Hyper-Raman Spectroscopy of CeO_2

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Abstract

Cerium dioxide (CeO_2) belongs to the fluorite structure group (O_h^5 point group) resulting in one Raman active T_{2g} mode and two IR active T_{1u} TO and LO modes. The T_{2g} Raman band in CeO_2 has been used to probe the symmetric Ce-O vibrational mode of different sized nanoparticulates. Far infrared studies of the Ce-O interactions are difficult to conduct due to low optical transmission, efficiency of the detector and water absorption bands interfering with the measurements. The selection rules of hyper-Raman spectroscopy (HRS) allow the study of IR bands in the far infrared spectral region, such as the motion of the Ce atoms. For the first time, HRS was used to investigate the T_{1u} TO and LO IR modes in CeO_2. The position and full-width half-maximum (FWHM) of the TO and LO bands in the HRS spectrum were used to investigate the spectral response in relation to particle size (i.e., phonon confinement). The investigation of CeO_2 with HRS provides a research platform for future work in the study of ThO_2, UO_2 and PuO_2 IR modes.

Keywords: cerium dioxide, hyper-Raman spectroscopy, lattice damage

Introduction

Crystalline material of cerium dioxide (CeO_2) belongs to the fluorite structure group and described with a face centered cubic (fcc) sublattice. Group theory analysis of the fluorite structure (O_h^5 point group) results in six optical-phonon branches, the triply degenerate Raman T_{2g} mode, the doubly degenerate infrared T_{1u} TO and the non-degenerate infrared T_{1u} LO mode.[1,2] Literature reports these bands at 465, 272 and 595 cm^{-1}, respectively.[1,3] The indicia of the IR bands at 272 and 595 cm^{-1} have been observed in the Raman spectrum of CeO_2 nanoparticulates. Studying compounds with a fluorite structure in the far infrared spectral region is difficult and is further complicated by large full-width half-maximum (FWHM) of the IR bands. Hyper-Raman spectroscopy (HRS) can provide a different method to study bands in the IR spectral region. HRS is a nonlinear spectroscopy where two photons interact with the material and produce a single photon of Raman scattered light at a little less than twice the excitation wavelength. The nonlinear effect changes the symmetry selection rules by allowing nonactive, silent modes and IR modes to become active. The high laser power density required to induce the nonlinear effect can cause sample degradation. Dielectric breakdown is a common problem in HRS experiments of dark-colored and powder samples with large surface areas. Fortunately, high signal-to-noise (S/N) ratio measurements were achieved in the HRS experiments of CeO_2. The high S/N ratios in the HRS measurements of CeO_2 enabled us to measure the effect of material particle size on the peak position and FWHM of the TO and LO modes.

Materials and Methods

CeO_2 samples were used as received from the manufacturer. Four different spherical particle sizes were investigated in this work: <5 μm (Aldrich Chemical Company), 100 nm (US Research Nanomaterials), 50 nm (US Research Nanomaterials) and 10 nm (US Research Nanomaterials). Samples were compacted with a spatula reducing the potential for dielectric breakdown. The particle size distribution of these samples is estimated to be 99 ± 6, 51 ± 2 and 15 ± 1 nm (95% confidence interval) from analysis of 100 particles in SEM images provided by the manufacturer (US Research Nanomaterials) and no SEM image was available for the <5 μm sample.

The Raman spectra of these samples were acquired with a Raman microspectroscopy system following excitation with a 632.8 nm laser with powers <5 mW at the sample and 2 minute integration times, as described previously.[4-6] In contrast, HRS spectra of CeO_2 were measured with a home-built HRS setup consisting of a Mira 900 picosecond laser (Coherent), a modified microscope (Olympus) operating in an epi-illumination configuration and an iHR320 spectrograph (Horiba Jobin-Yvon) equipped with a Newton EMCCD (Andor 971N-BV) detector. LabSpec 5.93 software was used to control the spectrometer, detector and collect data in these experiments. Several laser wavelengths from 780 to 950 nm were used in these experiments although most work was conducted with a picosecond laser tuned to 814 nm and filtered with a longpass edge filter to eliminate any visible light that might interfere with the HRS signal in the 407 nm region. A shortpass dichroic mirror was used in the microscope to reflect light from 647-1050 nm toward the sample, while transmitting 350-647 nm toward the spectrometer. The laser light was focused on the sample with a 20x NIR objective. The hyper-Raleigh at 407 nm was used to maximize the HRS signal. A 785 nm shortpass filter was used to block any residual fundamental. Laser power as low as 25 mW were used to characterize the material although the reported work was conducted with the laser power intensity of ~120 mW at the sample, which maximized the signal. The HRS spectra were integrated for 20 minutes and two spectra were co-added for each sample to eliminate cosmic ray contributions. A quadratic relationship was observed for the measured HRS intensity as a function of the incident excitation intensity. The HRS signal intensity increased significantly for wavelengths shorter than 900 nm, suggesting a resonance/pre-resonance effect.

Results and Discussion

Figure 1 shows Raman spectra of the CeO_2 samples of varying size diameters in the spectral region of 400 to 540 cm^{-1} acquired with 632.8 nm laser light. The Raman peak near 465 cm^{-1} in Figure 1 corresponds to the T_{2g} mode. The acquired spectra are very similar to the spectra acquired by Kosacki et al.[7,8]

Figure 2 shows the HRS spectra of the CeO_2 samples in the spectral region of 140 to 1200 cm^{-1}. HRS data shows the two IR T_{1u} TO and LO modes in the HRS spectrum near 270 and 590 cm^{-1}, respectively. The growth of an additional band near 400 cm^{-1} in the HRS spectra with decreasing sample diameter was significantly stronger for the 10 nm sample. The 400 cm^{-1} band was measured with 25 mW laser power, much less than the typical ~120 mW used in these experiments. The 400/594 cm^{-1} band ratio was approximately constant for laser powers ranging from 25 to 165 mW and the shape of the bands did not change in this range, so it is unlikely that laser-induced damage contributes to the intensity of the 400 cm^{-1} band. The temperature of the 10 nm sample irradiated with a 70 mW laser beam was estimated using the anti-Stokes/Stokes intensity ratio to be close to room temperature, which agrees with the small spectral shift observed in the band peak position.[5] The shape of the HRS bands (frequency and FWHM) remained the same at laser powers of 70 and 138 mW, therefore eliminating the possibility of thermal decomposition. The 400 cm^{-1} band may be attributed to the 2TA overtone of CeO_2.[1,9] It is also possible that since the surface to volume ratio is much larger for the 10 nm sample, surface vibrational modes might begin playing a role in the HRS spectrum.

The T_{1u} TO and LO bands for the 5 μm sample are located at 267 and 594 cm^{-1}, respectively. The FWHM of the TO and LO bands are 17 and 34 cm^{-1}, respectively. Minimal asymmetry is observed for these two bands. The LO band is broader than the TO band suggesting a shorter total phonon dephasing time for the LO mode.[7,8] Inhomogeneous broadening could also lead to a broader LO band.[10-12] For the 100 nm sample the LO band becomes more asymmetric and both the TO and

LO bands become broader. A progression in the asymmetry of the LO bands and broadening of the TO and LO bands is observed for decreasing sample diameter toward the 10 nm particles. The asymmetry becomes significant with decreasing sample size, especially for 10 nm particles.

Table 1 presents the peak positions and FWHM of the T_{2g}, T_{1u} TO and T_{1u} LO modes in the Raman and HRS spectra. The peak positions of the T_{2g}, T_{1u} TO and T_{1u} LO modes shift to lower energies as the sample diameters decrease. The FWHM of the T_{2g}, TO and LO modes in the Raman and HRS spectra broaden and become more asymmetric with decreasing sample diameter. The red-shifting of the peak positions, broadening and asymmetry of the Raman and HRS bands with decreased sample size may be attributed to the combined effects of inhomogeneous strain and phonon confinement in the structure of CeO_2 for smaller diameter samples which reduces the phonon lifetime.[1,7,8,10-12]

Conclusion

The HRS spectra of varying sizes of CeO_2 particles (5 μm, 100 nm, 50 nm and 10 nm) are reported here for the first time and were compared to Raman spectra of the same CeO_2 particles. The particle size dependent spectra provide a unique view of the T_{1u} LO IR and the T_{1u} TO IR vibrational modes in the HRS spectra. With decreasing particle size the peak position of the Raman and HRS bands shift to lower energies, broaden and become more asymmetric. The HRS spectra, in contrast to the Raman scattering spectra, were more sensitive to the particle size. HRS will allow for the study of actinide compounds with fluorite structures, such as, ThO_2, UO_2 and PuO_2 and the effect of dose radiation and damage to the crystal lattice.

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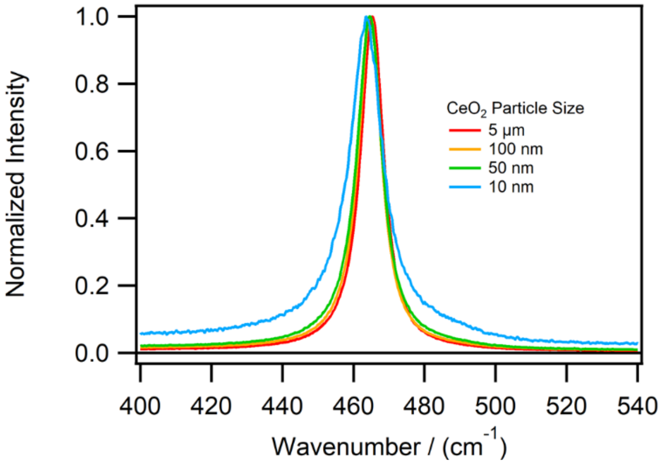

Figure 1: Raman spectra of CeO$_2$ particles of different sizes (5 µm (red), 100 nm (orange), 50 nm (green) and 10 nm (blue)) following excitation with 632.8 nm laser light.

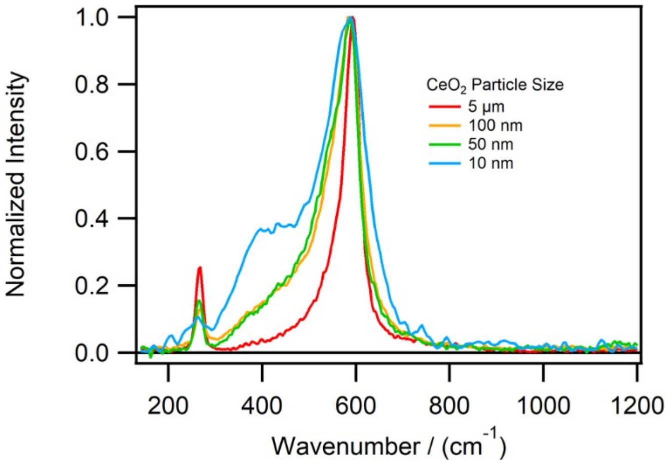

Figure 2: Hyper-Raman spectra of CeO$_2$ particles of different sizes (5 µm (red), 100 nm (orange), 50 nm (green) and 10 nm (blue)) following excitation with two photons of 814 nm laser light.

Table 1: Raman and hyper-Raman vibrational modes, frequencies and full-width half-maximum (FWHM) of CeO_2.

Raman

Particle Size (nm)	Mode	Frequency (cm^{-1})	FWHM (cm^{-1})
5000	T_{2g}	465	8
100	T_{2g}	464	8
50	T_{2g}	464	9
10	T_{2g}	463	15

Hyper-Raman

Particle Size (nm)	Mode	Frequency (cm^{-1})	FWHM (cm^{-1})	Mode	Frequency (cm^{-1})	FWHM (cm^{-1})
5000	TO	267	17	LO	594	34
100	TO	267	17	LO	588	48
50	TO	265	18	LO	588	55
10	TO	259	26	LO	587	64