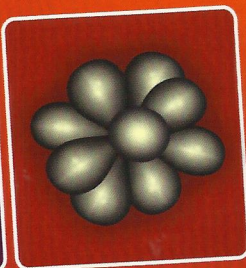


20
RE

13
Mat

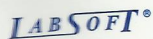


ABSTRACTS BOOK

International Conference on
RARE EARTH MATERIALS
Advances in Synthesis,
Studies and Applications
Wrocław, Poland, 26-28 April, 2013

THE CONFERENCE IS HELD UNDER THE HONORARY PATRONAGE OF THE MAYOR OF WROCLAW

SPONSORS



INNOWACYJNA
GOSPODARKA
NARODOWA STRATEGIA SPÓJNOŚCI



ORGANIZERS

PATRONAGE

DOPANT VALENCE CONTROL IN $Zr_{0.99-x}Gd_xR_{0.01}O_2$ (R: Pr AND Tb) MATERIALS BY CO-DOPING EFFECT

J.M. Carvalho^{1,*}, C.C.S. Pedroso¹, M.C.F.C. Felinto², L.C.V. Rodrigues^{1,3}, M. Lastusaari^{3,4}, J. Hölsä^{1,3,4}, H.F. Brito¹

¹Universidade de São Paulo, Instituto de Química, São Paulo-SP, Brazil

²Instituto de Pesquisas Energéticas e Nucleares, São Paulo-SP, Brazil

³University of Turku, Department of Chemistry, FI-20014 Turku, Finland

⁴Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland

*corresponding author: jose.miranda.carvalho@usp.br

Keywords: Zirconia, Valence Control, Praseodymium, Terbium

A change in the rare earth valence can affect significantly the optical properties of the materials and consequently their application. Luminescence can be quenched dramatically by recombination processes or energy transfer. For this purpose, different processes in materials science seek to control the valence of rare earth ions to obtain the desired optical properties. Despite a number of reports [1] on rare earth doped zirconia, the knowledge about the valence change of key rare earths in zirconia is still serendipitously poor. The valence of Pr and Tb in ZrO_2 changes from four to three with increasing concentration of the Gd^{3+} co-dopant according to XANES measurements (Fig.). The valence conversion of Pr differs from Tb in zirconia, partly due to different redox potentials [2]. The effect of charge compensation when R^{3+} occupies the Zr^{IV} site must be considered. For each oxide vacancy, two R^{3+} are required. As the concentration of the co-dopant increases, the number of defect clusters ($R_{Zr}^{3+}-V_O^{2-}-R_{Zr}^{3+}$) increases and involve not only Gd^{3+} but also Pr/Tb stabilizing the trivalent state. The created oxide vacancies could store the electrons for posterior reduction of R^{IV} by thermostimulation of the populated defects. As a conclusion, EXAFS studies may be required to clarify the change of dopant valence.

[1] J.D. Fidelus, S. Yatsunenko, M. Godlewski, W. Paszkowicz, E. Werner-Malento, W. Łojkowski, *Scripta Mater.* **61** (2009) 415.

[2] L.R. Morss, *Chem. Rev.* **76** (1976) 827

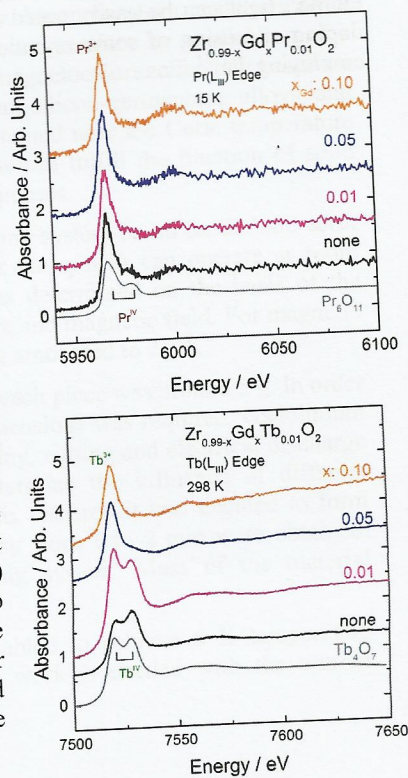


Fig. Synchrotron radiation XANES spectra for $Zr_{0.99-x}Gd_xPr_{0.01}O_2$ (top) and $Zr_{0.99-x}Gd_xTb_{0.01}O_2$ (bottom) materials.