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Anomalous fading in TL, OSL and TA – OSL signals of Durango apatite for various grain size fractions; from micro to nano scale

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ABSTRACT

Anomalous fading (AF) of luminescence signals has been studied extensively both experimentally and by simulations. This paper reports a new type of study of anomalous fading in grains of Durango apatite, a naturally occurring luminescent material that yields very intense anomalous fading. Grains of Durango apatite were ball milled (BM) for various durations, up to 48 h. Different ball milling durations resulted in different average grain size fractions as low as 200 nm, as it was indicated by Scanning Electron Microscopy (SEM) measurements. The anomalous fading effect was studied for optically stimulated luminescence (OSL), thermoluminescence (TL), as well as thermally-assisted OSL signals (TA – OSL). Anomalous fading was found to be ubiquitous for all luminescence signals, and for all apatite grain size fractions. The anomalous fading rate is weakly affected by the grain size for the cases of OSL and TL, while the TA – OSL signals were found to fade in a much slower rate than either the TL or the conventional OSL signals. An important experimental result is that the fading rate of TA – OSL decreases as the grain size fraction is decreased. For average grain size fractions between 200 and 450 nm, the TA – OSL signal is unaffected by the AF effect. A differential analysis on the TL glow curves showed that the AF rate decreases with increasing temperature along the glow curve, and also with increasing BM time. Finally, a component resolved de-convolution analysis was performed for both OSL and TA – OSL decay curves and recombination lifetimes are reported for both localized and delocalized components. FTIR analysis indicates that the ball milling procedure does not induce a new phase in this material.

1. Introduction

Anomalous fading (hereafter AF) of thermoluminescence (TL) signals is the term adopted for the rapid decay of luminescence at room temperature, instead of the stability expected for it according to standard luminescence kinetic models [1–7]. During the last 20 years, AF has also been studied in optically stimulated luminescence (OSL) and infrared stimulated luminescence (IRSL) signals [2,4–7]. It is now well established [8,9,12] that the AF effect is due to quantum mechanical tunneling, which is an important mechanism for loss of trapped electrons, inducing a source of signal instability in many types of phosphors. This loss of charge can take place directly from the ground state [11], or can be forced via an external stimulus through the excited state of the electron trap [13,14]. Recently Jain et al. [14] proposed a comprehensive model for the latter case, which will be referred to in this paper as localized tunneling recombination (LTR) model. In this model thermal or optical stimulation raises the trapped electrons into a higher energy level, from which they tunnel to the nearest neighbor luminescence center and recombine emitting light. Two important parameters of the LTR model are the trap-to-recombination center distance and a dimensionless parameter termed ρ′, which represents the concentration of the luminescence centers [14]. Kitis and Pagonis [15] quantified the semi-analytical model of Jain et al. [14] by deriving exact analytical expressions for different experimental stimulation modes. Later on, Pagonis et al. [16] obtained approximate expressions for the time development of nearest neighbor distribution during various types of luminescence experiments. Jain et al. [17] have extended their LTR model [14] by introducing Arrhenius analysis, and by analyzing IRSL signals that arise from truncated nearest-neighbor distributions.

Besides feldspar minerals which yield moderate AF, Durango apatite stands as an example of a material exhibiting very strong anomalous

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fading; this mineral has been thoroughly studied as a reference material for AF studies [2,3,18–22]. It was shown that the AF phenomenon is ubiquitous in TL, OSL and IRSL signals of Durango apatite. In this material the AF of TL signals was studied as a function of (a) grain size in the micrometer range, (b) annealing temperature, (c) pre-dose and irradiation temperature, (d) heating rate as well as (e) the occupancy of the recombination sites. These previous detailed studies have provided strong evidence that tunneling is most likely the mechanism responsible for AF in this material [18,19,22,23]. In important recent work, Kitis et al. [20] and Polymeris et al. [3] showed that thermally assisted OSL (hereafter TA – OSL [24]) is a much more stable signal than signals measured at room temperature. These TA – OSL signals arise from much deeper traps [24] in all types of apatites including Durango, and demonstrate a much slower fading rate. TA – OSL provides an experimental way to access the luminescence signal from a number of traps that are thermally inaccessible in typical TL/OSL measurements, where all luminescent materials are heated up to a maximum of 500 °C [25].

The original LTR model [14] has been a major development in this research area, and has contributed in the understanding of tunneling phenomena in a random distribution of electron-hole pairs. The LTR model of Jain et al. [14], via the analytical equations by Kitis and Pagonis [15] has been successfully applied in descriptions of luminescence of feldspars [16,26,27], apatites [3,23], contaminated quartz [28], aluminium nitride ceramics [29], YPO_4 [30], de-proteinated tooth enamel [33], and MgB_4O_7:Dy,Na [31]. Recently, Şahiner et al., [32] have used the same model to study the dependence of conventional, post Infrared IRSL (pIR IRSL) and multi-elevated pIR IRSL (MET pIR IRSL) signals from a pure microcline K-feldspar on the stimulation temperature.

The main purpose of this work is to study experimentally the AF effect as a function of grain size, at the edge between the micro- and the nano-scale.

The specific goals of this work are:

1. To fabricate nanocrystalline powder samples of various sizes, by applying a dry ball milling process on Durango apatite.
2. To quantify the effective grain sizes of the powder samples using Scanning Electron Microscopy (SEM) techniques.
3. To compare and analyze the luminescence signals from these powder samples of different grain sizes, with emphasis on the g-factors which describe the AF.
4. To look for possible changes in the structure of Durango apatite due to prolonged ball milling, by using Fourier Transform Infrared (FTIR) spectroscopy.

2. Experimental procedure

2.1. Sample preparation & Ball milling conditions

The sample used in these experiments was a natural crystal of Durango apatite which is a nearly pure fluorapatite, having the chemical formula $Ca_{9.80}Sr_{0.02}Fe_{0.02}Ce_{0.04}(PO_4)_{5.92}(SiO_4)_{0.04}(SO_4)_{0.06}(F_{1.90}Cl_{0.16})$ [34,35] with a maximum of 3.47 wt% F and of 0.37 wt% Cl [36]. This is the same bulk material that has been previously used in similar reference fading studies [2,3,18–23].

The single piece of monocrystal was crushed gently using an agate mortar and grains of dimensions within the range 100–180 μm were obtained after dry sieving. The grains were annealed at 1000 °C for 1 h, followed by rapid cooling to room temperature; this was selected as the reference grain size fraction. This annealing treatment is necessary to empty all very deep traps, which may have been filled by the natural irradiation of the material. Previous work has shown that this annealing process does not influence the anomalous fading effect in Durango apatite [18]. Aliquots with mass of 7.5 mg each, were prepared by mounting the material on stainless-steel disks of 1 cm^2 area.

In order to achieve grains in the nano-size fractions, the sample was ball milled. Ball milling (hereafter BM) process was carried out inside a Retsch centrifugal ball mill, Pulverisette 6, Fritsch (model S 100). The milling was carried out in oxygen atmosphere, in a cylindrical stainless steel jar of 50 ml, using 7 steel balls of 10 mm diameter each and a rotation speed of 500 rpm. The apatite samples were milled for 0 (reference grain size fraction), 2, 4, 8, 12, 24 and 48 h in dry conditions. The initial ball-to-powder mass ratio was 40:1. The process was interrupted several times and some powder was taken out for examination. The ball milling conditions applied were previously described elsewhere [37]. Ball milling conditions were chosen to avoid the extensive agglomeration that is known to be a major problem for the ball milling of this material. After each BM time, all luminescence measurements were performed on cold-pressed pellets of the same mass, because the ball milled material was very brittle. Pellets were prepared by vacuum pumping, using a $5{\cdot}10^{-3}$ m cylindrical pressing die and 10^9 Pa pressure. The pressing time was 60 min while the mass of each pellet was 35 mg. For the conditions of the cold pressing, the authors could refer to Stathokostopoulos et al. [38].

2.2. Electron Microscopy

The morphology and the grain size distribution after each ball milling duration was obtained using a Jeol 840A scanning microscope with an energy-dispersive spectrometer attached (model ISIS 300; Oxford). Detailed SEM statistics have been applied to better monitor the particle size variation due to the milling process. The beam spot area was of 1 μm in diameter, the accelerating voltage was 20 kV, the beam current was 0.4 nA, the working distance was 20 mm, and the counting time was 60 s real time.

2.3. FTIR spectroscopy

Fourier Transform Infrared analysis was performed with a Bruker FTIR spectrometer, model IFS113v, operating under vacuum. The spectra were collected in the mid-IR region (spectral range between 4000 and 400 cm^{-1}), with 32 scans and a spectral resolution of 2 cm^{-1}. Potassium bromide pellets of 200 mg were prepared -with a 0.5–1% content of the produced apatite grains- and were examined in transmittance configuration. All collected spectra showed substantially low signal-to-noise ratio. All measurements of pellets were performed in the transmittance configuration; a single Durango fluorapatite crystal was also examined in reflectance mode.

2.4. Apparatus and measurement conditions for luminescence

All luminescence measurements were carried out using a Risø TL/OSL Reader (model TL/OSL–DA–20), equipped with a high power blue LED light source (470 nm, FWHM 20 nm) and a $^{90}Sr/^{90}Y$ beta particle source, delivering a nominal dose rate of 0.1083 Gy/s [39]. A 9635QB photomultiplier tube with a Hoya (U-340) blue filter was used for light detection (340 nm, FWHM 80 nm). All TL measurements and heatings were performed in a nitrogen atmosphere with a low constant heating rate of 1 °C/s, to avoid significant temperature lag between the sample heater and the top surface of the sample [40]; TL measurements were performed up to the maximum temperature of 500 °C. The OSL stimulation wavelength is (470 ± 20) nm for the case of blue stimulation, delivering at the sample position a maximum power of 40 mW/cm^2. Both conventional OSL as well as TA – OSL measurements were performed in the continuous wave configuration (CW-OSL), with the power level being software controlled and set at 90% of the maximum stimulation intensity for blue LEDs. TA – OSL was measured according to the protocol suggested by Polymeris et al. [41,42]; the optimum temperature for the OSL measurement that was determined and adopted by Polymeris et al. [3] as well as by Kitis et al. [20] has been used, namely 200 °C.