Synthesis of nanocrystalline materials through reverse micelles: A versatile methodology for synthesis of complex metal oxides

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Abstract. We have been successful in obtaining monophasic nanosized oxides with varying chemical compositions using the reverse micellar method. Here we describe our methodology to obtain important metal oxides like ceria, zirconia and zinc oxide. The oxalate of cerium, zirconium and zinc were synthesized using the reverse micellar route. While nanorods of zinc oxalate with dimension, 120 nm in diameter and 600 nm in length, could be obtained, whereas spherical particles of size, 4–6 nm, were obtained for cerium oxalate. These precursors were heated to form their respective oxides. Mixture of nanorods and nanoparticles of cerium oxide was obtained. ZrO_2 nanoparticles of 3–4 nm size were obtained by the thermal decomposition of zirconium oxalate precursor. ZnO nanoparticles (55 nm) were obtained by the decomposition of zinc oxalate nanorods. Photoluminescence (PL) studies at 20 K shows the presence of three peaks corresponding to free excitonic emission, free to bound and donor–acceptor transitions. We also synthesized nanoparticles corresponding to $\text{Ba}_{1-x}\text{Pb}_x\text{ZrO}_3$ using the reverse micellar route. The dielectric constant and loss were stable with frequency and temperature for the solid solution.

Keywords. Reverse micelles; nanorods; photoluminescence; dielectric properties.

1. Introduction

Nanomaterials have fascinated the scientific community in the recent past. These materials exhibit unusual properties compared to their bulk counterparts. The physical laws applicable to the materials change as the size of the particles decreases to the nanoregime. Surface and quantum effects result in the modification of the properties, (optical, magnetic and dielectric) of nano-sized particles (figure 1). The dielectric and magnetic properties of oxides depend considerably on the size and shape of the particles. For example, in materials having dipoles show disorder in the dipole and magnetic moments with decrease in size (figure 2). This disorder leads to changes in the dielectric and magnetic properties. A very important property of nano-structured materials is that they can be dispersed in different types of matrix media to impart useful characteristics to the composite. These have immense consequences in flexible polymer composite films with functional properties due to the nano-metals or ceramic additives.

Various methods have been formulated to synthesize nano materials. These include physical methods such as chemical vapour deposition (Roth and Williams 1981; Maruyama and Shionoya 1992), plasma synthesis (Lin *et al* 2000), spray pyrolysis (De Merchant and Cocivera 1995). Chemical methods include solvothermal (Komarneni *et al* 1998), oxidant precipitation (Sartale and Lokhande 2000), electrodeposition (Erb 1995), sol–gel synthesis (Chatter-

jee *et al* 1993) etc. Such bottom-up approaches followed for the synthesis of nanomaterials should restrict the growth of the nuclei, prevent the agglomeration of particles and maintain the size distribution of these materials. A versatile chemical method to synthesize nanoparticles is the reverse micellar route (Pileni *et al* 1992; Ahmad *et al* 2005a; Ahmad and Ganguli 2006). The synthesis via this method does not require specialized or expensive equipments as is required by several physical methods. The reaction takes place in the aqueous cores of the reverse micelles which are dispersed in an organic solvent and are stabilized by a surfactant. The product obtained after the reaction is homogeneous. The morphology of the product can also be controlled as the surfactant aggregates form a variety of structures which are used as templates. The size of the core of the reverse micelles can also be controlled by changing W_o ($[\text{H}_2\text{O}]/[\text{surfactant}]$). Thus one can alter the morphology as well as the grain size of the product. We have synthesized a variety of materials using this method. These include dielectric oxide nanoparticles (Ahmad *et al* 2005a; Ahmad and Ganguli 2006) and several metal oxalates such as nanorods of copper and nickel oxalates (Ahmad *et al* 2005b). In this paper we discuss the synthesis and characterization of ceria, zirconia, zinc oxide and $(\text{Ba}, \text{Pb})\text{ZrO}_3$ by the above method.

2. Experimental

The experimental section is divided into the synthesis of (a) cerium oxalate and its decomposition to form cerium

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oxide nanoparticles, (b) zirconia from zirconium oxalate, (c) zinc oxalate nanorods and its decomposition to zinc oxide, and (d) (Ba, Pb)ZrO₃.

For synthesis of cerium oxalate, zirconium oxalate and zinc oxalate, two different microemulsions with CTAB (surfactant) (spectrochem), 1-butanol (co-surfactant) (qualigens), and isooctane (organic solvent) (spectrochem) and aqueous solution were prepared. One microemulsion contained 0.1 M Ce(NO₃)₃·6H₂O solution, 0.1 M zirconyl oxychloride and 0.1 M zinc nitrate solution for cerium oxalate, zirconium oxalate and zinc oxalate, respectively. The other contained 0.1 M solution of ammonium oxalate. The two microemulsions were mixed and allowed to stir for 15 h. The precipitates were centrifuged and washed with 1 : 1 mixture of chloroform and methanol and dried at room temperature. The cerium oxalate and zirconium oxalate precursors were decomposed at 500°C for 6 h to obtain cerium oxide and zirconium oxide nanoparticles. Zinc oxalate was decomposed at 450°C (6 h) to obtain ZnO.

The synthesis of the entire solid solution of Ba_{1-x}Pb_xZrO₃ was carried out using microemulsions with Tergitol (surfactant) (Aldrich), 1-octanol (co-surfactant) (spectrochem), cyclohexane (organic solvent) (Ranbaxy)

and aqueous solution. For (Ba, Pb)ZrO₃, four different microemulsions were prepared containing 0.1 M solution of barium acetate (Aldrich), lead acetate (BDH), zirconyl oxychloride (CDH) and sodium hydroxide (BDH, 97%), respectively. The microemulsions were mixed and stirred overnight at room temperature. A transparent solution was obtained. On evaporating the solvent from the solution at 60 ± 5°C, a brown precipitate was obtained which was washed with acetone, centrifuged and then dried in an oven at 60°C for 1 h. The product obtained was further heated in air at 500°C for 20 h and subsequently at 800°C for 20 h to get the pure product.

Powder X-ray diffraction studies (PXRD) were carried out on a Bruker D8 advance diffractometer using Ni-filtered Cu-Kα radiation. Normal scans were recorded with a step size of 0.02° and step time of 1 s. Raw data was subjected to background corrections and Kα₂-lines were stripped off. The grain size was calculated using the Scherrer's formula

$$t = 0.9\lambda/B\cos\theta,$$

where t is the diameter of the grain, λ the wavelength of radiation (λ for CuKα is 1.5418 Å) and B the line broadening which is measured from the full width at half maximum (FWHM) and calculated by the Warren's formula

$$B^2 = (B_M^2 - B_S^2),$$

where B_M is the full width at half maxima of the sample and B_S the full width at half maximum of the standard quartz with a grain size of around 2 μm. The cell parameters were determined using a least square fitting procedure on all reflections using quartz as the external standard. TGA/DTA experiments were carried out on Perkin Elmer Pyris Diamond TGA/DTA system on well ground samples in flowing nitrogen atmosphere with a heating rate of 10°C/min. TEM and HRTEM studies were carried out on JEOL JEM 3010 electron microscope operated at 300 kV.

Dielectric measurements were carried out on disks of (a) CeO₂ nanoparticles sintered at 1000°C, (b) ZrO₂ nanoparticles (synthesized from zirconium oxalate) sintered at 1000°C and (c) (Ba, Pb)ZrO₃ sintered at 1000°C. The measurements were carried out using Hewlett Packard 4284L multifrequency LCR meter in the range 50 Hz–500 kHz. Temperature variation studies of the dielectric constant and dielectric loss were carried out in the range 30–300°C.

For photoluminescence (PL) studies the samples were housed in an optical cryostat with front surface excitation and emitted radiation was collected. The samples were kept in a closed-cycle He refrigerator and excited with 325 nm line of a He–Cd laser. The PL signal was collected into a 0.46 m Jobin–Yvon grating monochromator in the wavelength region of 340–900 nm and detected with a UV-enhanced Si detector. The PL data were processed

Figure 1. Flowchart showing changes in various properties in nanodimension.

Figure 2. Schematic diagram showing the increase in disorder of dipoles with decrease in the size of particles.

using lock-in technique. The spectral response of the system was calibrated using a blackbody source.

3. Results and discussion

Cerium oxalate precursor was indexed on the basis of a monoclinic cell with refined lattice parameters of $a = 11.311(3) \text{ \AA}$, $b = 9.653(3) \text{ \AA}$, $c = 10.390(3) \text{ \AA}$ and $\beta = 114.5^\circ$. The particles were found to be 4–6 nm as observed from the HRTEM (figure 3a). Note that we have obtained nanoparticles and not nanorods (as earlier obtained for other transition metal oxalates) (Ahmad *et al* 2004, 2005b). This could be explained due to the trivalent

state of cerium in cerium oxalate whereas in earlier studies (Ahmad *et al* 2004, 2005b) as in transition metal oxalates, the transition metals were always in the divalent state. The divalent state of the metal ion is appropriate for linear geometry due to the 1 : 1 ratio of $M^{2+} : C_2O_4^{2-}$ (oxalate ion) and has resulted in the formation of rod like morphology whereas it appears that the trivalent state in case of Ce may be responsible for not allowing the formation of rod-like structure. The cerium oxalate precursor was heated at 500°C for 6 h to form cerium oxide. XRD shows monophasic ceria with lattice parameters close to values reported earlier (JCPDS No. 81-0792). Mixture of nanoparticles and nanorods of CeO_2 were observed (Vaidya *et al* 2007) from the HRTEM studies (figure 3b). The nanoparticles of CeO_2 are 10 nm in size; however, the dimensions of the nanorods are 7 nm in width and around 30 nm in length as seen from the HRTEM

Figure 3. HRTEM images of (a) cerium oxalate and (b) cerium oxide nanoparticles. Inset shows HRTEM images of cerium oxide (obtained from cerium oxalate) showing the growth of nanorods.

Figure 4. TEM images of nanocrystalline ZrO_2 . Inset shows HRTEM images for ZrO_2 .

Figure 5. TEM micrograph of zinc oxide nanoparticles. The inset shows TEM micrograph of the nanorods of zinc oxalate.

Table 1. Average particle size and dielectric parameters of (Ba, Pb)ZrO₃ powders obtained from TEM studies.

Ba _{1-x} Pb _x ZrO ₃	Particle size (nm)	ε (100 kHz)	D (100 kHz)	$d\varepsilon/dF$ (Hz ⁻¹)	$d\varepsilon/dT$ (°C ⁻¹)
$x = 0$	25 (± 5)	18.5	0.3	2.01×10^{-5}	0.0033
$x = 0.25$	22 (± 3)	76	0.01	8.00×10^{-6}	0.0738
$x = 0.50$	40 (± 5)	93.3	0.09	1.48×10^{-5}	0.1040
$x = 0.75$	50 (± 4)	69	0.09	1.13×10^{-5}	0.0046
$x = 1$	65 (± 5)	30.5	0.02	3.2×10^{-6}	0.0115

image (figure 3b). It seems that the particles aggregate to form rods as observed in the inset of figure 3b.

The zirconium oxalate precursor was found to be amorphous. Heating the precursor at 500°C for 6 h led to tetragonal zirconia with 10% impurity of monoclinic zirconia (Vaidya *et al* 2007). The refined cell parameters were found to be $a = 3.957(9)$ Å and $c = 5.16(3)$ Å. Note that the tetragonal zirconia is in high temperature phase which has been stabilized at low temperature (500°C). The particle size was found to be around 3–5 nm (figure 4). HRTEM image shows lattice fringes corresponding to (101) plane of tetragonal ZrO₂ (inset of figure 4).

The powder X-ray diffraction pattern of zinc oxalate precursor obtained by the reverse micellar route was indexed on the basis of a monoclinic cell (Ahmad *et al* 2006). The average dimensions of the nanorods were 120 nm in diameter and 600 nm in length as observed from the TEM image (inset of figure 5). Zinc oxide nanoparticles, obtained by the thermal decomposition of nanorods of zinc oxalate were indexed on the basis of hexagonal cell with the refined lattice parameters of $a = 3.2498(4)$ Å and $c = 5.209(1)$ Å. Figure 5 shows the average size of ZnO nanoparticles to be 60 nm.

For the oxides corresponding to Ba_{1-x}Pb_xZrO₃, the X-ray pattern of $x = 0$ (BaZrO₃) and $x = 0.25$ composition was indexed on the basis of a cubic cell. The orthorhombic phase was observed as the value of x in Ba_{1-x}Pb_xZrO₃ increases beyond $x = 0.25$ ($0.50 \leq x \leq 1$). The lattice parameters decrease slightly with increase in the value of x (Pb content). This is expected due to the smaller ionic radius of Pb(II) compared to Ba(II) ($r_{\text{Pb}^{2+}} = 1.19$ Å, $r_{\text{Ba}^{2+}} = 1.35$ Å). The particle size for different members of the solid solution (heated at 800°C) is given in table 1. The products sintered at 1000°C show slightly higher grain size (55 and 90 nm for $x = 0$ and 1, respectively).

Dielectric properties of CeO₂ nanoparticles synthesized from the oxalate precursor were studied after sintering the compacted disks at 1000°C. The dielectric constant and loss were found to be stable with frequency. The dielectric constant (15 at 500 kHz at room temperature) was nearly stable with temperature, while the dielectric loss shows a constant value (~ 0.08 at 500 kHz at room temperature) till 200°C beyond which it rises sharply. The dielectric constant for bulk CeO₂ was earlier reported (Logothetidis *et al* 2004) to be 26. However, there was no mention of the grain size and the sintering temperature.

Figure 6. PL spectra of ZnO nanoparticles at 20 K.

The dielectric constant (~ 12 at 500 kHz) and loss (~ 0.31 at 500 kHz) for ZrO₂ nanoparticles were highly stable with frequency at room temperature. Temperature variation studies show that the dielectric constant was stable after 100°C, however, the dielectric loss falls to ~ 0.03 at 100°C from 0.31 at room temperature.

The variation in dielectric constant and dielectric loss with composition (x) for Ba_{1-x}Pb_xZrO₃ (table 1) (at room temperature and at 100 kHz frequency) shows a maximum in the dielectric constant value ($\varepsilon = 93$) for $x = 0.5$ composition. The dielectric properties of nanocrystalline Ba_{1-x}Pb_xZrO₃ ($0 \leq x \leq 1$) over the entire range of x values have been reported for the first time. To the best of our knowledge, this is the first report to show the presence of a maximum in the value of the dielectric constant with Pb content corresponding to $x = 0.5$ composition. The explanation of this trend may lie in the presence of a structural phase transition close to this composition.

We have carried out the photoluminescence studies of nanocrystalline ZnO. Figure 6 shows three peaks in the deconvoluted photoluminescence (PL) spectra of nanocrystalline ZnO. The peak at 3.34 eV corresponds to free excitonic transition, 3.04 eV peak corresponds to free-to-bound transition (FB) and 2.78 eV peak corresponds to donor–acceptor pair (DAP). A weak peak at 2.5 eV is due

to the chromium present in the quartz substrate. The strong peak of the PL intensity suggests excellent sample quality.

4. Conclusions

Monophasic nanoparticles of CeO_2 , ZrO_2 and ZnO were synthesized from the thermal decomposition of their respective oxalate precursors. The precursors were synthesized using the reverse micellar route. Zinc oxalate was obtained as nanorods whereas cerium oxalate particles were spherical in shape. Nanoparticles of the solid solution of $\text{Ba}_{1-x}\text{Pb}_x\text{ZrO}_3$ have been reported for the first time and the dielectric properties show a maximum at $x = 0.5$. The reverse micellar route was found to be a versatile route for the synthesis of a variety of oxide nanomaterials.

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References

- Ahmad T and Ganguli A K 2006 *J. Am. Ceram. Soc.* **89** 1326
- Ahmad T, Ramanujachary K V, Lofland S E and Ganguli A K 2004 *J. Mater. Chem.* **14** 3406
- Ahmad T, Kavitha G, Narayana C and Ganguli A K 2005a *J. Mater. Res.* **20** 1415
- Ahmad T, Chopra R, Ramanujachary K V, Lofland S E and Ganguli A K 2005b *J. Nanosci. Nanotechnol.* **5** 1840
- Ahmad T, Vaidya S, Sarkar N, Ghosh S and Ganguli A K 2006 *Nanotechnology* **17** 1236
- Chatterjee A, Das D, Pradhan S K and Chakravorty D 1993 *J. Magn. Magn. Mater.* **127** 214
- De Merchant J and Cocivera M 1995 *Chem. Mater.* **7** 1742
- Erb U 1995 *Nanostruct. Mater.* **6** 533
- Komarneni S, D'Arrigo M C, Leonelli C, Pellacani G C and Katsuki H 1998 *J. Am. Ceram. Soc.* **81** 3041
- Lin Y, Tang Z and Zhang Z 2000 *J. Am. Ceram. Soc.* **83** 2869
- Logothetidis S, Patsalas P, Evangelou E K, Konofaos N, Tsiaoussis I and Frangis N 2004 *Mater. Sci. Eng.* **B109** 69
- Maruyama T and Shionoya J 1992 *J. Mater. Sci. Lett.* **11** 170
- Pileni M P, Motte L and Petit C 1992 *Chem. Mater.* **4** 338
- Roth A P and Williams D F 1981 *J. Appl. Phys.* **52** 6685
- Sartale S D and Lokhande C D 2000 *Indian J. Eng. Mater. Sci.* **7** 404
- Vaidya S, Ahmad T, Agarwal S and Ganguli A K 2007 *J. Am. Ceram. Soc.* **90** 863