

Valence Control of Pr in ZrO₂ by Gd³⁺ Co-Doping

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Summary

In this work, a set of praseodymium doped materials was prepared *via* sol-gel route and structurally characterized. The addition of the Gd³⁺ co-dopant gradually changes the zirconia structure from monoclinic to cubic. Photoluminescence studies show intensification of the Pr³⁺ luminescence with the increasing Gd³⁺ co-dopant concentration. This was related to the valence change of Pr in the ZrO₂ lattice.

Keyword

Praseodymium, Zirconia sol-gel materials, Red phosphors, Valence control.

Results and Discussion

Zr(O(CH₂)₃CH₃)₄ and R(NO₃)₃·6H₂O (R: Pr and Gd) were used as the precursors of the sol-gel reaction [1] yielding Zr_{0.99-x}Gd_xPr_{0.01}O₂ (x_{Gd}: 0.01, 0.05, 0.10 and 0.20) nanocrystals. The as-prepared materials were calcined in air for 5 h at 1000 °C and characterized by X-ray powder diffraction, UV excited luminescence and X-ray absorption spectroscopy (XANES).

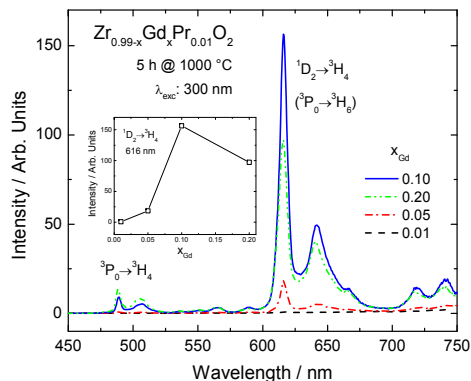


Figure 1. Emission spectra of the Zr_{0.99-x}Gd_xPr_{0.01}O₂ materials. Inset shows the peak intensity for the ¹D₂→³H₄ transition as a function of the Gd³⁺ concentration.

The enhancement of red Pr³⁺ luminescence in zirconia has been reported to result from the sensitization by the Y³⁺ co-dopant [2]. However, little is known about the oxidation state and environment of Pr. Indeed, the emission spectra of the Zr_{0.99-x}Gd_xPr_{0.01}O₂ materials (Fig. 1) show an initial strengthening of the red emission of Pr³⁺ (mainly the ¹D₂→³H₄ transition) with increasing Gd³⁺ co-doping. However, the luminescence is quenched at the highest Gd³⁺ concentration - possibly due to strongly increased concentration of the charge compensation defects. The enhanced red emission is due to the conversion of Pr^{IV} to Pr³⁺ as a result of increasing participation of Pr in the R_{Zr}-V_O^{**}-R_{Zr} defect clusters. The valence change is

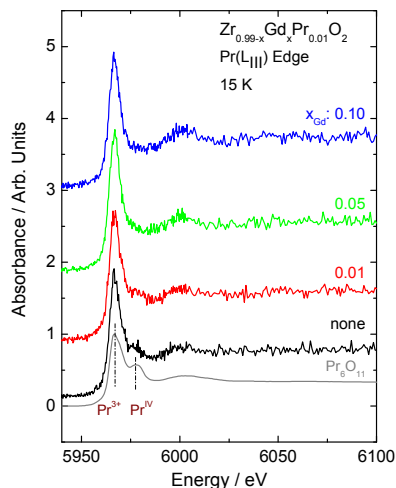


Figure 2. Synchrotron radiation XANES spectra for the Zr_{0.99-x}Gd_xPr_{0.01}O₂ materials, at 15 K with the Pr₆O₁₁ spectrum as a reference.

Conclusions

The control of Pr valence in zirconia was achieved by Gd³⁺ co-doping. As a by-product of the clustering of the charge compensation defects, efficient red luminescence was obtained due to quenching of the blue-green emission. Excessive Gd³⁺ co-doping leads to the quenching of the red emission, as well.

References

1. L.L. Hench, J.K. West, *Chem. Rev.* **90**, 33 (1990).
2. J.D. Fidelus, S. Yatsunenko, M. Godlewski, W. Paszkowicz, E. Werner-Malento, W. Łojkowska, *Scripta Mater.* **61**, 415 (2009).
3. L.C.V. Rodrigues, H.F. Brito, J. Hölsä, R. Stefani, M.C.F.C. Felinto, M. Lastusaari, T. Laamanen, L.A.O. Nunes, *J. Phys. Chem. C* (2012) (in press).