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Alexandrite: investigation of a natural material for radiation dosimetry

Alexandrite: investigation of a natural material for radiation dosimetry

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Abstract. In this work we performed experimental analyses of the dose-response curves of natural alexandrite, using thermoluminescence (TL) and optically stimulated luminescence (OSL). The natural alexandrite crystals from Bahia, Brazil, were pulverized and the optical absorption measurements were carried out in the range of 200 to 800 nm, comparing a non-irradiated sample with a 10 Gy beta irradiated one. OSL and TL measurements were performed using the Risø equipment (model DA-20) with irradiation doses from 1 to 5 Gy. Glow curve analysis was done using GlowFit software for TL, and R Studio software for OSL measurements. The irradiated sample (10 Gy) shows an absorption spectrum similar to the non-irradiated one, containing the same bands. The samples of natural alexandrite showed a linear dose-response for both OSL and TL measurements. From the TL and OSL analyses, it was possible to infer a correlation between the slow OSL component with the most intense TL peaks of alexandrite.

1. Introduction

Ionizing radiation plays a central role in many activities. We all take advantage of the benefits that ionizing radiation provides especially to medical diagnosis, radiography, and cancer therapy, among other activities. On the other hand, the risk of exposure increases with the expanding use of ionizing radiation [1,2]. Therefore, it is necessary to verify whether irradiation doses delivered to the environment or absorbed by humans are appropriate in each situation. Consequently, it is necessary to develop quantitative methods for the determination of deposited energy by ionizing radiation in a given medium directly or indirectly, a field known as dosimetry [3].

Dosimetric materials are essential for the evaluation of personal and environmental doses, including irradiation doses received in medical, spatial, and industrial activities [4]. Hereupon, natural dosimeters like minerals find application, e.g., in retrospective dosimetry, geological and archaeological dating. Also, natural materials can have a lower cost in production than synthetic ones and may be more readily available in large quantities [5].

Within this context, Brazilian soil is rich in minerals. Many of them have already been investigated from the point of view of geologic and mineralogic properties. However, for most of them, the physical properties have not been investigated. As already reported by some authors [3, 6–9], minerals may present luminescent properties and can be of interest in the dosimetry field. In this work, the potential of natural alexandrite ($BeAl_2O_4:Cr^{3+}$) as an ionizing radiation dosimeter was investigated by thermoluminescence (TL) and optically stimulated luminescence (OSL) measurements. TL and OSL are techniques widely used to determine radiation doses. Both are a type of phosphorescence, defined by the process of stimulation that can be either heat (TL) or light (OSL). Under these conditions, the emission of light is related to previously absorbed energy from sources of ionizing radiation in the form of trapped charged carriers [5, 10].

The alexandrite mineral consists of a variety of chrysoberyl, and its chemical composition suggests a potential application as a dosimeter since it consists of 80.2% Al_2O_3 and 19.8% BeO, which are the only two commercially used materials for OSL dosimeters [5]. Another motivation is the development of functional and low-cost dosimeters, since Brazil is one of the largest suppliers of gemstones in the world, including natural alexandrite.

2. Experimental Procedure.

In this work, natural alexandrite crystals from Bahia State (Brazil) were investigated. Firstly, thermal treatment at 673 K for 2 hours was carried out to extinguish effects of accumulated doses from background radiation. Then, samples were pulverized and sieved by selecting grain sizes on a micrometer scale. The pulverization of the materials was carried out using a Chiarotti mortar and pestle and a granulometric sieve from the Granutest with a 0.35 mm mesh opening (for TL and OSL measurements) and 75 µm (for optical absorption measurements). Fig. 1 illustrates the powder and pellets production process. For the TL measurements, powdered samples were used, distributed in the cups of the Risø equipment, with an average mass of 25 ± 1mg. For OSL measurements, pellets were produced by incorporating natural alexandrite powder in a polymeric matrix with a proportion of 20wt% of alexandrite (tests were performed and the binder used does not show any OSL response).

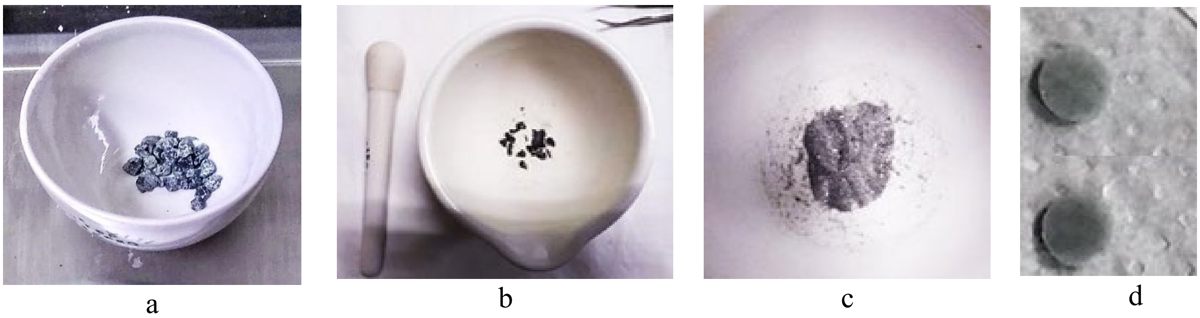


Figure 1. Samples of natural alexandrite (a), crushed sample (b), powder sample used in TL measurements (c) and pellets used in OSL measurements (d).

The optical absorption measurements were carried on a Shimadzu UV-2600 spectrophotometer in the wavelength range from 200 to 800 nm and spectral resolution of 0.1 nm. The absorbance measurements were performed in reflection mode adopting $BaSO_4$ as the reference material, and each spectrum was registered using around 30 mg of irradiated and non-irradiated alexandrite powder. For the X-ray diffraction (XRD) measurements, a Philips X'PERT-MPD diffractometer was used (operating at 45 kV-40 mA), and Cu Kα radiation (1.5405 Å), in a 2θ interval between 2° and 50°. The identification of crystalline phases was performed by comparing the sample diffractogram with PDF2 databases from ICDD - International Center for Diffraction Data and ICSD - Inorganic Crystal Structure Database using HighScore Plus software from Malvern Panalytical. TL and OSL measurements were carried out using a Risø OSL/TL reader (model DA-20). Beta irradiation was executed at room temperature using the built-in $^{90}Sr/^{90}Y$ beta source of the TL/OSL reader delivering a dose rate of 10 mGy/s and a cumulative dose within 1 to 5 Gy. TL glow curves were obtained using a heating rate of 1 K/s. OSL signal was stimulated in constant wave mode (CW) using blue LEDs (470 nm, FWHM = 20 nm) delivering a maximum power density of 80 mW/cm^2 at the sample position. The TL and OSL signals were detected with a bialkali photomultiplier tube behind an UV-transmitting, visible-absorbing glass filter (Hoya U-

340, 7.5 mm thick) that blocks the stimulation light while transmitting the OSL/TL signal in the UV-violet range.

3. Results and Discussion

3.1. Structural characterization

Fig. 2 shows a XRD analysis. The curve in red is from the alexandrite sample, and in blue and green lines correspond to the diffraction lines of the phases presented by quartz and chrysoberyl, according to the database (ICDD 01-081-1049 and 01-085- 0794).

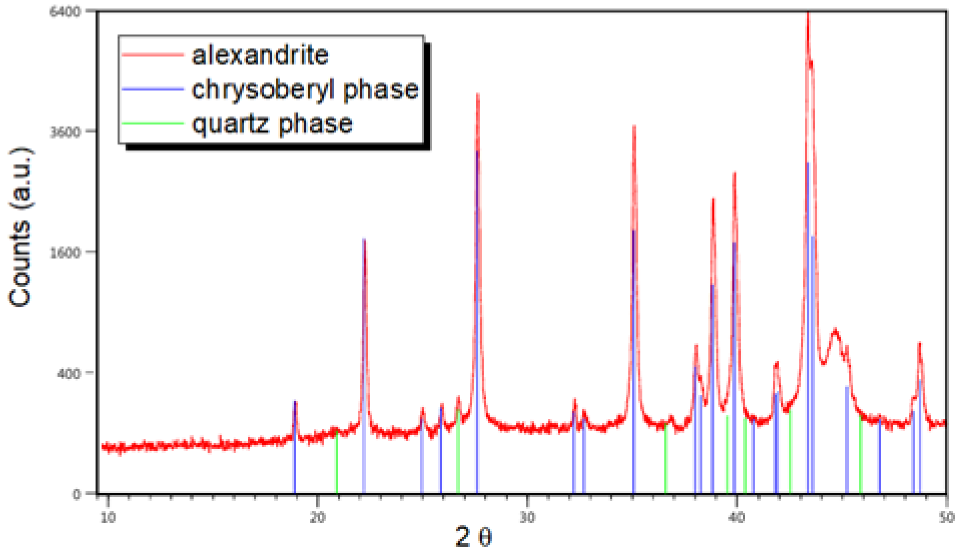


Figure 2. Diffractogram of natural alexandrite (red) and lines (blue and green) from database (ICDD 01-081-1049 and 01-085- 0794, respectively).

Through the XRD analysis it was possible to identify two mineral phases, chrysoberyl ($BeAl_2O_4$) and quartz (SiO_2). As expected, most of the diffractogram of the analyzed sample corresponds to chrysoberyl. In addition, other phases were found by phase contrast image analysis using scanning electron microscopy (SEM) and their chemical compositions were determined by EDS (energy dispersion X-ray spectroscopy) analysis performed by [11] using the same samples. The samples show 62% by weight alexandrite, 22% by weight apatite-calcium phosphate, 13% by weight mica, 3% by weight rare earth calcium aluminum silicates - alanite and traces of fluorite.

3.2. Optical absorption

Fig. 3 shows the results of the optical absorption measurements of the non-irradiated and irradiated powder samples (10 Gy beta dose).

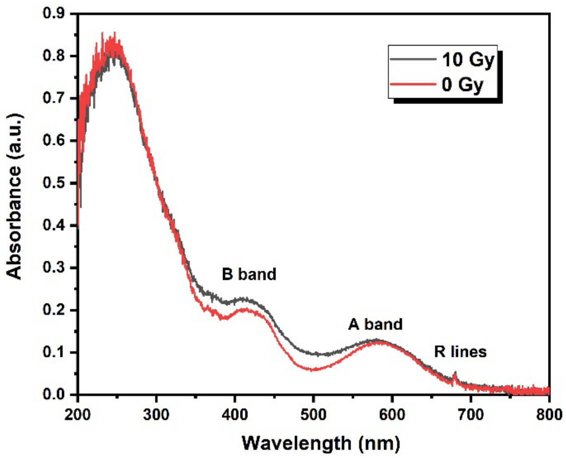
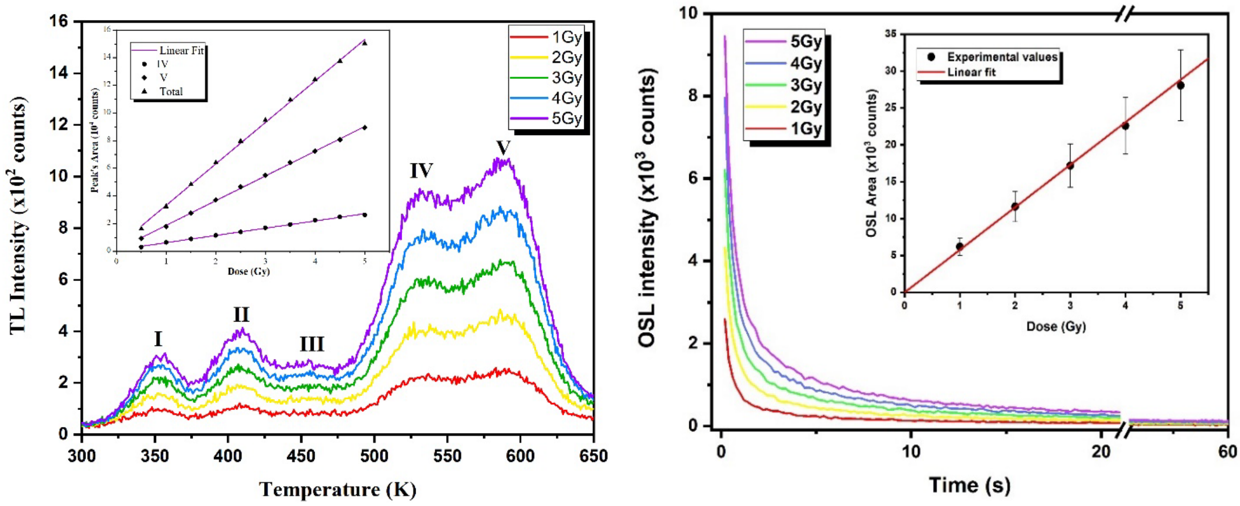


Figure 3. Optical absorption spectra of non-irradiated and beta-irradiated powdered alexandrite (d <75 μm).

The spectra have several absorption bands. The A Band is located between 550 and 600 nm and characterized by a superposition of two absorption bands due to Cr^{3+} ions distributed at Al_1 and Al_2 sites of the alexandrite crystal lattice. The B band is located between 400 and 450 nm and represents the absorption of Cr^{3+} and Fe^{3+} ions, also incorporated in different symmetrical sites [12, 13]. The R lines (located at 680 nm [13–15]) are related to Cr^{3+} ions present in the Al_2 sites [6, 16, 17]. The mineral also has a band located in the ultraviolet spectral region, which is related to Cr^{3+} ions in the sample (in agreement with SEM-EDS analysis [18]). The irradiated sample (10 Gy) shows an absorption spectrum similar to the non-irradiated one, containing the same bands.

3.3. TL and OSL

The alexandrite samples were irradiated with beta doses ranging from 1 to 5 Gy. The TL and OSL responses were determined (Fig. 4) and evaluated in terms of the dose-dependence of TL signal (peak area). Also, to understand better the detrapping mechanism, a peak analysis was done with GlowFit software [19]. The alexandrite TL peaks followed the first-order kinetics [18] and the deconvoluted glow curve was used to extract the area of the individual peaks, especially to isolate peaks IV and V, as shown in the example in Fig. 5.



a b

Figure 4. (a) TL glow curves of natural alexandrite. The inset shows the peak areas as a function of the irradiation dose for the most intense peaks. (b) OSL decay curves of natural alexandrite. The inset shows the OSL area under the curve as a function of irradiation dose.

As previously noted by the authors [18, 20, 21], natural alexandrite (Fig. 4a) shows five TL glow peaks, labelled I (~355K), II (~405K), III (~445K), IV (~530K), and V (~580K), with peak positions independent of the beta dose, thus corroborating that all the TL peaks presented a first-order kinetics mechanism. Only the two most intense TL peaks (IV and V) were used for the TL analysis. In addition, we observe that the intensity of the signal increased with the intensity of the irradiation dose. A linear fit of the dose-response curve (inset of Fig. 4a) was performed with good quality ($R^2 \approx 1$). Fig. 4b shows that the OSL curves have the same shape, regardless of the irradiation dose. For OSL, about 20s of illumination were enough to essentially extinguish the signal leaving less than 10% of the original signal remaining.

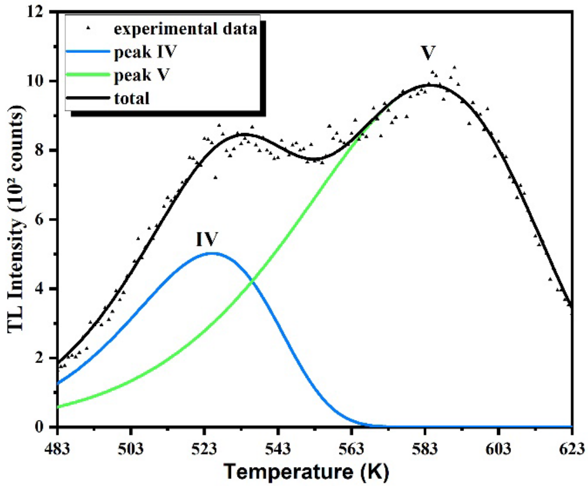


Figure 5. Peaks IV and V fitted by the GlowFit software with FOM parameter = 4.01%.

For TL analysis, the GlowFit software [19] was used. It is based on the first-order kinetics model by Randall-Wilkins [22], and a first-order kinetics mechanism fits well all the TL peaks of alexandrite [18, 20]. In this case, peaks IV and V were investigated (Fig. 5), because they present more useful characteristics for dosimetry. The results of the GlowFit analysis of peak IV were $T_m = (524.69 \pm 0.46)$ K; $E = (0.95 \pm 0.02)$ eV and the frequency factor was of the order of 10^{13} s^{-1}. For peak V, the results were $T_m = (587.09 \pm 0.21)$ K; $E = (0.87 \pm 0.01)$ eV and the frequency factor was of the order of 10^9 s^{-1}. Moreover, within the standard deviation, the peak position and the energy values were independent of the beta irradiation, in agreement with the expected behavior related to a first-order kinetics recombination mechanism.

For OSL analysis, deconvolutions of the OSL curves were also performed using the R Studio software [23, 24]. When performing deconvolutions in R Studio, it is possible to obtain parameters such a proportion of the charges initially trapped at type i trap (n_{0i}) as well as the charge escape probability (α_i) [6]. Fig. 6a shows the results of the best fit performed for the 1 Gy curve and Fig. 6b shows the trend of parameters n_{0i} for each of the analyzed curves as a function of the beta dose.

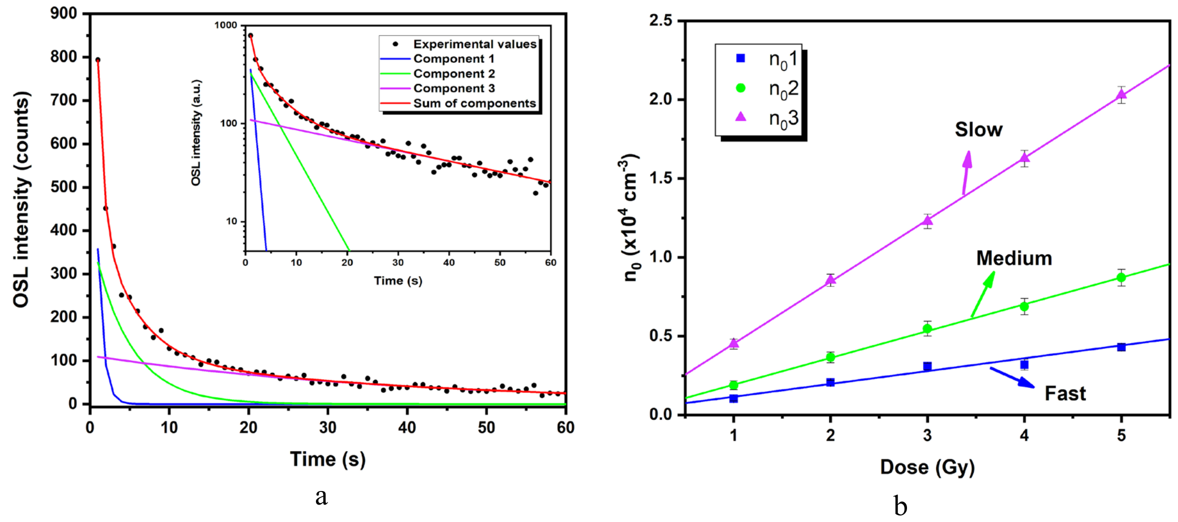


Figure 6. (a) Analysis of the 1Gy OSL decay curve and (inset) a logarithmic scale representation. (b) Parameter n_0 as a function of irradiation dose.

Fig. 6a shows that in order to describe the OSL curves of alexandrite, 3 components are needed, one being slow (purple), one medium (green) and one fast (blue). It is possible to notice that the sum of the components is close to the experimental curves, a result that can also be evaluated by the coefficient of determination obtained for this deconvolution, $R^2 = 0.99$. Thus, as shown by Fig. 6b, the results of each n_0 present a linear trend with the dose as the integrated OSL signal of Fig. 4b, that is, the 3 components obtained are related to at least 3 trapping centers.

According to [7, 10] each TL curve is linked to a trapping center of the material, and in the case of alexandrite the deepest trap centers are those of peak IV and V that corresponds to the most intense TL emission. Correlating with the OSL components we can verify that the slow component is the most intense of the three, and therefore probably can be linked to deeper traps such as peak IV and V. This result was also verified in samples of alexandrite mixed with a fluorinated polymer [6]. Using the following relation $\tau = 1/\alpha$ [5, 25], we can find the decay time of each OSL component, for the slow $\tau = 40.86$ s, for the medium $\tau = 4.93$ s and for the fast $\tau = 0.78$ s. Additional results related to this work can be found in [6, 26].

4. Conclusions

Integrated OSL and TL signals show linear increase with the irradiation dose, including a strong correlation observed between either OSL or TL signal with the beta irradiation dose, as demonstrated by the coefficient of correlation ($R^2 = 0.99$). Analysis of the glow curves showed that most intense TL peaks (IV and V) follow a first-order kinetics mechanism with an average kinetic energy of ~ 0.96 eV for peak IV and ~ 0.90 eV for peak V. OSL analysis showed that the characteristic OSL curve of alexandrite has at least three components, the fast, the medium and the slow component. The slow component could be related to a deep luminescence center and a large trap population due to its higher intensity, likewise the peaks IV and V of alexandrite.

5. References

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