



## NON-ALKOXIDE SOL-GEL SYNTHESIS OF RHOMBOHEDRAL $\text{CeZrO}_{3.5}$ NANOPOWDER AND ITS NANOCOMPOSITE

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### Abstract

A general sol-gel route using propylene oxide as a gelation agent was successfully applied to the synthesis of homogeneous and nanocrystalline  $\text{CeZrO}_{3.5}$  powders. Through this simple technique, sol-gel materials were prepared from solutions of metal nitrate without the need for alkoxides, polymeric gel agents, or elaborate reaction schemes. The gels were dried in ambient conditions, resulting in mesoporous xerogels with networked nanostructures interconnecting particulate regions. Calcination of the dried gels resulted in the crystallization of single-phase by  $800^\circ\text{C}$ , after decomposition of intermediate hydroxide, nitrate, and organic compounds. The formed nanopowder can be characterized by using XRD, UV-Vis spectroscopy and TEM analysis. The average crystallite size of the formed nanopowder is 30-50nm. In-situ polymerization method will be adopted for the synthesis of PMMA/ $\text{CeZrO}_{3.5}$  nanocomposite.

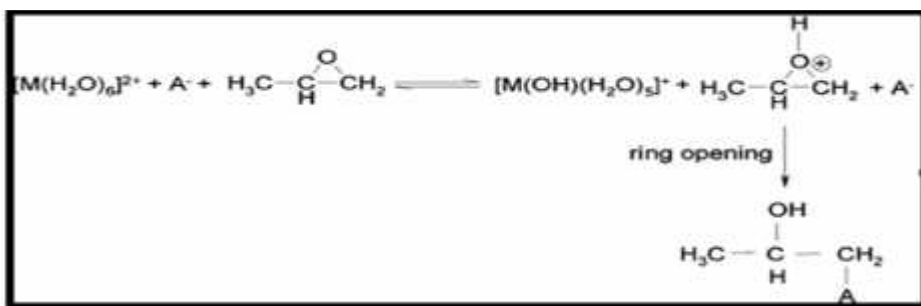
**Keywords:** Sol-Gel Materials, Mixed Oxides, Epoxide, Nanocomposite.

### 1. INTRODUCTION

Polymer-inorganic nanocomposites have attracted considerable interest since they usually combine desirable properties from the inorganic and organic components [1-3]. Polymethyl methacrylate (PMMA) has been the primary choice for the preparation of polymeric nanocomposites due to its superior properties such as high strength, compatibility with ceramics, dimensional stability and optical clarity. High performance materials usually require the use of small sized particles, especially in the range of nanometer. Rare earth elements offer a vast opportunity for development of environmentally secure alternatives for many of the eco-constrained materials. India is rich in rare earth resources and occupies the third place in the world in terms of rare earth deposits. Industrial utilization of rare earths is growing very rapidly because of their known low toxicity. Electronic configuration of the valence layer of the trivalent rare earth ions,  $[\text{Xe}]4f^n$ , involves the activity of internal f electrons, strongly protected by 5s and 5p electrons. Therefore, the resulting crystalline field caused by their interaction with neighboring ions is very low and usually optical spectra of lanthanide compounds present weak and profuse bands.

For the preparation of mixed oxide nanoparticles, the sol-gel method offers great advantages as compared to the conventional solid-state method. Comparison with the conventional ceramic routes, such as co-precipitation, grafting, impregnation, the sol-gel exhibits many advantages. Among them the low process temperature, the high control of purity, composition, microstructure and textural properties of the final material [4-5] are prominent. Particularly, for mixed-oxides this synthesis procedure allows to obtain materials characterized by a high dispersion of the active phase in the matrix on both molecular and nanometer scale [6-7].

Gash and co-workers have reported an alkoxide free, sol-gel synthesis technique for preparing various transition, main group, and rare-earth metal oxides. Through the use of an organic epoxide that acts as a proton scavenger, solutions of common hydrated metal salts undergo hydrolysis and condensation reactions to form metal oxide sol-gel materials [8]. The "epoxide addition method" eliminates the need for the often difficult preparation and handling of metal alkoxide precursors for non-traditional sol-gel metals and is complementary to traditionally prepared sol-gel materials (i.e.,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , etc.). Some examples of metal oxide gels prepared by the epoxide addition method include,  $\text{Cr}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ , and  $\text{ZrO}_2$ , and the method has also proven useful in the synthesis of a variety of binary metal oxide systems, including yttria-stabilized zirconia [9].



Equation (1)



According to the reaction Eq. (1), the epoxide consumes protons from the aqua complexes of  $[M(H_2O)_x]^{n+}$ , which promotes the hydrolysis and condensation of the complexes resulting in the formation of a gel. This method has been used for the preparation of metal-oxide aerogels [10] metal oxide/silica compounds [11] and metal-oxides nanoparticles [12]. The major disadvantage of this epoxide method is that metal oxide gels cannot be prepared from aqueous metal ions that have a formal charge of less than  $3^+$ , due to the lower acidities of  $[M(H_2O)_x]^{2+}$  complexes [13]. This lower acidity slows down the protonation of the added epoxide and the subsequent rise in the pH, allow in an alternative side reactions to occur to a significant degree and causing precipitation to take place. In the recently published works, the possibility of obtaining homogeneous gels from mixed ions having a formal charge of  $2^+$  and  $3^+$  was demonstrated for the preparation of spinel nanoparticles [14-16]. This epoxide addition method is a general technique for preparing gels of a variety of mixed metal oxides of transition, rare-earth, and main group elements. In this work, the epoxide assisted sol-gel process will be used to establish a general and facile way to synthesize  $CeZrO_{3.5}$  with small particle size and its nanocomposite through in-situ polymerization technique.

## 2. EXPERIMENTAL SECTION

**2.1. Synthesis of nanopowder:** Sol-gel materials were prepared from metal chloride solutions by the epoxide addition method from  $Ce(NO_3)_2 \cdot 6H_2O$  (99.9%), (Aldrich),  $ZrO(NO_3)_2 \cdot xH_2O$  (99.9%) and propylene oxide (PPO) supplied by Sigma Aldrich. Gels were prepared by dissolving the appropriate amounts of metal nitrate in ethanol separately. After the solution are mixing together at room temperature followed by stirring for half an hour. Subsequently, calculated amount of propylene oxide was added rapidly and the solutions were stirred vigorously. An exothermic reaction occurred within several minutes, followed by a rapid formation of a rigid gel. The gels were aged in a closed vessel at room temperature for 24 h, dried in an open vessel at 50 C for 12 h and then treated at 100°C for another 12 h to obtain xerogels. The resulting xerogels were ground to powder and calcined at 800°C.

**2.2. Synthesis of  $CeZrO_{3.5}$ /PMMA nanocomposites:** An in-situ polymerization method will be adopted for the synthesis of nanocomposite of proposed nano-powder with PMMA. The monomer (MMA) will be added in nanopowder dispersed solution and polymerize using 2, 2'- azobisisobutyronitrile (AIBN). The polymer modification or the nanocomposite imparts gloss and color retention of the powder as well as scratch and stain resistance.

## 3. CHARACTERIZATION METHODS

The thermal behaviour of xerogels (TG/DTA) of the samples was studied by a Seiko SSC/5200 (TG/DTA 320U) in static air atmosphere from ambient temperature to 1000 C with a heating rate of 10 C/min. The XRD patterns of the samples were measured in a Siemens D8 diffractometer using  $CuK$  radiation. Optical reflectance of the powder was measured with UV-Vis spectrophotometer (Shimadzu, UV-2450) using barium sulphate as a reference. Particle size and size distribution were estimated in the TEM micrograph. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 670 spectrometer in the range of 600–4000  $cm^{-1}$  using KBr pellets.

## 4. RESULTS AND DISCUSSION

### 4.1. Thermal behavior of xerogel

TG/DTG measurements were carried out in order to study the thermal behaviour of the dry gels (Fig.1), including the decomposition temperature of the organic matter and the weight loss. The DTG scan of  $CeZrO_{3.5}$  has an endothermic peak at 217.2 C followed by a sharp exothermic peak at 342.23°C shows the organic compound degradation and a second endotherm is observed at 452.23°C due to the elimination of nitrous oxide. The peak observed at 771.3°C is responsible for the crystalline phase formation

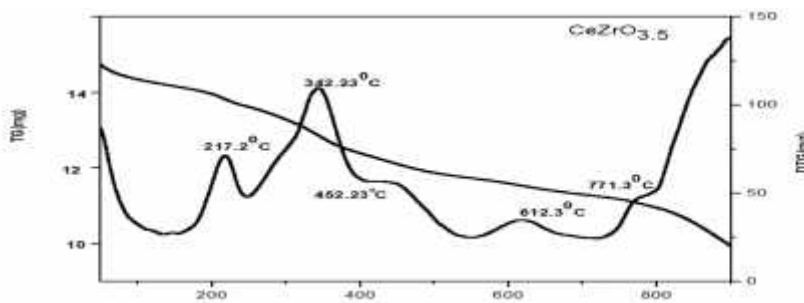


Fig.1. Thermogravimetric analysis of  $CeZrO_{3.5}$  xerogel



#### 4.2. Powder X-ray Diffraction analysis

Fig.2. shows the powder X-ray diffraction patterns for  $\text{CeZrO}_{3.5}$  prepared at various calcinations temperatures. The XRD pattern indicates that the synthesized sample has a standard rhombohedral phase of  $\text{Ce}_2\text{Zr}_2\text{O}_{7.98}$  (JCPDS 89-8532) at  $800^\circ\text{C}$ . The average crystalline size can be calculated using Debye Scherer equation and shows the particles are 30-50 nm in size.

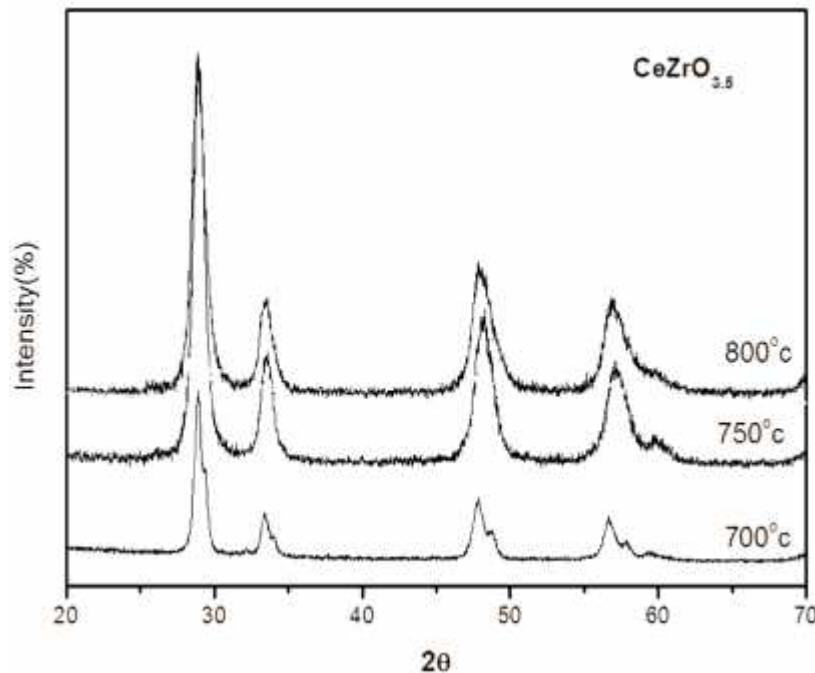


Fig.2. powder X-ray diffraction patterns for  $\text{CeZrO}_{3.5}$

#### 4.3. Optical studies of the nano $\text{CeZrO}_{3.5}$ and $\text{CeZrO}_{3.5}/\text{PMMA}$ nanocomposite

The reflectance spectrum of the  $\text{CeZrO}_{3.5}$  nanopowder and  $\text{CeZrO}_{3.5}/\text{PMMA}$  nanocomposite was shown in Fig. 3. The reflectance spectrum of the  $\text{CeZrO}_{3.5}$  powder with maximum reflectance (85%) at a wavelength of about 780 nm was observed. The  $\text{CeZrO}_{3.5}$  powder has a band gap value at 3.51 eV falls in the near visible region of spectrum and hence a complementary white color is observed for the powder sample.

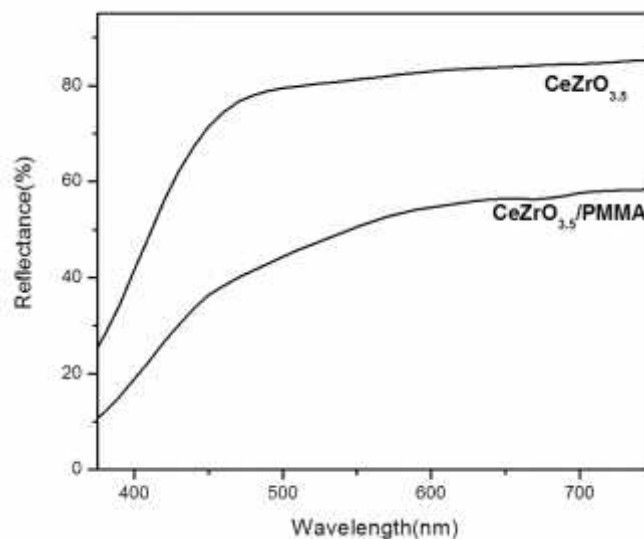


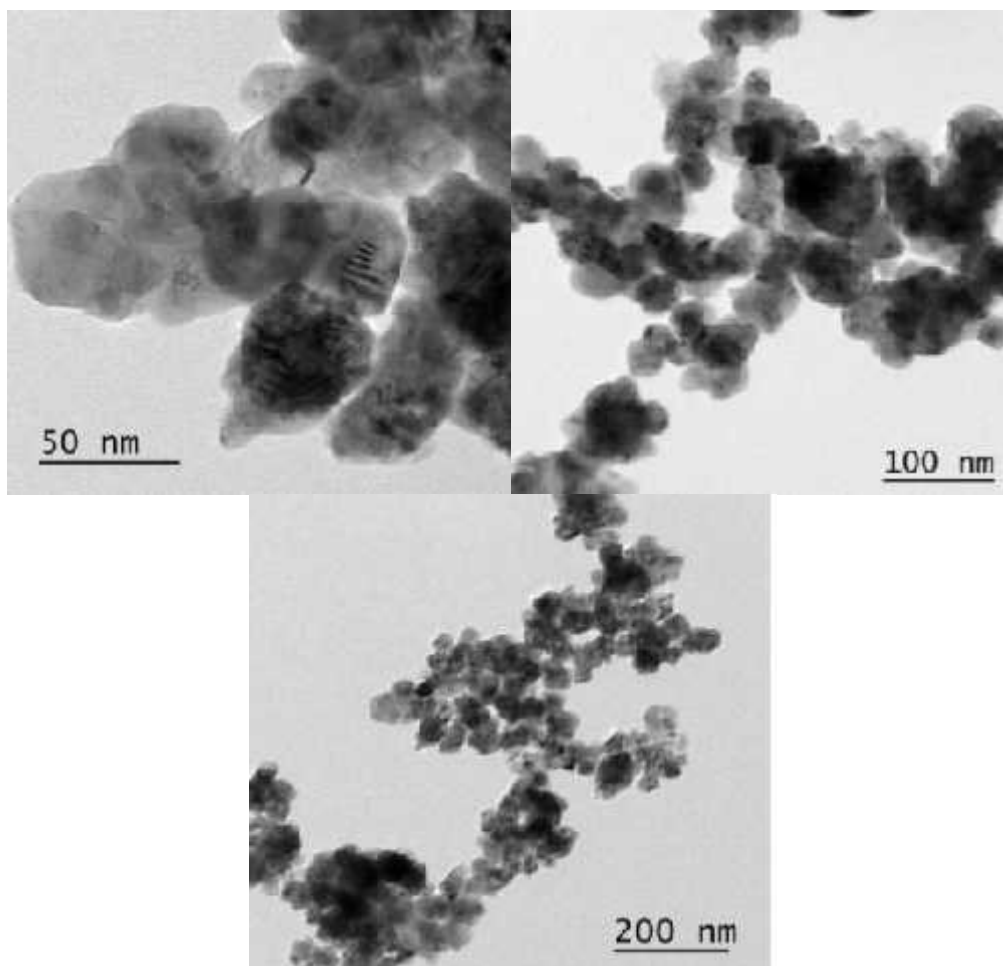
Fig.3. UV-Vis reflectance spectra of  $\text{CeZrO}_{3.5}$  and  $\text{CeZrO}_{3.5}/\text{PMMA}$  nanocomposite



**Fig.4.** Photographs of  $\text{CeZrO}_{3.5}$  nanopowder and  $\text{CeZrO}_{3.5}/\text{PMMA}$  nanocomposite

#### 4.4. TEM analysis of the nano $\text{CeZrO}_{3.5}$ powder

The TEM images of the  $\text{CeZrO}_{3.5}$  sample are shown in the Fig.5 exhibits well dispersed, non-agglomerated, and nearly spherical nanoparticle with crystalline size of 30-50nm. A high magnification representative micrograph of mixed metal oxide nanoparticle is given in the figure provide a fine characterization of their size and morphology.



**Fig.5.** TEM image  $\text{CeZrO}_{3.5}$  nanopowder

#### 4.5. FTIR Analysis of $\text{CeZrO}_{3.5}/\text{PMMA}$ nanocomposite

Fig.6 shows the FT-IR spectrum of  $\text{CeZrO}_{3.5}/\text{PMMA}$  nanocomposite and from the spectrum we can understand that the nano-particles are well dispersed in the polymer matrix. For PMMA, the peak at  $3441\text{ cm}^{-1}$  is attributed to hydroxyl stretching vibration, the peak at  $2954\text{ cm}^{-1}$  is assigned to the C-H stretching vibration of the methyl group ( $\text{CH}_3$ ), the peak at



1729  $\text{cm}^{-1}$  is attributed to the C=O stretching vibration of PMMA, the peak at 1430  $\text{cm}^{-1}$  is attributed to the C-H bending vibration, the peak at 1147  $\text{cm}^{-1}$  is associated with the C-O-C symmetrical stretching vibration, peaks at 984 and 831  $\text{cm}^{-1}$  correspond to the C-H bending wagging vibration and the deformation vibration of O-C-O of PMMA. The peak at 753  $\text{cm}^{-1}$  is attributed to the puckering vibrations of the PMMA chains. The FT-IR spectrum of PMMA/CeZrO<sub>3.5</sub> nanocomposites is almost identical to that of pure PMMA.

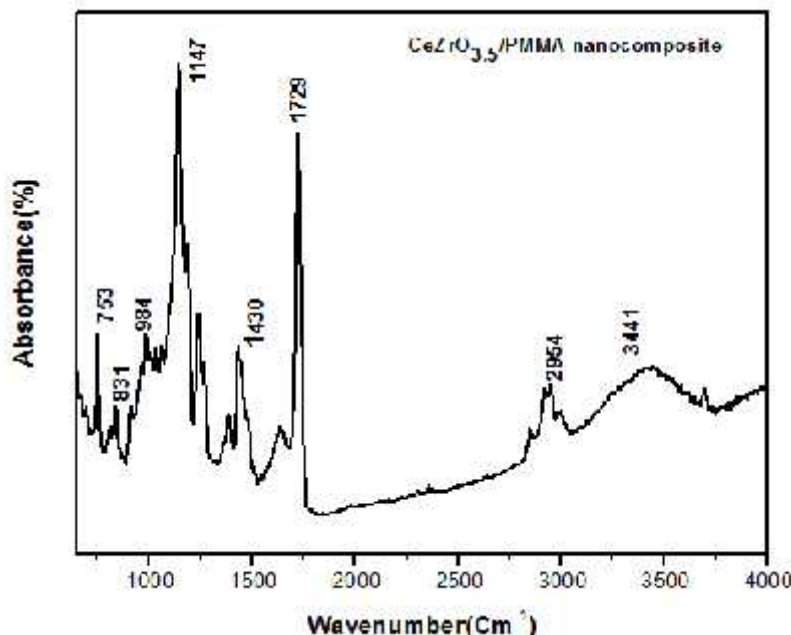


Fig.6.The FT-IR spectrum of CeZrO<sub>3.5</sub>/ PMMA nanocomposite

## 5. CONCLUSIONS

A sol-gel method using propylene oxide as gelation agent has been successfully used to synthesize rhombohedral CeZrO<sub>3.5</sub> nanoparticles of 30-50 nm size. The usage of this epoxide method results in a substantial reduction of calcination temperature and time as compared to the solid state route and other sol-gel routes. The formed nanocomposite show good dispersion of nanoparticle in the PMMA matrix.

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## REFERENCES

1. Ahmad Z, Sarwar M I and Mark J E 1997 *J. Mater. Chem.* 7 259
2. Schmidt H, Schloze H and Tunker G 1986 *J. Non-Cryst. Solids* 80 557
3. Caruso F, Lichtenfeld H, Giersig M and M'ohwald H 1998 *J. Am. Chem. Soc.* 80 8523
4. BrinkerC, J Scherer, S.W. “, Academic Press, New York, 1990.
5. FidalgoA, RosaME,Ilharco LM(2003) *Chem. Mater.* 15:2186.
6. FranciscoM.S.P, LandersR, GushikemY (2004) *Solid. State Chem.* 177:2432.
7. AronneA,turcoM, Bagnasco, Marena E, FanelliE,(2005) *Chem. Mater.* 17:2081.
8. Christopher N, Brady, Wei Chiu, H, AlexanderE, (2006) *Chem. Mater.* 18:1928.
9. Christopher N, Gash,Joe H. Satcher, Jr. and Susan M (2006)*Chem. Mater.* 1:1928.
10. Hongtao C, MarcosZ, DavidL (2006) *Sol-Gel Sci Techn:* 2006:83
11. Hongtao C, MarcosZ, DavidL (2007) *Sol-Gel Sci Techn.*41:313
12. Hongtao C, MarcosZ, David L(2015)*Sol-Gel Sci Techn*35:175.
13. Hongtao C, Marcos Z, David L (2006) *Non-Crystalline Solids* 352: 3035.
14. Hongtao Cui, Marcos Z, David L (2009) *Alloys and Compounds* 2474:292.
15. Masoud SN, Fatemeh D, MasoudF, (2009) *Sol-Gel Sci Techn.*51:48
16. MarauoD, Cenk G,Courtney K, Louisa J, HopeW(2011) *Sol-Gel Sci Techn*58:535.