



On the cathodoluminescence and thermoluminescence emission of lithium titanate ceramics



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ABSTRACT

We herein report on the radiation effects of Li_2TiO_3 ceramics sintered at 1150 and 1350 °C by means of its UV-IR cathodoluminescence (CL) and thermoluminescence (TL) properties. The CL spectral emission decreases in ceramic samples with the higher sintering temperature, which could be associated with subtle changes in the lattice structure (the beta-to-gamma transformation as illustrated in a XRD analysis). The study of the TL response to gamma-ray dose (17, 168 and 1400 kGy) and the fading effect (up to 2184 h of storage time) of these samples indicates that the UV-blue glow emission (i) exhibits a saturating exponential behaviour with dose, regardless the elapsed time from the irradiation process; (ii) displays an initial rapid decay (ca. 20%) with storage time, maintaining the stability from 30 to 40 days onwards after 3 months of storage following a first-order decay behaviour and (iii) seems to confirm a continuum in the trap distribution, after applying tests of thermal stability at different temperatures. Additionally, successive irradiation-heating cycles give rise to a progressive increase in the TL intensity due to an increase of holes concentration in luminescence centres.

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1. Introduction

Lithium titanate is a promising candidate for solid breeding blanket (BB) concepts of future fusion reactors. A fusion BB is a critically important component since it involves tritium breeding and energy extraction. During operation, the BB will be influenced by high-energy neutrons and energetic particles from the plasma nuclear reactions, and severe irradiation damage may occur in the material. Irradiation-induced defects were observed in ternary lithium compounds irradiated by electrons, neutrons and ion beams, when applying ESR, optical absorption and luminescence techniques [1,2]. F^+ -type centres (F^+ and F^0 defects), commonly observed in ionic crystals, were also identified as the resultant defects after light ion irradiation of some breeder ceramic candidates (Li_2O , Li_2TiO_3 , Li_2ZrO_3 , ...). In these Li_2SnO_3 -type lithium ternary compounds with C2/c spatial group irradiation-induced lithium colloids and decomposition products have been also identified in samples heavily irradiated by thermal neutrons. These authors have used ion beam-induced in-situ luminescence measurements to study in detail the kinetics of the production of the above-mentioned defects. On the other hand, isochronal and isothermal annealing experiments were used to study the recovery of both F^+ centres and metal colloids, suggesting that with temperature

the charged oxygen vacancies partly transform or associate into colloidal species [3].

The dependence of luminescence signals with wavelength and temperature has been widely used to study imperfections in different type of crystals: ionic [4], insulators [5], semiconductors [5], etc. Even slight modifications in the crystalline lattice sites are highly sensitively reflected by changes in the luminescence. In fact, 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 semiconductor and insulator materials during excitation with temperature, electrons, ions, UV or ionizing radiation. Thus, luminescence techniques, thermoluminescence (TL), cathodoluminescence (CL), optically stimulated luminescence (OSL) and radioluminescence (RL) are usually employed not only for the assignment of defects associated with the impurities or impurity-intrinsic complexes, but also for dosimetric purposes (i.e. dating, retrospective dosimetry or radiological terrorism).

This paper focuses on the luminescence behaviour of lithium titanate ceramics based on its cathodoluminescence (CL) and thermoluminescence (TL) properties. Both CL and TL provides information about the trapped charge recombination sites related to metastable defects inside the lattice depending on whether the detrapping process is due to electron exposure or heat, respectively. All the 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

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the presence of inclusions, impurities, substituted ions or surface defects in ppm concentrations show changes in the intensity and wavelength position of the emission spectra. Then, lithium metatitanate samples were sintered at different temperatures to achieve the required crystallinity, porosity and microstructure and then were studied by means of CL and TL as a function of total radiation dose, that in the scope of our knowledge, have been never reported before. Such luminescence characterization was performed considering (i) the ionizing radiation sensitivity, (ii) the dose dependence (up to 1.4 MGy) and (iii) the fading effect, i.e. the evolution of the TL signal with the elapsed time since the irradiation process took place.

2. Materials and methods

Lithium titanate commercial powders from Alpha Aesar (99.9% purity) were used to prepare the ceramic samples [6]. Fine-grained powders were isostatically pressed up to 200 MPa in pellets of about 20 mm in diameter prior to be sintered in air up to temperatures ranging from 1150 to 1350 °C. Dwell times at maximum temperature were fixed to 2 h. Heating and cooling rates were set both to 5 °C min⁻¹.

Sintered pellets were structurally analyzed by means of X-ray diffraction (XRD) using a Phillips PW1710/00 diffractometer with a Cu K α radiation source, equipped with a graphite monochromator. Patterns were obtained by step scanning from 2° to 64° (2 θ in steps of 0.020°; 4 s per step) and compared with the XRD card files of the Joint Committee on Powder Diffraction Standards.

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 (wavelength resolution better than 5 nm), being the most sensitive in the blue part of the spectrum. The samples were placed on polished slabs at low-vacuum mode without coating, to keep an 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 30 kV electron beam, where the depth of the beam penetration is considered up to 2–3 μ m [7]. Since changes in ion beam energy and current density may modify the emission spectra and intensity, all spectra shown here were recorded at the same conditions.

Thermoluminescence (TL) measurements were carried out using an automated Risø TL system model TL DA-12 [8]. This reader is provided with an EMI 9635 QA photomultiplier and the emission was observed through a blue filter (a FIB002 of the Melles-Griot Company) where the wavelength is peaked at 320–480 nm; FWHM is 80 \pm 16 nm and peak transmittance (minimum) is 60%. It is also provided with a ⁹⁰Sr/⁹⁰Y source with a dose rate of 0.012 Gy s⁻¹ calibrated against a ¹³⁷Cs photon source in a secondary standards laboratory [9]. All the TL measurements were performed using a linear heating rate of 5 °C s⁻¹ from RT up to 500 °C in a N₂ atmosphere. The samples were carefully powdered with an agate mortar to avoid triboluminescence [10]. Three aliquots of powdered lithium titanate samples, each weighing 2.0 \pm 0.1 mg, were used for each measurement. The incandescent background was directly subtracted from the TL data.

Small glass containers were filled with the milled sintered powders and introduced inside of a jig in N₂ atmosphere for ionizing irradiation experiments. Gamma irradiation was performed using the ⁶⁰Co radionuclide source placed at the NAYADE unit of CIEMAT, usually employed in food irradiation processes due to its high penetrating capability, very effective for thick or dense products. Powders were exposed to 17, 168 and 1400 kGy at a dose rate of

2.33 Gy/s. Temperature was controlled and monitored with the aid of thermocouples located beside the jig containers. During irradiation temperature was always below 80 °C. The source was calibrated using a Fricke system.

3. Results and discussion

The cathodoluminescence (CL) spectra registered in the UV-IR region of lithium metatitanate ceramic samples sintered at 1150 and 1350 °C are shown in Fig. 1. One can observe (i) a blue-green broad emission that exhibits at least two main components of fairly similar intensity located at about 430 and 470 nm, (ii) an intense emission over 600 nm that seems to be the resultant of several overlapped narrow peaks, and (iii) a remarkable decrease in the luminescence intensity for the higher temperature sintered sample. The higher energy waveband observed in both samples has been already referred in the literature by Alarcón and Blasse [11] as due to the main emission of the titanate groups. Moreover, the resulting glow emission located between 400 and 600 nm has been attributed to the radiative recombination of excitons associated to octahedral positions of Ti⁴⁺ ions. The 2p O²⁻ electron of the valence band trapped in the 3d orbitals of Ti⁴⁺ ions, when excited interact with the lattice vibrations being followed by the emission of luminescence during the de-excitation process. But it must be pointed out that it is the first time that the higher wavelength luminescence activity has been published; in this sense, several studies are in progress in our laboratory to determine whether it corresponds to point defects due to impurities or Ti redox reactions.

The similar intensities of the blue-green CL emission bands suggest rather similar luminescent processes of comparable origins. The existence of several bands was previously reported by Moritani and Moriyama [1] in ion-induced luminescence of lithium titanate as a consequence of the different distribution of lithium and titanium ions in the crystalline network. According to it, the responsible for the slight CL band shift is here explained as due to the different environments affecting the titanate groups. Such differences can be detected by luminescence techniques since the glow emission is significantly affected by thermal treatments that induce changes in the oxygen vacancy concentration and therefore in the electron traps with energies in the forbidden gap [12]. In other words, the slight charge transfer transitions to equivalent levels are being registered as a consequence of the thermal-induced crystal reordering or defect production during sintering of these titanate ceramics.

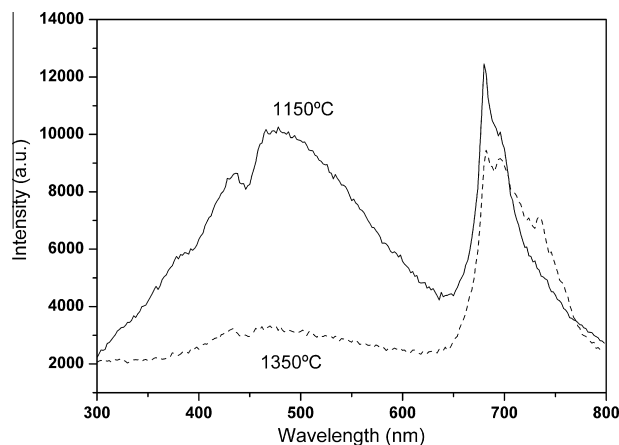


Fig. 1. The cathodoluminescence spectra of Li₂TiO₃ compositions sintered at 1150 and 1350 °C.

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