

# Far-infrared spectroscopic study of CeO<sub>2</sub> nanocrystals

Z. V. Popović · M. Grujić-Brojčin · N. Paunović ·  
M. M. Radonjić · V. D. Araújo · M. I. B. Bernardi ·  
M. M. de Lima · A. Cantarero

Received: 20 August 2014 / Accepted: 5 January 2015 / Published online: 13 January 2015  
© Springer Science+Business Media Dordrecht 2015

**Abstract** We present the far-infrared reflectivity spectra of 5 nm-sized pure and copper-doped Ce<sub>1-x</sub>Cu<sub>x</sub>O<sub>2-y</sub> ( $x = 0; 0.01$  and  $0.10$ ) nanocrystals measured at room temperature in the 50–650 cm<sup>-1</sup> spectral range. Reflectivity spectra were analyzed using the factorized form of the dielectric function, which includes the phonon and the free carriers contribution. Four oscillators with TO energies of approximately 135, 280, 370, and 490 cm<sup>-1</sup> were included in the fitting procedure. These oscillators represent local maxima of the CeO<sub>2</sub> phonon density of states, which is also calculated using the density functional theory. The lowest energy oscillator represents TA(L)/TA(X) phonon states, which become infrared-active E<sub>u</sub> modes at the L and X points of the

Brillouin zone (BZ). The second oscillator originates from TO(Γ) phonon states. The oscillator at ~400 cm<sup>-1</sup> originates from Raman mode phonon states, which at the L point of BZ also becomes infrared-active E<sub>u</sub> mode. The last oscillator describes phonons with dominantly LO(Γ) infrared mode character. The appearance of phonon density of states related oscillators, instead of single F<sub>2u</sub> infrared-active mode in the far-infrared reflectivity spectra, is a consequence of the nanosized dimension of the CeO<sub>2</sub> particles. The best fit spectra are obtained using the generalized Bruggeman model for inhomogeneous media, which takes into account the nanocrystal volume fraction and the pore shape.

**Keywords** Nano ceria · Far-infrared spectroscopy · Phonon density of states · Bruggeman model · Nanoparticle characterization

Z. V. Popović (✉) · M. Grujić-Brojčin · N. Paunović  
Center for Solid State Physics and New Materials,  
Institute of Physics, University of Belgrade, Pregrevica  
118, 11080 Belgrade, Serbia  
e-mail: zoran.popovic@ipb.ac.rs

M. M. Radonjić  
Scientific Computing Laboratory, Institute of Physics  
Belgrade, University of Belgrade, Pregrevica 118,  
11080 Belgrade, Serbia

V. D. Araújo · M. I. B. Bernardi  
Instituto de Física, Universidade de São Paulo-USP,  
São Carlos, SP 13560-970, Brazil

M. M. de Lima · A. Cantarero  
Instituto de Ciencia de Los Materiales, Universidad de  
Valencia, 46071 Valencia, Spain

## Introduction

There are plenty of nanoscopic, microscopic, and other techniques that are used to study nanosized materials and structures (Popović et al. 2011). Among them, the most frequently used spectroscopic techniques are vibrational (phonon) spectroscopy techniques, such as Raman (R) and infrared (IR). The use of these techniques for nanostructure characterization is discussed in Popović et al. (2011), Grujić-Brojčin et al. (2005), and Cantarero (2013).

Ultrafine ceria powders represent an important material for solid oxide fuel cells or catalytic applications, which are attributed to CeO<sub>2</sub> remarkable oxygen-storage capability, i.e., the ability to undergo rapid redox cycles by releasing and storing oxygen (Popović et al. 2012).

In a nanocrystal, the phonons are confined in space, and all the phonons over the entire Brillouin zone (BZ) will contribute to the first-order vibrational spectra. The weight of the off-center phonons increases as the crystal size decreases, and the phonon dispersion causes a mode shape change and the frequency shift. The influence of all these effects on the CeO<sub>2</sub> Raman mode intensity, line shape, and energy were discussed in Popović et al. (2011) and Cantarero (2013).

Infrared spectroscopy is widely used in the 400–4,000 cm<sup>-1</sup> spectral range to characterize un-wished residuals during the synthesis of CeO<sub>2</sub> nanoparticles (Orel 1999). To the best of our knowledge there are no study regarding infrared-active lattice vibrations in ceria nanocrystals. In this paper, we have measured room-temperature far-infrared reflectivity spectra of the pure and copper-doped Ce<sub>1-x</sub>Cu<sub>x</sub>O<sub>2-y</sub> ( $x = 0, 0.01$  and  $0.10$ ) nanocrystals in the 50–650 cm<sup>-1</sup> spectral range. In order to assign the obtained features we performed lattice dynamics calculation of CeO<sub>2</sub>. Reflectivity spectra were analyzed using the factorized form of the dielectric function, which includes several oscillators and the free carriers contribution to the dielectric function. The oscillators represent the phonon density of states (PDOS)-related IR active modes. The best fit spectra are obtained using the generalized Bruggeman model for inhomogeneous media, which takes into account the volume fraction of nanopowder and the pore shape.

## Experiment and numerical method

Ceria samples were prepared in one step by the polymeric precursor method (Araújo et al. 2013). The sizes of nanocrystals obtained by Raman scattering technique are about 5 nm. Specific surface area of the samples (BET-method) were estimated from the N<sub>2</sub>-adsorption/desorption isotherms, at liquid nitrogen temperature, using a Micromeritics ASAP 2000 analyzer. The infrared reflectivity measurements were carried out at room temperature with a BOMEM DA-8

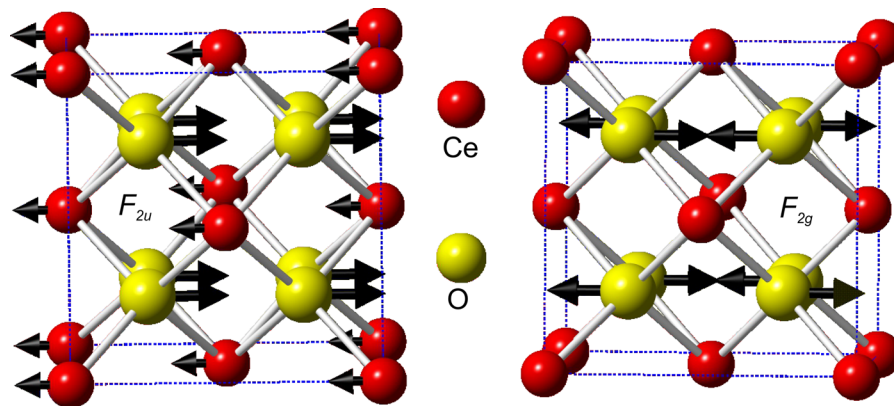
Fourier-transform IR spectrometer. A deuterated triglycine sulfate (DTGS) pyroelectric detector was used to cover the wave number region from 50 to 650 cm<sup>-1</sup>. Spectra were collected with 2 cm<sup>-1</sup> resolution, with 1,000 interferometer scans added for each spectrum.

In order to interpret the experimental data, we have performed density functional theory calculations implemented within the QUANTUM ESPRESSO package (Giannozzi et al. 2009). We have used the ultrasoft pseudopotentials with PBE exchange–correlation functional with 4f<sup>1</sup>, 5s<sup>2</sup>, 5p<sup>6</sup>, 5d<sup>1</sup>, 6s<sup>2</sup> valence electrons of cerium and 2s<sup>2</sup>, 2p<sup>4</sup> valence electrons of oxygen. The energy cutoffs for the wave functions and the electron densities were 60 and 900 Ry, determined to ensure stable convergence. We have sampled the BZ with a 32 × 32 × 32 Monkhorst–Pack **k**-space mesh.

The phonon frequencies are calculated within density functional perturbation theory (Baroni et al. 2001), over the BZ sampled with 8 × 8 × 8 Monkhorst–Pack **q**-point mesh. We have calculated the PDOS using that mesh, and the phonon dispersion curves are obtained from interpolation along the chosen path.

## Results and discussion

Cerium dioxide crystallizes in the fluorite-type cubic crystal structure (Fig. 1), space group *Fm* $\bar{3}$ *m* (no. 225), in which Ce is located in (4a) (0,0,0), surrounded by eight oxygen atoms located at (8c) (1/4, 1/4, 1/4) Wyckoff positions. This structure has one infrared ( $F_{2u}$ ) and one Raman ( $F_{2g}$ ) active mode, each of them being triple degenerated. The normal modes of these vibrations are sketched in Fig. 1. The  $F_{2u}$  mode represents vibrations of both the Ce and O atoms in opposite directions, whereas  $F_{2g}$  mode originates from the stretching vibrations of only oxygen atoms around Ce. In the CeO<sub>2</sub> single crystals and polycrystalline samples, the infrared and Raman active modes appear at 283/596 cm<sup>-1</sup> ( $\omega_{TO}/\omega_{LO}$ ) (Marabelli and Wachter 1987; Santha et al. 2004) and 465 cm<sup>-1</sup> (R) (Kourouklis et al. 1988; Weber et al. 1993; Nakajima et al. 1994), respectively. In our less than 5 nm CeO<sub>2-y</sub> nanocrystals (Popović et al. 2012) the Raman mode is centered at about 456 cm<sup>-1</sup>.



**Fig. 1** The normal modes of the infrared ( $F_{2u}$ ) and Raman ( $F_{2g}$ ) active lattice vibrations of  $CeO_2$  (Color online)

Because our nano  $CeO_2$  samples are inhomogeneous (they consist of  $CeO_2$  nanoparticles and air pores) we have applied the effective medium approximation (EMA) method to calculate infrared reflectivity of inhomogeneous media, taking into account the macroscopic volume fractions and local microstructural geometry (Grujić-Brojčin et al. 2005; Gonzalez et al. 1997; Spanier and Herman 2000; Bruggeman 1935). Two widely used effective medium theories are the Maxwell–Garnett theory (Maxwell–Garnett 1904) and the Bruggeman theory (Bruggeman 1935). In both theories the effective dielectric constant does not depend explicitly on the size of the grains or inclusions occurring inside the medium. Maxwell–Garnett approximation treats the effective medium as consisting of a matrix in which are embedded inclusions of a specific shape, where the fraction of the inclusions is very small ( $<0.15$ ), so that the inclusions are spatially separated and can be treated as a perturbation (Spanier and Herman 2000; Saarinen et al. 2003; Gehr et al. 1997). The other widely used approximation is the Bruggeman’s, which has no such limitations, and can be used for entire range of fraction values from 0 to 1. That was the reason why we used Bruggeman approach for analysis of infrared reflectivity spectra of inhomogeneous  $CeO_2$  nanocrystals.

As nanophase  $CeO_2$  is a porous material with a relatively large specific surface (see Table 1), the porosity of the nanopowder is included in modeling its dielectric function. The best agreement between calculated and experimental results is obtained by the generalized Bruggeman EMA (B-EMA), which introduces the effect of pore shape using the adjustable depolarization factor  $L$  for ellipsoidal voids ( $L = 1/3$

for spherical cavities and  $1/3 < L < 1$  for prolate spheroidal cavities).

Similar to the B-EMA, in the generalized Bruggeman model (Grujić-Brojčin et al. 2005, 2006; Spanier and Herman 2000), porous nanopowder with effective dielectric function  $\epsilon_{eff}$  is assumed to be an inhomogeneous media composed of nanopowder ( $\epsilon_{nano}$ ) and air ( $\epsilon_{air} = 1$ ) with volume fractions  $f_{nano}$  and  $f_{air}$ , respectively. The basic Bruggeman model is modified to include the influence of porosity:

$$\left( \frac{\epsilon_{nano} - \epsilon_{eff}}{\epsilon_{eff} + L(\epsilon_{nano} - \epsilon_{eff})} \right) f_{nano} + \left( \frac{\epsilon_{air} - \epsilon_{eff}}{\epsilon_{eff} + L(\epsilon_{air} - \epsilon_{eff})} \right) f_{air} = 0 \tag{1}$$

Generally, a decrease of nanopowder volume fraction results in a decrease of reflectivity and broadening of the IR features, due to the greater air fraction in the powder. Also, the decrease of depolarization factor  $L$ , from prolate spheroidal voids ( $L = 1$ ) to spherical pores ( $L = 1/3$ ), leads to the increase in the reflectivity, with characteristic IR features becoming more pronounced (Grujić-Brojčin et al. 2005).

Since the analysis of the far IR reflectivity spectrum of ceria nanopowders has revealed a presence of a plasmon mode, it was necessary to include both contributions of the phonon and the plasmon (free carrier contribution) to the dielectric function. Therefore, the factorized form of dielectric function has been decomposed into a sum of two independent terms (Gonzalez et al. 1997; Grujić-Brojčin et al. 2006; Gervais 1983):

**Table 1** The characteristic TO and LO phonon frequencies ( $\omega$ ) and damping factors ( $\gamma$ ) (all given in  $\text{cm}^{-1}$ ) of  $\text{Ce}_{1-x}\text{Cu}_x\text{O}_{2-y}$  nano- and poly-crystals, used in the fitting procedure together with the corresponding plasmon parameters for pure, 1, and 10 % Cu-doped  $\text{CeO}_2$  samples

Parameters	0 % Cu	1 % Cu	10 % Cu	10 nm nano	Polycrystal
$\omega_{\text{TO}}$ ( $\gamma_{\text{TO}}$ )	135 (190)	137 (220)	137 (300)	130 (132)	135 (130)
$\omega_{\text{LO}}$ ( $\gamma_{\text{LO}}$ )	155 (95)	147 (180)	147 (180)	160 (188)	161 (187)
$\omega_{\text{TO}}$ ( $\gamma_{\text{TO}}$ )	282 (37)	280 (28)	280 (25)	273 (57)	272 (25)
$\omega_{\text{LO}}$ ( $\gamma_{\text{LO}}$ )	375 (180)	380 (165)	385 (180)	280 (108)	416 (137)
$\omega_{\text{TO}}$ ( $\gamma_{\text{TO}}$ )	370 (100)	360 (95)	370 (140)	448 (159)	–
$\omega_{\text{LO}}$ ( $\gamma_{\text{LO}}$ )	407 (100)	407 (150)	407 (120)	468 (105)	–
$\omega_{\text{TO}}$ ( $\gamma_{\text{TO}}$ )	490 (180)	480 (140)	485 (180)	493 (113)	428 (157)
$\omega_{\text{LO}}$ ( $\gamma_{\text{LO}}$ )	580 (10)	580 (60)	585 (40)	585 (385)	587 (47)
$\omega_{\text{TO}}$ ( $\gamma_{\text{TO}}$ )	–	–	–	333 (67)	–
$\omega_{\text{LO}}$ ( $\gamma_{\text{LO}}$ )	–	–	–	350 (88)	–
$\omega_p$ ( $\gamma_p$ )	390 (400)	385 (580)	320 (550)	100 (50)	–
$f_{\text{nano}}$	0.80	0.83	0.86		
Pore shape $L$	0.74	0.70	0.70		
Specific surface area $S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	40	40	44		
Average pore diameter (nm)	10.8	12.4	9.1		

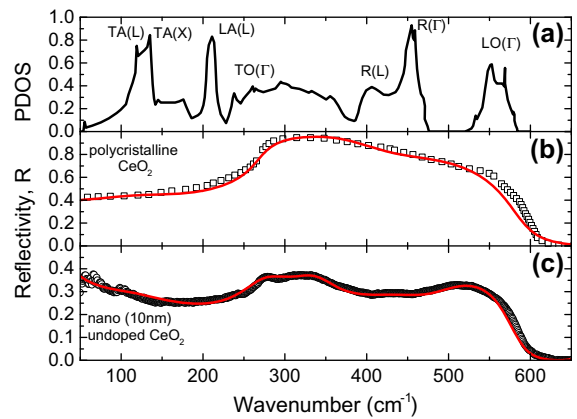
The fitting parameters from Bruggeman model (powder volume fraction  $f_{\text{nano}}$  and the pore shape  $L$ ) together with the specific surface area and pore diameter values are listed for each nanopowder sample

$$\epsilon(\omega) = \epsilon_\infty \left[ \prod_{j=1}^n \frac{\omega_{\text{LO},j}^2 - \omega^2 + i\omega\gamma_{\text{LO},j}}{\omega_{\text{TO},j}^2 - \omega^2 + i\omega\gamma_{\text{TO},j}} - \frac{\omega_p^2}{\omega(\omega - i\gamma_p)} \right] \quad (2)$$

where  $\omega_{\text{LO},j}$  and  $\omega_{\text{TO},j}$  are longitudinal and transverse frequencies of the  $j$ th oscillator,  $\gamma_{\text{LO},j}$  and  $\gamma_{\text{TO},j}$  are their corresponding dampings,  $\omega_p$  ( $\gamma_p$ ) is the plasma frequency (damping), and  $\epsilon_\infty$  is the high-frequency dielectric constant.

Figure 2a shows the PDOS of  $\text{CeO}_2$ . This PDOS is in complete agreement with previously published ones (Marabelli and Wachter 1987; Nakajima et al. 1994; Gürel and Eryigit 2006; Buckeridge et al. 2013).

The  $\text{CeO}_2$  IR reflectivity spectra of polycrystalline sample (Santha et al. 2004) and 10-nm particle size undoped  $\text{CeO}_2$  nanocrystal are given in Fig. 2b, c, respectively. These spectra are fitted using dielectric function model, Eq. (2), with parameters given in Table 1. In the case of the polycrystalline sample three oscillators are used to obtain a rather good agreement with experimental data. The lowest energy oscillator with TO energy of  $135 \text{ cm}^{-1}$  represents phonon states from the X and L point of BZ. Other two oscillators represent  $F_{2u}$  mode. Appearance of two instead of one IR active mode in this spectral range is related to the anharmonicity (Santha et al. 2004). In the case of the



**Fig. 2** a The phonon density of states of  $\text{CeO}_2$ . b The IR reflectivity spectra of polycrystalline  $\text{CeO}_2$  sample (Santha et al. 2004); c nanocrystalline undoped  $\text{CeO}_2$  sample (particle size  $\sim 10 \text{ nm}$ ). Solid lines represent the calculated reflectivity spectra obtained by the fitting procedure based on Eq. (2), with the parameters given in Table 1 (Color online)

nanosized sample (Fig. 2c) five oscillators are included in the fitting procedure, as well as, plasma term (see Table 1). Origin of these oscillators will be discussed later.

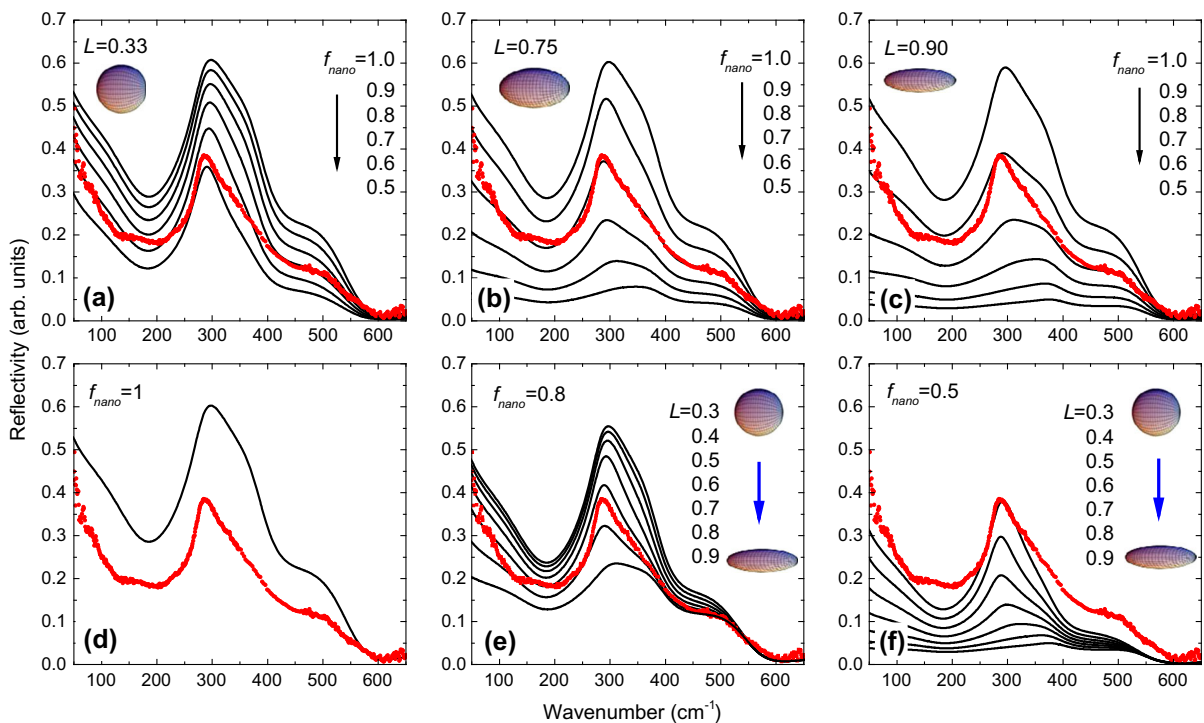
The influence of nanopowder volume fraction and the pore shape on the IR reflectivity spectra is analyzed in Fig. 3a–c, which show the IR reflectivity spectra

calculated with the generalized B-EMA, with the variation of powder volume fraction  $f_{\text{nano}}$  and fixed value of depolarization factor (pore shape factor)  $L = 0.33, 0.75,$  and  $0.90,$  respectively. The spectra are calculated with the set of parameters corresponding to the pure  $\text{CeO}_2$  sample, listed in the Table 1 (0 % Cu), whereas  $f_{\text{nano}}$  is varied from 0.5 (50 % of  $\text{CeO}_2$  powder in porous sample) to 1 (nonporous powder). The pore shape factor  $L = 0.33$  defines ideally spherical pores and for given TO/LO parameters, the best volume fraction fit corresponds to values of  $f_{\text{nano}}$  between 50 and 60 % of powder content in the sample (Fig. 3a).

The pore shape factor  $L = 0.75$  defines pores with elongated structure, as indicated in Fig. 3b. For given TO/LO parameters (Table 1) the best volume fraction fit corresponds to values of  $f_{\text{nano}}$  around 80 % of powder content in the sample. In Fig. 3c the variation of powder volume fraction  $f_{\text{nano}}$  with depolarization factor  $L = 0.90$  is shown. The pore shape factor  $L = 0.90$  corresponds to extremely elongated pores.

For given TO/LO parameters (Table 1) the best volume fraction fit corresponds to values of  $f_{\text{nano}}$  between 80 and 90 % of powder content in the sample.

The pore shape variation is analyzed in Fig. 3d–f. In Fig. 3d the calculated spectrum for powder volume fraction  $f_{\text{nano}} = 1,$  i.e., nonporous powder is shown together with experimental IR reflectivity of the pure  $\text{CeO}_2$  sample. The spectrum is calculated with the set of parameters corresponding to the pure  $\text{CeO}_2$  sample, listed in Table 1 (0 % Cu), whereas the pore shape factor ( $L$ ) variation has no influence in this calculation. Figure 3e, f show the IR reflectivity spectra calculated with the generalized Bruggeman EMA with powder volume fraction of 80 % and 50 %. The pore shape factor varied from  $L = 0.3$ – $0.9.$  It may be noticed that in both cases, the intensity of the reflectivity is getting lower with the increase in pore shape factor. For given TO/LO parameters (Table 1) the best pore shape fit is obtained for values of  $L$  from 0.7 to 0.8 (Fig. 3e), corresponding to the area of elongated pores. These



**Fig. 3** The IR reflectivity spectra calculated with the generalized B-EMA. **a** The volume fraction of nanopowder is in the range from 0.5 to 1.0 and the pore shape factor  $L = 0.33$  (spherical shape of pores); **b** pore shape factor  $L = 0.75$  (elongated pore structure); **c** pore shape factor  $L = 0.90$  (extremely elongated pore structure); **d** the IR reflectivity spectra calculated with the generalized B-EMA with the volume

fraction of the nanopowder  $f_{\text{nano}} = 1$  (nonporous powder); **e** fixed volume fraction of nanopowder ( $f_{\text{nano}} = 0.8$ ) with pore shape factor varying from 0.3 to 0.9; **f** fixed volume fraction of nanopowder ( $f_{\text{nano}} = 0.5$ ) with pore shape factor varying from 0.3 to 0.9. Experimental IR reflectivity spectrum (red curve) of pure  $\text{CeO}_2$  sample (0 % Cu) is given for comparison (Color online)

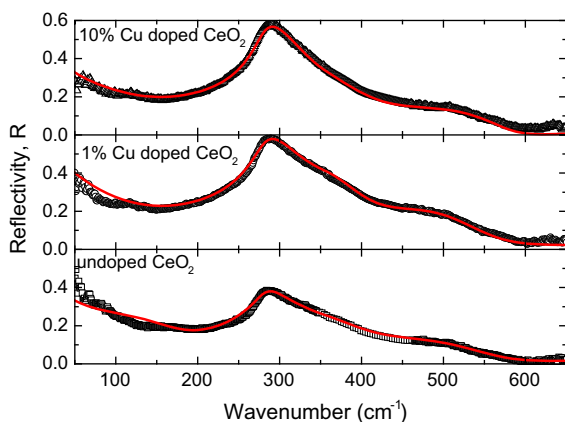


results correspond to those shown in Fig. 3b. Finally, in Fig. 3f the best pore shape fit is obtained for values of  $L$  around 0.3, corresponding to ideally spherical pores.

By analyzing the results shown in Fig. 3, we came to the following conclusions:

- (i) Bruggeman EMA model can be used to fit the experimental reflectivity spectra of inhomogeneous nanomaterials, in our case  $\text{CeO}_2$  nanocrystals.
- (ii) The B-EMA model parameters that best describe the experimental  $\text{CeO}_2$  reflectivity spectra are close to  $f_{\text{nano}} = 0.8$  and  $L = 0.75$ . (see Fig. 3b). Refinement of these parameters for samples under investigation gives values shown in Table 1.
- (iii) The very good agreement between the calculated and the experimental spectra illustrated in Fig. 4 suggests that the use of more specific model, which may include the pore shape distribution, instead of the B-EMA general and simple model, is not necessary.

In Fig. 4 experimental IR reflectivity spectra of 5 nm-sized pure, 1, and 10 % Cu-doped  $\text{CeO}_2$  samples are shown, together with the corresponding spectra calculated with the generalized B-EMA. Fitting parameters for these spectra are listed in Table 1. As can be seen from Table 1, four oscillators with TO energies of approximately 135, 280, 370, and  $490 \text{ cm}^{-1}$  were included in the fitting procedure, Eq. (2), for 5 nm-sized  $\text{CeO}_2$  samples. These



**Fig. 4** Experimental IR reflectivity spectra of pure, 1, and 10 % Cu-doped  $\text{CeO}_2$  samples, with the corresponding spectra obtained by the fitting procedure based on Eq. (2) and the generalized B-EMA, Eq. (1). Parameters are given in Table 1

oscillators represent local maxima of the PDOS. The lowest energy oscillator represents TA(L)/TA(X) phonon states, which become IR-active  $E_u$  modes (Buckeridge et al. 2013) at the L and X points of BZ. The second oscillator originates from TO( $\Gamma$ ) phonon states. The oscillator at  $\sim 400 \text{ cm}^{-1}$  originates from Raman mode phonon states which at the L point of BZ also becomes IR-active  $E_u$  mode (Buckeridge et al. 2013). The last oscillator describes phonons with dominantly LO( $\Gamma$ ) IR mode character. The appearance of PDOS-related oscillators, instead of single  $F_{2u}$  IR-active mode in the far-infrared reflectivity spectra, is a consequence of the nanosized dimension of the particles, as mentioned earlier. Besides that, the oscillator energies appear at lower energies than the maxima of PDOS. This is also related to the particle size. In fact, in nanocerium the unit cell dimensions abruptly increase by particle size reduction (Tsunekawa et al. 2000; Wu et al. 2004). Consequently, the PDOS softens with the particle size lowering due to an increase in the internal strain, as it was discussed in Buckeridge et al. (2013).

A small variation in the frequencies of TO (LO) modes of the pure and doped samples is noticed, whereas the damping parameters are clearly affected by the variation between pure and doped samples. Plasmon modes are registered in all samples, with significant plasma frequency decrease and damping parameter increase with Cu doping. The values of parameters used in the generalized Bruggeman EMA are varied with doping: similar porosity has been estimated in all studied samples. Namely, the volume fraction parameter is estimated from  $f_{\text{nano}} = 0.80$  in pure  $\text{CeO}_2$  (which means 80 % of  $\text{CeO}_2$  fraction in a porous sample) to 0.86 in 10 % Cu-doped  $\text{CeO}_2$  sample. The depolarization factor  $L$ , defining pore shape is estimated as 0.74 in pure  $\text{CeO}_2$  sample and slightly lower (0.70) in doped samples, therefore describing pores filled with the air as very elongated. Comparing these with textural measurement results, we find that in the 10 % Cu-doped sample, the reduction of  $L$  and an increase in volume fraction is correlated with a decrease of pore diameter and an increase in specific surface area (see Table 1).

## Conclusion

We have measured the unpolarized far-infrared reflectivity spectra of the  $\text{CeO}_2$  nanocrystals at room

temperature. Reflectivity spectra were analyzed using the factorized form of the dielectric function, which includes the phonon and plasmon contribution to the dielectric function. The best fit spectra are obtained using the generalized Bruggeman model for inhomogeneous media, which takes into account the volume fraction of CeO<sub>2</sub> nanocrystal and the air pore shape.

**Acknowledgments** This work was supported by the Serbian Ministry of Education, Science and Technological Development under Projects ON171032, ON171017 and III45018, the Spain–Serbia bilateral Project AIB2010SE-00160, the Spanish Grant MAT2012-33483, and the Brazilian governmental research funding agencies FAPESP, CAPES, and CNPq.

## References

- Araújo VD, de Lima MM Jr, Cantarero M, Bernardi MIB, Bellido JDA, Assaf EM, Balzer R, Probst LFD, Fajardo HV (2013) Catalytic oxidation of *n*-hexane promoted by Ce<sub>1-x</sub>Cu<sub>x</sub>O<sub>2</sub> catalysts prepared by one-step polymeric precursor method. *Mater Chem Phys* 142:677–681
- Baroni S, de Gironcoli S, Dal Corso A, Giannozzi P (2001) Phonons and related crystal properties from density-functional perturbation theory. *Rev Mod Phys* 73:515–562
- Bruggeman DAG (1935) Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen. *Ann Phys* 24:636–664
- Buckeridge J, Scanlon DO, Walsh A, Catlow CRA, Sokol AA (2013) Dynamical response and instability in ceria under lattice expansion. *Phys Rev B* 87(21):214304
- Cantarero A (2013) Review on Raman scattering in semiconductor nanowires: I. Theory. *J Nanophotonics* 7(1):071598
- Gehr RJ, Fischer GL, Boyd RW (1997) Nonlinear-optical response of porous-glass-based composite materials. *J Opt Soc Am B* 14(9):2310–2314
- Gervais F (1983) High-temperature infrared reflectivity spectroscopy by scanning interferometry. In: Button KJ (ed) *Infrared and millimeter waves*. Academic Press, New York, pp 279–339
- Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti GL, Cococcioni M, Dabo I, Corso AD, de Gironcoli S, Fabris S, Fratesi G, Gebauer R, Gerstmann U, Gougoussis C, Kokalj A, Lazzeri M, Martin-Samos L, Marzari N, Mauri F, Mazzarello R, Paolini S, Pasquarello A, Paulatto L, Sbraccia C, Scandolo S, Sclauzero G, Seitsonen AP, Smogunov A, Umari P, Wentzcovitch RM (2009) QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J Phys* 21(39):395502
- Gonzalez RJ, Zallen R, Berger H (1997) Infrared reflectivity and lattice fundamentals in anatase TiO<sub>2</sub>. *Phys Rev B* 55(11):7014–7017
- Grujić-Brojčin M, Šćepanović MJ, Dohčević-Mitrović ZD, Hinić I, Matović B, Stanišić G, Popović ZV (2005) Infrared study of laser synthesized anatase TiO<sub>2</sub> nanopowders. *J Phys D* 38(9):1415–1420
- Grujić-Brojčin M, Šćepanović MJ, Dohčević-Mitrović ZD, Popović ZV (2006) Infrared study of nonstoichiometric anatase TiO<sub>2</sub> nanopowders. *Sci Sinter* 38:183
- Gürel T, Eryiğit R (2006) Ab initio pressure-dependent vibrational and dielectric properties of CeO<sub>2</sub>. *Phys Rev B* 74(1):014302
- Kourouklis GA, Jayaraman A, Espinosa GP (1988) High-pressure Raman study of CeO<sub>2</sub> to 35 GPa and pressure-induced phase transformation from the fluorite structure. *Phys Rev B* 37(8):4250–4253
- Marabelli F, Wachter P (1987) Covalent insulator 2: optical reflectivity measurements. *Phys Rev B* 36(2):1234–1238
- Maxwell-Garnett JC (1904) Colours in metal glasses and in metallic films. *Philos Trans R Soc Lond, Ser.4* 203:385–420
- Nakajima A, Yoshihara A, Ishigame M (1994) Defect-induced Raman spectra in doped CeO<sub>2</sub>. *Phys Rev B* 50(18):13297–13307
- Orel Z (1999) Characterization of cerium dioxide dip-coated films by spectroscopic technique. *Internet J Vib Spec Vol 3*, Edition 4, Section 6 ([www.ijvs.com](http://www.ijvs.com)). Accessed 20 June 2013
- Popović ZV, Dohčević-Mitrović Z, Šćepanović M, Grujić-Brojčin M, Aškračić S (2011) Raman scattering on nanomaterials and nanostructures. *Ann Phys* 523(1–2):62–74
- Popović ZV, Dohčević-Mitrović ZD, Paunović N, Radović M (2012) Evidence of charge delocalization in Ce<sub>1-x</sub>Fe<sub>2+(3+)</sub>O<sub>2-y</sub> nanocrystals ( $x = 0, 0.06, 0.12$ ). *Phys Rev B* 85:014302
- Saariinen JJ, Vartiainen EM, Peiponen KE (2003) On tailoring of nonlinear spectral properties of nanocomposites having Maxwell Garnett or Bruggeman structure. *Opt Rev* 10(2):111–115
- Santha NI, Sebastian MT, Mohanan P, Alford NM, Sarma K, Pullar RC, Kamba S, Pashkin A, Samukhina P, Petzelt J (2004) Effect of doping on the dielectric properties of cerium oxide in the microwave and far-infrared frequency range. *J Am Ceram Soc* 87(7):1233–1237
- Spanier JE, Herman IP (2000) Use of hybrid phenomenological and statistical effective-medium theories of dielectric functions to model the infrared reflectance of porous SiC films. *Phys Rev B* 61(15):10437–10450
- Tsunekawa S, Ishikawa K, Li ZQ, Kawazoe Y, Kasuya A (2000) Origin of anomalous lattice expansion in oxide nanoparticles. *Phys Rev Lett* 85(16):3440–3443
- Weber WH, Hass KC, McBride JR (1993) Raman study of CeO<sub>2</sub>: second-order scattering, lattice dynamics, and particle-size effects. *Phys Rev B* 48(1):178–185
- Wu L, Wiesmann HJ, Moodenbaugh AR, Klie RF, Zhu Y, Welch DO, Suenaga M (2004) Oxidation state and lattice expansion of CeO<sub>2-x</sub> nanoparticles as a function of particle size. *Phys Rev B* 69(12):125415