Characterization, dielectric and optical studies of nano-cerium phospho iodate synthesized by chemical co-precipitation method

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Nanoparticles of cerium phospho iodate belong to the class of tetravalent metal acid (TMA) salt are synthesized by chemical co-precipitation method. The particle size obtained from X-ray diffraction spectrum is found to be in the range of 30 nm. Surface morphology is studied from SEM images. The chemical composition of the sample has been verified using EDAX. The optical studies are carried out using FTIR and UV techniques. The stretching and bending frequencies of the sample are studied using the FTIR spectrum. The optical direct band gap of the material calculated using the Tauc’s relation is found to be 3.4 eV. The dielectric behaviour of the samples is studied at various temperatures and frequencies and ac electrical conductivity is also calculated. It is found that dielectric constant decreases with increase in frequency.

Keywords: Nanoparticles, XRD, Optical band gap

Nowadays there is a constant effort for miniaturization of electronic components, which demands the search for new materials with a very high dielectric constant1. Nanocrystalline and ultrafine particles of material are technologically important because surface to volume ratio of atoms is large compared to their bulk counterparts2. Reducing the size of metallic and semiconducting materials to the nano scale can dramatically influence their structural, electrical and optical properties. These properties can be selectively controlled by engineering the size, morphology and composition of the compounds3. The rare earth materials exhibit high dielectric behaviour and superior conductivity in the nano form and hence these materials have potential applications in memory devices, capacitors and sensors4-6. In the present work a systematic study related to the variation of dielectric behaviour with temperature and frequency have been carried out. The studies on the effect of frequency in the dielectric behaviour and ac conductivity give valuable information about the conduction phenomenon in nanostructured materials7. It is well known that dielectric properties of every solid are very sensitive to the local electric field distribution in the sample. Therefore, the temperature and frequency dependence of dielectric constant and ac electrical conductivity can explore useful information about structure changes, transport mechanism and defect behaviour.

Experimental Procedure

Nanoparticles of cerium phospho iodate (CPI) was prepared by arrested precipitation from analytical grade ammonium ceric sulphate, disodium hydrogen ortho phosphate and potassium iodate using ethylene diamine tetra-acetic acid (EDTA) as the capping agent8. The samples were prepared from 0.1M solution. The choice of the selection of 0.1M is a compromise between quantity and quality. If we go for low molarities, the quantity obtained will be very small; on the other hand high molarities will increase the size of the nanoparticles. The precipitate was formed by mixing all the chemicals in to EDTA solution, by constant stirring using a magnetic stirrer. The precipitate was separated from the reaction mixture and washed several times with distilled water and then with alcohol to remove the impurities, including the traces of EDTA and the original reactants if any. The wet precipitate was dried and thoroughly ground using an agate mortar to obtain the sample in the form of fine powder.

XRD study was carried out using XPERT-PRO powder diffractometer (make PAN analytical, Netherlands) employing Cu-Kα radiation in the 2θ range.
range 10° to 90° at 30 mA, 40 kV. The infrared spectroscopic study of the sample was done using Perkin-Elmer FTIR spectrophotometer between 400 cm\(^{-1}\) and 4000 cm\(^{-1}\). The TGA and DTA of the sample were taken using Perkin-Elmer, Diamond TG/DTA apparatus. The morphology of the powder sample was characterized by a scanning electron microscope JEOL/EO JSM-6390 apparatus and the chemical composition was found out using the energy dispersive analysis of X-rays (EDAX). The powder samples were pressed at a high pressure of 10 tons with a hand operated hydraulic press in 1 mm stainless steel dye. Using those pellets, the dielectric measurements as a function of frequency in the range of 100 Hz to 1 MHz were carried out using an Agilent 4284A Precision LCR Meter for different temperatures ranging from 50-110°C.

The dielectric permittivity of nano sized sample was calculated using the relation, \(C = \frac{(\varepsilon_0 \varepsilon_r A)}{d}\), where \(C\) is the capacitance of the sample, \(A\) is the surface area of the sample, \(\varepsilon_0\) is the permittivity of free space and \(\varepsilon_r\) is the dielectric permittivity of the sample. The ac conductivity of the sample was evaluated from the values of dielectric permittivity (\(\varepsilon_r\)) and loss factor (\(\tan\delta\)) using the equation, \(\sigma_{ac} = \frac{2\pi\varepsilon_0 \varepsilon_r f \tan\delta}{\beta}\), where \(f\) is the frequency. The UV study was carried out using Shimadzu UV-2550 UV visible spectrophotometer.

**Results and Discussion**

**XRD studies**

The XRD spectrum of the samples at 0.1M concentration and at room temperature is shown in Fig. 1. The XRD line broadening study reveals that the particles formed are nanocrystalline. The fine particle nature of the sample is reflected in the X-ray line broadening. The size of the synthesized nanoparticles calculated using Scherrer equation, \(d = \frac{0.9\lambda}{\beta\cos\theta}\), is found to be around 30 nm and the crystal system is found to be monoclinic; where \(\beta\) represents the full width at half maximum (FWHM) of X-ray lines, \(\lambda = 1.54060\ \text{Å}\). The nanocrystals have lesser lattice planes compared to the bulk, which contributes to the broadening of peaks in the diffractogram. This broadening of the peaks could also arise due to the micro straining of the crystal structures arising from the defects like dislocations and twinning\(^\text{10}\). These are believed to be associated

![Fig. 1—XRD Pattern of CPI](image-url)
with the chemically synthesized nanocrystals as they grow spontaneously during the chemical reaction. As a result, chemical ligands get negligible time to diffuse to an energetically favorable site. It could also arise due to the lack of sufficient energy needed by an atom to move to a proper site in forming the crystallite.

**Thermo gravimetric analysis**

A TGA/DTA curve of the sample is shown in Fig. 2. The TGA analysis is performed in the temperature range 30-950°C. Thermal behaviour of cerium phospho iodate has been investigated and examined for loss of moisture, loss of external water molecules and condensation of structural hydroxyl groups. The TGA profile shows decomposition in three distinct states: (i) initial weight loss up to 170°C, (ii) another weight loss region in the temperature range 170-430°C and (iii) a major weight loss region in the temperature range 430-540°C. Almost no weight loss was observed at above 540°C indicating the crystalline formation of CPI, the final product.

**Microstructural studies**

For microstructural analysis, the sample is directly transferred to the chamber of the SEM without disturbing the original nature of the product. The

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![Fig. 2—DTA/TGA curve of CPI](image)

![Fig. 3—SEM image of CPI](image)

![Fig. 4—EDAX of CPI](image)
SEM images of the samples are shown in Fig. 3. The SEM picture reveals that the particles are agglomerated. Moreover, the particle size can be estimated to be lying in the nano meter range. The energy dispersive spectrum has shown in Fig. 4 gives the chemical composition of the sample. About 42% of Ce ion by mass is present in the sample.

**FTIR spectra analysis**

The FTIR spectrum of the pure CPI sample is shown in Fig. 5. The FTIR spectrum shows a strong peak at 3382 cm$^{-1}$ corresponding to the (O-H) mode of (H-bonded) water molecules$^{12}$. Another strong and sharp peak with a maximum of 1627 cm$^{-1}$ may be due to H-O-H bending$^{13}$. The spectrum also shows strong band in the region 830-500 cm$^{-1}$ indicating the presence of iodates and metal oxide$^{14}$.

**UV spectral studies**

The UV spectrum of the sample taken in the range 200-1800 nm with 1 nm resolution is shown in Fig. 6a. The UV spectra provide important information about the details related with band gap of the material. The energy band of the material is related to the absorption coefficient $\alpha$ by the Tauc relation$^{15}$, $\alpha h\nu = A(h\nu - E_g)^n$, where $A$ is a constant, $h\nu$...
is the photon energy \((\nu = c/\lambda)\), \(E_g\) is the band gap and \(n = 1/2\) for an allowed direct transition. Figure 6b indicates \((\alpha h\nu)^2\) versus \(h\nu\) graph, which gives the value of direct band gap \(^16\). The optical band gap of the sample has been determined from the absorption spectra and is found to be 3.4 eV, which is almost equal to the band gap observed in the case of CeO\(_2\) \(^17\).

**AC conductivity studies**

The variations in the dielectric constant with frequency of the applied field at different temperatures from 50 to 110°C of the samples are shown in Fig. 7a. The dielectric constant and thus the capacitance decreases rapidly with increase in frequency and reaches a constant value showing that it is independent of frequency at high frequency range. According to the theory, the dielectric behaviour of the nanostructured material is primarily due to different types of polarizations present in the material \(^18\). The nanostructured material possess enormous number of interfaces, and the large number of defects present in these interfaces can cause a change of positive or negative space charge distribution. When an electric field is applied these space charges move and are trapped by these defects resulting in the formation of dipole moments. This is called space charge polarization. Interface in nanostructured materials possess many oxygen ion vacancies, which are equivalent to positive charges giving dipole moments. Exposed to an electric field, these dipoles will rotate, giving a resultant dipole moment in the direction of the applied field. This is called rotation direction polarization \(^19\). Thus the high value of dielectric constant at low frequencies is mainly due to the space charge polarization and rotation direction polarization \(^20\). As the temperature increases, more and more dipoles will be oriented \(^21\) resulting in an increased value of dipole moment. This is why the dielectric constant increases with increase in temperature for fixed frequencies.

The ac conductivity is found to be high for higher frequency, shows a trend necessary for a small polaron hopping. From the electrical conductivity (ac) versus frequency curve shown in Fig. 7b, it is clear that for higher temperatures as frequency increases the conductivity also increases. The nature is similar for other temperatures, but the values are shifted upwards as the temperature is raised. This nanoparticle system exhibits conductivity with highly localized carriers bound to the lattice with an accompanying lattice strain, i.e., with polaron conduction. Thus, the dielectric properties change with the frequency of the applied field \(^22\).

**Conclusions**

It is concluded that the material synthesized by chemical co-precipitation method in the nano range exhibits enhanced dielectric properties. The method is
found to be simple and economical for the bulk preparation of the samples with required characteristics. XRD and SEM suggest the average size of the particles that comes to be in the nano range. The SEM picture reveals that the particles are slightly agglomerated with more or less spherical in shape. From the UV spectrum, the direct band gap of the material is found to be 3.4 eV. The dielectric properties and electrical transport for nanostructured materials differ from those for micron sized materials due to increased interfacial atoms or ions and sinking of large amount of defects at or near the grain boundaries. Each interface acts as a capacitor, thus changing the dielectric value of the material.

References
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