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## The Role of Titanium Valence on the Luminescence of $\text{ZrO}_2$ Materials

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### 1. Introduction

The optical properties of zirconia materials have received much attention though no outstanding applications have been established so far. The advantage of combining the efficient luminescence of the trivalent rare earths ( $\text{R}^{3+}$ ) and the stable and versatile zirconia host has finally been ruined by the incompatibility of these two systems: the charge compensation defects created by the aliovalent substitution of the tetravalent zirconium with trivalent (or divalent) rare earths have jeopardized the luminescence efficiency [1]. So far, no efficient tetravalent luminescent rare earth has been found and, undoubtedly, will not be in the future either. The room temperature UV excited luminescence of the non-doped  $\text{ZrO}_2$  or zirconates or even hafnates have been noted in several reports. In addition to Ti impurity luminescence, defects as oxygen vacancies and colour centers have been offered as origins to luminescence. The Ti impurities were mentioned as the luminescence center and a mechanism to the persistent luminescence was proposed recently [2]. Regarding the details of the luminescence mechanism, synchrotron radiation techniques such as X-ray absorption and vacuum UV (VUV) spectroscopy can unveil more details on the elements' valences as well as energy transfer processes.

### 2. Results

The monoclinic  $\text{ZrO}_2$  nanomaterials were prepared using the sol-gel route followed with annealing at 1000 °C for 5 h. The typical VUV excited luminescence was observed as a broad band centred at 500 nm (Fig. 1, left). Starting with opposite hypotheses to explain this emission, the materials were doped either with  $\text{Ti}^{3+}$  or  $\text{Lu}^{3+}$  (both 0.5 mole-%) supposed to enhance the  $\text{Ti}^{3+}$  or defect emission, respectively. The emission spectra at room temperature show clearly that the 500 nm luminescence is due to a  $\text{Ti}^{3+}$  impurity, albeit at a trace element level [2]. The analogy between  $\text{Ti}^{3+}/\text{IV}$  and  $\text{Tb}^{3+}/\text{IV}$  suggests the dopant can exist in both oxidation states in  $\text{ZrO}_2$  depending on the post-preparation treatment of the material. The XANES measurements (Fig. 2) on the Ti K edge proved inconclusive due to complicated pre-edge structure, however. Low temperature emission spectra with VUV excitation agree with the emission of both  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$  species in the  $\text{Lu}^{3+}$  doped and non-doped material.  $\text{Lu}^{3+}$  doping enhances slightly the  $\text{Ti}^{3+}$  emission. The  $\text{Ti}^{4+}$  charge transfer emission centered at 390 nm agrees with the UV-vis absorption edge of  $\text{TiO}_2$ . The broad bands at 750 nm may be attributed to  $\text{Ti}^{4+}$   $\text{Ti}^{3+}$  polarons [3] supporting the presence of both ions. The Ti doped materials reveal only the 520 nm transition due to the  $\text{eg} \rightarrow \text{t}_{2g}$  transition of  $\text{Ti}^{3+}$  splitting when symmetry lowers from Oh. The UV-VUV excitation spectra (Fig. 1, right) show energy transfer from the  $\text{ZrO}_2$  host to  $\text{Ti}^{3+}/\text{IV}$  with Eg at 5.25 eV which decreases with increasing temperature as usual.

**Are you currently a postgraduate student? (Yes/No)**

Yes

**At what level of studies are you currently? (Hons/MSc/PhD)**

PhD

**Please provide the name and email address of your supervisor.**

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