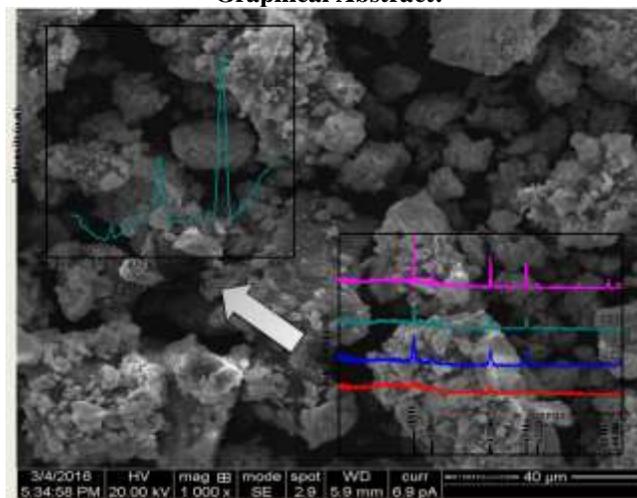


**EFFECT OF REACTION TEMPERATURE ON SYNTHESIS AND
CHARACTERIZATION OF CERIUM OXIDE (CeO₂) NANO PARTICLES VIA
MODIFIED CO-PRECIPIATION METHOD**^{1,2}M.Ramachandran, ³M.Shanthi, ¹R.Subadevi, ¹M.Sivakumar*¹ #120, Energy Materials Lab, Department of Physics, Alagappa University, Karaikudi-630003. Tamil Nadu, India.² Department of Physics, Arumugam Pillai Seethai Ammal College, Tiruppattur 630 211.³ Department of Physics, Kamaraj College of Engg. And Tech, Virudhunagar 626001, Tamil Nadu, India.**Highlights:**

- ❖ The CeO₂ particles were successfully synthesized using PVP as surfactant by Modified co-precipitation method.
- ❖ The formation cubic phase CeO₂ was confirmed through XRD.
- ❖ The presence of fine spherical particles together with nanotubes like morphology was observed through SEM
- ❖ The bandgap of the CeO₂ nano particle was estimated as 3.67 eV by PL analysis.
- ❖ The as prepared CeO₂ nano particle has been used filler in the lithium secondary battery fabrication.

Graphical Abstract:**Abstract**

Cerium oxide (CeO₂) is a technologically important rare earth material because of its keen properties for various engineering and electrochemical applications. In this attempt, CeO₂ filler samples were synthesized from a cerium nitrate solution and Poly vinyl pyrrolidone (PVP) as surfactant by modified co-precipitation method as a function of reaction temperatures such as 400, 500, 600 and 700°C. The products were characterized by XRD, SEM, EDX analyses. XRD patterns confirmed the formation of cubic CeO₂ with crystallite size of 11 to 55nm (JCPDS.no: 81-0792). FESEM images confirmed the presence of fine spherical particles with nano tube like morphology. The presence of Ce and O were confirmed through EDX analysis. The representative sample was characterized by Photoluminescence study. The band gap of the CeO₂ nanoparticle was estimated as 3.67 eV. The optimized sample has been used as filler in the Lithium polymer battery fabrication.

Key words: Cerium oxide, PVP, modified co-precipitation method.

Introduction:

Cerium is the most lavish among rare earth elements, occupying about 0.0046 wt.% of the earth crust, and also currently a subject of great interest due to its extensive array of applications. e.g., as associate materials for three-way catalysis, oxygen sensors, solid oxide fuel cells that employ the oxygen storage capacity, oxygen sensors, glass-polishing,

ceramics and uv absorbent [1,2]. Rare earth oxide nanoparticles have exceptional luminescence, magnetic and electronic properties due to their unfilled 4f electronic structure. In recent years, due to excellent physical and chemical properties of nano-sized particles, which are significantly different from those bulk materials. Numerous methods, including precipitation from solution [3], Microwave assisted method [4], Hydrothermal synthesis[5], Sol-gel[6], Solvo thermal method[7] have been used to prepare Ceria nano particles with different morphologies and size such as nano belts, nano spheres, nano fibres and flower-like morphologies.

Among these, Modified co-precipitation method has been an extensively accomplished assembly of homogeneous high-purity and crystalline oxide at low cost, also simple procedure allows scaling up for mass production[8]. In this attempt, Ceria (CeO_2) was synthesized using Cerium nitrate as source material, Sodium hydroxide (NaOH) as precipitation agent and PVP as surfactant by using modified co-precipitation method by varying reaction temperature such as 400, 500, 600 and 700°C. The as prepared powders were systematically studied the structural and morphology analyses. The representative samples were analyzed using EDX and PL studies.

Materials and methods

Ceria (CeO_2) was synthesized by a modified co-precipitation method. The method involves the slow addition of an aqueous solution containing the stoichiometric amount of Cerium nitrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Merck, GR 99%) to an aqueous solution of the surfactant PVP (sigma Aldrich, Mol.wt.40,000) under stirring condition. The resulting aqueous mixture was stirred further for 10min at room temperature and then aqueous Sodium hydroxide (NaOH) (Merck) was added drop wise under vigorous stirring when $\text{pH} > 9$. The resulted in the appearance of a yellow-precipitate which was further stirred for about 90m, when it was transformed into light yellow slurry. The precipitate was centrifuged at 200 rpm and washed with deionized water and acetone several times to ensure the complete elimination of surfactant. Finally, the precipitation was dried in oven at 110°C for 2h and consequently calcined in air at 400°C, 500°C, 600°C and 700°C for 2h to get the CeO_2 material.

Results and discussion

The XRD patterns of as-prepared CeO_2 nanoparticles as a function of varying reaction temperature, such as 400°C (a), 500°C (b) 600°C (c) and 700°C (d) are shown in Fig.1. All diffraction peaks are well harmonized with those of pure phase of CeO_2 fluorite cubic structure (JCPDS Card No.81-0792). The peak at (111) orientation has higher intensity than the other peaks, which was attributed to high crystalline nature of the particular orientation of the samples. No obvious XRD peaks arising from impurities or other phases are found, which undisputedly indicates the high purity of the as-prepared crystalline CeO_2 . The intensity of the diffraction peaks increases while increasing the reaction temperature. The average crystalline size was estimated as 11.5 nm, 21.2 nm, 35.4 nm and 55.3nm for samples a, b, c and d, respectively, using Debye-Scherrer formula [9] and the values are comparable with the previous literatures [10,11]

Fig 2(a)-(e) display the SEM images and EDX spectra of CeO_2 samples prepared using modified co-precipitation method with magnification of 1K. It could be seen that the particles were observed in spherical shape and distorted structures in Fig.2 (a and b). In Fig.2.c, It could be seen that the particles have two distinct shapes, one is rod like morphology ($1.2 \mu\text{m} \times 0.04 \mu\text{m}$) or nanotube which are long narrow and some spherical particles (40 nm) were observed. Also shows that the reaction temperature at 700°C produced the particles were in spherical shapes and cauliflower like morphology was observed. The method of preparation is identical in all cases, however, it is interesting to note their morphology and nanoparticle size are very different, clearly indicating the role of reaction temperature on the synthesis of CeO_2 nanoparticles. Further, the EDX spectrum of CeO_2 sample is shown in Fig. 2.e. The result clearly exhibits the presence of Ce and O.

The Photoluminescence spectra Fig.3 has observed a typical fluorescence spectrum with an excitation wavelength of 270nm, whereas a high intense broad fluorescence band was also perceived around 369nm with corresponding energy of 3.67 eV is called the near band edge emission. This is likely to be related with band to band emission probably involving localized or free excitons. The peaks at 434 and 516 nm respectively, with corresponding energies 2.86 and 2.37 eV, are evidently lower than the deduced band gap, it should be due to the mid-gap trap states such as oxygen vacancies or defect states.

Conclusion

The CeO_2 nano particles have been synthesized via the modified co-precipitation method using various reaction temperatures viz., 400°C, 500°C, 600°C and 700°C. The cubic structure with a Fm-3m space group was confirmed through (JCPDS: 81-0792) using XRD analysis. Further, the presence of Ce, O species was ascertained through EDX analysis. The morphology of CeO_2 nano particles was highly dependent on the reaction temperature. The well dispersed nano rod together with spherical morphology was observed at 600°C. Also, it has a band gap of 3.67 eV, which was lower than bulk. Based on these analyses, one can realize that this material can ultimately be used as filler for Lithium polymer secondary battery electrolyte fabrication.

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Figure Captions:

Figure 1: XRD pattern of CeO₂ nano particle a) 400°C b) 500°C c) 600°C and d) 700°C as reaction temperature.

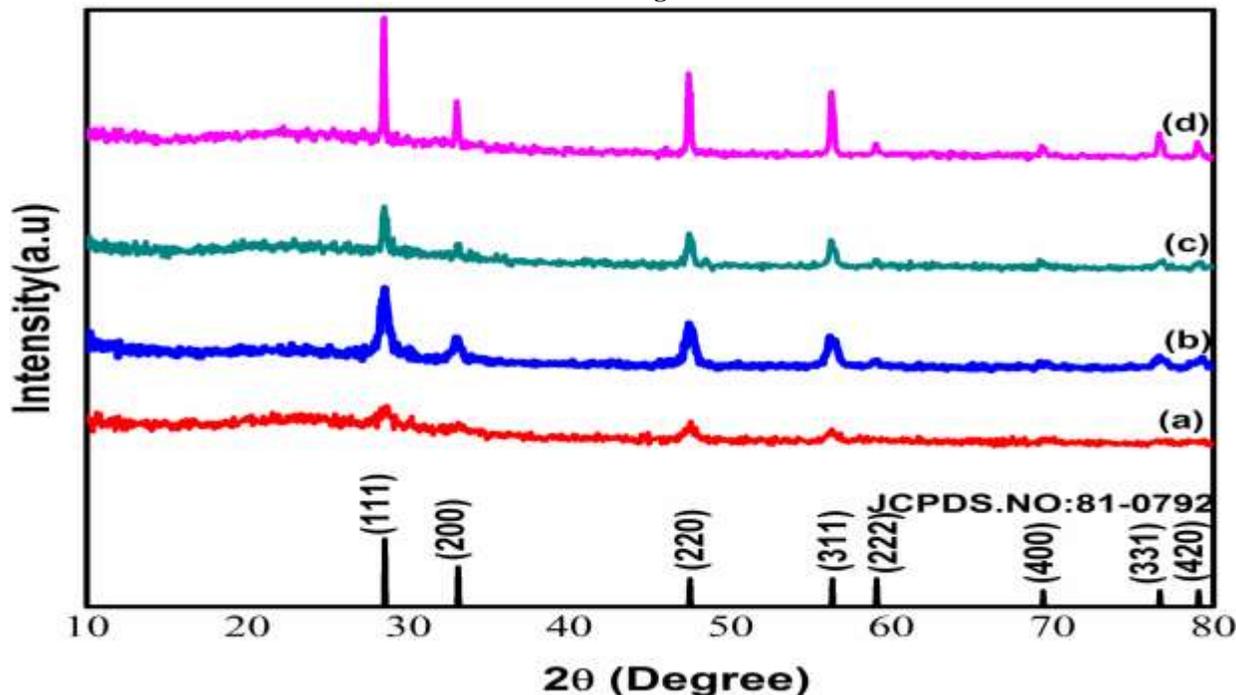
Figure 2: SEM Image a) 400°C b) 500°C c) 600°C and d) 700°C as a reaction temperature e) EDX spectrum of CeO₂ nano particle.

Figure 3: Photoluminescence spectra of CeO₂ nano particle.

Name of the author: ^{1,2}M.Ramachandran, ³M.Shanthi, ¹R.Subadevi, ¹M.Sivakumar*

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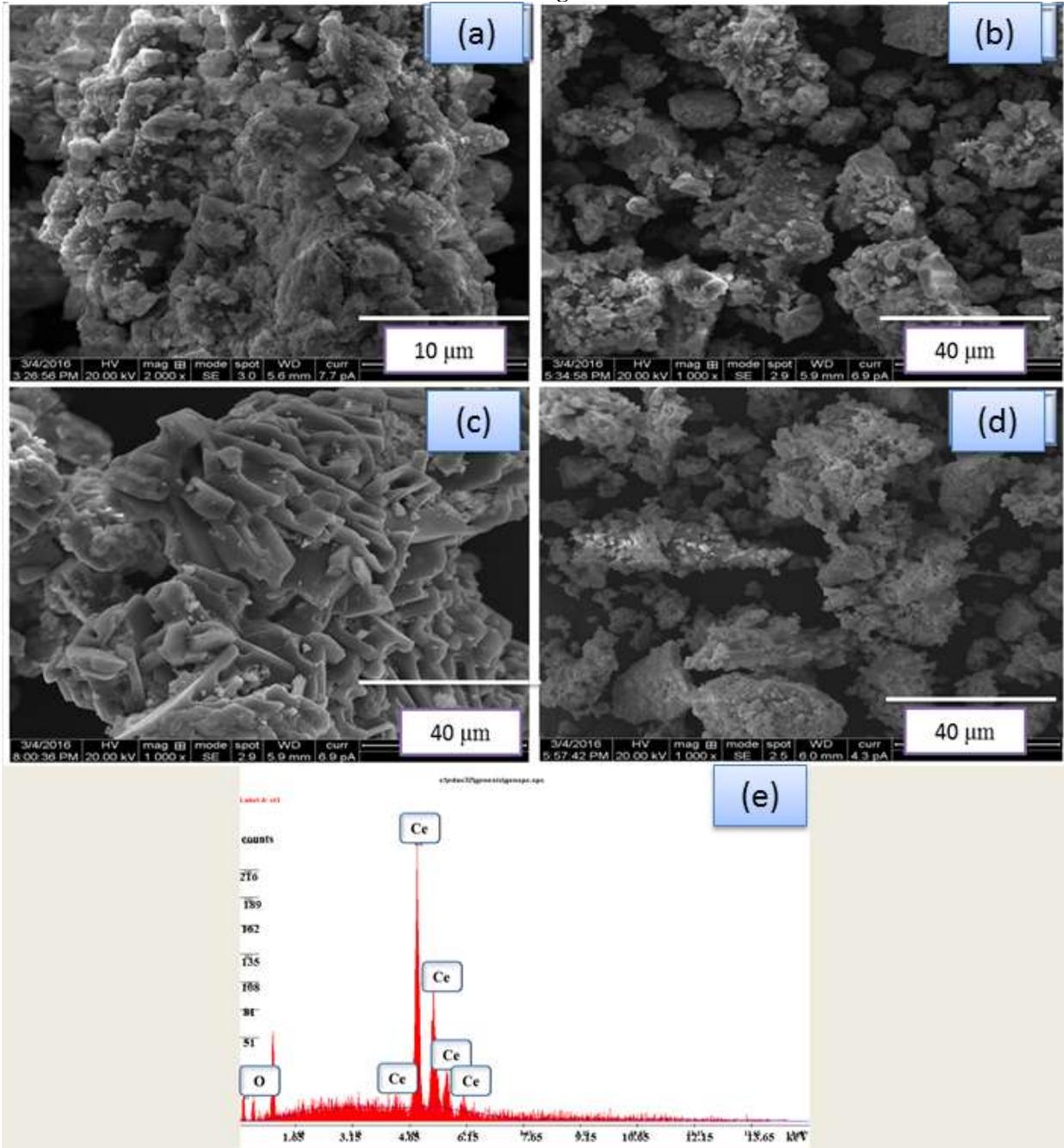
Figure 1



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Figure 2



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Figure 3

