Effect of Temperature on Crystallite Size of Lanthanum Cerium Oxide (La$_2$Ce$_2$O$_7$) and its Optical Properties

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The effect of the calcination process on the crystallite size and optical properties of Lanthanum Cerium Oxide (La$_2$Ce$_2$O$_7$) nanopowders synthesized using co-precipitation process were reported. X-ray diffraction analysis revealed that the synthesized nanopowders calcined at various temperatures have cubic fluorite phase. Thermal Gravimetric Analysis (TGA), X-ray Diffraction (XRD), Energy Dispersive Spectroscopy (EDS), Transmission Electron Microscopy (TEM), Laser Raman Spectroscopy, and UV-visible spectroscopy were utilized to characterize phase structure and morphology of the products.

Keywords : Crystallite Size, Co-precipitation Method, Thermal Properties, Optical Properties, Structural Properties.

Introduction : Rare earth doped ceria (REC) with a fluorite structure is used in wide applications such as solid oxide fuel cells (SOFC) due to its higher oxygen conductivity than that of ZrO$_2$ solid solution [1, 2, 3] and thermal barrier coatings [4, 5] due to its properties such as high melting point, low thermal conductivity, thermal expansion match with metallic substrate, no phase transformation between room temperature and operation temperature, chemical stability, good adherence to the metallic substrates and low sintering rate of the porous microstructure [6, 7]. Recent work done for the preparation of La$_2$Ce$_2$O$_7$ include the work by Benjaram et al. [8], Andrievskaya et al. [9], Cao et al. [10], Wang et al. [11]. Different methods were used in the preparation of La$_2$Ce$_2$O$_7$, such as hydrothermal method [11, 12], solid state method [13], cold pressing and sintering [14], conventional co-precipitation method, [15]. Some of these methods are multistep [19], costly [14], and produces particles greater than nano-size [13, 14]. Long heating time is essential for solid state method, and cold pressing method, but results in formation of micron sized particles. In hydrothermal and conventional co-precipitation method, water is used as solvent for the synthesis of La$_2$Ce$_2$O$_7$, since water is used externally, results in the formation of hard agglomerates, due to hydrogen bonding. Thus by the elimination use of additional water, we can eliminate the formation of agglomerate [16].

Preparation of lanthanum cerium oxide nanopowders and studying its thermal and optical properties is a new research subject, practical
methods are still needed for synthesizing high quality ultrafine powders with required characteristics in terms of their size, uniformity, morphology, specific surface area and crystallinity. Very few techniques have been proposed to synthesize nano-sized lanthanum cerium oxide (La$_2$Ce$_2$O$_7$) with promising control of properties.

In the present study we report the effect of the calcination process on the crystallite size and optical properties of Lanthanum Cerium Oxide (La$_2$Ce$_2$O$_7$) nanopowders synthesized using co-precipitation process using Thermal Gravimetric Analysis (TGA), X-ray Diffraction (XRD), Energy Dispersive Spectroscopy (EDS), Transmission Electron Microscopy (TEM), Laser Raman Spectroscopy, and UV-visible spectroscopy.

**Experimental Method** : The co-precipitation process for making lanthanum cerium oxide La$_2$Ce$_2$O$_7$ was followed according to the work reported by Li et al [17]. The whole precipitation process was performed at room temperature. The cerium nitrate hexahydrate Ce(NO$_3$)$_3$·6H$_2$O (Spectrochem 99%) and lanthanum nitrate hexahydrate La(NO$_3$)$_3$·6H$_2$O (Loba Chemie 99 %) were used as source for synthesizing lanthanum cerium oxide La$_2$Ce$_2$O$_7$ powder. Triethylamine (C$_2$H$_5$)$_3$N and ethanol were used as precipitant and solvent respectively. Ce(NO$_3$)$_3$·6H$_2$O, La(NO$_3$)$_3$·6H$_2$O and (C$_2$H$_5$)$_3$N were dissolved into the solvent separately. The final concentrations were 0.1 M for mixture of cerium nitrate and lanthanum nitrate solution and 0.4 M for triethylamine solution.

0.1 M mixture of cerium nitrate and lanthanum nitrate solution was mixed in a flask and titrated using 100 ml of 0.4 M triethylamine precipitant solution kept in another flask under mild stirring. The stirring was continued till the solution of cerium nitrate and lanthanum nitrate were empty, and solution was filtered by a suction filter using Whatman 42 (pore diameter 2.5 µm) filter paper. Precipitates was washed with solvent alcohol many times, then again washed with acetone to remove the remaining alcohol, unreacted triethylamine, and other byproduct. Then the precipitates was dried for 24 hours, and calcined at different temperatures for 3 hours [16].

Thermogravimetric analysis (TGA, TGA-701, Rikagu, Japan), X-ray diffraction (XRD, Bruker X-ray diffractometer (D2 Phaser)), Transmission electron microscopy (TEM, Philips Tecnai 20, Holland), Electron dispersive spectroscopy (EDS), Raman Spectroscopy, and UV-visible spectroscopy were used as analytical tools to characterize the as prepared powder.

**Results and Discussion** :

**Thermal Gravimetric Analysis (TGA) :**

![Figure 1](image1.jpg)

Figure (1) : Graph showing the weight loss of sample with respect to increment in temperature.

![Figure 2](image2.jpg)

Figure (2) : Graph showing the weight loss of sample with respect to increment in temperature.

TGA Analysis was done using RIGAKU TGA-701, at SIC, Mechanical Engineering Department, SVNIT. Figure (1a) shows the graph of weight loss vs temperature. In this graph the weight of
the substance decreases up to around 500 °C, but after that there is zero or negligible weight loss. Which suggest that all the volatile material is removed around that temperature.

**X-Ray Diffraction (XRD) Analysis**: Bragg showed in 1913 that diffraction from a crystal is described by the equation now known as Bragg's law:

$$2d_{(hkl)} \sin \theta = n\lambda$$  \hspace{1cm} (1)

This equation allows one to measure the perpendicular distance ($d_{(hkl)}$) between imaginary planes which form parallel families and which intersect the repeating unit cell filled with atoms in a way described by the Miller indices ($hkl$). X rays of wavelength $\lambda$ may be thought of as reflecting from these imaginary planes at the measurable angle $\theta$, where $n$ is the order, $\theta$ is one-half of the diffraction angle. A powder pattern therefore contains a set of diffraction peaks at 2$\theta$ positions that correspond to the interplanar spacings in the crystal [18].

Detailed analysis indicates that XRD pattern match well with the standard cubic fluorite phase of CeO$_2$. No evidence of La$_2$Ce$_2$O$_7$ pyrochlore phase (Fd3m) could be found. Furthermore, no peaks corresponding to the individual oxides (La$_2$O$_3$) were observed. This feature can be attributed to the formation of La$_2$Ce$_2$O$_7$ solid solution

**Energy Dispersive Spectroscopy (EDS)**: Elemental composition of Lanthanum Cerium Oxide (La$_2$Ce$_2$O$_7$) as observed from EDS is show in the table below:

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>16.98</td>
<td>64.08</td>
</tr>
<tr>
<td>La</td>
<td>41.36</td>
<td>17.97</td>
</tr>
<tr>
<td>Ce</td>
<td>41.66</td>
<td>17.95</td>
</tr>
</tbody>
</table>
EDS measurements were carried out at M.S. University, Baroda. EDS measurements carried out on the as-prepared La$_2$Ce$_2$O$_7$ nanopowders indicates, the chemical composition of La$_2$Ce$_2$O$_7$ is closing to the stoichiometric composition of La$_2$Ce$_2$O$_7$.

**Transmission Electron Microscopy (TEM) :**

TEM analysis was done using Philips Tecnai 20, at SICART, Vallabh vidya nagar, Anand. The morphology, particle size and structure of the synthesized La$_2$Ce$_2$O$_7$ were illustrated by TEM. Figure (3a) and (b) illustrate the TEM images of the La$_2$Ce$_2$O$_7$ nanocrystals calcined at 900ºC. The particles appear to posses the particle size 55 to 80 nm with cubic shape.

Laser Raman Spectroscopic Analysis:

Laser Raman Spectroscopic Analysis was done using Ar:Laser; 4W power (all lines), Ramnor HG-2S Spectrometer, at IIT Bombay, The exposure time was 50 sec and the wavelength of laser source was 514.5 nm. Cubic fluorite structure metal dioxides have only a single allowed Raman mode, wich has F$_{2g}$ symmetry and can be viewed as a symmetric breathing mode of the O atoms around each cation. In above spectra two broad peaks are observed. 1\textsuperscript{st} peak is at 451 frequency and 2\textsuperscript{nd} peak is at 570 cm$^{-1}$. The 1\textsuperscript{st} peak is CeO$_2$ peak it is shifted from 464.5 cm$^{-1}$ to 451 cm$^{-1}$. This shifting is due to change in the M-O vibration frequency after incorporation of La in
CeO₂, which account for the difference in the ionic radius [21, 22, 23]. Vibrations are rapid for contracted lattice and slow down for expanded lattice so that band shifts to higher and lower wavenumbers, respectively. The peak at 570 cm⁻¹ is the new feature, and is due to the effect of dopant. Due to doping the O vacancies increases.

**Results and Discussion :**

**Conclusions :** La₂Ce₂O₇ nanocrystals were produced via co-precipitation method. Thermo gravimetric analysis (TGA) of Nanoparticles in hydroxide form shows that weight loss is negligible as temperature increases above 500°C, and TGA of sample Calcined at 750°C also shows that the weight loss is negligible. From X-ray diffraction (XRD) Analysis of sample Calcined at 600°C, 750°C, 900°C and 1050°C standard cubic fluorite phase of Lanthanum Cerium Oxide (La₂Ce₂O₇) is observed. Electron Diffraction Spectroscopy (EDS) confirms L₂Ce₂O₇ phase. From Transmission Electron Microscope (TEM) morphology, particle size and structure of the synthesized La₂Ce₂O₇ was observed. Laser Raman Spectroscopy reveal the presence of vacant spaces due to doping of Lanthanum. And from UV-visible Spectroscopy it is observed that there is change in bandgap with increase in calcinations temperature. The products are cubic fluorite in structure. The nanoparticles have size in range 55-80 nm. This method is found to be simple and economical for the preparation of La₂Ce₂O₇ nanoparticles. XRD and TEM results suggest that the nanoparticles are cubic fluorite in structure. Laser Raman Spectroscopy reveals an extra peak at 570 nm.

**References :**

La$_2$(Zr$_x$Ce$_{1-x}$)$_2$O$_7$ oxide system Kwak, Mater. Lett. 65 (2011) 2937-40.


