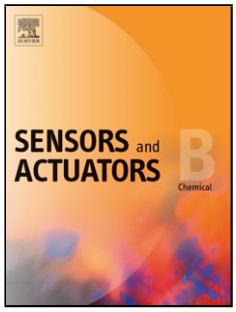

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Modeling of luminescence-based oxygen sensing by redox-switched energy transfer in nanocrystalline TiO_2:Sm^{3+}

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Highlights

- Oxygen sensitivity of Sm-doped TiO_2 was studied from 100 ppm to 100% of O_2
- Oxygen responses of stationary and time-resolved luminescence were measured
- An original model is developed for rare-earth-doped semiconducting materials
- Model describes oxygen dependence of complex time-resolved luminescence decays
- Luminescence sensitivity is linked to defect densities and surface-to-volume ratio

Abstract

It is shown that the luminescence of Sm^{3+} ions, which were doped into anatase nanopowder, is highly sensitive to the presence of oxygen gas. The luminescence was effectively excited through TiO_2 band-to-band absorption and exhibited oxygen sensitivity in a wide concentration range from pure O_2 gas down to 100 ppm of O_2 in a nitrogen atmosphere. An increase in oxygen concentration led to a stronger intensity and longer lifetime of Sm^{3+} luminescence, an exactly opposite behavior to luminescence-based sensors described by Stern-Volmer law. An original physical model is developed for describing such luminescent enhancement mechanism: it is proposed, that the adsorbed oxygen suppresses the inherent luminescence quenching of Sm ions taking place via a resonant energy transfer to acceptor defects in the material. Electron transfer between the adsorbed oxygen and these defects changes the structure of electronic energy levels and hence the energy accepting ability of the latter. The model allows describing the oxygen-dependent non-exponential luminescence decays in a quantitative manner and relates the luminescence characteristics to the material parameters such as the surface-to-volume ratio of nanocrystallites and the density of acceptor defects and gas adsorption sites.