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Structural, Optical, Electrical Characteristics of Synthesized Nanoparticles of Cerium Orthophosphate

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Abstract: Nanoparticles of cerium orthophosphate synthesized via chemical co-precipitation method belong to the monoclinic crystal system. The surface morphologies reveal that the particles have spherical shape with the grain size ranging from 80 – 90 nm. The photoluminescence emission spectrum shows the broad emission peak at 400 nm which is due to the optically allowed transition from 5d – 4f. The dielectric constant ($\varepsilon^{/}$) reveals the dispersion is due to a Maxwell-Wagner type of interfacial polarization. The continuous decrease in dielectric constant with increase in frequency suggests that the conduction mechanism is due to hopping of the charge carriers from one site to another.
Keywords- Rare earth elements; XRD; Photoluminescence; Dielectric properties.

1. Introduction and Experimental

Cerium orthophosphate ($CePO_4$) is a synthetic cognate of the naturally occurring mineral monazite and is considered to be thermally stable material. Due to interesting chemical and physical properties, they become a centre of attraction for the material scientist. Several researchers have reported the synthesis of cerium orthophosphate nanomaterials by various method including reverse micelles [1], sol-gel [2] and hydrothermal methods [3]. Hexagonal and monoclinic $CePO_4$ nanowires were prepared through hydrothermal reaction [4]. The optical reflection spectrum of $CePO_4$ is affected critically by their crystallization which in turn depends on the method of preparation as well as the calcination temperature [5]. This paper deals with study of cerium orthophosphate nanospheres synthesized by co-precipitation method calcinated at 800°C and then studying its optical and electrical behaviour.

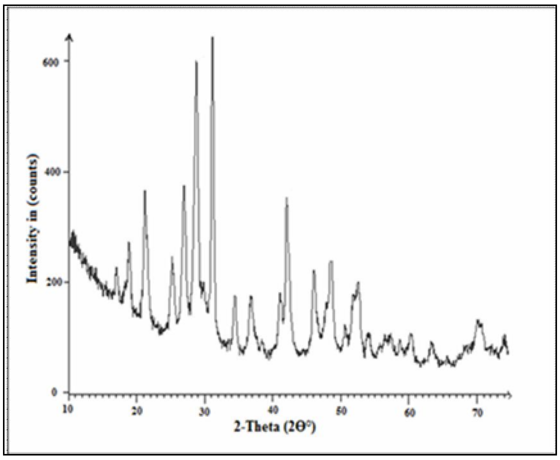
Cerium nitrate hexahydrate {Ce $(NO_3)_3.6H_2O$} 99.9% pure (Alfa Aesar) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) as precursor were used for the preparation of cerium orthophosphate nanoparticles by co–precipitation technique. The cerium orthophosphate nanoparticles were characterized using various physico– chemical techniques like X-ray diffraction analysis, scanning electron microscopy, photoluminescence spectrophotometer and dielectric characteristics.

2. Results and Discussion

X-ray diffraction (XRD) pattern of the $CePO_4$ (Fig.1) consist of highly resolved peak at specific 2θ Bragg’s angle depicting crystalline phase and purity of the grown nanoparticles. The particles belong to the monoclinic structure which was compared with JCPDS no. 32-0199. The crystallite size calculated from the Debye-Scherer method comes out to be 49 nm. Fig. 2 shows electron microscopic features consisting of nanosphere morphology slightly agglomerated and almost uniformly distributed throughout the material with an average grain size ranging from 80–90 nm. The photoluminescence (PL) emission spectra recorded for cerium orthophosphate nanoparticle using an excitation wavelength of 330 nm is shown in Fig.3. As observed from the spectra strong ultraviolet emission band at 400 nm exists which is caused by the transition from the 5d – 4f state. Basically, the cerium emission consists of two transitions from the 2D state to the spin orbit components of the ground state, $^2F_{7/2}$ and $^2F_{5/2}$ and the maximum absorption of cerium (Ce^{3+}) was observed in the UV-VIS region which correspond to the transitions from the ground state $^2F_{5/2}$ ($4f^1$) to the crystal field splitting level of the Ce^{3+} ^2D ($5d^1$) excited states [6].

Fig. 4 shows the variation of dielectric constant ($\varepsilon^/$) with frequency of the applied ac field (5 kHz to 1 MHz) in the temperature range of 40 - 500°C. The maximum value of dielectric constant ($\varepsilon^/$) obtained in the present case is 67 at 5 kHz. As the frequency increases the dielectric constant ($\varepsilon^/$) decreases and remained constant at higher frequency 1 MHz. The continuous decrease in the value of the dielectric constant ($\varepsilon^/$) with increasing frequency may be attributed to different types of polarization viz. ionic, electronic, dipolar and interfacial or space charge polarization at low frequencies [7]. At low frequencies, the dielectric constant can be explained on the basis of the Maxwell-Wagner model. In this model, the dielectric structure consist of two layers, the first layer at higher frequencies shows a large number of grains that act as a conducting medium and the second layer at low frequency consist of grain boundaries that act as a highly resistive medium [8]. In $CePO_4$ nanoparticles the polarization mechanism at low frequency are explained as a local displacement of electrons by the hopping mechanism between Ce^{3+}/Ce^{4+} and an orientation of dipoles in the direction of the applied ac field. The continuous fall of dielectric constant with increasing frequency occurs because dipoles are not able to follow faithfully the impressed oscillating field and the low value of dielectric constant ($\varepsilon^/$) are observed at high frequencies.

From the present investigation, it is concluded that the cerium orthophosphate nanoparticles can be successfully synthesized by co-precipitation method calcinated at 800°C. Detailed investigation reveals that the material belongs to the monoclinic phase with spherical morphology and grain size ranging from 80 – 90 nm. The optical characteristics of $CePO_4$ nanoparticles shows strong emission band at 400 nm which is due to the 5d – 4f emission. The gradual decrease in dielectric constant with frequency indicates that the material may be having different types of polarisation which can be explained on the basis of Maxwell – Wagner model.



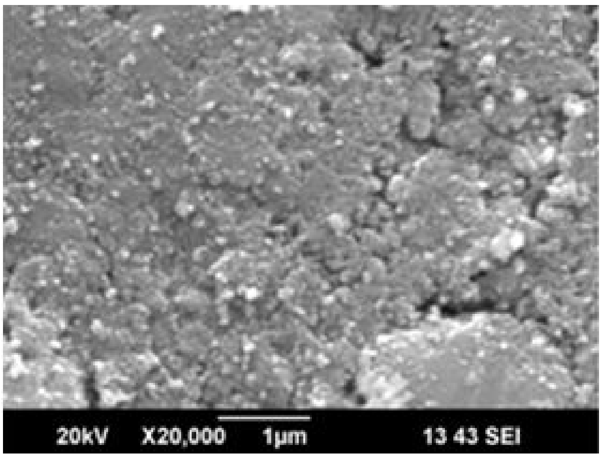


Fig. 1 **Fig.2**

Fig. 1 Powder X-ray diffraction pattern of cerium orthophosphate ($CePO_4$) nanoparticles.
Fig. 2 Scanning electron micrograph reveals the spherical particles which are agglomerated.

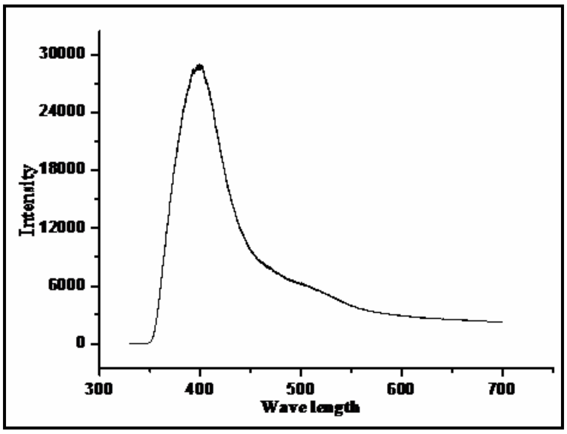


Fig. 3

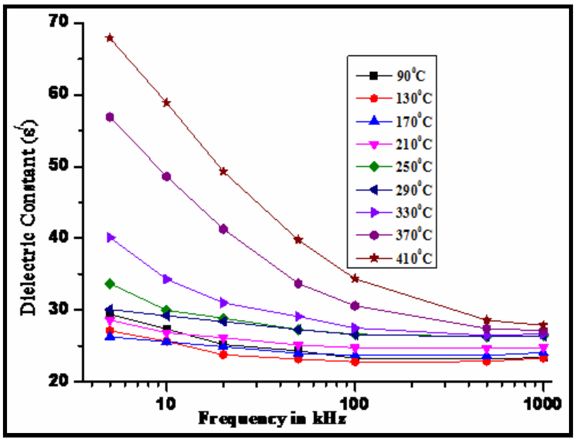


Fig.4

Fig. 3 Photoluminescence emission spectra excited at 330 nm.

Fig. 4 Variation of dielectric constant (ε′) with frequency at different temperatures.

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