

# Dopant Valences in ZrO<sub>2</sub> Based Persistent Luminescence Materials

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The urgency on the development of new photonic materials has increased in the last three decades due to the needs of the efficient light converting and energy storage, and their respective applications on solar cells and sustainable energy [1,2]. Persistent luminescence materials continue emitting light for up to 24+ hours after ceasing the irradiation [3]. These materials are inserted in this context with a wide variety of applications, such as emergency lighting and even medical diagnostics [4]. The most studied persistent luminescence materials are doped with rare earth ions [3], though the rare earth precursors are now suffering from higher prices and new alternatives are needed to comply with this problem. One solution could be zirconia, ZrO<sub>2</sub>, based materials.

Regarding the luminescence arising from the non-doped zirconia several explanations have been offered in literature, such as: emission from defects, self-activated emission and metal impurities. With a more profound investigation, the titanium present as an impurity in zirconia has provided an unambiguous explanation for the serendipitous spectroscopic behaviour [5].

In this work, the presence, valence and environment of Ti, Tb, Lu and Hf dopants in ZrO<sub>2</sub> persistent luminescence materials were studied by XANES and EXAFS measurements using the beamlines A1 and C at HASYLAB (DESY, Hamburg, Germany). The measurements were carried out at 10 and 300 K in the fluorescence mode using the SDD-MI 7 channel silicon drift and PIPS detectors. The extraction of interatomic distances from the EXAFS data was performed by the EXAFSPAK program package [6].

Previous luminescence measurements [5] have confirmed the presence of a titanium impurity in “non-doped” ZrO<sub>2</sub> materials showing persistent luminescence. The UV excited emission has shown a bright white-blue luminescence at *ca.* 500 nm assigned to the Ti<sup>3+</sup> e<sub>g</sub> → t<sub>2g</sub> transition. The persistent luminescence originates from the same Ti<sup>3+</sup> center. Due to the low content of the titanium impurity and the rather low sensitivity of the A1 beamline setup around the TiK edge (4966 eV) and its corresponding K $\alpha$  doublet emission (*ca.* 4510 eV), this impurity could not be detected using XANES or X-ray emission. Moreover, with intentional 0.5 mole-% Ti doping, the fluorescence XANES signal at the TiK edge was rather noisy and no conclusions could be made on the valence of titanium. Therefore, to simulate the Ti<sup>3+</sup> ↔ Ti<sup>IV</sup> redox pair, the Tb<sup>3+</sup> ↔ Tb<sup>IV</sup> one was studied instead.

The TbL<sub>III</sub> edge XANES data showed that the as-prepared product obtained by sol-gel synthesis has only trivalent terbium (Figure). Annealing at 800 °C produces a significant amount of tetravalent Tb and with heating at 1000 °C, Tb<sup>IV</sup> dominates. The distance distributions calculated from EXAFS data agreed (Figure): The as-prepared product possesses Tb-O distances of *ca.* 2.5 Å similar to the longer Tb-O ones in Tb<sub>4</sub>O<sub>7</sub>. For the product heated at 1000 °C, the *ca.* 2.2 Å distance, similar to the shorter Tb-O in Tb<sub>4</sub>O<sub>7</sub>, prevails. This corresponds to the regular Zr-O distance in ZrO<sub>2</sub> suggesting no more than minor structural distortion.

The present XANES measurements also revealed the presence of a Hf impurity, which seems only natural if Ti is present, as well. The EXAFS calculations indicated that it occupies the Zr site(s) in the matrix and has

not formed another phase. These results will be analyzed further to elucidate the possible role of Hf in the persistent luminescence process.

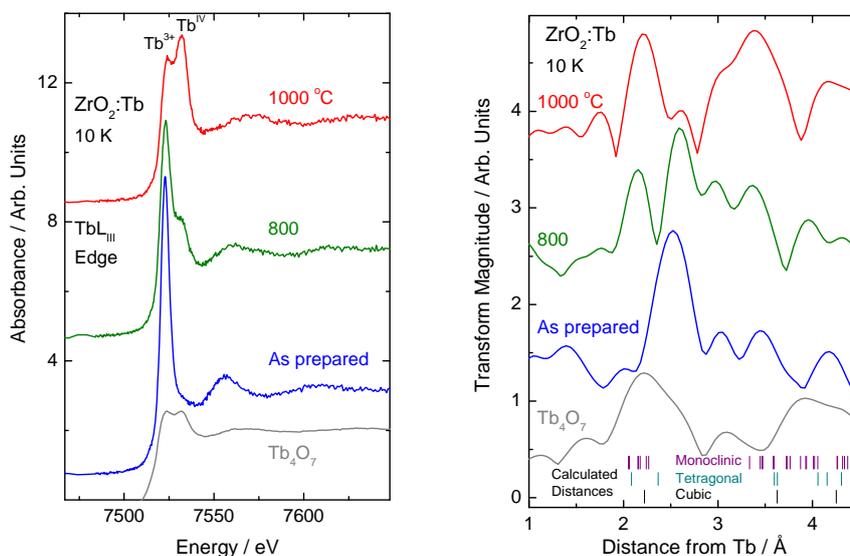


Figure: Tb<sub>LIII</sub> edge XANES spectra (left) and distance distribution around Tb (right) in ZrO<sub>2</sub>:Tb<sup>3+</sup> ( $x_{\text{Tb}}$ : 0.005) at 10 and 300 K. Distances calculated for the monoclinic, tetragonal and cubic forms from the crystal structures are given, as well. The results for Tb<sub>4</sub>O<sub>7</sub> are shown for comparison.

Together with data obtained from HASYLAB/SUPERLUMI and thermoluminescence measurements, the present results were used to construct for the first time the mechanism of persistent luminescence for Ti<sup>3+</sup> (in ZrO<sub>2</sub> materials). Measurements were also made for other persistent luminescence materials. The data treatment and analysis is currently in progress. The results will be published promptly in appropriate international journals.

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