Abstract

Mixed zirconium and titanium oxides have been the subject of a number of studies investigating their structural and textural properties, as well as their catalytic activity. Among various binary oxides, the TiO$_2$-ZrO$_2$ exhibited very good catalytic activity and high surface acidity. They exhibit relatively high surface area, thermal stability and mechanical strength. The ZrO$_2$ content leads to an improved chemical durability of the matrix and also prevent phase transformations of TiO$_2$ from anatase to rutile, thus, promoting the thermal stability of the catalysts. The TiO$_2$-ZrO$_2$ materials are potential candidates for the fabrication of refractory ceramics and development of advanced coating process. These materials are used for preparing photosensitive materials and photostable pigments. The TiO$_2$-ZrO$_2$ matrices act as suitable host for doping rare earth elements and semiconductors. Thus these materials are quite interesting for a variety of applications due to their remarkable properties.

The thesis describes the preparation of titania- zirconia based xerogels with an optimum composition of TiO$_2$:ZrO$_2$ = 75:25 wt% by the ultra-low hydrolysis sol-gel route. Various techniques like FTIR spectroscopy, TGA/DTA, XRD, TEM, Raman spectroscopy, UV-VIS spectroscopy and fluorescence spectroscopy were used to assess the structural and optical properties of these titania- zirconia based materials.

The structural and spectroscopic properties of CdS nanocrystallites/Sm$^{3+}$/Tb$^{3+}$ doped titania-zirconia xerogels were described. The fluorescence spectra reveal that the intensity of the characteristic emission of samarium and terbium increases considerably in the presence
of CdS nanocrystallites. The fluorescence enhancement of the Sm\textsuperscript{3+}/CdS and Tb\textsuperscript{3+}/CdS codoped samples are due to the nonradiative energy transfer from CdS surface trap levels to the Sm\textsuperscript{3+} and Tb\textsuperscript{3+} ions. The titania-zirconia matrices doped with CdSe/Tb\textsuperscript{3+} and CdSe/Sm\textsuperscript{3+} were also prepared through the sol-gel process. From the fluorescence spectra the fluorescence intensity of Sm\textsuperscript{3+} and Tb\textsuperscript{3+} ions were increased due to the presence of CdSe nanoparticles. Enhancement in the emission spectra can be attributed to the nonradiative energy transfer from the electron-hole recombination of the CdSe nanoparticles to the rare earth ions.

Phonon side band analysis is carried out in Eu\textsuperscript{3+}, Eu\textsuperscript{3+}/CdS and Eu\textsuperscript{3+}/CdSe doped titania-zirconia matrices. A correlation between the Raman spectral data and phonon side band analysis gives an average structure of the bulk glass and a near estimate of the maximum vibrational state energy. In order to obtain white light emission the terbium ions were also codoped into the above samples. The spectroscopic parameters of Sm\textsuperscript{3+} ions and CdS/CdSe nanocrystallites in titania-zirconia matrices were well elucidated in the thesis using Judd-Ofelt theoretical analysis. It was observed that the titania-zirconia matrices were good candidates as host matrices for rare earth ions in realizing optical amplification and optically active devices.

**Keywords**: Sol-gel, Nanocomposites, Titania-zirconia, Rare earths, Nanocrystallites, Fluorescence, phonon side band, Colorimetry, J-O parameters.