# Thermo- and cathodoluminescence properties of lepidolite

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HIGHLIGHTS

- UV–IR CL shows seven peaks centered at 330, 397, 441, 489, 563, 700, and 769 nm.
- CL bands are due to the presence of point defects and structural defects.
- TL indicate a structure of a continuous trap distribution, i.e., multiorder kinetics.

GRAPHICAL ABSTRACT
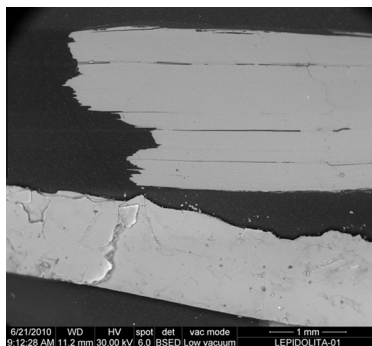
ABSTRACT

Lepidolite, $K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$, and many of the related phyllosilicate mineral of the mica group have been well studied from the chemical and structural point of view; however, to the best of our knowledge, studies on their luminescence properties have been scarcely reported. This work focuses on the thermoluminescence (TL) and cathodoluminescence (CL) response of a natural lepidolite from Portugal previously characterized by means of environmental scanning electron microscope (ESEM) and X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) techniques. The complexity of the thermoluminescence glow curves of non-irradiated and 1 Gy irradiated samples suggests a structure of a continuous trap distribution involving multiorder kinetics. UV–IR CL spectral emission shows seven peaks centered at 330, 397, 441, 489, 563, 700, and 769 nm. Such emission bands could be due to (i) structural defects, i.e., $[AlO_4]$ or non-bridging oxygen hole centers and (ii) the presence of point defects associated with Mn^{2+} and Fe^{3+}.

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Introduction

Lepidolite, $K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$, is a secondary source of lithium and is one of the major sources of rubidium and cesium elements. Besides the well known application of lithium compounds in dosimetry (TLD-100 [1], Gr-200 [2]), ^6Li is used as raw material for tritium production and as a neutron absorber in nuclear fusion [3]. Additionally, lithium minerals are employed in batteries [4] and in the manufacture of glass [4] and ceramics [5] among others. This is a phyllosilicate mineral of the mica group showing complex variable compositions because of the tendency for isovalent and heterovalent isomorphism substitutions to form series with muscovite and other Li-rich micas such as zinnwaldite [6]. It appears in granite pegmatites, in some high-temperature quartz veins, greissens, and granites. Lepidolite, like other micas, has a layered structure of lithium aluminum silicate sheets weakly bonded together by layers of potassium ions, where all the three octahedral sites are occupied by the cations. The composition depends on their relative amounts of Al and Li in octahedral

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coordination where, additionally, monovalent cations (mainly Na, Rb, and Cs) can replace K. All of the intrinsic (i.e. lattice defects) and/or extrinsic (i.e. impurities) defects as well as structural defects and their distribution in the lattice are responsible for the luminescence emission that is commonly observed in insulator materials during excitation with temperature, electrons, ions, UV, or ionizing radiation. In fact, luminescence techniques, e.g., thermoluminescence (TL), cathodoluminescence (CL), optically stimulated luminescence (OSL), and radioluminescence (RL), are usually employed not only for dosimetric purposes (dating, retrospective dosimetry, or radiological terrorism), but also for material characterization. Both TL and CL provide information about the trapped charge recombination sites related to metastable defects inside the lattice depending on whether the detrapping process is due to heat or electron exposure, respectively. All factors 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 variations in the lattice structure due to the presence of inclusions, impurities, substituted ions, or surface defects in ppm concentrations show changes in the intensity and wavelength position the emission spectra [7]. Information on the trap structure can be obtained by means of initial rise (IR) analysis. It consists in the premise that occupancies of the relevant states remain almost constant for the lowest temperature side of the TL peak, and therefore, this side of the peak will follow an exponential dependence regardless of the kinetic order [8,9].

To the best of our knowledge, thermoluminescence properties of micas in general (muscovite [10,11], sericite [10] and phlogopite [10]) and lepidolite in particular have been scarcely studied. Only Kasuya and coworkers [12] analyzed the annealing effects on the sensitivity of gamma-induced thermoluminescence on natural lepidolite mica from Madagascar. This work reports on the study of the CL and TL emission of a natural lepidolite collected from the pegmatite of Mangualde (northern Portugal). The sample has been structural and chemically characterized by means of Impact-S microscope (ESEM), XRF, and AAS techniques.

Experimental

The natural lilac-pink lepidolite collected from Mangualde (Viseu, Portugal) was examined on an ESEM microscope, of FEI Company, settled in the Spanish National Museum of Natural Sciences (MNCN). It is a low-vacuum ESEM with a large sample chamber wide enough to hold large samples without the sputtered covering onto sample. The chemical composition was determined in the Spanish MNCN Museum by XRF using a PHILIPS PW-1404 spectrometer with a Sc-Mo tube, Ge, LIF220, LIF200, PE, and TLAP analyzer crystals and Super-Q manager from Panalytical-Spain as analytical software. For the XRF measurements, lepidolite pellets of 8 g of milled sample with 0.1 g of elbacite were pressed under 20 TM and dried at 40 °C in a climatic chamber. The lithium amount was obtained by means of the AAS technique (Perkin Elmer spectrometer Mod. 2380) with a specific AAS intensitron lamp M-705 for the element Li. Nondestructive chemical analyses of major and minor elements were performed by electron microprobe analysis (EMPA) to provide spatially resolved information on the chemical homogeneity. The sample was bound together with a polymer and softly polished, offering a flat surface to the EMPA beam. The crystal-chemical characteristics of the aluminosilicate were determined on data series of electron microprobe analyses (JEOL Superprobe JXA-8900M), bulk and channel selected (TAP, PETJ, LIF, PETH) X-ray spectra search, and by identification routines. The used standards were natural and synthetic crystals from the collection of the "Servicio de Microscopia Electronica

Lluis Bru," Universidad Complutense de Madrid. The ZAF program was used for correction of matrix effects. The spot diameter of the probe was ca. 5 μm, and the operating conditions were 15 kV and 20 nA. The lithium light element of lepidolite burns under e-beam or X-irradiation, it is unstable to be analyzed by XRF o by EPMA. In addition to the X-ray Fluorescence Spectrometry method, the total concentration of fluorine element contained in the lepidolite phases was also determined using a Fluoride Ion-Selective Electrode (ELIT 8221) on free fluorine element previously dissolved in water. Lepidolite grinded sample with Na_2CO_3 flux was melted at high temperature (800 °C) into a platinum crucible by acid attack with hydrochloric and nitric acid (1:1). Later, we added a high ionic strength, weakly acidic buffer to the standards and analysis solutions. The used buffer was a total ionic strength adjustment buffer (TISAB) being 1 M in both acetic acid and NaCl with pH 5.2–5.4 that was necessary to avoid interferences (OH bindings, HF formation, to control the ionic strength, etc.). The analytical procedure for using the fluoride electrode consists of preparing a series of fluoride solutions of varying but known concentrations containing TISAB. The standards will be made from a 100 μg/mL F-stock standard solution.

The stability of TL signal has been studied for natural non-irradiated samples (NTL) and 1 Gy beta irradiated samples (ITL) using a preheat technique that consists of linear heating of the samples up to a temperature T_{stop} followed by quick cooling to room temperature and final readout to record the whole remaining TL glow curve [13], where thermal preheating varies from 190 to 280 °C. The TL measurements were performed using an automated Risø TL reader model TL DA-12 provided with an EMI 9635 QA photomultiplier [14]. The emission was observed through a blue filter (a FIB002 of the Melles-Griot Company) where the wavelength (in nm) is peaked at 320–480 nm; FWHM is 80 ± 16 nm; and peak transmittance (minimum) is 60%. The TL reader is also provided with a $^{90}Sr/^{90}Y$ source with a dose rate of 0.021 Gy s^{-1} calibrated against a ^{137}Cs photon source in a secondary standard laboratory [15]. The sample was carefully powdered with an agate pestle and mortar to avoid triboluminescence [16]. All the TL measurements were performed using a linear heating rate of 5 °C s^{-1} from room temperature up to the corresponding temperature in a N_2 atmosphere. Aliquots of 5.0 ± 0.1 mg of the sample were used for TL measurements.

The CL spectra were measured using a Gatan MonoCL3 detector with a PA-3 photomultiplier tube attached to the ESEM model XLS30. The detector covers a spectral range of 250–850 nm and is the most sensitive in the blue parts of the spectrum. The samples were placed on polished slabs, at low-vacuum mode without coating to keep open way out to the CL emission. The emission of the samples was collected and amplified using a retractable parabolic diamond mirror and a photomultiplier tube. The distance between the sample and the bottom of the CL mirror assembly was 15 mm. The excitation for CL measurements was provided at 25 kV electron beam.

Results and discussion

An ESEM image of two pieces of the lepidolite sample is shown in Fig. 1. The structure is homogeneous and with laminar texture characteristic of the mica. Li-micas, like lepidolite, are principally linked to the core margin and the replacements units of the pegmatites. However, book micas are the most homogeneous since they were collected from the intermediate zone of the pegmatite. Micas from core margins or intermediate units of the pegmatites usually exhibit inhomogeneities with different replacements and disequilibrium textures. Deformation after crystallization can produce patchy zoning, cellular texture, among others [17] giving rise