

Report on WP3 and WP4 activities

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

Appendix D:

**Training in the μ -Raman and the μ -PL spectroscopy at low temperatures,
high magnetic fields and high pressure**

Table of Contents

- A. Training in the μ -Raman and the μ -PL spectroscopy at low temperatures and high magnetic fields/3**
- B. Training in high-pressure μ -Raman and μ -PL spectroscopy research/4**

A. Training in the μ -Raman and the μ -PL spectroscopy at low temperatures and high magnetic fields

Micro-Raman spectra were taken at room temperature in backscattering configuration and analyzed using a Jobin Yvon T64000 spectrometer, equipped with a nitrogen cooled charge-coupled-device detector. As an excitation source we used the 514.5 nm line of an Ar-ion laser. Raman scattering measurements of pure and Fe-doped ceria nanopowders are presented in Fig. 1. Raman spectra showed that there is evident redshift and broadening of the F_{2g} Raman mode with an increase of oxidation state of Fe dopant while the Raman mode due to intrinsic oxygen defect states also increases with oxidation state of Fe dopant (see Fig. 2). The presence of defect states in ceria lattice implies the presence of $Ce^{3+}-O^{2-}$ complex in ceria lattice. Therefore, this redshift and broadening can be a consequence of the coupling between charge located at $Ce^{3+}-O^{2-}$ complex and F_{2g} vibration responsible for the room temperature ferromagnetism in these compounds.

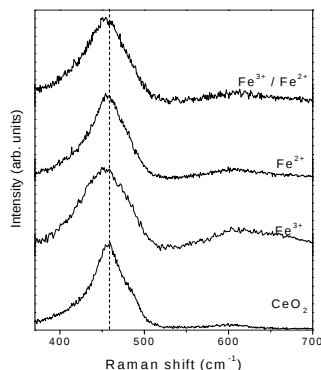


Figure 1 Raman spectra of pure and Fe-doped CeO_2 nanopowders.

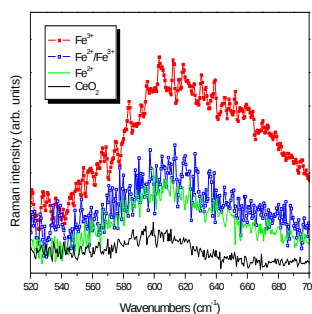


Figure 2 Raman spectra of oxygen defect states

The observation of RT-FM in pure CeO_2 nanocrystalline powder has given a strong evidence of oxygen vacancy induced ferromagnetic ordering in this nonmagnetic oxide (Fig. 3) whereas Fe doping of CeO_2 causes an enhancement of ferromagnetism with increased valence state of Fe, almost three times higher in Fe^{3+} sample as compared with the pure CeO_2 . This is presented in Fig. 4.

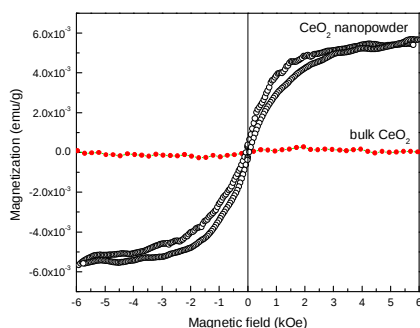


Figure 3. Room temperature magnetization vs magnetic field for bulk and nanopowdered CeO_2 .

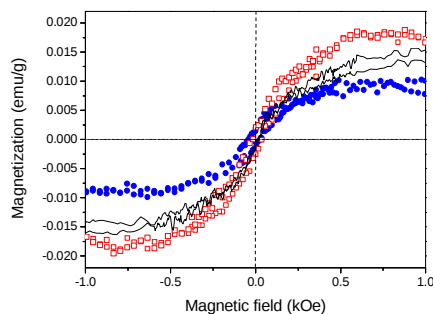


Figure 4 Room temperature magnetization versus magnetic field for Fe-doped samples.

Our results indicated that the RT-FM in Fe doped samples originates from a combination effect of oxygen vacancies and TM doping and can be significantly enhanced through a F-centre exchange (FCE) coupling mechanism, in which both oxygen vacancies and magnetic ions are involved.

B. Training in high-pressure μ -Raman and μ -PL spectroscopy research

The high pressure Raman scattering measurements were performed on undoped TiO_2 nanopowders with an average particle size of 7 nm obtained from XRD results. Measuring of the μ -Raman spectra of anatase TiO_2 nanocrystalline sample at high pressures were performed at Jobin-Yvon T64000 triple spectrometer equipped with a liquid nitrogen cooled CCD and a microscope (magnification 40x) was used for detection. High pressure measurements were achieved with a Merrill-Basset type diamond anvil cell (DAC) fitted under the microscope allowing micro-Raman study in a back scattering geometry. The pressure transmitting medium was a mixture of methanol-ethanol (4:1). The Raman spectra of anatase TiO_2 nanocrystals for all five Raman modes under increasing (1atm-4.7GPa) and decreasing pressure are given in Fig. 1. The Raman energy shift and bandwidth dependence on pressure is presented in Fig. 2. From frequency shift of five Raman modes it was possible to deduce the values for a Grüneisen parameter γ of each Raman mode. This analysis revealed that the Grüneisen parameters γ for each Raman mode are of the same sign and have slightly higher values than in the corresponding monocrystalline sample. These results were of crucial importance regarding our further investigation of phonon-phonon interactions in nanocrystalline anatase TiO_2 whose E_g modes experience unusual temperature behaviour.

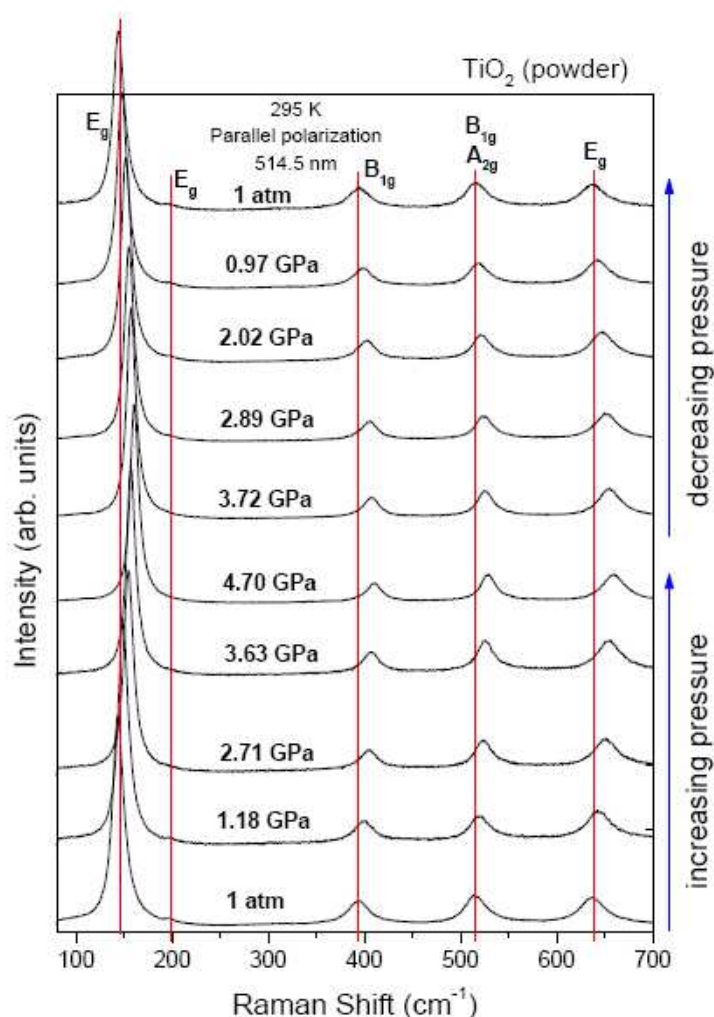


Figure 1 High-pressure Raman spectra of anatase TiO_2 nanocrystals

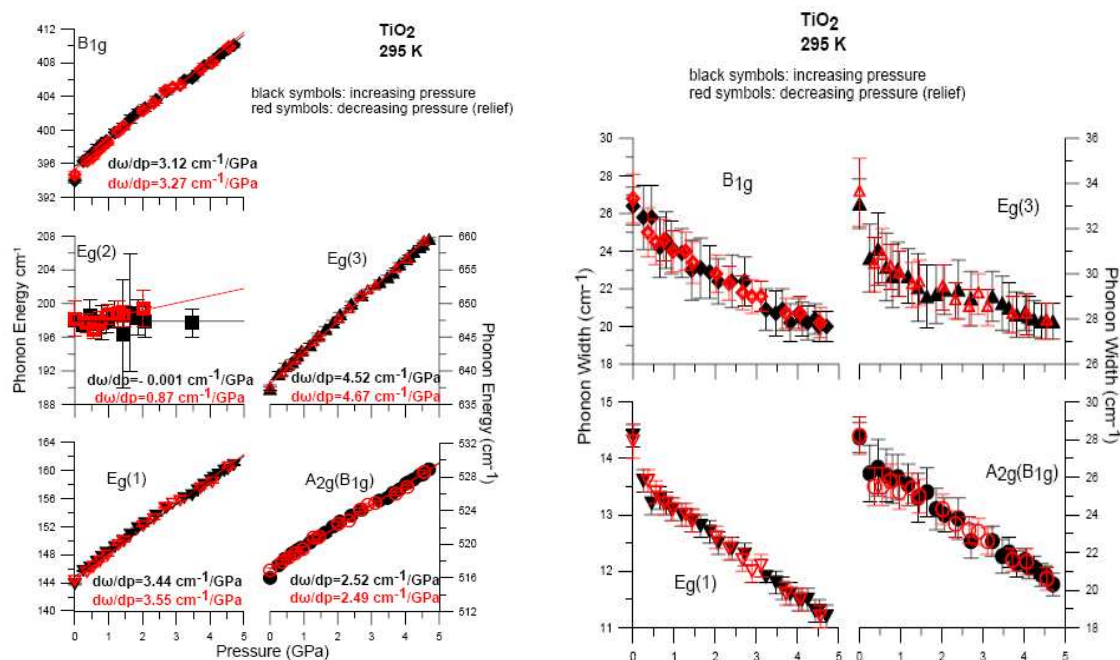


Figure 2 Frequency and bandwidth dependence of anatase TiO₂ Raman modes on pressure.

Photoluminescence (PL) spectra of the TiO₂ nanopowders prepared by a laser-induced pyrolysis have been measured by TriVista 557 spectrometer (Fig. 3). The peaks appearing at the high-energy side of the PL spectra shown in figure below belong to the Raman signal characteristic for anatase TiO₂ samples. Under laser irradiation with photon energy of 2.41 eV (514.5 nm) and 2.54 eV (488 nm) the TiO₂ nanocrystals displayed strong visible light emission. The line shape and position of this broad luminescence band vary with excitation energy. As the excitation photon energy increases the PL maximum has a blueshift, whereas the PL peak intensity has small variation. This indicates that a series of localized levels within the forbidden gap have a distribution and are suitable for luminescence, and that these levels might have nearly the same luminescence efficiency.

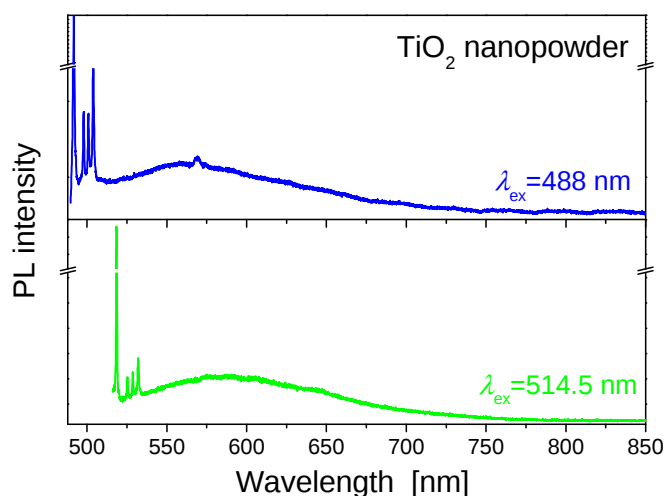


Figure 3 Room temperature μ -PL spectra of laser synthesized TiO₂ nanopowders excited by 488 and 514.5 nm line of mixed Ar⁺/Kr⁺ laser.