Unusual photoluminescence of undoped hafnia perovskite nanoparticles synthesized via non-aqueous sol-gel process

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Perovskite compounds are among the most interesting mixed metal oxide materials in terms of their optical, magnetic, ferroelectric and multiferroic properties. The synthesis of these compounds as nanoparticles is of fundamental importance as size reduction and shape engineering allow modification and tuning of their fundamental properties,[1] thus opening new possibilities for micro-, opto- and nanoelectronic applications.[2]

Hafnia perovskite nanoparticles with size as small as 1.6nm in diameter were synthesized via a non-aqueous sol-gel process.[3] The synthesis procedures were carried out in a glove box using metallic strontium (Sr) or calcium methoxide ($Ca(OCH_3)_2$) and hafnium (IV) tert-butoxide ($Hf(O^tBu)_4$) mixed into benzyl alcohol. The mixture was transferred into a stainless steel autoclave, carefully sealed and then heated in a furnace at 300ºC for 2 days. An important advantage of this method is the possibility to synthesize pure and highly crystalline nano-sized perovskite (ABO_3)-type oxide nanoparticles without use of surfactant.[4]

The structural properties of these nanoparticles were studied by XRD, TGA, SEM, HRTEM, Cs corrected TEM and XPS. High-resolution transmission electron microscopy micrographs presented in Figures 1 reveal high crystallinity of the defect free nanoparticles and that they possess the perovskite structure (power spectrum inset figure 1b). Cs corrected study enabled to differentiate the perovskite phase from the cubic HfO_2 phase.

Literature shows that upon cerium[4] or europium doping, these perovskite nanoparticles exhibit certain luminescence from an otherwise optically inactive matrix material. UV-visible diffuse reflectance measurements allowed for the detection of impurity phases ($CaCO_3$) that were not visible using XRD measurements and HRTEM study (Fig. 2).[5] Under these measurements it was also possible to estimate the optical band gaps of the $CaHfO_3$ and $SrHfO_3$ nanoparticles. Photoluminescence (PL) study of these undoped perovskite nanoparticles at room temperature revealed two important features. Firstly, an unexpectedly strong luminescence in the UV-visible region was observed for both types of nanoparticles. Secondly, spectral instability under continuous UV illumination became immediately apparent, exhibiting different trends for $SrHfO_3$ and $CaHfO_3$ nanoparticles. To get a better insight into these processes, more systematic PL measurements were carried out as a function of temperature (10-300K) (Fig. 3), UV-exposure time (0-15min) and surrounding ambient (air/vacuum). The influence of these parameters will be discussed and a tentative model will be proposed to explain these phenomena in terms of luminescent centers located at the surface of the nanoparticles.

Acknowledgements

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Figures

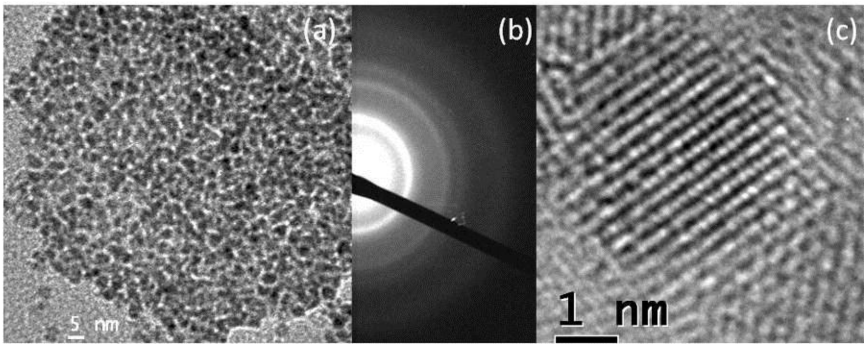

Figure 1: TEM micrographs of $CaHfO_3$ showing (a) general appearance of these particles, (b) electron diffraction pattern indicating $CaHfO_3$ cubic structure, (c) HRTEM image of a single particle oriented along <001> zone axis.

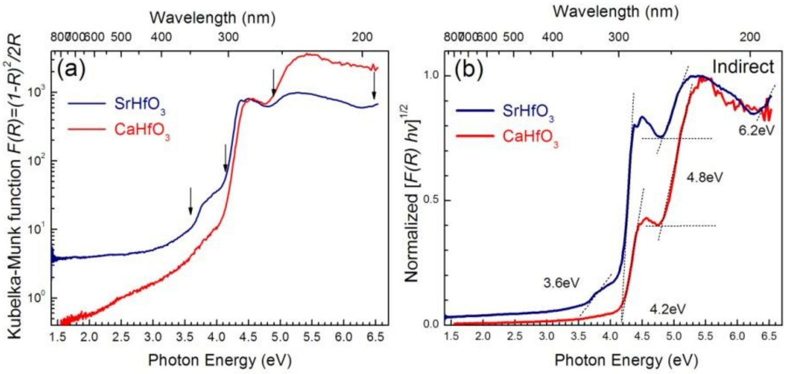

Figure 2: Diffuse-reflectance spectra measured in the UV-visible region at 300K for $SrHfO_3$ and $CaHfO_3$ nanoparticles; arrows indicate apparent absorption thresholds. Normalized Tauc plots considering (b) indirect optical transitions for $SrHfO_3$ and $CaHfO_3$.

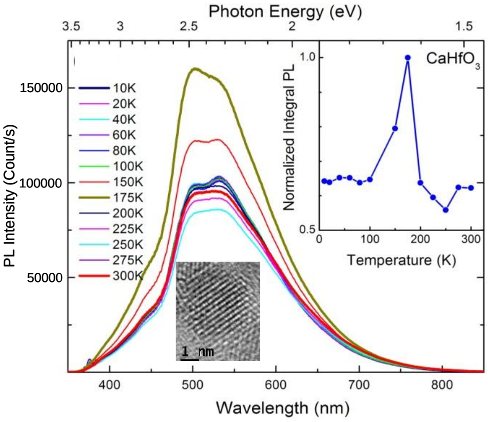

Figure 3: Temperature-dependent PL spectra of $CaHfO_3$ nanoparticles; insets show corresponding evolutions of the integral PL yield as a function of temperature.