Photoluminescence properties of different ZrO_2 polymorphs obtained by sol-gel method

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Luminescent nanocrystalline ZrO_2 materials were prepared with a simple one-pot sol-gel method. A low post-annealing temperature (600 °C) favoured the tetragonal ZrO_2 (*t*-ZrO_2) form whilst higher temperatures (800 and 1000 °C) yielded the monoclinic one (*m*-ZrO_2). The luminescence centre in the non-doped ZrO_2 is trivalent titanium and the emission is due to the $3d^1$ $e_g \rightarrow t_{2g}$ transition [1]. Due to larger Stokes shift in *m*-ZrO_2, the Ti^{3+} emission is red-shifted from 410 in *t*-ZrO_2 to 496 nm. The non-doped ZrO_2 excitation seems to involve photoionization of Ti^{3+} to Ti^{IV} in addition to the $t_{2g} \rightarrow e_g$ transition of Ti^{3+} (Fig., right). Subsequently, the freed electron is trapped to the oxygen vacancies created by Ti^{3+}/Ti^{IV} charge compensation, so this can be considered as a metal-to-host/ligand charge transfer. Most of the excitation results in immediate emission; the traps are probably very shallow though deeper ones lead to the persistent luminescence from *m*-ZrO_2 observed previously [1]. The properties of ZrO_2 luminescence as a function of temperature will be discussed also.

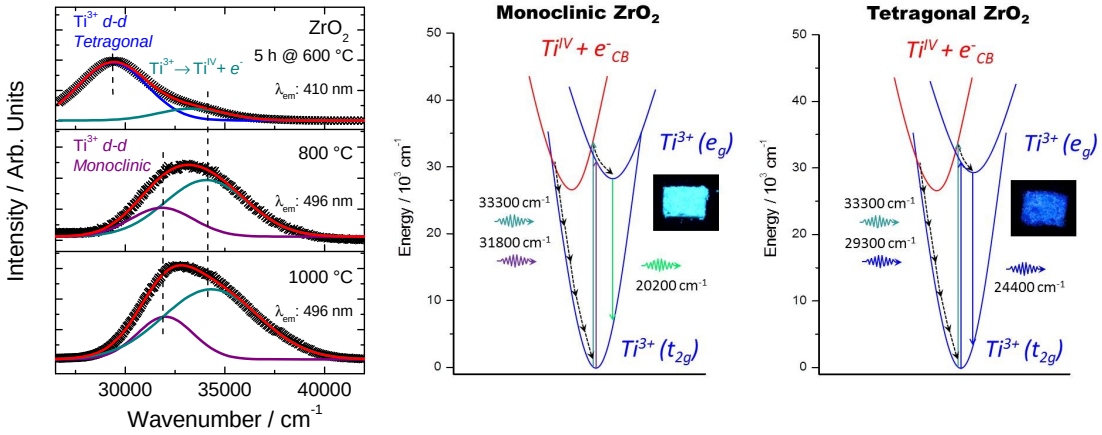

Figure 1: Deconvoluted excitation spectra of non-doped ZrO_2 obtained by sol-gel method (left). Schematic representation of luminescence processes for *m*- and *t*-ZrO_2 (center, right).

References:

[1] J.M. Carvalho, L.C.V. Rodrigues, J. Hölsä, M. Lastusaari, L.A.O. Nunes, M.C.F.C. Felinto, O.L. Malta, H.F. Brito, Opt. Mater. Exp. 2 (2012) 331.