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Preliminary results on the relationship between luminescence and crystalline structure of lithium metatitanate

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ABSTRACT

Lithium metatitanate is a luminescent ceramic material of promising properties for numerous applications (breeder blanket in fusion reactors, ionic conductors). In some cases, the material will be submitted to aggressive environments (radiation, chemicals, high temperatures), which could induce changes in the crystalline structure. Small variations (presence of inclusions, impurities, or surface) in the lattice of crystalline solids are known to change the light emission behaviour, i.e. intensity and wavelength position of photoluminescence. Li_2TiO_3 ceramic samples were sintered in the range of 1050 and 1350 °C to modify the high temperature crystalline structure, and then were characterized by means of their cathodoluminescence (CL) and thermoluminescence (TL) properties as a function of total radiation dose and time of storage.

1. Introduction

Lithium titanate could be employed as solid breeding blanket (BB) in future fusion reactors that will be influenced by high-energy neutrons and energetic particles from the plasma nuclear reactions, and consequently severe irradiation damage may occur in the material. The irradiation-induced defects could be observed not only by means of ESR and optical absorption, but also by luminescence techniques [1,2]. F-type centers (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, …). These authors have used ion beam-induced in situ luminescence measurements to study in detail the kinetics of the production of the aforementioned defects. Additionally the dependence of luminescence signals with wavelength and temperature has been widely used to study imperfections in different type of crystals: ionics [3], insulators [4], semiconductors [4], etc. Changes in the lattice induce variation in the luminescence spectra. 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. Such response is 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 due to 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. 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. Samples and experimental

Lithium titanate commercial powders from Alpha Aesar (99.9% purity) were used to prepare the ceramic samples. 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

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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 CuKα radiation source, equipped with a graphite monochromator. Patterns were obtained by step scanning from 2° to 64° (2θ 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. 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 [5]. 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 ± 16 nm and peak transmittance (minimum) is 60%. It is also provided with a ^{90}Sr/^{90}Y source with a dose rate of 0.012 Gy s^{-1} calibrated against a ^{137}Cs photon source in a secondary standards laboratory [6]. All the TL measurements were performed using a linear heating rate of 5 °C s^{-1} from RT up to 500 °C in a N$_2$ atmosphere. The samples were carefully powdered with an agate mortar to avoid triboluminescence [7]. Three aliquots of powdered lithium titanate samples, each weighing 2.0 ± 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 N$_2$ atmosphere for ionizing irradiation experiments. Gamma irradiation was performed using the ^{60}Co 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

3.1. X-ray diffraction

XRD technique was used to characterize the crystalline structure of the samples sintered at different temperatures chosen to be below and above the characteristic beta-to-gamma phase transition temperature (1150 or 1250 °C, depending on the phase equilibrium diagram of reference). The diffraction peaks could be indexed assuming monoclinic symmetry according to the PDF#33-0831 (ICDD powder diffraction database). Additionally, the split of several peaks is observed in the pattern of the higher temperature sintered sample (Fig. 1). Over this transition temperature, volatile lithium compounds are easily formed. Then during cooling, the TiO$_2$-rich composition formed decomposes into Li$_2$TiO$_3$
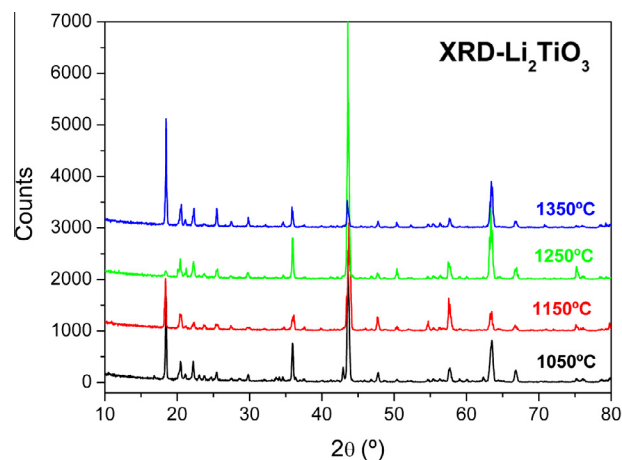

Fig. 1. The X-ray diffraction patterns obtained from the titanate compositions sintered in the range of 1050 and 1350 °C.

and Li$_4$Ti$_5$O$_{12}$ solid solutions. The monoclinic Li$_2$TiO$_3$ and Li$_4$Ti$_5$O$_{12}$ compounds show very similar XRD patterns the differences being the appearance of extra weak peaks at lower 2θ angles. The upper XRD pattern could also be then evidencing the slight deficiencies in the lithium concentration in a Li$_4$Ti$_5$O$_{12}$ type-structure by showing small diffractions at the left hand side of the main monoclinic peaks, the more intense being that at 20°, 30°, 47° and 74°.

3.2. Spectral analyses of Li$_2$TiO$_3$: CL and TL

The CL spectra registered in the UV-IR region of lithium metatitanate ceramic samples sintered in the range of 1050–1350 °C (Fig. 2) displays: (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 the samples could be associated with the main emission of the titanate groups [8]. Moreover, the resulting glow emission located between 400 and 600 nm has been attributed to the radiative recombination of excitons associated with octahedral positions of Ti^{4+} ions.

The TL emission was investigated placing a blue or a red filter before the detector to acquire the emissions peaked at 400 and 700 nm, respectively. In case of red filtering, the high wavelength
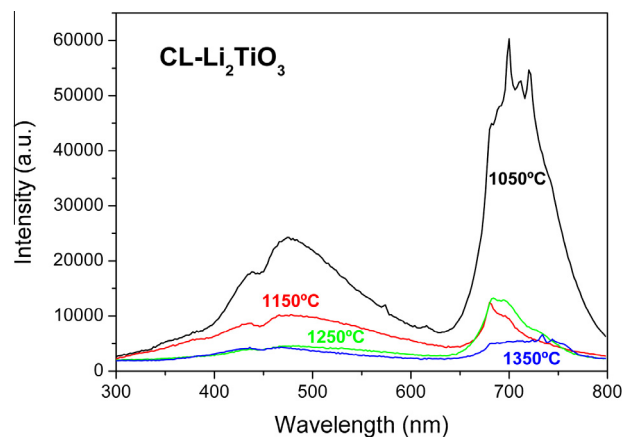

Fig. 2. Cathodoluminescence spectra at RT of the sintered samples.