



Thermoluminescence of natural $\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$ Brazilian mineral: Preliminary studies

Neilo Marcos Trindade^{a,b,*}, Henrique Kahn^c, Elisabeth Mateus Yoshimura^b

^a Federal Institute of Education, Science and Technology of São Paulo - IFSP, Rua Pedro Vicente, 625, 01109010 São Paulo, SP, Brazil

^b University of São Paulo - USP, Institute of Physics, Rua do Matão, 1371, 05508090 São Paulo, SP, Brazil

^c University of São Paulo - USP, Graduate Program in Mineral Engineering, Av. Prof. Mello Moraes, 2373, 05508900 São Paulo, SP, Brazil



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ABSTRACT

Alexandrite ($\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$) is a variety of the chrysoberyl mineral widely found in Brazil. This mineral is expected to have potential as a natural dosimeter since its composition contains 19.8 wt% BeO and 80.2 wt% Al_2O_3 , both oxides being commercially used as dosimeters. We report the investigation of thermoluminescence (TL) properties from alexandrite in natural form. Samples 1.0 mm-thick and mass of 0.045 g were cut of a stone originated in Bahia, Brazil. Sample composition was determined through x-ray fluorescence and scanning electron microscopy/energy dispersive x-ray spectroscopy measurements. Irradiations were performed at room temperature using a $^{90}\text{Sr}/^{90}\text{Y}$ beta source of the Riso TL reader (dose rate = 10 mGy/s). TL measurements were made at 5 °C/s within the dose range from 1 to 50 Gy. The glow curve consists of a dominant peak at 350 °C and three additional peaks at 110, 160 and 280 °C. Results showed that the TL signal increases linearly with beta irradiation dose. Our results suggest that Fe and Cr ions together with the presence of secondary phases such as mica and apatite play important roles in the TL process. Based on the linearity of the TL response, we conclude that alexandrite shows potential for use in dosimetry.

1. Introduction

Currently, Brazil is one of the largest producers of natural alexandrite mineral in the world. Nevertheless, despite belonging to families of gems of high economic and technological interest [1], there are few studies about the physical properties of natural alexandrite, for example, thermoluminescent properties.

Alexandrite, with chemical composition of $\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$, has a chrysoberyl type structure with the incorporation of chromium in its lattice [2]. The chrysoberyl (BeAl_2O_4) has the theoretical composition of 42.5 wt% Al, 7.1 wt% Be and 50.4 wt% O, a chemical composition similar to that of spinel mineral group, and structurally isomorphic to olivine [3]. The chrysoberyl structure has orthorhombic symmetry ($Pmn2_1$) that corresponds to dense hexagonal packing, influencing oxygen atom (atomic radius 2.7 Å) positions, which are slightly distorted by the presence of aluminum atoms. The unit cell contains four molecules with eight Al^{3+} ions (0.54 Å) occupying distorted octahedral sites, and four Be^{2+} ions (0.47 Å) occupying distorted tetrahedral sites formed with oxygen ions located in planes perpendicular to the c-axis [4]. Due to the small ionic radius of Be^{2+} , the crystal structure of chrysoberyl has a lower symmetry than the spinel mineral group with similar chemical composition [5]; this small ionic radius also results in

a bond length of 1.637 Å for Be-O [6]. Two of the three oxygen positions are located in a reflection plane and the third oxygen occupies a general position [7].

These distortions give rise to two sites of different symmetries: site, Al_1 , average Al–O bond length of 1.890 Å, set in an inversion center symmetry and a site, Al_2 , average Al–O length of 1.938 Å, located in a reflection plane [5,8,9]. In alexandrite, Cr^{3+} ions preferably occupy the largest of these sites, Al_2 . Chromium impurities are responsible for the optical properties of this mineral, being used as laser emitter [4,6,10]. This mineral also has a photochromatic effect that can be explained by the relative presence of chromium in both positions: $\text{Cr}^{3+}(\text{Al}_2)/\text{Cr}^{3+}(\text{Al}_1)$ [3]. This property, known in the literature as the alexandrite effect [11], results in the popularity and high market value of alexandrite as a gem [12]. Furthermore, the alexandrite crystal is mechanically rigid and has good thermal conductivity [12]. Alexandrite in synthetic form is also well known in the medical field as an active laser medium, first reported by Bukin et al. [13], with superior characteristics when compared to other types of laser media with emission in the range between 700 and 800 nm [9,14]. Comprehensive reports on the applications of the alexandrite laser in medicine can be found in [15–21].

This work presents results of thermoluminescence (TL) of natural samples of alexandrite mineral investigated under beta irradiation. TL

* Corresponding author.

E-mail addresses: ntrindade@ifsp.edu.br (N.M. Trindade), henrkahn@usp.br (H. Kahn), e.yoshimura@if.usp.br (E.M. Yoshimura).

is the light emitted under heating by insulating materials that were previously exposed to ionizing radiation. It is a thermally stimulated emission originating from the energy that was previously stored in the material during the irradiation [22]. Therefore, the material exposure to ionizing radiation generates charge carriers that populate trapping levels, with heating leading to the release of these carriers from the trapping centers [23]. The light emitted during heating is caused by the recombination of the released carriers with the opposite charge carriers in defects called recombination centers, where radioactive deexcitation occurs [24].

There are some naturally occurring minerals, such as quartz [25], topaz [26], feldspar [27] and mica [28] that present characteristics desired for TL dosimetry. However, in the literature, although there are many papers related to optical properties of alexandrite, to our knowledge, only one of them, by Yarovoi et al. [29], studied the ionizing radiation effects in synthetic alexandrite and another paper, by Ferraz et al. [30], investigated the TL properties of natural alexandrite and chrysoberyl.

Yarovoi et al. [29] studied the creation of color centers in alexandrite irradiated by X rays and gamma rays and found out that the TL peak at 712 K (439 °C) was related to these centers, with Cr^{3+} ions serving as the recombination centers. Ferraz et al. [30] showed TL measurements with the presence of the peaks at 170, 260 and 320 °C, the latter being the most intense. The authors also claimed that chrysoberyl samples exhibits TL peaks at the same temperatures as in alexandrite samples, but with the glow curves being more than 200 times less intense.

In this work, the main motivation to investigate chrysoberyl is the fact that it contains 19.8 wt% BeO and 80.2 wt% Al_2O_3 [5]: both these crystals are commercially used as TL materials. BeO is used for ionizing radiation TL dosimetry, with high sensitivity, linear dose response and an effective atomic number ($Z_{\text{eff}} = 7.2$) near to that of human soft tissue ($Z_{\text{eff}} \sim 7.6$) [31]. Similarly, Al_2O_3 is a sensitive, well established material for luminescence dosimetry [32–34]. In both cases, studies are still in course to improve TL properties of these materials using different dopants [35,36]. For example, there are works with single crystals of Al_2O_3 :Fe,Mg,Cr [37], and Al_2O_3 :Cr,Ni [38]; additionally, recent works show Al_2O_3 :C,Mg as a highly sensitive alternative luminescent material [39–41].

In this paper, we will present a series of experimental TL results of Brazilian alexandrite, relating the observations with the material impurities in order to explain the mechanism of the luminescence and the effects of ionizing radiation in this mineral.

2. Materials and methods

2.1. Samples and preparation for analyses

Our sample is a natural stone of alexandrite originated from Bahia, Brazil, with a dark green color. Two 1.0 mm-thick slices with mass of 0.045 g and perfectly parallel faces were cut from this stone, and denominated as *Ale I* and *Ale II*.

2.2. Chemical analysis and photoluminescence

Chemical analysis was carried out on polished sections of the samples by means of scanning electron microscopy (SEM)/electron dispersive X-ray spectroscopy (EDS) using Stereoscan 440 (LEO) with an energy dispersive spectrometer (EDS) (x-act, Oxford), imaged at accelerating voltage of 20 kV. For each section, back-scattered electron (BSE) imaging was used in complement to chemical characterization by EDS; EDS standardization was based on standards from Smithsonian Institute and Micro-Analysis Cons. Ltd. The characterization procedure also included standardless chemical analysis (total oxides) by non-destructive X-ray fluorescence (XRF) for major oxides (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO, MgO, CaO, Na_2O , K_2O , P_2O_5). The analyses were

carried out using a Bruker S8 Tiger WD X-ray fluorescence spectrometer, with QuantExpress Full Analysis mode. The alexandrite samples were mounted in 40 mm diameter epoxy resin section blocks (Epofix–Struers) and then ground and polished with diamond for both SEM / EDS and XRF bulk analyses. Blank epoxy resin blocks were also analyzed to assure that there was no interference on analyses of the oxides.

Photoluminescence (PL) spectra were obtained using a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer equipped with double monochromators for both excitation and detection, and a 450 W xenon lamp as the excitation source. All measurements were carried out in ambient conditions and detection spectral resolution of 1 nm and integration time of 1 s.

2.3. TL measurements

TL measurements were carried out using a commercial automated TL/OSL reader produced by Risø National Laboratory (model DA-20). TL glow curves were obtained using a heating rate of 5 °C/s, from room temperature to 450 °C. The TL signals were detected with a bi-alkali photomultiplier tube (PMT) behind an UV transmitting filter (Hoya U-340, 7.5 mm thick). Irradiations were performed at room temperature using the built-in $^{90}\text{Sr}/^{90}\text{Y}$ beta source of the TL/OSL reader (dose rate of 10 mGy/s) at a dose range from 1 to 50 Gy. Before use of a sample in a TL experiment, the sample was heated at 20 °C/min up to 700 °C and kept at this temperature for 1 h, in a muffle furnace, to empty the traps and erase any TL signal.

3. Results

3.1. Sample composition

The emission and excitation spectra of the samples are shown in Fig. 1. The results agree with previously published results for both natural and synthetic alexandrite samples [1,42], therefore, this outcome is consistent with the presence of Cr^{3+} in the samples.

Table 1 shows the results of standardless XRF bulk concentration of major oxides in both samples. Unfortunately, it is not possible to quantify beryllium with this technique, as only elements with atomic numbers above B ($Z = 5$) in the periodic table can be detected, and only above F ($Z = 9$) can be quantified with the QuantExpress mode. Fig. 2 presents BSE images of both samples, *Ale I* and *Ale II*. In these images, it is possible to identify other minerals in the samples, besides alexandrite, a fact that is common with natural samples. In order to identify these secondary phases some points were selected for ESD analysis based on the BSE images. In Tables 2, 3 it is possible to see the results of

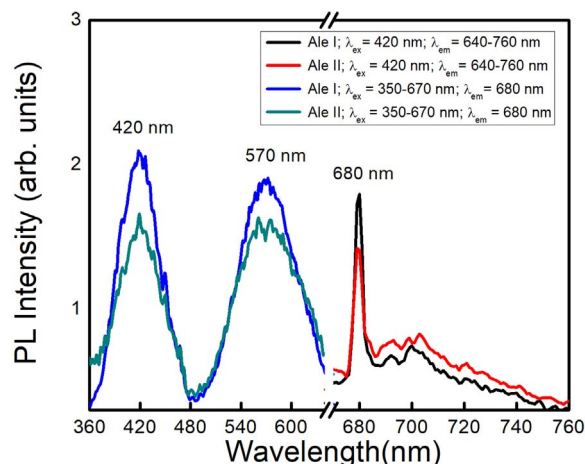


Fig. 1. Excitation and emission spectra of *Ale I* and *Ale II* samples of natural alexandrite.

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