

Short Communication

Synthesis and Characterization of Ce-Fe Composite Nanoparticles via Sol-gel Method

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Inorganic-organic hybrid materials exhibit a vast application potential due to their tailorable mechanical and optical properties. These hybrid materials are hi-tech and sometime show unexpected properties different from organic/inorganic molecule. In the present study, the nanosized Ce-Fe composites of perovskite structure were synthesized via sol-gel method using mixture of hybrid materials, i.e. polyvinyl alcohol (PVA) and cerium nitrate, and calcined at different temperatures. The as-synthesized Ce-Fe composites were characterized using XRD, SEM, FTIR, UV-Vis techniques to study their structural, morphological and optical properties. Characterization study shows crystalline nature of particles with a size ranging from 22.04 nm to 57.73 nm with agglomeration and porous nature. These composites show the characteristic metal-oxygen absorption band in wavelength range of 500-400 nm and band gap energies from 4.0 to 5.2 eV. The formation of Ce-Fe composite material is reported at calcination temperature of 800-1000 °C. Further calcination at a higher temperature may lead to the formation of CeFeO₃ which offers scope of further study.

Keywords: Ce-Fe composites, Polyvinyl alcohol, XRD, FTIR, UV-Visible, Sol-gel synthesis.

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1. INTRODUCTION

Perovskites are a family of oxides having general formula ABO₃, where B is a transition metal. Members of the perovskite family of reduced symmetry are important for their magnetic and electrical properties. Recently, the synthesis of rare earth metal oxide (RFeO₃) nanoparticles has gained attention due to their peculiar optical, magnetic and electrical properties. A rare earth metal reacts with oxygen or precursor of oxygen or oxidant and forms rare earth element oxide of two types having the general formula R₃Fe₅O₁₂ and RFeO₃, where R is a rare earth element. Among these oxides R₃Fe₅O₁₂ possesses garnet structure and RFeO₃ possesses perovskite structure. CeFeO₃ structure possesses the 12-fold coordinated A-site which is mostly occupied by large rare earth metal ions, while the 8-fold coordinated B-site usually hosts iron metal cations [1]. Due to oxidizing tendency of Ce³⁺ into Ce⁴⁺, it is difficult to prepare CeFeO₃ since Ce³⁺ is mostly oxidized and converted into CeO₂ [2]. Hence some authors tried to prepare CeFeO₃ by various means like using reducing agent and under reduced pressure. CeFeO₃ is a narrow band gap inorganic semiconductor that acts by absorbing photons to create electron-hole pair, which can subsequently participate in the redox reaction [3].

These RFeO₃ nanoparticles have many potential applications such as ultrafast spin reorientation [4], photomagnetic recording [5], photocatalyst [6], solar hydrogen production [7], and multiferroicity [8]. Vivekananthan et al. used Ce-Fe oxide in a mixed form as a potential material to remove organic and inorganic contaminants through affinity-based binding [9]. In RFeO₃ family, CeFeO₃ possesses single-phase orthorhombic structure with space group Pbnm [10]. Distorted oxide of the

perovskite family has a reduced symmetry which is important for its magnetic and dielectric properties.

In this work, CeFeO₃ nanoparticles are prepared using polyvinyl alcohol (PVA) as a complexing agent adopting sol-gel method. However, it is observed from the XRD pattern that instead of CeFeO₃, Ce-Fe composite material is obtained as a result.

2. MATERIAL AND METHOD

To prepare CeFeO₃ nanoparticles, an appropriate quantity of PVA was dissolved in de-ionized water at 80 °C and continuously stirred for 2 h. A stoichiometric amount of rare earth metal salt Ce(NO₃)₃·6H₂O and transition metal salt Fe(NO₃)₃·9H₂O was suspended in de-ionized water and added gradually to the main solution containing PVA; and the temperature was maintained at 60-80 °C. A molar ratio of 2:1 of positively charged valences of metal nitrate to hydroxyl groups (Mⁿ⁺/-OH) of PVA was used during the process. The solution was thoroughly stirred continuously for 24 h until the gelation started to appear and it was followed by heating the gel in the microwave oven (600 W power). The resulting brown, puffy and porous mass was ground into a fine powder and was calcined in a temperature range from 800 °C to 1000 °C for a period of 3 h to obtain CeFeO₃ nanoparticles.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction (XRD)

XRD peaks of cerium iron composite nanoparticles (2:1) calcined at 800 °C, 900 °C, and 1000 °C well indexed to the JCPDS card 01-081-0792 for CeO₂ and 00-013-0534 for Fe₂O₃ (Fig. 1) confirm the formation of Ce-Fe compo-

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site instead of CeFeO_3 . The most intense reflection peak is taken as a reference to calculate the crystallite size using Debye-Scherrer formula [10]. The particle sizes are obtained to be 22.04 nm, 39.48 nm, and 57.73 nm for samples calcined at a temperature of 800 °C, 900 °C, and 1000 °C respectively. It is experimentally observed that the crystallite size increases with the increase in calcination temperature. It is possibly due to coalescence of small grains at a temperature higher than 300 °C [8]. Besides, the peak intensity of the diffraction peaks also increases with the calcination temperature, indicating the enhancement of crystallinity [11, 12].

3.2 Fourier Transform Infrared (FTIR) Analysis

FTIR analysis of Ce-Fe composite nanoparticles is scanned in the range of 400-1000 cm^{-1} (Fig. 2). The peaks occurring below 1000 cm^{-1} are characteristic of metal-oxygen stretching and bending vibrations [10]. The calcined samples show two characteristic IR bands for metal-oxygen stretching at 400-420 cm^{-1} and 455-470 cm^{-1} . The sample before heating displays a broad IR band at 3300 cm^{-1} , 1600 cm^{-1} , 1300 cm^{-1} due to $(\text{OH})^{-1}$, CO and other groups present. These absorption bands were removed from the calcined sample and only metal-oxygen characteristic band is observed at 500-400 cm^{-1} for all the samples, thus confirming the formation of cerium iron composite material at 800 °C.

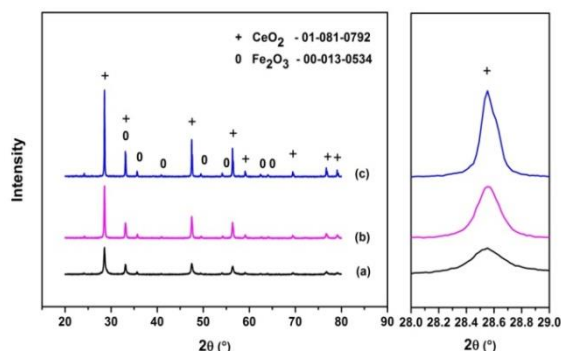


Fig. 1 – XRD graph of Ce-Fe composite nanoparticles calcined at 800 °C (a), 900 °C (b), 1000 °C (c)

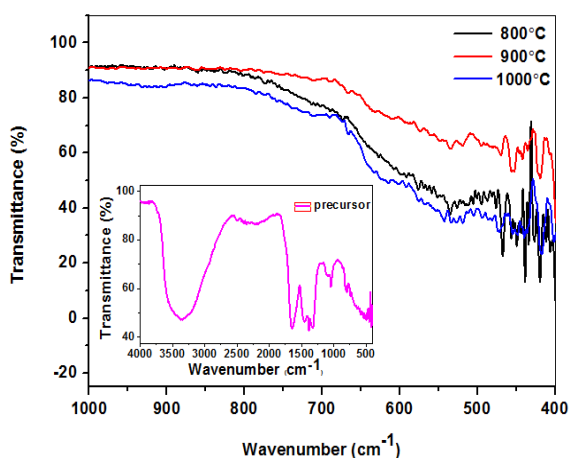


Fig. 2 – FTIR graph of Ce-Fe composite nanoparticles before heating (inset) and powder calcined at 800 °C, 900 °C, 1000 °C

3.3 UV-visible Analysis

The study of absorption spectra of Ce-Fe composite material before and after calcination was carried out from 200-400 nm to find the optical absorption and band gap. Ce-Fe composite material has high absorption in the UV region instead of visible region. Extrapolation of the linear portion of the plot of $(\alpha \times h\nu)^{1/n}$ versus the photon energy ($h\nu$) to the energy axis for zero absorption [10] gives the band gap energy for the electronic transitions. The value of the energy band gap decreases with an increase in calcination temperature (Table 1). The value of the energy band gap in this study is 5.2-4.0 eV, which is higher as compared to the band gap of 1.77 eV reported by Tang et al. [6]. The obtained results can be interpreted in terms of the fact that the band gap value can be affected by a number of factors such as crystallite size, synthesis route, carrier concentration, stoichiometry of precursors and presence of impurity.

3.4 Scanning Electron Microscopy Analysis

Ce-Fe composite calcined at 800 °C shows porous and foamy structure which is due to the formation of CO_2 and CO gases during the calcination of precursor (Fig. 3). The presence of a porous network is one of the characteristics of combustion-synthesized powders [10]. The nanoparticles prepared by the sol-gel process followed by thermal treatment show a highly porous open network consisting of agglomerated particles. This is the result of the effervescence of various gaseous products in the thermal process combined with the short reaction time, which prevented further particle growth. If we compare the results with the nanoparticles prepared by the high-temperature solid-state reaction it consists of micron size particles that are sintered together to form a dense non-porous network. Further calcination increases the interparticle interaction among the cerium, iron and oxygen ions [5]. The image clearly indicates the homogenous aggregation of nanoparticles. The particle size of cerium iron grows as the annealing temperature increases and leads to the formation of large feather-like agglomerates due to the thermal annealing process and subsequent phase transformations under temperature.

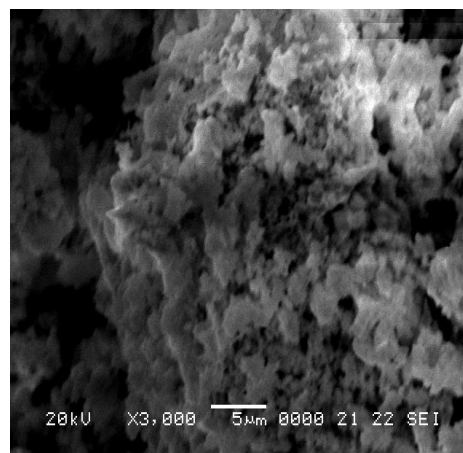


Fig. 3 – SEM images of Ce-Fe composite nanoparticles calcined at 800 °C

Table 1 – Absorption maxima and band gap of cerium iron composite

| Metal/hydroxyl valences | Samples | λ_{max} | Band gap |
|-------------------------|---------------------|-----------------|----------|
| M-OH 2:1 | Before | 204 nm | 5.2 eV |
| | Calcined at 800 °C | 203 nm | 5.0 eV |
| | Calcined at 900 °C | 201 nm | 4.9 eV |
| | Calcined at 1000 °C | 199 nm | 4.0 eV |

4. CONCLUSIONS

Ce-Fe composite nanoparticles are prepared via sol-gel method using PVA as a complexing agent. FTIR spectra show a peak within the range of 500-400 cm^{-1} which is the characteristic of metal-oxygen stretching. UV-Visible spectra of Ce-Fe composite nanoparticles give the absorption maxima around 199-204 nm and the bandgap in the range of 4.0-5.2 eV. X-ray diffraction pat-

tern revealed the formation of well crystalline Ce-Fe composite with a crystal size ranging from 22.04 nm to 57.73 nm. SEM studies revealed that Ce-Fe composite shows agglomeration and porous nature. The present study confirms the formation of Ce-Fe composite material at calcination temperature of 800-1000 °C. Further calcination at a higher temperature may lead to the formation of CeFeO_3 which can be a scope of further study.

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Синтез та характеристика наночастинок композиту Ce-Fe методом золь-гелю

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Неорганічно-органічні гібридні матеріали виявляють величезний потенціал застосування завдяки своїм механічним та оптичним властивостям. Ці гібридні матеріали є високотехнологічними і часом виявляють несподівані властивості, відмінні від органічної/неорганічної молекули. У дослідженні нанорозмірні композити Ce-Fe перовскітної структури були синтезовані методом золь-гелю із застосуванням суміші гібридних матеріалів, тобто полівінілового спирту (PVA) та церівної селітри, які прожарені при різних температурах. Синтезовані композити Ce-Fe характеризувались методами XRD, SEM, FTIR та UV-Vis для вивчення їх структурних, морфологічних та оптичних властивостей. Дослідження характеристик показує кристалічну природу частинок розміром від 22,04 нм до 57,73 нм з агломерацією та пористою структурою. Ці композити виявляють характерну смугу поглинання металу та кисню в діапазоні довжин хвиль 500-400 cm^{-1} та енергії забороненої зони в діапазоні від 4,0 до 5,2 eV. У роботі повідомляється про формування композиційного матеріалу Ce-Fe при температурі прожарювання 800-1000 °C. Подальше прожарювання при більш високій температурі може призвести до утворення CeFeO_3 , що дає можливість подальшого вивчення.

Ключові слова: Композити Ce-Fe, Полівініловий спирт, XRD, FTIR, Ультрафіолетовий та видимий діапазони, Золь-гель синтез.