Preparation of Cerium Orthophosphate Nanosphere by Coprecipitation Route and Its Structural, Thermal, Optical, and Electrical Characterization

Seema Verma and K. K. Bamzai

Crystal Growth and Material Research Laboratory, Department of Physics & Electronics, University of Jammu, Jammu 180006, India

Correspondence should be addressed to K. K. Bamzai; kkbamz@yahoo.com

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Cerium orthophosphate (CePO₄) nanoparticles were synthesized via wet chemical coprecipitation technique using cerium nitrate hexahydrate for Ce³⁺ ion and ammonium dihydrogen phosphate for PO₄³⁻ ion source. X-ray diffraction (XRD) analysis suggests that the material belongs to monoclinic crystal system with crystallite size of 49.3 nm. Scanning electron microscope (SEM) and transmission electron microscope (TEM) reveal the surface morphology of the prepared nanoparticles as nanospheres having grain size in the range of 30–50 nm. The energy dispersive X-ray analysis (EDAX) gives elemental composition present in the grown nanomaterial. Thermogravimetric analysis suggests that the structural phase transition is above 800 °C. The optical properties include UV-VIS-NIR absorption and the photoluminescence spectrum shows the absorption and emission peaks in the ultraviolet region. The dielectric constant (ε') and ac conductivity properties were investigated with regard to change in temperature (40 to 500 °C) and frequency (5 kHz to 1 MHz). The dielectric measurement indicates that the transition is diffused and the activation energy values decrease suggesting that the conduction mechanism is due to hopping of the charge carriers from one site to another.

1. Introduction

Rare earth elements (REEs) known as lithophile are the elements enriched in the earth crust which occur naturally because all are trivalent and form a special group of transition elements in the periodic table. Among these REEs, cerium (Ce) is found in abundance which makes it one of the cheapest rare earth metals. However, cerium is found in several minerals like monazite (Ce, La, Nd, Th) PO₄, xenotime (Y, Ce) PO₄, bastnasite (Ce, La) CO₃ (F, OH), and cerite (Ce, La)₉(Mg, Fe)Si₆(O, OH, F)₉₈. Orthophosphates are substances that are composed of isolated PO₄ tetrahedra analogous to “orthosilicates.” The most common naturally occurring orthophosphates are apatite [Ca₅(PO₄)₃F; CI, OH] and monazite (LnPO₄) where “Ln” refers to rare earth elements. Rare earth orthophosphates with the general formula RXO₄ (where R = rare earth and X = P, As, or V) belong to a family that crystallizes in different structural types like hexagonal, tetragonal, and monoclinic depending on the radius of ions and temperature. The rare earth compounds with large ionic radii, namely, RPO₄ with R = La, Ce, Pr, Nd, Sm, Eu, and Gd, crystallize in the monoclinic monazite structure, whereas rare earth compounds with small ionic radii, namely, RPO₄ (R = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc), crystallize in the tetragonal zircon (or xenotime) structure [1]. The hexagonal structure is the low temperature phase and it can transform into the monoclinic structure, while the tetragonal maintains its structure after calcinations at 900 °C [2–4].

Cerium orthophosphate (CePO₄) has attracted attention of many researchers because of its use in the area of fluorescence, catalytic materials, ceramic composite materials with high mechanical properties, and ion exchange [5–7]. CePO₄ doped with different rare earth elements can be used in colour
mixing in 1:1 molar ratio

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Ce(NO₃)₃⋅6H₂O + NH₄H₂PO₄ + 2NH₄OH
→ CePO₄ + 3NH₄NO₃ + 8H₂O ↑

2. Material and Methods

2.1. Material Preparation. Cerium orthophosphate nanoparticles were prepared by coprecipitation method using cerium nitrate hexahydrate (Ce(NO₃)₃⋅6H₂O) 99.9% pure (Alfa Aesar) and ammonium dihydrogen phosphate (NH₄H₂PO₄) 99.9% pure (Alfa Aesar) as precursor. Figure 1 illustrates the schematic diagram for synthesis of cerium orthophosphate (CePO₄) via coprecipitation method. Cerium nitrate hexahydrate of 0.5 molarity (M) was prepared in deionized water under stirring using a mechanical stirrer. Synthesis of CePO₄: Tb nanoparticles was reported by liquid phase synthesis in high boiling coordinating solvents, whose structure is monazite [12]. Hexagonal and monoclinic CePO₄ nanowires were prepared through hydrothermal reaction by Zhang and Guan [13]. The optical reflection spectrum of CePO₄ is affected critically by their crystallization which in turn depends on the method of preparation and the calcination temperature [14, 15]. Therefore, formation and structure of phosphate depend on rate and time of heating, the cooling rate of melt, the atmosphere, kind of cations of phosphate, and the ratio of phosphorous/cation [16]. As per the literature survey, cerium orthophosphate nanomaterials were synthesized by techniques which involve low basic pH value. However, the novelty of the present research work is the preparation of cerium orthophosphate nanoparticles by coprecipitation technique which is based on high pH value. Therefore, in the present investigation, the authors report the synthesis of monoclinic CePO₄ nanospheres by simple coprecipitation method calcinated at 800°C for 2 hr and then carried out its detailed characteristics viz-a-viz optical and electrical.
2.2. Characterization. The cerium orthophosphate nanoparticles were characterized using various physicochemical techniques like X-ray diffraction analysis, particle size analyzer, transmission electron microscope, and scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDAX); optical properties include UV-VIS-NIR spectroscopy and photoluminescence spectrophotometer, and electrical properties include dielectric constant, dielectric loss, and conductivity. The phase identification was carried out by X-ray diffraction patterns using PANalytical X’Pert Pro diffractometer with a CuKα radiation ($\lambda = 1.54060 \, \text{Å}$), the intensities of the diffraction beam were obtained in the $2\theta$ range between 20° and 70°. Debye-Scherer relation was used to determine the crystallite size. The particle size was measured with Zetasizer Nano ZS (Malvern Instruments Ltd., UK). In order to see the microstructure studies scanning electron microscope of JEOL Model JSM-6390 LV supplemented with energy dispersive X-rays analysis (EDAX) of model number JEOL JED-2300 was used. The size and shape of nanoparticles were observed under transmission electron microscope of Tecnai G² 20 S-Twin working at a 200 kV accelerating voltage. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves were recorded simultaneously on the thermal analyzer (Shimadzu make DTG-60) over the temperature range from room temperature to 1000 °C at the heating rate of 10 °C/min at a flow rate of 30 mL/min. Fourier transform infrared (FTIR) spectrum was obtained on IR Prestige-21 (Shimadzu) spectrophotometer in the region from 400 to 3500 cm$^{-1}$ using KBr pellet. The optical absorption was measured in UV-VIS-NIR region with Varian Carry 5000 spectrophotometer. The photoluminescence (PL) was investigated by Perkin Elmer Luminescence Varian Carry 5000 spectrophotometer. The photoluminescence (PL) was investigated by Perkin Elmer Luminescence Varian Carry 5000 spectrophotometer. The size and shape of nanoparticles were observed under transmission electron microscope of Tecnai G² 20 S-Twin working at a 200 kV accelerating voltage. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves were recorded simultaneously on the thermal analyzer (Shimadzu make DTG-60) over the temperature range from room temperature to 1000 °C at the heating rate of 10 °C/min at a flow rate of 30 mL/min. Fourier transform infrared (FTIR) spectrum was obtained on IR Prestige-21 (Shimadzu) spectrophotometer in the region from 400 to 3500 cm$^{-1}$ using KBr pellet. The optical absorption was measured in UV-VIS-NIR region with Varian Carry 5000 spectrophotometer. The photoluminescence (PL) was investigated by Perkin Elmer Luminescence Varian Carry 5000 spectrophotometer. The phase, purity, and crystallite size of the material. The X-ray data was compared with JCPDS card number 32-0199 which suggests that material is a low temperature phase. The details of the XRD pattern depicting interatomic ($d$) spacing and corresponding ($hkl$) planes are given in Table 1. The line broadening of diffraction peaks can be used to calculate the crystallite size by Scherer’s formula:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where “$D$” is the crystallite size (nm), “$\lambda$” is the wavelength of monochromatic X-ray beam (Å) (λ = 1.54184 Å for CuKα radiation), “$\beta$” is the full width at half maximum for the diffraction peak under consideration (rad.), “$\theta$” is the diffraction angle (°), and “$k$” is a constant varying with crystal habit and chosen to be 0.9. The crystallite size comes out to be 49.3 nm. Figure 3 is the graph showing the particle size (nm) by Zeta particle size analyzer. From the particle size analyzer graph and XRD results, it may be concluded that the synthesized cerium orthophosphate is in the nanoscale range.

Figures 4(a) and 4(b) show scanning electron micrograph which reveals the surface morphology. These nanoparticles

### Table 1: Data regarding interatomic ($d$) spacing, the {hkl} planes corresponding to specific $2\theta$ angles.

| $d$-Spacing | 2 theta (°) | {hkl} planes |
|------------|-------------|--------------|
| 4.56       | 18.93       | 011          |
| 4.82       | 21.23       | -111         |
| 3.62       | 25.38       | 020          |
| 3.32       | 26.85       | 200          |
| 3.10       | 28.77       | 120          |
| 2.87       | 31.12       | 012          |
| 2.14       | 42.03       | -103         |
| 1.97       | 46.07       | 212          |
| 1.88       | 48.47       | 103          |
| 1.74       | 52.55       | -232         |
are composed of agglomerated spherical particles. The possible growth mechanism for the formation of agglomerated spherical particles requires the surface potential to be low so that the attractive interaction between the grain boundaries dominates over the repulsive interaction forces. So the magnitude of the attractive interaction depends on the various factors like ionic strength, the dielectric constant of the solvent, and its viscosity which affects the kinetic agglomeration [18–20]. Further insight into the morphology and size distribution. The corresponding selected area electron diffraction (SAED) pattern in the inset of Figure 5(b) reveals that the samples are consistent with the high crystallinity, and diffraction spots can be indexed as the phase formed is spherical instead of any other shape. Therefore, the coprecipitation process in the present investigation leads to homogeneous powder with small spherical particles with a narrow size distribution. The corresponding selected area electron diffraction (SAED) pattern in the inset of Figure 5(b) reveals that the samples are consistent with the high crystallinity, and diffraction spots can be indexed as the phase formed is purely monoclinic in monazite structure which has also been confirmed from the powder XRD results.

The spectrum obtained from energy dispersive X-ray analysis (EDAX) is shown in Figure 6. The EDAX spectrum shows peaks corresponding to all the major elements present in the grown composition as should be expected in case of cerium orthophosphates. The spectra show peaks corresponding to all major elements like cerium, oxygen, and phosphorous. No such impurity was found in the grown material. The weight % and atomic % as observed in the experiment are given in Table 2.

3.2. Thermal Analysis. Thermogravimetric and differential thermal analyses (TGA/DTA) were used to identify different phase transition and to assess the stability of a prepared material. Figure 7 shows the recorded thermograph for cerium orthophosphate dried at 100°C. TGA/DTA was carried out between 14°C and 1000°C at uniform heating rate of 10°C/min and the mass was found to lose continuously as a function of temperature. The material starts to decompose at 21°C and decomposition went up to 335°C; thereafter the material is thermally stable up to 1000°C. The total weight loss observed is 15.81%. From the graph, it is clear that the thermal decomposition can be divided into three stages. The first stage of decomposition begins at 21°C and terminates at 127°C. During this temperature range, the mass loss observed is 9.31%. In this first stage of decomposition, the endothermic peak is observed at 54°C which is attributed to the loss of physisorbed water. The second stage of decomposition starts at around 127°C and is completed at around 255°C and net weight loss observed is 3.92%. Second stage of decomposition involves conversion of hydrated hexagonal cerium orthophosphate into anhydrous in nature as indicated in the following equation [21]:

(\text{CePO}_4 \cdot n\text{H}_2\text{O})_{\text{Hexagonal}} \rightleftharpoons (\text{CePO}_4)_{\text{Hexagonal}} + n\text{H}_2\text{O}

(3)

The third stage of decomposition occurs in the temperature range from 255 to 335°C. The weight loss in this stage is 2.58%. During this decomposition stage, this weight loss is accompanied by an exothermic peak at 285°C which is attributed to the transformation of cerium orthophosphate from the amorphous state to the crystalline phase. After the third decomposition stage (255–335°C), the material is thermally stable up to 1000°C. A weak exothermic peak at 817°C may be due to the crystallization of monoclinic monazite, cerium orthophosphate from hexagonal form (\text{CePO}_4)_{\text{Hexagonal}} \rightarrow (\text{CePO}_4)_{\text{Monoclinic}}. From the thermal analysis of the system, we can therefore confirm that the product formed is in the monoclinic phase above 800°C which support the results obtained by powder XRD.

3.3. Fourier Transform Infrared Spectroscopy (FTIR). In order to identify and characterize the inorganic species and analyse the chemical bonds, functional groups, and internal structure of molecules present in the grown nanomaterial, Fourier transform infrared spectroscopy (FTIR) was used. Figure 8 shows the FTIR spectra of cerium orthophosphate (\text{CePO}_4). Fundamentals IR frequencies observed in other phosphate compounds were also found in the present case, which confirms the presence of orthophosphate group in the grown material. The band observed in the range 2885.51–2341.58 cm\(^{-1}\) shows the presence of absorption of water vibration in addition to the wide bands associated with the OH group and another peak at 1635.64 is due to the scissor bending mode of associated water molecule [21]. The bands around wave numbers 1043.49, 623.01, and 543.93 cm\(^{-1}\) correspond to P–O stretching, O=P–O bending, and O–P–O bending mode of vibration, respectively. The bands from orthophosphate (\text{PO}_4^{3–}) functional group appeared at 493.78 to 395.41 cm\(^{-1}\) in the lanthanide phosphates of monoclinic (monazite structure) and agree well with the literature data [22]. Table 3 gives complete information about the type of
Figure 4: (a) Scanning electron micrograph of CePO$_4$ at lower magnification. (b) Scanning electron micrograph reveals the nanoparticles are composed of agglomerated spherical particles.

Figure 5: (a) TEM micrograph clearly depicting nanosphere morphology having grain size in the range of 30–50 nm. (b) TEM micrograph and corresponding SAED patterns of cerium orthophosphate nanoparticles.

Figure 6: Energy dispersive X-ray analysis (EDAX) spectrum revealing the presence of all the major elements present in cerium orthophosphate (CePO$_4$).

Table 2: Data regarding weight% and atomic% present in the cerium orthophosphate (CePO$_4$) composition as observed in the experiment.

| Elements    | Weight% | Atomic% | KeV   |
|-------------|---------|---------|-------|
| Oxygen (O)  | 11.95   | 43.53   | 0.525 |
| Phosphorous (P) | 13.53 | 25.47   | 2.013 |
| Cerium (Ce) | 74.52   | 31      | 4.839 |

3.4. Optical Characterization

3.4.1. UV-VIS-NIR Absorption Spectrophotometer. Rare earth compounds are one of the most important types of phosphors so it is essential to understand their optical properties, namely, electronic transitions and optical band gap energy. The UV-VIS-NIR absorption spectrophotometer for cerium
Ortphosphate is shown in Figure 9. It can be seen that there are two absorption bands at 208 and 274 nm in the ultraviolet range which is assigned to transitions from ground state $^2{F}_{5/2}$ to the excited state, namely, $^2{D}_{5/2}$ and $^2{D}_{3/2}$ energy level. The cerium absorption band shows a weak extension from 300 to 450 nm, which is caused by the presence of a small amount of Ce$^{4+}$ and a small peak is observed at 1452 and 1939 nm due to the presence of phosphate in the NIR region.

The obtained results are consistent with the data for the transition of Ce$^{3+}$ where the transition in case of Ce$^{5+}$ is assigned from 4f ground state ($^2{F}_{5/2}$) to the 5d energy level split ($^2{D}_{5/2}$, $^2{D}_{3/2}$) within monoclinic crystal field [17, 23]. UV-Visible absorption spectra also give the optical band gap of the material. The energy band gap is related to the absorption coefficient "α" by the Tauc relation, $αhv = A(hv − E_g)^n$ [24], where "A" is constant, "hv" is the photon energy ($\nu = c/\lambda$), "$E_g$" is the band gap energy of the material, and $n = 1/2$ for an allowed direct transition. For allowed direct transition, the band gap energy can be obtained from extrapolation of the straight line ($αhv$) versus $hv$ as shown in Figure 10. From the intersection of the extrapolated linear portion, the optical band gap energy ($E_g$) of the material was found to be 1.07 eV; it means the absorption of photon with energy is greater than the optical band gap energy for direct transition from the occupied state in the valence band to unoccupied states in the conduction band. From the optical results, one can conclude that the cerium orthophosphate shows the properties of direct band gap material. In direct band gap material the electron wave vector remains the same (there is no phonon interaction); that is, if the momentum of electrons and holes is the same in both the conduction band and valence band, an electron can directly emit a photon.

### Table 3: Presence of various functional groups along with their frequency bands.

| Serial number | Assignments of bands/peak | IR bands (cm$^{-1}$) |
|---------------|---------------------------|---------------------|
| 1             | OH stretching             | 2885.51–2341.58     |
| 2             | H–O–H bending            | 1635.64–1514.12     |
| 3             | P–O stretching           | 1043.49             |
| 4             | O=P–O bending            | 623.01              |
| 5             | O–P–O bending mode of vibration | 543.93            |
| 6             | PO$_4^{3-}$ vibration    | 493.78–395.41       |
3.5. Electrical Properties. The investigation of electrical property is an elegant tool for understanding the dielectric behaviour of the material in response to an applied electric field. The study includes finding dependence of dielectric constant ($\varepsilon'$) and dielectric loss ($\tan \delta$) on temperature and frequency. In order to carry out these investigations, the agglomerated nanoparticle was mixed with 1-2% PVA (polyvinyl alcohol) which acts as a binder and then pressed into a shape of circular pellet of the size 13.11 mm in diameter and 1.43 mm in thickness with the help of hydraulic press. The pellet was heated up to a temperature of 250°C at a heating rate of 2°C/min. before performing any measurement in order to overcome the effect of binder. The conducting silver paste was applied on both sides of the circular pallet which acted as capacitor with the material as dielectric. The material was then mounted on specially designed two terminal sample holders. The instrument directly provides the value of capacitance ($C$) and dielectric loss ($\tan \delta$). The dielectric constant was calculated using the relation:

$$\varepsilon' = \frac{Ct}{\varepsilon_0 A},$$

where “$C$” is the capacitance (F), “$t$” is the thickness (m), “$A$” is the area (m$^2$), and “$\varepsilon_0$” is the absolute permittivity in the free space having a value of $8.854 \times 10^{-12}$ Fm$^{-1}$.

3.5.1. Dependence of the Dielectric Constant and Loss Tangent on Temperature. Figure 12 shows the variation of dielectric constant ($\varepsilon'$) with temperature (40–500°C) as a function of frequencies (5 kHz–1 MHz). The dielectric curve shows two anomalies, one at 60°C and another at 260°C. This behaviour was observed for other materials which exhibit two-phase transition [26]. In first phase of transition, the value of $\varepsilon'$ increases with increase in temperature attaining a maximum value of 31 followed by a decreasing pattern. The second phase transition occurs at 260°C and the maximum value of $\varepsilon'$ is 34. The first transition is attributed to the space charge polarization effect and the second phase transition may be due to ferroelectric to paraelectric transition. Similar behaviour was also observed in the thermal analysis results. From the thermal analysis graph, the peak observed at 285°C is nearly equal to the peak observed at 260°C in
the dielectric results suggesting that the transition takes place in the material. During this phase transition, the peak observed is broadened and as frequency increases from 5 kHz to 50 kHz the peak around the dielectric constant becomes more broadened and the dielectric shifts towards the higher temperature. At higher frequencies (1 MHz), the value of dielectric constant shows less variation with temperature because space charge polarization decreases as the frequency increases. So, one can observe that the value of transition temperature shifts towards higher temperature with increase in frequency thereby showing the relaxational behaviour of the material. For most of the relaxor ferroelectrics, the peak of the dielectric constant ($\varepsilon'$) shifts to higher temperature with increasing frequency, which has been attributed to decreasing relaxation time with increasing temperature [27]. However, after the second phase transition and above 300°C the value of dielectric constant ($\varepsilon'$) shows further increase with increase in temperature. The maximum value of dielectric constant ($\varepsilon'$) obtained for 5 kHz at 500°C is 77, but due to instrument constraint we cannot perform our experiment beyond 500°C. The dielectric loss (tan\(\delta\)) was observed in the temperature range of 315–500°C (Figure 13) and behaviour is almost similar to that of variation of dielectric constant ($\varepsilon'$) within this temperature range.

3.5.2. Diffusivity Study. The region around the dielectric peak is broadened, which is a diffuse phase transition. The diffuse phase transition (DPT) takes place in materials where the composition fluctuations lead to large fluctuations in the Curie temperature. The structural disorder arises due to the presence of a number of voids and impurities of different size. The degree of diffusivity ($\gamma$) is calculated using the expression:

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon_{\text{max}}} = A(T - T_c)^{\gamma}.$$  \hspace{1cm} (5)

Here $\varepsilon_{\text{max}}$ is the peak value of the dielectric constant and $\gamma$ is the critical exponent which lies in the range $1 < \gamma \leq 2$. $\gamma = 1$ represents the ideal Curie-Weiss behaviour while being between 1 and 2 indicates diffuse behaviour [28]. The diffuse phase transition in ferroelectric is characterized by extending the phase transition in a wide temperature interval around the transition temperature where the dielectric constant assumes its maximum value. Figure 14 shows the variation of $\ln(1/\varepsilon' - 1/\varepsilon_{\text{max}})$ versus $\ln(T - T_c)$ at 5 and 10 kHz. The value of $\gamma$ calculated from the slope of the curves comes out to be 1.8 at 5 kHz and 2.0 at 10 kHz. Thus, the value of “$\gamma$” suggests the diffuse phase transition, which may be due to the compositional fluctuations and structural disordering in the arrangement of cations in one or more crystallographic sites in the structure that finally results in a microscopic heterogeneity in the grown materials with local Curie points [29].

3.5.3. Dependence of Dielectric Constant and Loss Tangent on Frequency. The dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan\(\delta\)) on frequency of the applied ac field was studied in the temperature range of 40–500°C and a frequency range of 5 kHz to 1 MHz. Figures 15 and 16 show that the dielectric constant ($\varepsilon'$) and dielectric loss go on decreasing continuously with frequency in the lower frequency range and to attain saturation at 1 MHz. The continuous decrease in the value of the dielectric constant ($\varepsilon'$) and loss tangent with increasing frequency may be attributed to different types of polarisation, namely, ionic, electronic, dipolar, and interfacial or space charge polarisation at low frequencies [30]. This continuous fall occurs because dipoles are not able to follow faithfully the impressed oscillating field and the low value of dielectric constant ($\varepsilon'$) was observed at high frequencies. Similarly, the loss tangent also decreases in the same manner like dielectric constant. The observed dielectric constant at
Dielectric constant ($\varepsilon$)

![Graph showing the variation of dielectric constant with frequency at different temperatures.](image1)

**Figure 15:** Graph showing the variation of dielectric constant with frequency at different temperatures.

low frequencies can be explained on the basis of the Maxwell-Wagner model. In this model, the dielectric structure consists of two layers: the first layer shows a large number of grains that act as a conducting medium at higher frequencies and the second layer consists of grain boundaries that act as a highly resistive medium at low frequencies [31]. In cerium orthophosphate nanoparticles, the polarisation mechanism at low frequency is explained as a local displacement of electrons by the hopping mechanism between $\text{Ce}^{3+}/\text{Ce}^{4+}$ and an orientation of dipoles in the direction of the applied ac field. At low frequencies, the dielectric constant value is very high because the charge carriers are collected at the boundaries between the conductive grain region and the highly resistive grain boundary region. When the frequency increases, the electric dipoles and the $\text{Ce}^{3+}/\text{Ce}^{4+}$ electrons transfer decreases the net displacement of charge in one direction thereby decreasing the dielectric constant value.

3.5.4. AC Conductivity and Activation Energy. In order to understand and authenticate the conduction mechanism, the alternating current conductivity $\sigma_{ac}$ ($\Omega^{-1} \text{m}^{-1}$) was calculated in the high temperature region using the relation:

$$\sigma_{ac} = 2\pi f_{ac} \varepsilon_0 \varepsilon' \tan \delta,$$

where “$f_{ac}$” is the frequency of the applied field (kHz) “$\varepsilon_0$” is the absolute permittivity of free sample having a value of $8.854 \times 10^{-12}$ Fm$^{-1}$, “$\varepsilon'$” is the dielectric constant and “$\tan \delta$” is the dielectric loss.

The variation of ac conductivity was measured at different frequencies from 5 kHz to 1 MHz in the temperature range of 315–500°C. Figure 17 shows the variation of ac conductivity “$\ln(\sigma_{ac})$” with temperature. It was observed from the graph that the ac conductivity goes on increasing with increasing temperature. The influence of conductivity has been explained by considering the mobility of charge carrier responsible for hopping. As temperature increases, the mobility of hopping ions also increases thereby increasing conductivity. The variation of ac conductivity “$\ln(\sigma_{ac})$” with frequency at different temperatures ranging from 340 to
Figure 18: Variation of \( \ln(\sigma_{ac}) \) with frequency at different temperatures.

500\(^\circ\)C is shown in Figure 18. From the graph, it can be observed that the dependence of ac conductivity increases with increasing frequency at all temperature which is characteristics feature of material where hopping mechanism dominates. In the low frequency region, the conductivity was identical to the dc conductivity and was independent of frequency [32]. In the low frequency range, the applied field is not enough to initiate the hopping conduction. Therefore, the range of the low frequency conductivity plateau (\( \sigma_{ac} \)) was found to increase with temperature. As frequency increases, ac conductivity increases due to the strong mobility of charge carriers. One can conclude that the conductivity is a function of both temperature and frequency of the applied field as has been reported for other materials [33–35]. At high frequency, ac conductivity (\( \sigma_{ac} \)) increases linearly with frequency obeying the power law: 

\[
\sigma_{ac} = A \omega^n
\]

where “\( A \)” is the temperature dependent constant and “\( n \)” is the frequency exponent [33]. The variation of frequency exponent parameter “\( n \)” with temperature gives information about the specific mechanism. Figure 19 shows the variation of the exponent “\( n \)” with temperature and it is clear that with the increase of temperature, the value of “\( n \)” goes on decreasing. The decrease of (\( n \)) suggests that the correlated barrier hopping (CBH) [36] model is the predominant ac conduction mechanism, which considers the hopping of charge carriers between two sites over a barrier separating them.

The variation of ac conductivity (\( \sigma_{ac} \)) with temperature favours the thermally activated transport properties obeying Arrhenius formula. The activation energy for cerium orthophosphate nanoparticles was calculated from Arrhenius plot of \( \ln(\sigma_{ac}) \) using the relation:

\[
\sigma_{ac} = \sigma_0 \exp\left(-\frac{E_a}{K_B T}\right)
\]  

where “\( \sigma_{ac} \)” is the conductivity at temperature “\( T \),” “\( E_a \)” is the activation energy for the electrical process, and “\( K_B \)” is the Boltzmann constant. Activation energy was calculated from the slope of the graph (Figure 20) showing the variation of \( \ln(\sigma_{ac}) \) with \( 1000T^{-1} \) at different frequencies. The activation energy at frequencies 5, 10, 20, 50, 100, and 1000 kHz was calculated and is given in Table 4. The values of activation

**Figure 19:** The variation of frequency exponent parameter (\( n \)) with temperature for CePO\(_4\) nanoparticles.

**Figure 20:** Graph showing the variation of \( \ln(\sigma_{ac}) \) with \( 1000T^{-1} \) at different frequency.
energy comes out to be 0.037, 0.033, 0.029, 0.026, 0.025, and 0.018 eV at frequencies 5, 10, 20, 50, 100, and 1000 kHz, respectively. From the table, one can conclude that the value of activation energy decreases with increase in frequency. This type of behaviour suggests that the conduction mechanism may be due to the hopping of the charge carriers. The polarisation process in CePO$_4$ nanoparticles explained as a local displacement of electrons (i.e., n or p type) by the hopping mechanism between Ce$^{3+}$/Ce$^{4+}$ and an orientation of electric dipoles in the direction of the applied field from one site to another. Therefore, a very small amount of energy is required to activate the charge carriers/electrons for electrical conduction. It has been shown by Ang et al. [37] and Moretti and Michel-Calendini [38] that the value of activation energy depends on ionization level of the oxygen vacancy. Usually, activation energy less than 1.0 eV is connected to singly ionized vacancies [37] and/or electronic mobility in space charge region. Thus, the conduction process within this temperature range may be due to the hopping of charge carriers and/or singly oxygen vacancies.

| Serial number | Frequency (kHz) | Activation energy (eV) |
|---------------|----------------|-----------------------|
| 1             | 5              | 0.037                 |
| 2             | 10             | 0.033                 |
| 3             | 20             | 0.029                 |
| 4             | 50             | 0.026                 |
| 5             | 100            | 0.025                 |
| 6             | 1000           | 0.018                 |

4. Conclusions

In summary, cerium orthophosphate (CePO$_4$) nanoparticles having monoclinic monazite phase were prepared by coprecipitation method. From XRD results, the crystallite size comes out to be 49.3 nm and from particle size analyser one can confirm that the particles grown in the nanoscale range. Transmission and scanning electron microscopic analysis reveals that the particles prepared by this technique are nanosphere having grain size in the range of 30–50 nm which is comparable to the crystallite size. Thermogravitric and differential thermal analysis (TGA/DTA) suggests that the structural transition from hexagonal to monoclinic phase is taking place above 800°C. Optical studies using UV-VIS-NIR absorption spectrophotometer shows the maximum absorption in the ultraviolet region and the optical band gap energy of the material was found to be 1.07 eV for direct transition. The photoluminescence spectrum gives strong ultraviolet band at 400 nm which is caused by the 5d-4f emission. The electrical properties of these nanospheres show dependence of dielectric constant on both temperature and frequency. The variation of dielectric constant with temperature shows the transition peak shift towards higher temperature as the frequency increases. Therefore, it is suggested to have relaxor ferroelectric behaviour. From the ac conductivity behaviour, the value of activation energy decreases with increase in frequency, suggesting that conduction mechanism is due to the hopping of the charge carriers from one site to another.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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