shows a multiorder kinetic glow curve which can be interpreted as a dynamic continuous trapping-detrapping process during the luminescence measurements. At the same time as grinding and milling thermo-mechanical self-diffusion processes of alkali ions occurs which most probably escape along the planar defects. The atomic transport along interface-interphases destabilises the metastable equilibrium of the twin-domains and unmixed phases.

In addition to its thermolabile irreversible character[10], the 290nm spectra emission could also denote a mechanolabile irreversible configuration for the strained coherent exsolved alkali feldspars. These UV emissions present clear mechano-luminescence (ML) characteristics such as strain-rate, temperature, crystal-size, defect center density, etc [11-12]. The ML decay is related to the stress relaxation of lattices, the increase of grinding energy drops the 290nm peak while it increases the 420nm broad band. This ML hypothesis for the UV emissions (i.e. 290nm) agrees with both the classic background of fracture mechanics of rocks[13] and the mineralogy of perthitic feldspars. A credible hypothesis could link the 290nm UV emissions with the presence of Na atoms in the interfaces. This hypothesis can consider several associate mechanisms as follows: a) Thermoinduced alkali self-diffusion produces mass transport which can be the dominant mechanism for subcritical crack growth[14], b) Ion exchanges can facilitate crack extension, c) Na and K atoms are very different in size and a considerable strain is experienced in the Na/K exsolution interface-interphase, d) Dislocation mobility in aluminosilicates is known to be strongly influenced by

structurally bound alkali[15], e) ground surfaces of adularia adsorb more H$^+$ than leached or annealed surfaces because grinding-induced defects provide additional adsorption sites by weakening and breaking the Si-O and Al-O bonds to make the Si- and Al-surface sites more accessible to protonation. In addition, annealing will drive water from the surface and reduce the number of hydroxyl groups (i.e., $\equiv$Si—OH + HO—Si $\equiv \rightarrow \equiv$Si—O—Si $\equiv$ + H$_2$O). This typical adularia superlattice is composed by polycrystalline KAlSi$_3$O$_8$ micro-domains, however this mechanolabile UV 290nm emission could be explained by its perthitic composition (few NaAlSi$_3$O$_8$ cluster domains). Perthites are twin-domain structures in metastable equilibrium (twin-superstructures), at room temperature, twin-planes are metastabilized by Na accumulations. In these alkali feldspar superlattices the twin density increases with temperature. Slow cooling rates produce more K/Na exsolution and low twin densities. Fast cooling rates provide Na in the twin interfaces and consequently, higher twin densities. This geological frame could explain why pre-heatings and pre-mechanical treatments produce the irreversible collapse of the 290nm luminescence emission. The divergent results of the intensities of the broad band around 400nm could be explained by the complex alkali losses produced during the different thermo-mechanical handling and consequently with [AlO4]$^\circ$ defects[16].

CONCLUSION

The irreversible mechanical collapse of the UV 290nm peak is linked with the degree of grinding and milling and it seems to be conditioned by the cracks-strain-exsolution-twinning features of the adularia lattice. Luminescence analytical routines based on UV spectra emissions should not use crushed samples. The broad band around 400nm characteristic of alkali aluminosilicates remains the best representative region of the spectrum in which to record the luminescent emissions for dating and dosimetric purposes.

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