LUMINESCENCE AND RAMAN SCATTERING OF STABILIZED ZIRCONIA CRYSTALS. D. I. Torres and J. Llopis, 1 Department of Natural Science, Inter American University of Puerto Rico, Bayamón Campus, Puerto Rico 00957, 2 Departamento de Física de Materiales, F. CC Físicas, Universidad Complutense, Madrid 28040, Spain.

Introduction: Zirconium dioxide (ZrO$_2$) has monoclinic form at room temperature, but can be stabilized in cubic phase by partial substitution of Zr$^4+$ with metal cations like Ca$^{2+}$ or Y$^{3+}$. This cation substitution causes the creation of oxygen vacancies in order to preserve electrical neutrality. This base defect structure of stabilized zirconia (SZ) has a significant influence on their optical properties, and can be modified by exposing the samples to reducing conditions. As a result of thermal reduction, which generate new oxygen vacancies, the SZ become coloured modifying their main characteristic. The changes in coloration can be related to a broad absorption band centered at 365 nm, associated with defects formed with oxygen vacancies. However, the detailed structure of such defects is yet uncertain. Temperature dependent Photoluminescence (PL) and Raman spectra have been used to study the defect structure of untreated and thermochemically reduced Y-stabilized cubic zirconia (YSZ). The method of moments has been applied to the emission (EM) bands in order to obtain more information of the defects generated in the stabilization process, and in the reduction process.

Experiment setup: PL spectra were determined with a Perkin-Elmer LS-5 fluorescence spectrometer. Raman spectra were excited using 514.53 nm radiation line from a Coherent Innova99 Ar-ion laser. Spectra were measured in the backscattering geometry using a Raman microprobe (Olympus) attached to a triple spectrometer configured in the subtracting mode (Jobin Yvon T64000) and a multichannel detector charged coupled device (CCD). For the temperature dependence studies, we measured the EM in the range of 110-300 K, and the Raman spectra from 70-580 K. The YSZ single crystals used, purchased from Ceres Corp., contained 9.5 mol% Y$_2$O$_3$ with (100) orientation. For the thermochemical reduction, the samples were placed in a graphite box inside a furnace with a flowing inert atmosphere and then quenched in liquid nitrogen.

Results: PL spectra. Over the whole temperature range the EM spectrum of the untreated crystals can be decomposed into three broad bands, a red component peaked at 2.0 eV, a yellow-orange component peaked at 2.2 eV and a blue component peaked at 2.6 eV. The behavior of these bands with temperature and the parameters obtained from the moments theory (Huang-Rhys parameter $S$ and phonon mean energy $h\omega$) confirms that they can be associated with three different defects, $F_{A\alpha}$-center for the red component, $F_{A\alpha}$-center for the yellow-orange component, and F-center for the blue component. As a result of thermochemical reduction, the crystals became colored with tonalities ranging from pale-yellow to dark-brown, and there appeared a broad absorption band centered at ~365 nm similar to that previously reported. The rate of the luminescence decay with thermoreduction of each EM spectrum component was different, consistent with previous assumption of three different complexes. Results from moments theory applied to the EM bands in colored samples points out to $T$-centers as the main defect generated in the reduction process.

Raman spectra. The Raman spectra of the as-received crystals showed the characteristic broad T$_{2g}$ band centered at ~600 cm$^{-1}$. The Raman spectrum of the most reduced sample exhibited a decrease in intensity at frequencies below 300 cm$^{-1}$. This region mostly contains contributions from the acoustic modes, which arise from the in-phase motion between the oxygen and the cation sublattice, with the cations as the major contributors of the vibration. This observation is indicative of improved order since the acoustic modes are activated by disorder. This improvement of the lattice arrangement can be understood as indicating that the concentration of vacancies is not randomly distributed, but that they are arranged in periodic sequences. This is in agreement with our PL measurements and moments theory which associated a specific mean phonon frequency to each band component. The decrease in intensity at 300 cm$^{-1}$ can be associated with the decay of PL intensity of the blue band and the formation of $T$-centers.