PREPARATION AND CHARACTERIZATION OF $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$ NANOPOWDERS USING SOL-GEL METHOD

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Nanopowders of $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$ were prepared by sol-gel via hydrolysis method for different hours. The prepared powders are characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscope (SEM) and analyzed by UV-visible spectroscopy, Photoluminescence (PL) and Energy dispersive X-ray analysis (EDAX). Cubic fluorite structure of the prepared samples was confirmed by powder X-ray diffraction and the grain size of the prepared samples in the range of 12 to 33 nm. The functional groups of the prepared nanopowders are identified by FTIR spectra. The band gap energy obtained from the UV spectra. From the photoluminescence spectra, there is a mirror image relation between absorption and emission spectra. The purity of the prepared samples is confirmed by EDAX measurements.

Keywords: Sol-Gel; XRD; UV.

1. Introduction

Nanopowders are defined as particulate dispersions or solid particles with a size in the range of 10-1000 nm. Depending upon the method of preparation, nanopowders, nanospheres, nanocapsules or nanorods can be obtained. The properties of the nanopowders can change by different ways. Doping is one of the ways to alter the properties of nanopowders in desirable and controllable ways. Doped ceria improves the properties, compared to pure ceria [1-6].

Cerium is the most abundant element in rare earth family. Ceria-based materials are attractive due to their widespread applications in catalysis, fuel cells, optical films, polishing materials, gas sensors, and other fields. Particularly these materials are used as redox or oxygen storage promoters in the three way catalysts (TWCs) and catalysts for H_2 production from fuels and solid state conductors for fuel cells [7]. Another one

application for cerium and yttrium oxides are used in the medical field as a neuroprotective. CeO_2 and Y_2O_3 particles protect cells from death due to oxidative stress [8].

Nowadays, samarium or gadolinium doped ceria electrolyte is attracted much attention from the view point of the application in SOFC. It considered that, these doped ceria electrolytes exhibited high oxide ionic conductivity and a mixed conducting behaviour of both ionic and electric conductivity. But yttrium doped ceria has a high electrical conductivity in whole doped ceria electrolytes [9-13].

Rare earth doped ceria nanopowders were prepared by several wet chemical route methods such as co-precipitation, sol-gel, solvothermal, hydrothermal [14].

In the present study yttrium doped ceria nanopowders were prepared by sol-gel via hydrolysis process. Hydrolysis is a chemical reaction in which water is used to break down a compound; this is achieved by breaking a covalent bond in the compound by inserting a water molecule across the bond. Here hydrolysis is the forced one i.e. the forced hydrolysis. The prepared powders are characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), Scanning electron microscope (SEM) and analyzed by UV-visible spectroscopy, Photoluminescence (PL) and Energy dispersive X-ray analysis (EDAX). The results obtained from the above techniques are discussed in results and discussion.

2. Preparation of Samples

2.1. Materials and preparation methods

Cerium chloride hexahydrate (98.5%, Merck), Yttrium chloride (99.9%, Himedia), Ammonium hydroxide (99.0%, Merck) were used to prepare the samples. Acetone (99.5%) were purchased from Merck, and used for washing purpose. De-ionized water was used as a solvent.

Fig.1. (a) Method of preparation, (b) Hydrolysis set up

Here, the samples are referred to as $Ce_{1-x}Y_xO_2$ for convenience, where x denotes the molar ratio of yttrium. $CeCl_3$ and YCl_3 were weighted according to the molar ratio of $Ce_{0.8}Y_{0.2}O_2$ (when $x = 0.2$, $1-x = 0.8$).

The homogeneous solution was prepared by thoroughly mixing the both solutions for their respective molar ratios with 0.1N. Then the solution is subjected to forced hydrolysis and condensation. Ammonium hydroxide was added to convert the sol into gel. White gelatinous precipitate formed. The precipitate was washed thoroughly until traces of Cl^- were removed and it filtered using whatmann filter paper. This procedure has been repeated for three different hydrolysis hours namely 60, 100 and 120 hours. The prepared $Ce_{0.8}Y_{0.2}O_2$ nanopowders were ground well for several hours.

2.1.1. Reaction

It was further dried at ambient temperature and annealed at $1000^\circ C$ for 2 hours in air atmosphere.

3. Instrumentation

Powder X-ray diffraction measurements were taken from Panalytical X'PERT Pro powder X-ray diffractometer using $CuK\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray patterns are recorded from 10° to 80° (2θ). The 2θ and ($h k l$) values are used to index the XRD patterns using the respective JCPDS files. Fourier transform infrared (FTIR) spectra of $Ce_{0.8}Y_{0.2}O_2$ were recorded on Perkin Elmer spectrum RXI spectrophotometer over $400\text{--}4000\text{ cm}^{-1}$ region with resolution of 1 cm^{-1} for functional group analysis. The surface morphology of the crystalline is observed by JEOL/EO, JSM-5000 scanning electron microscope. The chemical compositions of the products are determined by energy dispersive X-ray absorption spectroscopy; this facility is available with SEM instrument. The PL studies were carried out using Perkin Elmer LS 55 luminescence spectrometer. UV analysis was carried out using the model Perkin Elmer lambda 35. The absorption is associated with the band gap of the material.

4. Results and Discussion

4.1. Powder X-ray diffraction

The prepared yttrium doped cerium oxide powders were characterized by X-ray powder diffractometer. X-ray diffraction pattern recorded for the as-prepared $Ce_{0.8}Y_{0.2}O_2$ nanopowders for different hydrolysis hours (60, 100 and 120 hours) and those annealed at $1000^\circ C$ for 2 hours are shown in Fig. 2. The size of the crystallite calculated from FWHM (β) of the (111) peak using Scherrer's formula $d = 0.9 \lambda / \beta \cos\theta$, where λ is the wavelength and θ is the Bragg's angle of the peak in degree. All the diffraction patterns were perfectly indexed as $Ce_{0.8}Y_{0.2}O_2$ with cubic fluorite structure (JCPDS-75-0175).

Fig.2. XRD patterns of annealed at 1000°C (2 hours) $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$ nanopowders for as-prepared and different hours hydrolysis (60, 100 and 120 hours).

From Fig.2, XRD patterns shows that the grain size of highest peak orientation (1 1 1) values is decreases with increasing hydrolysis hours. The average grain size of the yttrium doped ceria calculated by Scherrer's formula are 33.9 nm, 13.9 nm, 13.4 nm, 12.2 nm for as-prepared, 60 hours, 100 hours, 120 hours respectively.

M. Dukek et al., [15] were investigated that the crystallite size of the $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$ solid solutions powder is $D_{hkl} = 12.8$ nm. Shaowu Zha et al., [16] were investigated that the average crystalline sizes of the yttria doped ceria ($\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$) powder are calculated by Scherer's formula, and are 6, 22 and 43 nm for 500YCO, 700YCO and 900YCO samples respectively.

4.2. FTIR studies

Fourier Transform Infrared Spectroscopy (FTIR) spectrum of annealed YDC ($\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$) nanopowders for different hydrolysis hours (60, 100 and 120 hours) was obtained. An IR spectrum was recorded over 400-4000 cm^{-1} region with resolution of 1 cm^{-1} . The IR spectra of annealed YDC nanopowders for as-prepared different hydrolysis hours (60, 100 and 120 hours) are shown in the figure 3.1 to 3.4 respectively.

FTIR spectrum shows the characterization absorption bands at 851, 905, 1022, 1389, 1637, 2349 and 3448 cm^{-1} . A strong peak at 1400 cm^{-1} is attributed to stretching vibrations of Ce-O. The strong and broad bands at 3448, 1600 cm^{-1} are assigned to bending vibrations of H-O-H [17]. A strong peak near at 3400 cm^{-1} is assigned to stretching vibrations of O-H. A fine peak was observed near at 1000 cm^{-1} in the spectrum of all samples. To change the hydrolysis hours there is a slightly change in the absorption bands. Similar results were reported by Kang-Qiang Liu et al., [17] and Mickael Palard et al., [18].

Fig.3.1. FTIR spectra of as prepared YDC ($Ce_{0.8}Y_{0.2}O_2$) nanopowders annealed at $1000^{\circ}C$.

Fig.3.2. FTIR spectra of YDC ($Ce_{0.8}Y_{0.2}O_2$) nanopowders annealed at $1000^{\circ}C$. (60 hours hydrolysis)

Fig.3.3. FTIR spectra of YDC ($Ce_{0.8}Y_{0.2}O_2$) nanopowders annealed at $1000^{\circ}C$. (100 hours hydrolysis)

Fig.3.4. FTIR spectra of YDC ($\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$) nanopowders annealed at 1000°C . (120 hours hydrolysis).

4.3. Scanning electron microscope(SEM) analysis

SEM is one of the most widely used analytical techniques across all fields of science, technology and industry. Applications include imaging of highly three dimensional biological structures, imaging and microanalysis of semiconductor structures, magnetic domain imaging for data storage applications, and imaging of fracture surfaces in component failure analysis.

SEM micrographs of annealed YDC ($\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$) nanopowders for two different hours hydrolysis (60 and 120 hours) are shown in the figure 4.

The micrographs clearly indicate that the shapes of the particles are fairly irregular. It was found that each irregular particle is in fact a cluster of spherical particles which were agglomerated.

Fig.4. SEM images of $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$ nanoparticles annealed at 1000°C (60 hours hydrolysis and 120 hours hydrolysis)

4.4. EDAX results

The yttrium distribution across the annealed $Ce_{0.8}Y_{0.2}O_2$ (YDC) nanopowders for different hydrolysis hours (60 and 120 hours) was determined using energy dispersive X-ray spectroscopy (EDAX). The concentration distribution of yttrium in the ceria particles was determined. The element percentage and atomic percentage of the annealed YDC particles are given in the following Table 1.

The EDAX spectrum normally displays the peaks corresponding to the energy level for which the most X-rays had been received. An EDAX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well.

The EDAX spectrum confirms that the annealed YDC nanopowders are composed of yttrium and cerium compounds. The amount of energy possessed for the corresponding yttrium and cerium peak emitted by the electrons in the L-shell and for the corresponding oxygen peak emitted by the electrons in the k-Shell. The expected atomic percentage of YDC is 20 %. The results show that the percentage is 15.89 % instead of 20 % for 60 hours hydrolysis and slightly the percentage is increases for 120 hours hydrolysis (16.45% instead of 20%).

From that, the yttrium and cerium concentration distribution increases with increasing hydrolysis hours. The EDAX spectra for annealed YDC nanopowders for different hydrolysis (60 and 120 hours) are given in figures 5.(1) and (2).

Table 1. Annealed YDC nanopowders for different hour's hydrolysis.

Hydrolysis hours	Element	Concentration	Element percentage %	Atomic percentage %
60 hours	Y L	0.53	1.05	15.85
	Ce L	7.83	7.51	72.15
120 hours	Y L	0.72	1.43	16.45
	Ce L	12.05	11.45	83.55

Fig.5.1. EDAX spectrum of annealed YDC nanopowders for 60 hours hydrolysis.

Fig.5.2. EDAX spectrum of annealed YDC nanopowders for 120 hours hydrolysis.

4.5. UV absorption spectrum analysis

The ultra violet visible spectrum is taken for Yttrium doped Cerium oxide ($\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$) for different hydrolysis hours, annealed at 1000°C . This technique is based on the absorption of light in the ultra violet (10 - 420 nm) and visible (420-700 nm) regions by a powder sample. From UV spectrum, the absorbance in each sample is studied.

From the UV spectrum, the optical band gap energies of cerium oxide nanoparticles are determined. Figure 6.1 shows the UV spectrum of annealed ($\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$) Yttrium doped Cerium oxide nanoparticles at different hydrolysis hours.

Fig.6.1. UV Spectrum of $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$ nanoparticles annealed at 1000°C for 2 hours for different hours hydrolysis (60, 100 and 120 hours hydrolysis)

From the above UV spectrum, the optical band gap energies of cerium oxide nanoparticles are calculated from the plot of energy against $(\alpha h\nu)^2$ is shown in figure 6.2.

Fig.6.2. The plot of energy against $(\alpha h\nu)^2$ of $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$ nanoparticles annealed at 1000°C for 2 hours for different hours hydrolysis (60, 100 and 120 hours hydrolysis)

From the UV absorption analysis, it is observed that the prepared $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$ materials have energy band gap values in the range of 3.50 – 3.37 eV. From the comparison of UV absorption spectra annealed $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$ samples for different hydrolysis hours, the UV-vis absorption spectra exhibited a well-defined and strong absorption peak near range at 346-371 nm and weak absorption peak at 270-278 nm respectively.

Mickael Palard et al., [18] were synthesized $\text{Ce}_{0.75}\text{Y}_{0.15}\text{O}_{1.925}$ by different co precipitation protocols. The UV-vis absorption spectra exhibited a well-defined and strong absorption peak near 295nm (4.20 eV). The estimated band gaps were ranged between 3.56 and 3.72 eV.

Franck Tessier et al., [19] were prepared fluorite-type compositions within the $\text{Ce}_{0.7}\text{Y}_{0.3}\text{O}_{1.85}$ system. The possibility to tune the absorption edge position of ceria by substituting yttrium for cerium atoms towards the UV-vis transition (400nm) was showed.

4.6. Photoluminescence (PL) studies

Photoluminescence occurs when an external source of energy, in the form of electromagnetic radiation, is absorbed by an atom or molecule, resulting in the emission of photons.

Photoluminescence (PL) studies of annealed YDC ($\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$) nanopowders were determined for different hydrolysis hours (60,100, and 120 hours). PL emission spectra of annealed YDC nanopowders excited at fixed wave length 345 and 420 nm for different hydrolysis hours (60, 100, and 120 hours). Small changes in excitation wavelength bring along shifts in emission. Emission spectra of annealed YDC nanopowders for different hydrolysis hours excited at 345 and 420 nm are shown in the figure 7.1 and 7.2 respectively. Excitation spectra of annealed YDC nanopowders emission at wavelength 485 nm for different hydrolysis hours (60, 100, and 120 hours) are shown in the figure 7.3.

From figure 7.1, it show that broad peaks observed at 666 to 703 nm for different hydrolysis hours excited at 345 nm. There is a change in emission spectrum as increasing hydrolysis hours. That is, the broad peak is shifted to lower wavelength. There is a peak observed at UV region range at 400-600 nm and it's due to oxygen vacancies. There is a shift in intensity as increases hydrolysis hours.

From figure 7.2, it show that broad peaks observed at 484 to 596 nm for different hydrolysis hours excited at 420 nm. There is a change in intensity as well as emission spectrum as increasing hydrolysis hours. When compared to emission spectra excited at 345 nm, its show that there is shift in broad peaks near at 700 nm to around 590 nm.

Fig.7.1. Emission spectra of annealed YDC nanopowders for different hydrolysis hours excited at 345 nm.

Fig.7.2. Emission spectra of annealed YDC nanopowders for different hydrolysis hours excited at 420 nm.

Fig.7.3. Excitation spectra of annealed YDC nanopowders for different hydrolysis hours emission at 485 nm.

From the above figure 7.3, it shows that the excitation spectra for emission wavelength 485 nm for different hydrolysis hours. It has broad peaks around at 240 to 247 nm. There is a change in intensities and as well as excitation peaks with increases hydrolysis hours.

Mickael Palard et al., [18] were investigated that $Ce_{0.75}Y_{0.15}O_{1.925}$ nanopowders have the photoluminescence spectra of the pure and doped cerium oxides all exhibited a strong UV emission band near 400nm and a weak blue shoulder at about 415nm (2.99 eV). They were attributed to surface defects (oxygen vacancies) which existed between the Ce 4f state and O 2p valence band.

5. Conclusion

In this work yttrium doped cerium oxide nanopowders are prepared by sol-gel via the hydrolysis process for different hydrolysis hours and those annealed at 1000°C for 2 hours. From the XRD patterns, the nanocrystalline ($Ce_{0.8}Y_{0.2}O_2$) purity improved after annealing and also the grain size is increased. The grain size of the highest orientation peak (111) values is decreases with increasing hydrolysis hours for annealed samples. FTIR studies were carried out for prepared samples, to change the hydrolysis hours there is a slightly change in absorption bands. From SEM images, the micrographs clearly indicate that the shapes of the particles are fairly irregular. It was found that each irregular particle is a cluster of spherical particles which were agglomerated. EDAX spectrum confirms the presence of yttrium and cerium compounds in the prepared YDC samples. UV absorption analysis shows that the prepared $Ce_{0.8}Y_{0.2}O_2$ materials have energy band gap values in the range of 3.50-3.37 eV. The absorption spectra exhibited a well-defined and strong absorption peak near range at 346-341 nm. From the photoluminescence emission and excitation spectra of prepared samples, that is a same mirror image relation between the absorption and emission spectra.

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