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Short communication

Tight binding approximation in Nd^{3+} doped nano ceria prepared via gel combustion method

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Abstract

Neodymium doped nano ceria powder was synthesized through gel combustion route using urea formaldehyde as fuel. The powder was characterized through XRD, TEM and spectrophotometry. Small nanograins consisting of single crystals of around 5–15 nm size (against 10–20 nm as estimated by Scherrer equation) were observed under TEM. Decrease in crystallite size with corresponding lattice expansion follows quamtum confinement effect. The measured band gap ranges from 2.71 to 3.84 eVs. The effect of doping concentration on band gap of ceria nanocrystals along with simultaneous change in lattice parameter has been explained in the light of tight binding approximation.

Keywords: Ceramics; Functional; Nanocrystalline materials

1. Introduction

For more than a few decades, ceria has been known as a semiconductor materials [1] as well as three-way catalysts for reducing the emission of the toxic pollutants (CO, NOx, hydrocarbons, etc.) from automobile exhaust [2]. This is owing to its high oxygen storage capacity, associated with its rich oxygen vacancies and low redox potential between Ce^{3+} and Ce^{4+} [3]. Doping in ceria with aliovalent oxides creates further oxygen vacancy that gives rise to multi-functional properties encompassing high oxygen ion conductivity, oxygen storage capacity, photochemical activities, strong UV absorption properties and luminescence. Elaborate studies are available with rare earth cations such as Eu^{3+}, Tb^{3+}, and Er^{3+} [4–6]. Oxygen adsorption plays an important role in electrical transport properties of CeO_2. For example in gas sensing, the adsorbed oxygen obtains conduction electrons from the CeO_2 and therefore, lowers the conductance of CeO_2. When the sensors are exposed to reducing gases, for instance, CO or H_2S, the gases react with the adsorbed O^{2-} and release the trapped electrons back to the conduction band, resulting in an increase of the conductance of CeO_2 [7]. Since conduction band plays important role here, band gap is an important parameter. The band gap of metal oxide nanocrystals has, in general, different significant impacts on their electronic, optical, and catalytic properties. For instance, it has been shown that an increased band gap can enhance the photocatalytic efficiency of metal oxide nanostructures [8].

In the present work, neodymium doped nano ceria prepared through gel combustion route using urea-formaldehyde (UF) as fuel was characterized and effects of doping concentration on band gap of the prepared powder have been studied.

2. Experimental

Neodymium oxide (4–20 mol%) doped ceria have been prepared by UF gel combustion route [9]. Urea was hydroxymethylolated with the addition of formaldehyde solution followed by pH adjustment to 8.5, the ratio of urea to formaldehyde being 1:4. After 24 h of ageing time to complete methylolation, neodumium nitrate and cerium nitrate hexahydrate in stoichiometric amount were mixed with the earlier solution followed by subsequent addition of a second lot of urea to make the ratio of metal nitrates to urea as 1:2. The resultant solution was heat treated at 110 °C for water removal followed by UF resin formation. The resin was ignited to produce nano ceria.

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The produced powders were characterized by XRD (Philips PW-1730 Philips Corporation, Almelo, Netherlands) using Cu Kα radiation (1.5406 Å) in the angular region of 2θ to be 20–80°. The refined peak positions ($K\alpha_2$ stripping, background determination, peak searching, smoothening and fitting profile) were considered for lattice parameter determination by Cohen's method and crystallite size calculation by the Scherrer method [10]. Microscopy was done under TEM (TECNAI G2 30ST, FEI Company, Netherlands). Optical absorption study through spectroscopy (Lambda 20, Perkin Elmer) was carried out in the electromagnetic wave range of 200–700 nm to determine band gap. The onset frequency of the photon transition from a valence to conduction band was determined following an established procedure [11]: $\alpha_2(h\nu)^n = \text{constant}\ (h\nu - E_g)$ where $h\nu$ is the photo energy, α_2 is the absorption coefficient constant relative to the material. The dependence of the absorption coefficient (α_2) relates to the energy of the incoming photons ($h\nu$) with n equals to 2 for a direct transition (E_g).

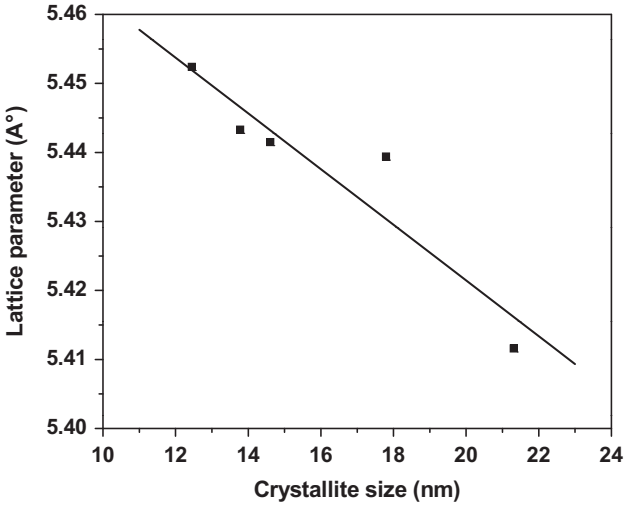

Fig. 1. Variation of lattice parameter with crystallite size.

3. Results and discussion

The phase formation of the product was confirmed through matching with JCPDS file no. 81–0792. A shift in diffraction angle was observed corresponding to the level of doping. Lattice parameter was found to increase with doping concentration. Cell dimension, as estimated from Scherrer equation, diminishes with crystallite sizes (fig. 1): the phenomenon is supported by earlier observations on other nano-oxides [12,13]. Microscopic study (fig. 2a) reveals that small nanocrystals of around 5–15 nm size were obtained. These are single-crystals, as evidenced by SAED patterns and HRTEM (Fig. 2b), respectively. From HRTEM image, distances between the adjacent lattice fringes corresponding to the interplanar distances of cubic doped CeO_2 have been measured. The exposed planes are (111) and (200) with interplanar distances of 3.16 and 2.76 Å, respectively. This corroborates to the findings of earlier study [14]. The phenomenon of lattice expansion at lower doping concentration may be viewed through quantum size effect. Literature report estimates that quantum size effect can be applicable for the crystallite size up to 19 nm [15]. In the present experiment, the minimum crystallite size as observed under microscopy and also as estimated by Scherrer equation (10–20 nm) coincides with the estimated effective range. Therefore, the effect may be presumed to be valid for the whole range of compositions.

Absorption spectra of all the compositions recorded from alcoholic suspensions of doped ceria powders are shown in fig. 3. The absorption in the UV region originates from a charge transfer from O^{2-} to Ce^{4+}, that is, the O2p→Ce 4f electronic transition [16]. The measured band gap ranges from 2.71 to 3.84 eV for 4–20 mol% of Nd doping (Table 1). The reported direct band gap of bulk ceria is 3.19 eV [17]. The reason behind the combination of widening of band gap and simultaneous lattice expansion as a function of dopant concentration can be explained by tight binding approximation or linear combination of atomic orbital approximation. This approximation stands on the assumption that wave functions of electrons of the adjacent atoms within a crystal

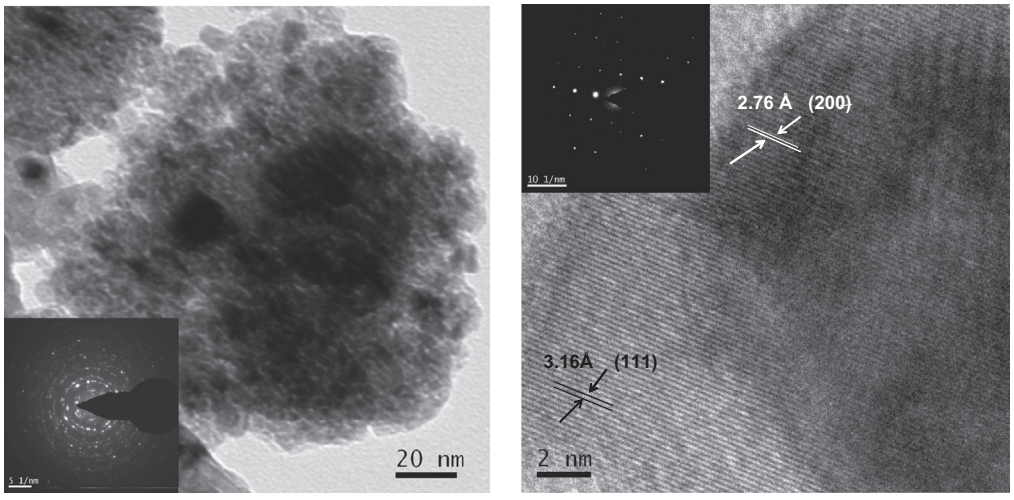

Fig. 2. (a) TEM images of crystallites with 4 mol% doping; inset—diffraction pattern, (b) HR pattern of crystallites in Fig. 2a; inset—diffraction pattern.

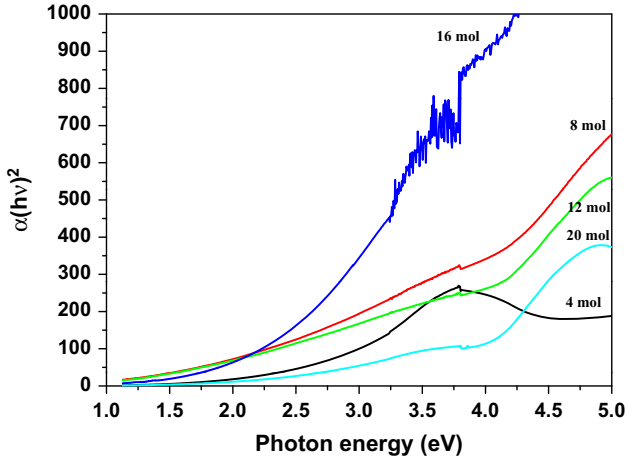

Fig. 3. Plot of $\alpha_2(h\nu)^2$ vs. photon energy of ceria samples with varying amounts of dopant.

Table 1
Comparison of properties.

Nd concentration (mol%)	Lattice parameter, a (Å)	Band gap (eV)
4	5.4116	2.71
8	5.4394	3.38
12	5.4433	3.54
16	5.4415	2.25
20	5.4524	3.84

interact with each other. The width of the energy band depends on the extent of overlap interaction among the wave functions of the neighboring atoms; stronger overlap interaction produces wider energy band and conversely, the weaker overlap creates narrower energy band [18]. In the present case, as lattice parameter increases with increase in doping, the interaction among the wave functions of electrons of neighboring atoms decreases. This decreasing interaction leads to narrower band which, in turn, increases forbidden bands between valence and conduction band.

4. Conclusion

UF gel combustion is a successful wet chemical route to produce very fine grained Nd-doped ceria. Reduction in crystallite size causes lattice expansion. The band gap measured with increasing Nd-doping ranges from 2.71 to 3.84 eV. The simultaneous widening of band gap with lattice expansion toward larger doping concentration has been explained through tight binding approximation.

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