

**Preparation and Characterization of CeO₂ via Co-Precipitation Method**G.Savithiri¹, M.Ramachandran^{1,2}, V.Priyanka¹, R.Subadevi¹, M.Sivakumar*¹¹#120, Energy Materials Lab, Department of Physics, Alagappa University,
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Abstract - Cerium oxide (CeO₂) nanoparticles were prepared through a facile method (co-precipitation method) by using various catalysts like sodium hydroxide (NaOH), Potassium hydroxide (KOH), sodium carbonate (Na₂CO₃) and ammonia (NH₃) in the absence of surfactants. The products were characterized by XRD, FTIR, Raman and SEM analyses. It was found that cubic structure with Fm-3m space group was confirmed through XRD analysis. The Ce-O stretching vibration was ascertained through FT-IR spectrum. Further triply degenerate F_{2g} Raman mode of the fluorite structure of CeO₂ was confirmed through Raman analysis and flakes like morphology with soft agglomeration was confirmed through SEM analysis. The CeO₂ formation mechanism is also discussed.

Key words: Cerium oxide, Sodium hydroxide, cubic structure.

I. INTRODUCTION

The major advances in civilization have been associated with increased consumption of energy. In fact, energy consumption today is related to the extent of industrialization of a country and the standard of living of its people. Widespread industrialization and an increasing demand for energy have led to the current energy crisis. In general terms, there are three main issues one needs to address while dealing with this problem such as the need to restrict increases in energy consumption, the need to evolve alternative energy sources as a substitute to conventional energy sources and the evaluation of how far these new energy sources can serve as a replacement for conventional energy sources. Developing electrical energy storage (EES) systems is critical to integrate intermittent renewable energy into constant and controllable power delivery [1]. The nanostructured materials have also led to major advances in electrochemical energy storage areas and more especially to Lithium-ion batteries. Nanostructured materials also promise to revolutionize the field of super capacitors, thus opening the doors to many applications, such as hybrid electric vehicles and portable electronic devices [2]. The demand for efficient and smart materials that can be used for multipurpose applications, such as visible light photo-catalysis, photo-electrode, electrolyte etc., Metal oxide nanostructure, such as CeO₂, serving supporting materials, have attracted increasing interest in catalyst because of their unique structure, properties, such as high surface area, uniform pore distribution and rigid frame work [3]. M.P.Kalamuei et.al.,[4] reported that CeO₂ nano particles have been synthesized from (NH₄)₂Ce(NO₃)₆ ethylenediamine and hydrazine by hydrothermal method. G.Wu.et.al.,[5] reported that 3D CeO₂ have been synthesized by using PEG 2000 assisted simple hydrothermal method. It is still difficult to synthesize the CeO₂ nano particles with aqueous solvent. Based on that an attempt is made to synthesize Nano sized CeO₂ particle via co-precipitation method using different catalysts. Thus the crystal structure, functional groups and morphology of the prepared materials were analyzed using XRD, FTIR, Raman and SEM.

II. EXPERIMENTAL METHODS

CeO₂ particles have been prepared by co-precipitation method using different catalysts. The 0.2 M of Ce(NO₃)₃.6H₂O was dissolved into deionized water. Precipitation was done by slowly adding 0.5 M of various catalysts such as NaOH, KOH, Na₂CO₃, NH₃ solution drop by drop separately with constant stirring (500 rpm) at room temperature for 1h. The precipitate was washed several times using deionized water and followed by acetone to remove the impurities and dried at room temperature. The dried precursor was annealed at 600°C for 4 hours and thus CeO₂ nanoparticles were obtained.

The crystalline phase structure of the as-prepared materials was analyzed using powder X-ray diffraction analysis (Model: PANalytical X-pert Pro diffractometer with CuK α radiation). The functional group vibrations were analyzed using a Thermo Nicolet 380 FT-IR spectrophotometer using KBr pellets in the range 4000 – 400 cm⁻¹ and through Laser Raman spectrometer, (STR 500, LASER RAMAN SPECTROMETER, SEKI, JAPAN). The surface and particle morphology of the prepared sample were observed using a scanning electron microscope (FEG quanta 250).

III. RESULTS AND DISCUSSION

Crystalline structure and phase purity of as-prepared CeO₂ materials have been determined using X-ray powder diffraction analysis. The XRD patterns of the sample prepared by co-precipitation method are shown in Figure 1. The diffraction peaks at different angles ($2\theta = 28.542, 33.075, 47.475$ and 56.332°) corresponds to the (111), (200), (220) and (311) planes of the samples. All samples correspond to cubic structure with space group Fm-3m. (JCPDS card.No.81-0792). Sharp and strong diffraction peaks indicates that as-prepared products well crystallized.

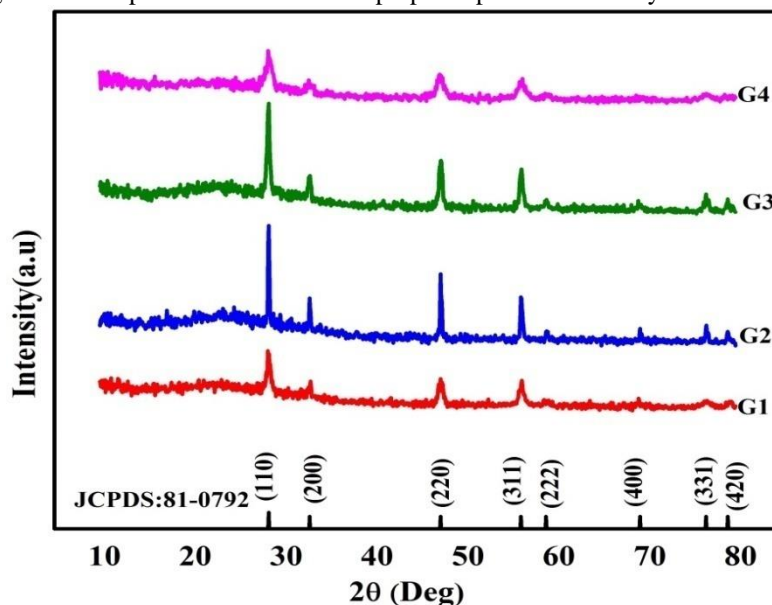


Figure 1. XRD pattern CeO₂ nanoparticles using G1) NaOH G2) KOH G3) Na₂CO₃ G4) NH₃ as catalyst

However, none of the impured diffraction peaks could be detected, which is due to clear observation of phase purity of the prepared samples. According to Debye Scherrer formula, the crystallite size of the samples is 49, 519, 205 and 61 nm correspond to NaOH, KOH, Na₂CO₃ and NH₃ as a catalyst.

The fundamental vibrations of the prepared nanoparticles were studied by FTIR spectroscopy as shown in Figure 2. The strong bands at 1635, 1382 and 407 are ascribed to the stretching vibration of O-H, absorption of non-bridging OH groups and characteristic of cubic CeO₂ respectively [6,7]. These peaks are shifted to 1626, 1390 and 423 cm⁻¹ in the complexes. The peaks obtained particularly at 855, 558 and 423 cm⁻¹ revealed due to Ce-O₂-Ce asymmetric stretching and Ce-O symmetric stretching respectively, which are the characteristic bonds of cubic phase of CeO₂.

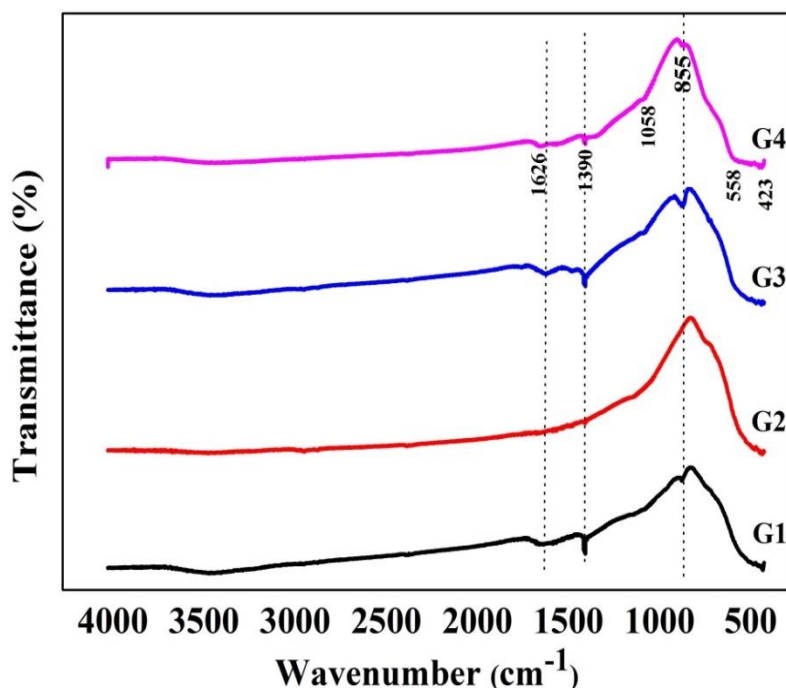


Figure 2. FTIR spectrum of CeO₂ nanoparticles using G1) NaOH G2) KOH G3) Na₂CO₃ G4) NH₃ as catalyst

Further, the confirmation of the cubic structure of CeO_2 nanoparticles, Raman analysis was performed for all samples. The cubic fluorite structure–metal dioxide has a single Raman mode at 459 cm^{-1} which has F_{2g} symmetry and can be noticed as a symmetric breathing mode of the O atoms around each cations.

In this study, we found that the catalyst has great influence on the morphology of the final product. The catalyst NaOH shows that the sample comprised of flakes morphology with soft agglomeration with grain size of $2.85\mu\text{m}$. (Fig.4.G1), whereas other catalysts such as KOH, Na_2CO_3 and NH_3 resulted in irregular shape and agglomerated particles as shown in Fig 4(G2-G4). Therefore, it is clearly seen that the catalyst NaOH is most favorable for the creation of uniformly sized CeO_2 nanoflakes. The process of the crystal growth and morphology growth can be pronounced in terms of Oswald ripening. Small size crystals act as nutrient for bigger crystals [8-10].

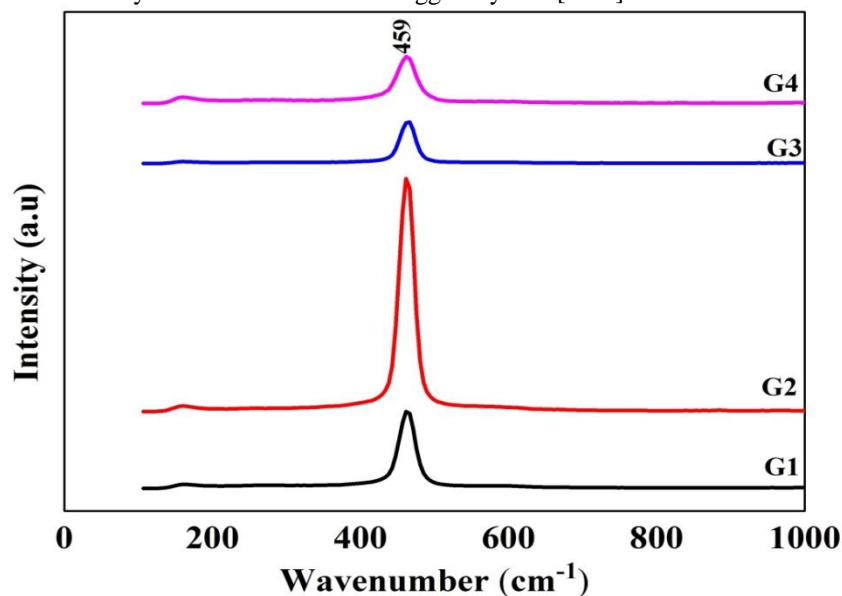


Figure 3. Raman spectrum of CeO_2 nanoparticles using G1) NaOH G2) KOH G3) Na_2CO_3 G4) NH_3 as catalyst

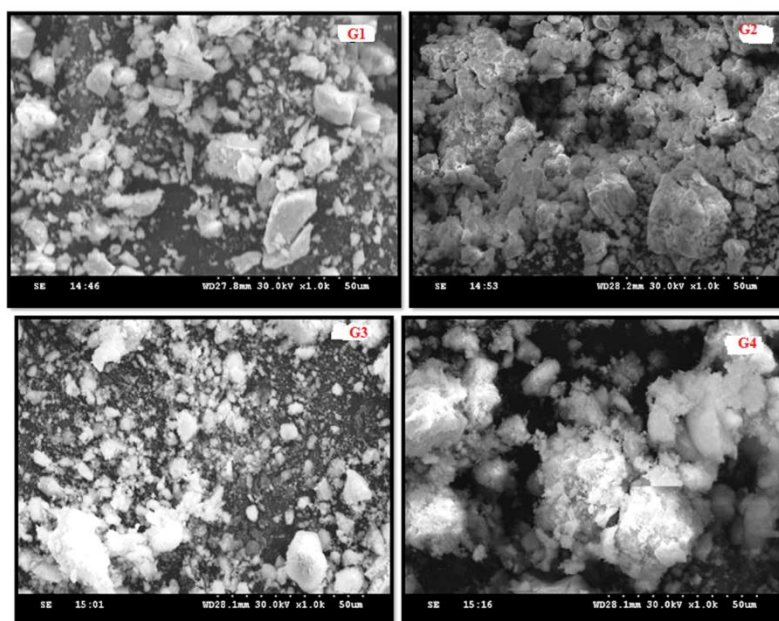


Figure 4. SEM images CeO_2 nanoparticles using G1) NaOH G2) KOH G3) Na_2CO_3 G4) NH_3 as catalyst

IV. CONCLUSION

The CeO_2 nano particles were successfully synthesized via the co-precipitation method as function of catalyst such as NaOH, KOH, Na_2CO_3 and NH_3 . The cubic structure with Fm-3m space group was confirmed through (JCPDS: 81-0792) using XRD analysis. Further the presence of Ce-O species was confirmed by FT-IR and Raman analyses. The morphology of the product highly depends on the catalyst. The uniform sized ($2.85\mu\text{m}$) Nano flakes was observed when NaOH acts as catalyst. One can realize that this material can ultimately be used as filler for lithium polymer battery electrolyte fabrication.

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