Structure of Er^{3+}-doped SiO_2-HfO_2 Glass and Glass-Ceramic Planar Waveguides using EXAFS and XRD

Nasser D. Afify*
School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NH, United Kingdom

Giuseppe Dalba
Dipartimento di Fisica dell'Università di Trento,
Via Sommarive 14, I-38050 Povo (Trento), Italy

Francesco Rocca
Istituto di Fotonica e Nanotecnologie del Consiglio Nazionale delle Ricerche,
Sezione CeFSA di Trento - Via Sommarive 14, I-38050 Povo (Trento), Italy

Er^{3+}-doped SiO_2 glasses represent the basic material used in the fabrication of photonics devices such as optical amplifiers. Having binary or ternary glassy hosts can lead to systems with better spectroscopic properties, compared to the basic SiO_2 glass. Introducing additional oxides is an attempt to enhance the limited solubility of the rare-earth ion. Another motivation is trying to alter the crystal field around these ions. Recently, this procedure has been extended to growing nanocrystalline phases of the co-dopant oxide, obtaining new materials where rare-earth ions are present in small nanocrystals dispersed in the host glass. Many co-dopant oxides such as Na_2O, TiO_2, and Al_2O_3 have been reported in literature, leading in most cases to improvement in the properties. Here we present results of introducing HfO_2 into the Er^{3+}-doped SiO_2 glassy system. Both the glassy and glass-ceramic regimes were covered in this study.

Planar waveguides with the nominal compositions 1 mol % Er^{3+}-doped (1-x)SiO_2-xHfO_2 ($x = 0.0, 0.9, 1.8, 5, 8, 10, 20, 30, 40,$ and 50 mol %) were prepared by the sol-gel route and dip-coated on amorphous SiO_2 substrates. All the samples were thermally annealed at 900^oC for duration depending on HfO_2 content, obtaining fully densified amorphous waveguides. Nanocrystals of HfO_2 were successively grown by appropriate further thermal annealing. The structure of the glass and glass-ceramic waveguides was characterized by XRD and both Er and Hf L_3-edges EXAFS measurements carried on ESRF Beamlines.

In the glassy regime, our EXAFS results at Er L_3-edge show the strong tendency of Er^{3+} ions to be present in HfO_2-rich regions for HfO_2 concentration $\geq$ 5 mol %, without altering its local structure between 10 and 50 mol % HfO_2. These results were confirmed by both Photoluminescence (PL) and Raman results. At lower concentrations of HfO_2, the local structure around Er^{3+} is modified with respect to the pure SiO_2 host. In the glass-ceramic regime, even with 5 mol % HfO_2, it was possible to grow HfO_2 nanocrystals. Both Hf L_3-edge EXAFS and XRD results evidence the substitution of Hf by Er ions in the nanocrystals. Er L_3-edge EXAFS results clearly show an ordered environment around the rare-earth ion. This environment is sensitive to the size of HfO_2 nanocrystals, which in turn is tunable by controlling the heat treatment. These findings were found coherent with the measured PL spectra. Very similar results were obtained on waveguides fabricated by the RF-sputtering technique.

* Electronic address: N.Afify@kent.ac.uk