

Report

Project no. **INCO-CT-2006-026283-OPSA**

Project title:

**Centre of Excellence for Optical Spectroscopy Applications in Physics, Material
Science and Environmental Protection**

Appendix E:

**Report from the training courses in optical characterization of
nano-sized structures and materials (WP5).**

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A. Infrared spectroscopy (FTIR)

Infrared spectroscopy (FTIR) of nanosized materials brings information on the bulk, and surface. From the infrared spectrum it is possible to obtain information about the interatomic bonds constituting the core of nanoparticles, size and shape of the nanoparticles, about material stoichiometry, chemical nature of the surface bonds and surface groups and the possible presence of contaminating species on the surface. This study also includes the bandgap study of nanomaterials. Using FTIR reflection spectroscopy for analyzing different kind of nano-sized materials we can obtain information about the dielectric function which on the other side can give more complete insight into the nanostructure nature of the materials.

FTIR reflection spectroscopy in the FAR and MID region was applied for analyzing different kind of nano-sized materials like anatase TiO_2 , pure CeO_2 and CeO_2 doped with Y and Nd, and ZnO. Reflectivity spectra were measured on BOMEM DA8 FTIR spectrometer at room temperature in vacuum using Hyper ($40\text{--}700\text{ cm}^{-1}$) and KBr ($500\text{--}5000\text{ cm}^{-1}$) beamsplitters and DTGS (far IR) or MCT (mid infrared) detectors.

FT-NIR.

1. Reflectivity spectra of TiO_2 samples in FAR and MID infrared region

FTIR reflectivity spectra were measured on anatase TiO_2 nanopowders synthesized by laser induced pyrolysis method. The IR reflection spectra of TiO_2 nanopowders pressed into pellets were measured at room temperature using a BOMEM-DA8 spectrometer in the spectral range between 80 and 1500 cm^{-1} . The dielectric function was modelled using the generalized Bruggeman EMA to account for the polycrystalline and porous character of the nanopowders. Comparison of reflectivity spectra calculated using this dielectric function with the experimental ones enable us to obtain the values of the main fitting parameters, namely the TO and LO mode frequencies and their damping factors as well as the volume fraction of TiO_2 (air) in nanopowders what is in accordance with their specific surface area and grain size values obtained from XRD results.

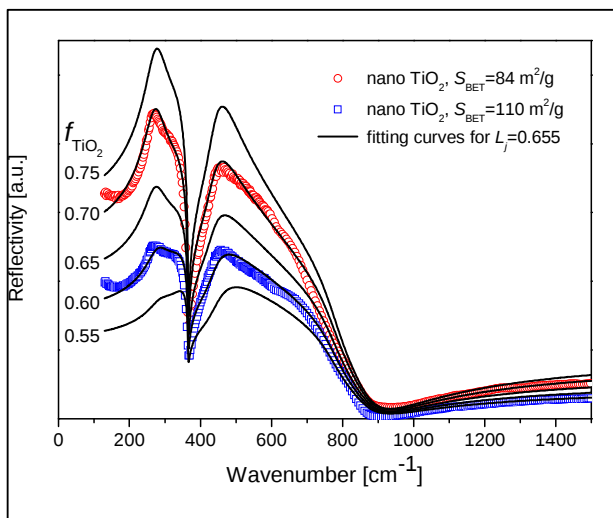


Figure 1 Experimental IR spectra (◻, ◻) of titania samples and fitted spectra (—) obtained by generalized Bruggeman EMA.

In Fig. 1 are presented reflectivity spectra of two TiO_2 nanocrystalline samples with specific surface area (SBET) of 84 and $110\text{ m}^2/\text{g}$. With black lines are presented the modeled reflectivity spectra varying volume fraction (f_{TiO_2}) of titania powders and introducing the effect of pore shape by adjustable depolarization factor L_j .

2. Reflectivity spectra of ZnO samples in FAR infrared region

FAR-IR spectra were collected by BOMEM DA8 spectrometer at room temperature (Fig. 2), in the range $50\text{--}650\text{ cm}^{-1}$. Differences between far infrared spectra of non-activated and activated samples point out to the changes in powder microstructure and appearance of small amount of iron or iron-oxides due to long time grinding in a vibro-mill with steel rings. These results also show decrease of plasma mode intensity with activation, as a consequence of decrease in free carrier concentration.

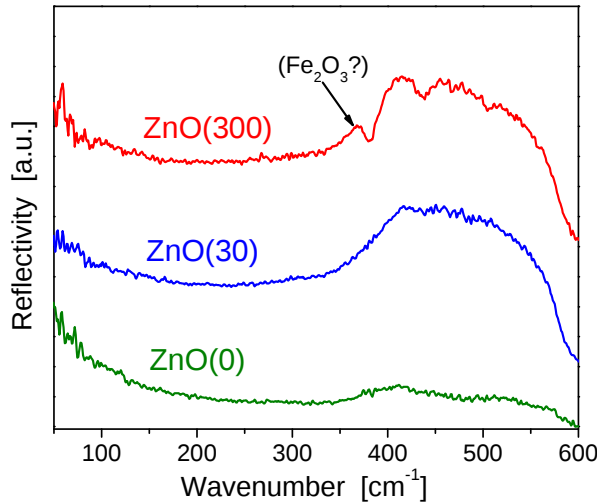


Figure 2 Infrared reflectivity spectra of the non-activated ZnO powders (ZnO(0)), and ZnO powders activated in vibro-mill during 30 and 300 min - ZnO(30) and ZnO(300).

3. Reflectivity spectra of pure and Nd(Y) doped CeO₂ samples in FAR and MID infrared region

FTIR reflectivity spectra were measured on pure and Nd(Y) doped CeO₂ nanopowders produced by self propagating room temperature synthesis method. The spectra of pure and doped samples are measured in the spectral range between 40 cm^{-1} and 700 cm^{-1} in vacuum at room temperature. The FAR-IR spectra of cerium dioxide are presented in Fig. 7. Cerium dioxide (CeO₂) of the fluorite type structure has two zone-center infrared frequencies: at 272 cm^{-1} (doubly degenerate TO mode), and at 595 cm^{-1} (nondegenerate LO mode). From KK analysis we were able to obtain frequencies of TO and LO modes for our nanocrystalline sample. Frequency of TO mode is estimated to be at 285 cm^{-1} while frequency of LO mode is about 550 cm^{-1} . Due to ionic nature of bonding in CeO₂ crystal, there is strong splitting of TO and LO modes in undoped ceria sample and they are shifted regarding the bulk values due to the nanostructured nature of the material (average particle size $\sim 7\text{ nm}$). In the spectra of Nd(Y) doped samples (Fig. 3) the TO and LO modes are shifted to lower (higher) values because of the different ionic radius of dopants. From the spectra of doped samples it can be deduced that with increasing dopant concentration the free carrier concentration increases with a pronounced screening of LO modes. The dielectric function of this materials are modeled as a Lorentz oscillators with plasma damping but we are currently developing a model based on effective medium theory where the size-effects will be incorporated through the size-dependant damping constant. On the spectra from Fig. 3, there is also evident a presence of new mode at $\sim 375\text{ cm}^{-1}$ (designated with * in Fig. 3) which can be ascribed to the surface mode.

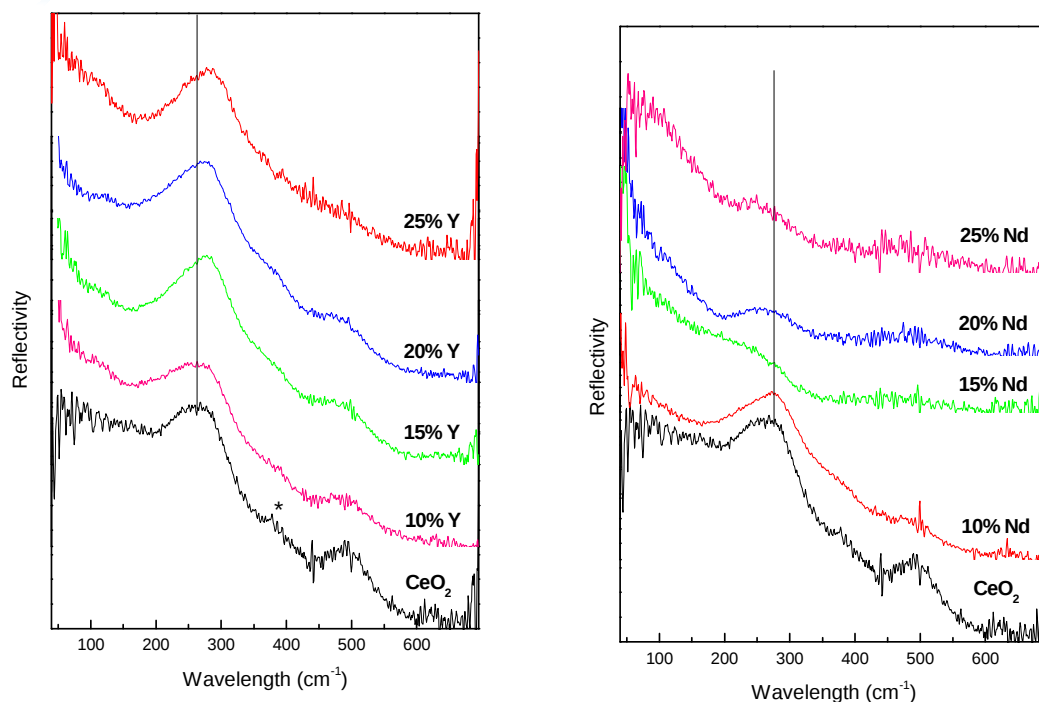


Figure 3. FAR-IR reflection spectra of (a) Y doped and (b) Nd doped ceria samples. The spectra of undoped CeO_2 are also presented.

In Fig. 4 is presented the FTIR spectra of CeO_2 nanocrystalline sample in FAR and MID infrared region ($40\text{--}4000\text{ cm}^{-1}$) where besides the TO(LO) phonon modes, there are bands in the frequency region from 1000 to 2000 cm^{-1} . These bands can be assigned to C–O stretches of carbonate species formed by coordination of CO_2 molecules onto the unsaturated CeO_2 surface. The identification of IR modes for adsorbed CO_2 molecules has important implications in characterization of cerium dioxide based catalysts.

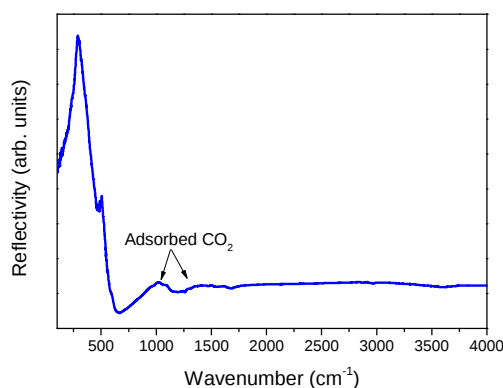


Figure 4. IR reflection spectra of CeO_2 nanocrystalline sample.

4. Reflectivity spectra of pure and Ba doped CeO_2 , TiO_2 and ZnO samples in NIR infrared region

The optical properties of metal oxide nanoparticles attract recently great attention because of important optical applications of nanocrystalline metal oxides which comprises better photonic bandgap materials, better optical limiting materials for eye protection and antireflective optical

coatings. Particle size of an oxide affects its color that in turn can affect its reflectance properties. In the present study the investigations were made on the NIR reflectance properties of pure and Ba-doped CeO_2 , TiO_2 and ZnO nanocrystalline samples. A comparison was made between the reflectance properties of these oxides with their macrocrystalline analogs. All measurements were performed on BOMEM DA8 spectrometer in the NIR region using NIR LN_2 InSb detector (IPH5000L) for the range $1800\text{--}8500\text{ cm}^{-1}$, a visible Si (IPH5600L) detector for the range $8500\text{--}50\,000\text{ cm}^{-1}$ and a Quartz visible beamsplitter (IMB2100L). The NIR reflectance measurements were performed at room temperature in vacuum.

The NIR spectra of pure and Ba-doped CeO_2 , TiO_2 and ZnO nanocrystalline samples are depicted in Fig. 5. The reflectance curves for macrocrystalline oxides are presented for comparison. A comparison between NIR reflectance properties of nanocrystalline metal oxides and their macrocrystalline analogs show that nanocrystalline metal oxides are more reflective compared to the bulk oxides. Low values of reflectivity in the region from $1300\text{--}2500\text{ nm}$ indicate strong absorption due to carbonates or adsorbed water and these features are usually stronger in nanocrystalline oxides. In fact, nanocrystalline metal oxides have high specific surface area and possess more adsorbed water molecules or CO_3^{2-} ions, compared to macrocrystalline oxides and hence stronger absorption. In the spectral region $750\text{--}1300\text{ nm}$ there is no absorption and the reflectivity is almost 15–20% higher then in bulk counterparts. Therefore, CeO_2 , TiO_2 and ZnO nanocrystalline samples can be used as NIR reflective pigments in this region.

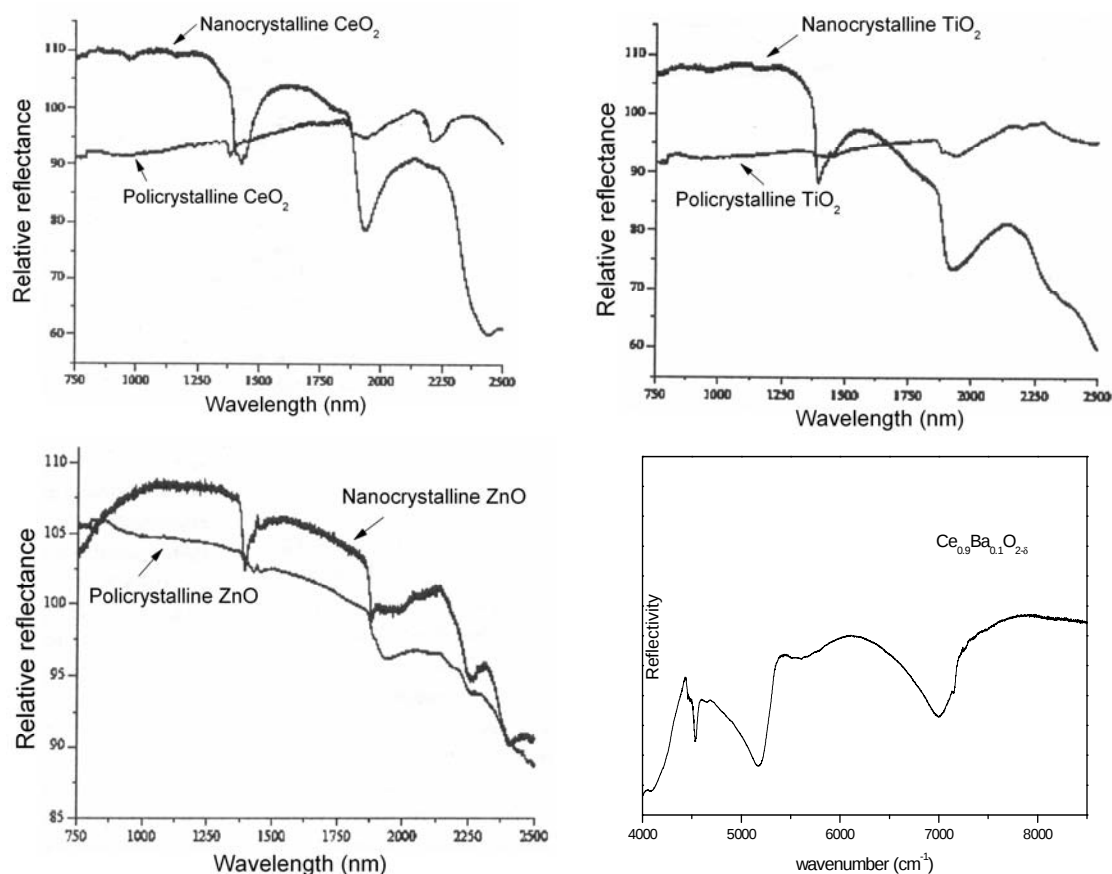


Figure 5 NIR spectra of Ba-doped CeO_2 , TiO_2 and ZnO nanocrystalline samples. NIR spectra of macrocrystalline samples are given as reference ones.

B. Training in XPS spectroscopy

During the second year of OPSA project we realized strong collaboration with several Italian Universities as University of Bari and University of L'Aquila where M. Scepanovic realized measurements and training in use of x-ray photoluminescence spectroscopy (XPS) for nano-sized materials characterization.

XPS measurements of the samples of nanocrystalline CeO_2 doped with Nd^{3+} and Y^{3+} (in concentration 25 wt.%) were performed by a VG ESCALAB 210 spectrometer with non-monochromatized $\text{MgK}\alpha_{1,2}$ (1256.6 eV) X-ray source and with operating pressure of 10^{-8} Pa. The spectra were collected in the constant pass energy mode of the analyzer, with values ranging from 50 and 20 eV. XPS of doped and pure ceria nanopowders provides interesting information about the concentration of Ce^{3+} sites in the material and thereby allows evaluation of oxygen vacancy behaviour in the material of interest for solid oxide fuel cells.

Acquired spectra are shown in the Figures 6 and 7 below.

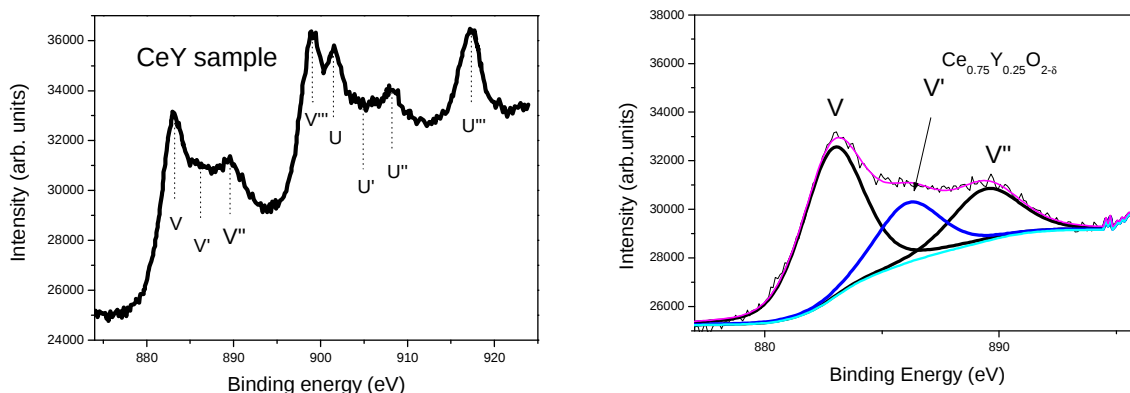


Figure 6 XPS spectra of 25%Y-doped ceria

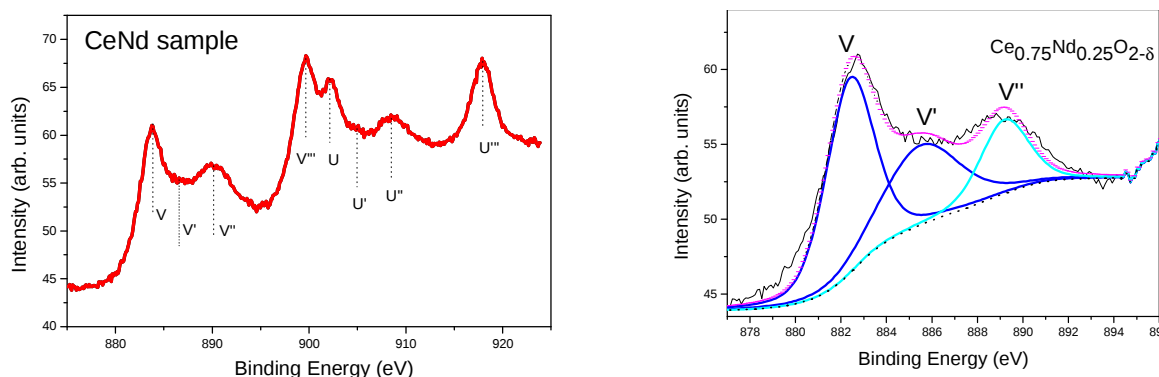


Figure 7 XPS spectra of 25%Nd-doped ceria.

It is accepted that 10 peaks appear for $\text{CeO}_{2-\delta}$ in the Ce_{3d} XPS spectrum. Peaks marked as V_0, V', U_0, U' are assigned to reduced CeO_2 containing mostly Ce^{3+} , whereas the peaks $V, V'', V''', U, U'', U'''$ are assigned to photoelectrons originating from Ce^{4+} . In the obtained spectra peaks V_0 and U_0 are of negligible intensities. XPS was applied to determine the concentration of Ce^{3+} ions in doped ceria samples. Applying the fitting procedure, it was possible to determine the concentration

of Ce^{3+} ions in doped samples. In such a way, the concentration of Ce^{3+} ions was 10.7% for Nd-doped and 23.1% for Y-doped ceria. Therefore, this analysis revealed that Y doped sample has a higher percentage of Ce^{3+} states than Nd doped sample what was in a very good accordance with previous Raman results obtained on the same samples which showed that surface layer of $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ has higher O^{2-} vacancy concentration than $\text{Ce}_{0.75}\text{Nd}_{0.25}\text{O}_{2-\delta}$ sample.