

Influence of titanium and lutetium on the persistent luminescence of ZrO_2

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Keywords: persistent luminescence, zirconia, titanium doping, nanocrystalline, sol-gel method

Zirconia is one of the most important metal oxides with applications in photonic devices due to the quite unique properties as thermal and chemical stability, high refractive index (2.15–2.18) and low phonon energy [1–5]. The stretching frequency of the Zr–O bond is about 470 cm^{-1} , which is much lower than for Al–O (870) or Si–O (1100) though higher than Y–O ($300\text{--}380\text{ cm}^{-1}$) [5]. The wide band gap (5.0–5.5 eV) is important for the use as luminescent materials to suppress non-radiative losses. The ZrO_2 system has a variety of applications, including fuel cell electrolytes, thermal barrier coatings, electro-optical materials, and oxygen sensors [3–6]. ZrO_2 exhibits well known polymorphism with three forms of different crystal structures: cubic, tetragonal and monoclinic [2,7]. Though the monoclinic phase is stable at the room temperature, it is transformed to the tetragonal one at 1170°C , and further to cubic at an even higher temperature (2370 °C) [8]. However, the tetragonal and cubic phases can be stabilized at the room temperature by doping with trivalent rare earth (R_3^{3+}), Mg^{2+} or Ca^{2+} ions, thus generating oxide vacancies [2,9]. In this work, the $\text{Ti}^{3+/IV}$ and Lu^{3+} doped as well as non-doped luminescent nanocrystalline ZrO_2 materials were prepared with a sol-gel method using different $[\text{H}_2\text{O}]/[\text{ZTB}]$ ($=W$) ratios (ZTB: zirconium tetrabutoxide) at temperatures between 600 and 1000°C . The nominal Lu or Ti dopant concentrations were 0.5 mole-% of the zirconium amount. The materials were characterized with X-ray powder diffraction (XRD), thermogravimetric analysis and infrared spectroscopy. The photo- and thermally stimulated luminescence were also investigated. The increasing calcination temperature increased the amount of the monoclinic phase whilst the increasing W ratio increased the amount of tetragonal phase as observed in the X-ray diffraction patterns (Fig. 1). The most intense persistent luminescence of the non-doped ZrO_2 was obtained for $W=3$ at 1000°C , thus the Ti and Lu doped ZrO_2 were prepared at these conditions. The excitation spectra (Fig. 2, top) of the materials show a broad band with a similar profile (though not position) independently of the presence of dopants. The emission spectra (Fig. 2, bottom) show a broad band with a maximum at 500 nm, characteristic to the monoclinic phase. The Ti doping increased only the intensity of the (excitation and) emission spectra, indicating that titanium is responsible for the luminescence of the non-doped ZrO_2 (present then as an impurity).

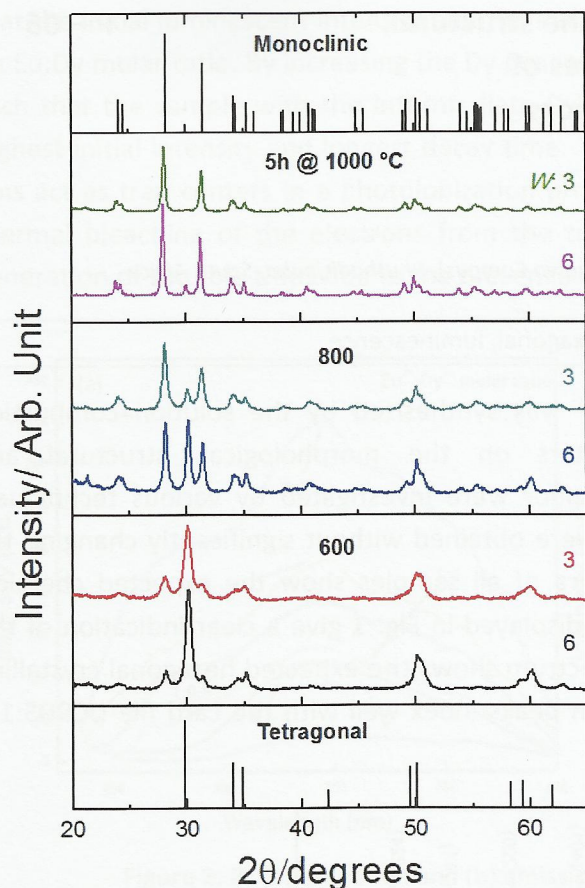


Figure 1: XRD patterns of the non-doped ZrO_2 for different W ratios.

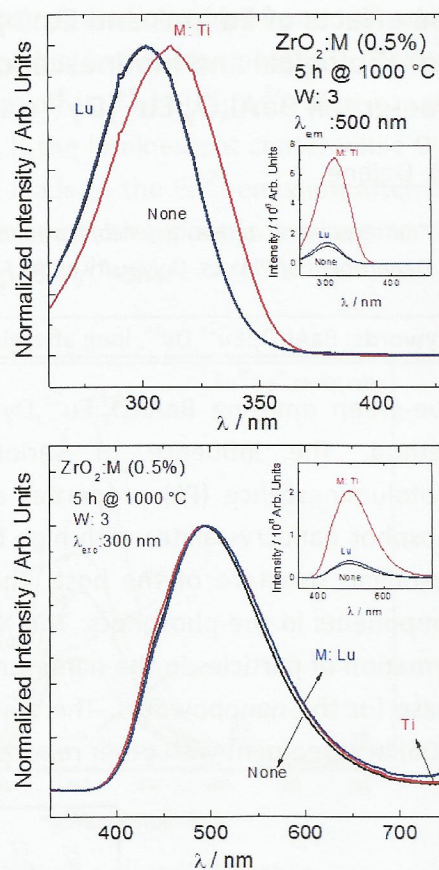


Figure 2: Luminescence excitation (top) and emission (bottom) spectra of non-doped and doped ZrO_2 systems
a) excitation and b) emission spectra

In conclusion, the persistent luminescence of the non-doped zirconia was shown to result from a Ti^{3+} impurity and the crystal structure was related to the persistent luminescence phenomenon. However, more detailed studies are needed to develop a mechanism of persistent luminescence for this system.

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