Raman scattering from low frequency phonons confined in CeO$_2$ nanoparticles

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Abstract. CeO$_2$ nanopowder samples synthesized by self-propagating room temperature method were investigated by Raman spectroscopy. The phonon modes observed in the low frequency region ($\omega < 70$ cm$^{-1}$) can be well described by the elastic continuum model, assuming that nanoparticles are of perfect spherical shape and isotropic. Both rigid boundary and stress-free surface cases were analyzed. The calculated vibrational frequency dependencies on the particle diameter were used to identify the modes: ($l=2$, $n=0$), ($l=0$, $n=0$) and ($l=0$, $n=1$). Using the facts that mode frequencies scale inversely with particle dimension ($\omega \sim 1/D$) and that mode-radiation coupling coefficient for this type of vibrations is $1/\omega$, the correspondence between the particle size distribution and the Raman intensity was made. Particle diameter values ranging from 7 to 8 nm for the rigid boundary condition give the best description of the experimental spectra. This coincides well with the average particle diameter value of 8 nm acquired from the phonon confinement model.

1. Introduction

Raman scattering from confined acoustic vibrations in nanoparticles was observed in the low frequency part of spectra of various materials. The elastic sphere model (ESM) was generally used to analyze the acoustic phonon confinement. This model describes the oscillations of homogeneous elastic sphere and was successfully applied to explain the experimental spectra of nanoparticles [1, 2, 3, 4, 5]. According to ESM, the frequency of an acoustic Raman mode is scaled as the inverse of the dimension of a vibrating particle.

In this paper we give an overview of the possibilities for the extraction of information on nanoparticle size distribution from the low-frequency Raman spectra of CeO$_2$ nanoparticles. We calculated linear coefficients relating vibrational frequency and the particle diameter from ESM [2, 6]. We regarded our experimental spectrum as a superposition of several ESM modes and treated the inhomogeneous broadening of the spectrum as a consequence of the non-uniform particle size distribution of the sample. Based on this, the average particle size was evaluated. Results were compared to the particle size value deduced from phonon confinement model (PCM) that accounts for the optical phonon confinement, size and inhomogeneous strain effects [7].

2. Experimental Results

The nanocrystalline CeO$_2$ samples were obtained by self-propagating room temperature synthesis [7] and analyzed by X-ray diffraction. The CeO$_2$ crystallite size was about 6 nm.
Micro-Raman spectra were taken in the backscattering configuration and analyzed using a Jobin Yvon T64000 spectrometer, equipped with nitrogen cooled charge-coupled-device detector. As an excitation source we used the 514.5 nm line of Ar-ion laser.

Figure 1 shows Raman spectra of nano- and polycrystalline CeO$_2$ samples measured at room temperature. The strongest intensity mode at about 457 cm$^{-1}$ (in polycrystalline sample at 464.3 cm$^{-1}$) represents the optical Raman F$_{2g}$ mode, which softens in nano-sample as a consequence of phonon confinement effects. From the fits of optical F$_{2g}$ mode with PCM the average particle size value can be deduced and for this sample it is 8 nm.

Weak intensity feature at about 270 cm$^{-1}$ is ascribed to the second order Raman scattering. In the inset of figure 1 we have shown corrected experimental Raman spectrum of nano-CeO$_2$ in the low-frequency region 0-110 cm$^{-1}$. The intensity of the elastic scattering background was subtracted by $A/\omega^n$ approximation [5].

3. Vibrations of homogenous elastic nanospheres of CeO$_2$

Low-frequency Raman peaks in nanocrystalline materials, ascribed to confined acoustic phonon-like vibrations, can be well interpreted as vibrations of a three-dimensional homogenous elastic sphere using Navier’s equation and imposing spherical symmetry:

$$\rho \ddot{u} = (\lambda + 2\mu) \nabla(\nabla \cdot u) - \mu \nabla \times (\nabla \times u),$$  \hspace{1cm} (1)

where $u$ represents mechanical displacement vector $u(r,t) = u(r)e^{-i\omega t}$, while $\lambda$ and $\mu$ are parameters of material known as the Lame’s constants and $\rho$ is the mass density. Mass density of CeO$_2$ is 7300 kg/m$^3$, transverse and longitudinal sound velocities are respectively: $v_T = \sqrt{\mu/\rho} = 2890$ m/s and $v_L = \sqrt{(\lambda + 2\mu)/\rho} = 6600$ m/s [8].

Different boundary conditions were applied in solving Eq.(1): rigid boundary condition (no displacement at the particle surface) [2, 3, 6] and stress-free surface condition (no force acting on the particle surface) [1, 4, 5]. Two types of vibrational modes were obtained: spheroidal and torsional modes [2]. The calculated solutions express the linear dependence of $\omega$ on the inverse diameter of a nanoparticle. The Raman frequency is related to the particle diameter $D$ as:

$$\omega_{ln} = \frac{\omega}{D_T} = \beta_n,$$

where $\beta_n$ characterize the solutions of the Eq.(1), $l$ is the angular momentum quantum number. The solutions $\beta_n$ for spheroidal $l=0$, $l=1$ and $l=2$ and torsional $l=1$ and $l=2$ modes for two different boundary conditions are presented in Table 1 (a) and (b), respectively. According to the group theory analysis the spheroidal $l=0$ and $l=2$ modes are Raman active [9].

4. Results and discussion

Intensity of Raman scattering by small particles is expressed by formula [10] :

$$I(\omega) = A \frac{n(\omega)}{\omega} C(\omega) g(\omega) \hspace{1cm} (2)$$
torsional (TOR) modes in CeO$_2$ for rigid boundary (a) and stress-free surface condition (b).

| (a) | spherical | torsional |
|-----|-----------|-----------|
| l   | n         | $\beta_{ln} \cdot 10^5$ | l   | n         | $\beta_{ln} \cdot 10^5$ |
| 0   | 0         | 314.42    | 0   | 0         | -          |
| 0   | 1         | 540.62    | 0   | 1         | -          |
| 2   | 2         | 763.31    | 2   | 2         | -          |
| 1   | 0         | 33.66     | 0   | 1         | 137.78     |
| 1   | 1         | 114.07    | 1   | 1         | 236.88     |
| 2   | 2         | 137.79    | 2   | 2         | 334.36     |
| 0   | 1         | 176.62    | 0   | 1         | 176.73     |
| 1   | 2         | 222.31    | 2   | 1         | 278.89     |
| 2   | 2         | 278.73    | 2   | 2         | 377.87     |

| (b) | spherical | torsional |
|-----|-----------|-----------|
| l   | n         | $\beta_{ln} \cdot 10^5$ | l   | n         | $\beta_{ln} \cdot 10^5$ |
| 0   | 0         | 199.96    | 0   | 0         | -          |
| 1   | 1         | 431.16    | 0   | 1         | -          |
| 2   | 2         | 654.20    | 2   | 2         | -          |
| 0   | 1         | 113.00    | 0   | 1         | 176.73     |
| 1   | 1         | 225.26    | 1   | 1         | 278.89     |
| 2   | 2         | 298.89    | 2   | 2         | 377.87     |
| 0   | 1         | 81.41     | 0   | 1         | 76.69      |
| 2   | 1         | 160.00    | 2   | 1         | 218.82     |
| 2   | 2         | 267.63    | 2   | 2         | 322.43     |

where $n(\omega)$ is Bose-Einstein factor, $C(\omega)$ is the mode-radiation coupling factor, $g(\omega)$ is the density of states and $A$ is the scaling constant. It had been shown that the mode-radiation coupling factor scales inversely with the vibrational frequency: $C(\omega) \sim \frac{1}{\omega}$ for small spherical particles [10]. According to ESM, Raman spectrum would consist of discrete peaks if all the particles were of same dimensions. We presumed that the density of states reflects the particle size distribution, $N(D)$, through the relation: $g(\omega) = N(D = \frac{D_0}{\beta})$ [5]. The most often size distributions encountered in different nanomaterials can be well approximated with Gaussian ($N(D) \sim e^{-\frac{(D-D_0)^2}{2\sigma^2}}$) or Log-normal ($N(D) \sim e^{-\frac{\ln(D/D_0)^2}{2\sigma^2}}$) distribution functions.

Table 1. Calculated values of dimensionless variables $\beta_{ln}$ for fundamental spheroidal (SPH) and torsional (TOR) modes in CeO$_2$ for: rigid boundary (a) and stress-free surface condition (b).

In the low frequency region of the obtained Raman spectrum, there is a broad structure with two maxima positioned at the frequencies 18 cm$^{-1}$ and 28 cm$^{-1}$. Due to the significant broadening, the low frequency Raman spectrum was fitted with three ESM modes ($l=2$, $n=0$), ($l=0$, $n=0$) and ($l=0$, $n=1$). Intensities of these modes were calculated according to Eq.(2) including Gaussian or Log-normal particle size distribution. Most frequent diameter, $D_0$, distribution width, $\sigma$ and constants $A$ corresponding to the three modes, were treated as free parameters. The position and broadening of each peak in the calculated spectra are determined by $\beta_{ln}$, $D_0$ and $\sigma$. A mode position shifts towards lower frequencies as $D_0$ and $\sigma$ increase and $\beta_{ln}$ decreases.

The theory implies that the spheroidal ($l=0$, $n=0$) mode should be the most intensive in the ($l=0$ series of solutions [10]. The same applies for the first quadrupolar mode ($l=2$, $n=0$) in the $l=2$ series. From the results shown in Table 1 (a) and (b) it is obvious that $\beta_{00} > \beta_{20}$, which implies that the most intensive mode from figure 2, at about 28 cm$^{-1}$ corresponds to the spherical ($l=0$, $n=0$) mode, while the mode at 18 cm$^{-1}$ can be ascribed to ($l=2$, $n=0$) mode.

We analyzed the case of rigid boundary particles first. Curves plotted in the figure 2 (a)
illustrate that the Gaussian distributions with $D_0$ having value from the interval $6 - 8 \text{ nm}$ coincide well with the experimental Raman spectra. The distributions with higher values of $D_0$ from this interval are more likely to occur since they need to be narrower and approach zero value more rapidly as the diameter approaches zero. The Log-normal distributions of the particle diameter for the values of $D_0$ in interval $7.5 - 8.5 \text{ nm}$ produced satisfactory fit of the experimental spectra (see figure 2 (b)). The best fits were acquired for the Gaussian distribution with parameters ($D_0 = 7 \text{nm}$, $\sigma = 3.1 \text{nm}$), and Log-normal distribution with parameters $D_0 = 8 \text{nm}$, $\sigma = 0.285$. If the results from these fits are compared to the value of the mean particle size diameter of $8 \text{nm}$, acquired from PCM, it can be concluded that values of $D_0$ from the interval $7 - 8 \text{ nm}$ (in the rigid boundary case) describe best the particle size distribution of the investigated sample.

In the case of stress-free surface the values of $\beta_{20}$ and $\beta_{00}$ led to sufficiently distinct peaks in the Raman spectrum for $D_0$ ranging from $5 \text{ nm}$ to $6.7 \text{ nm}$, without possibility to produce the satisfactory fit of the experimental data. Small size of the particles ($6 - 8 \text{ nm}$) often leads to high particles’ agglomeration which might be the reason for rigid boundary vibrations, since it can act as powder matrix [3].

5. Conclusion
We identified the low-frequency Raman feature as scattering from the vibrations of small spheres. Taking into account the correspondence between Raman intensity and particle size distribution, Raman intensity was calculated as the sum of three ESM modes intensities: $(l=2, n=0)$, $(l=0, n=0)$ and $(l=0, n=1)$. The best agreement between experimental and calculated spectrum was obtained for the rigid boundary case and not for stress-free boundary condition. The reason can be found in high agglomeration of the nanoparticles when the particles are of small dimensions as in our case or in the presence of microstrain effects that influence strongly the optical Raman mode in ceria nanopowder. The mean particle diameter could not be determined exactly because of the resemblance of the calculated curves for the particle diameter interval $6 - 8 \text{ nm}$ in the case of Gaussian size distribution and for the interval $7.5 - 8.5 \text{ nm}$ for Log-normal distribution. The idealization imposed by ESM model might be the reason for the lack of unique interpretation of the experimental results, but the actual particle size distribution might also differ from those used in our calculations.

Acknowledgments
This work is supported by the Ministry of Science of the Republic of Serbia, under the project No. 141047 and the OPSA-026283 project within EC FP6 Programme. S.A. wishes to thank M. Žepeanović for helpful discussions.

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