

Structural, magnetic and optical properties of Cr doped CeFeO₃ nanoparticles synthesized by co-precipitation method

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ABSTRACT

Structure, Characterization and magnetic properties of Cr-doped CeFeO₃ (CeFe_{1-x}Cr_xO₃) nanoparticles have been synthesized by co-precipitation method. The consequential samples are characterized by structural, optical and magnetic properties. The average crystallite size (D_c) is decreasing with a dopant and establish to be altering between 7nm-32.6nm. The morphology is analyzed using scanning electron microscope and the obtained results credited that E_g values are growing with dopant varying between 2.05 eV- 2.61 eV. The metal oxide (M-O) stretching vibrations and few functional groups are detected from infrared spectra. (VSM) Vibrating sample magnetometer analysed the weak ferromagnetic behavior is pragmatic from hysteresis loop behavior. As well, the large hysteresis loop behavior induces no saturation up to 15kOe in nanoparticles. According to the obtained grades, CeFeO₃ nanopowder can be raised as a visible light-driven photocatalyst,

Keywords: Crystallite size, Co-precipitation method, Nanoparticles, optical properties, Magnetic Properties.

1. INTRODUCTION

In recent years, perovskite oxides with common formula ABO₃ have ensnared much thought because of the properties that effect from highly correlated d-band strong electron–lattice couplings and electrons. In addition, are very essential materials exhibiting special properties such as ferroelectricity [1,2,3], huge magnetoresistance and ferromagnetism [4,5], dielectric properties, piezoelectricity, [6,7], and semiconductor [8].

The Fe-O-Fe bond angle is a scale to analyse the degree of deformation which affects the structural, optical, dielectric, magnetic and other properties of the compound [9]. Nowadays, RFeO₃ ceramic objects have been the target of thought of researchers due to their helpful properties in different applications ranging from solid oxide fuel cells [10], sensors [11], environmental catalysts [12] to magnetic materials [13]. As

well, high domain-wall velocity as well as the continuation of Bloch lines production them applicable in magneto-optical data storage devices [14].

Mixed oxides type photocatalysts as well as perovskite (ABO_3) type structures are also between the large number of photocatalyst compositions explored [15]. TiO_2 [16, 17], $SrTiO_3$ [18] and $NaTaO_3$ [19] are between the most possible photocatalysts for hydrogen generation because they have benign stability, immobile nature and thermodynamically optimum band structures. The co-precipitation is the main method for the research of $CeFeO_3$ [20–21], in which the precursors of $CeFeO_3$ are first prepared and then subjected to high temperature calcinations. The $CeFeO_3$ is a narrow band gap semiconductor material, which has large view for applications in visible-light photocatalysis [22-23].

2. EXPERIMENTAL TECHNIQUES

$CeFe_{1-x}Cr_xO_3$ ceramic powders are synthesized by Co-precipitation method with the aqueous solutions of $Ce(NO_3)_2 \cdot 6H_2O$ (99.6 % purity, Sigma-Aldrich), $Fe(NO_3)_2 \cdot 9H_2O$ (99.6 % purity, Sigma-Aldrich) and $Cr(NO_3)_2 \cdot 6H_2O$ (99.6 % purity, Sigma-Aldrich) mixtures respectively in alkaline medium. The solutions of $Ce(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_2 \cdot 9H_2O$ and $Cr(NO_3)_2 \cdot 6H_2O$ in their stoichiometry (1g of $Ce(NO_3)_2 \cdot 6H_2O$ in 50 ml), (0.8g of $Fe(NO_3)_2 \cdot 9H_2O$ in 50 ml), (0.2g of $Cr(NO_3)_2 \cdot 6H_2O$ in 50 ml) were dissolved in double distilled water with a constant stirring. The pH maintained in between 10-11 by adding NaOH solution was additional drop wise to the mixture. Later, the solution forms a precipitate which was stirred (350 rotation/min) at room temperature for 30 min and then kept at $80^\circ C$ for 3 hrs. The resultant sample was chilled to room temperature. The sample is filtered and washed several times with double distilled water. The sample was then dried at $100^\circ C$ for over night. The dried sample was downy mass in form that is grind for 2hrs, and the consequential powder was sintered for 3hrs at $800^\circ C$. After sintering the sample is once more grinded for 4hrs using the Motor pestle apparatus and the resulting powder is analysed to XRD, FTIR, SEM / EDAX and VSM.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

XRD pattern depicts the $CeFe_{1-x}Cr_xO_3$ nanoparticles as shown in figure(1). All the reflection planes are in good agreement with the standard JCPDS: 22-0166 of orthorhombic structure. The maximum intensity peak was observed at 32.3° corresponding to (112) plane of $CeFeO_3$ structure. Other characteristics peaks at 2θ values 22.6° , 39.8° , 46.5° , 52.5° , 57.8° , 67.6° and 77° were besides observed for respective planes of (002), (202), (004), (311), (204), (224) and (116). All the peaks obtained in XRD pattern are intense and sharp, which suggests highly crystalline orthorhombic single phase of nanoparticle $CeFeO_3$ material, synthesized by Co-precipitation method. The average diameter (D) of the sample is evaluated for the intense peak positions using Scherrer's formula [24]:

$$D = \frac{k\lambda}{\beta \cos\theta} \text{-----(1)}$$

Where 'k' is a constant and is approximately equals to 0.9 for a spherical symmetry, ' λ ' is X-ray wavelength of $\text{CuK}\alpha = 1.5418 \text{ \AA}$, ' θ ' is diffraction angle and ' β ' is full-width half maxima (FWHM).

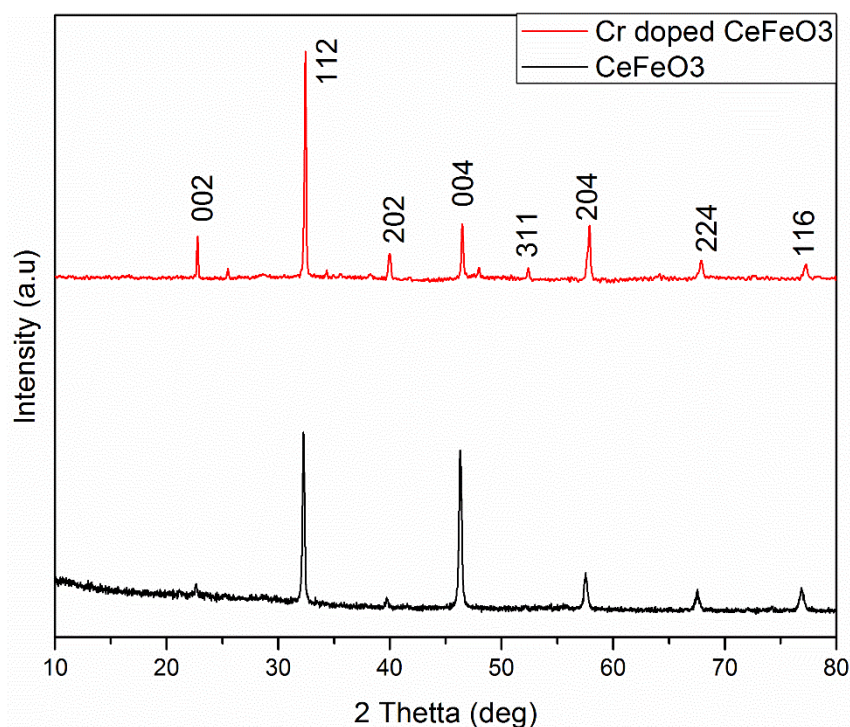


Figure 1: XRD pattern of CeFeO_3 and $\text{CeFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x=0, 0.2$)

3.2 FTIR ANALYSIS

The Fourier transform infrared spectra (FT-IR) of $\text{CeFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x=0, 0.2$) nanopowders. The absorption bands are formed. The higher wave number metal oxide (M-O) $848.66 \text{ cm}^{-1} - 877.61 \text{ cm}^{-1}$ this range is approximately 3462.22 cm^{-1} are more absorption bands observed (25). Which are assigned to the asymmetry stretching mode and symmetry of water molecules. At approximately 1435.04 cm^{-1} and 1639.4 cm^{-1} wave number the bending mode is O-H band are observed. The peak is 848.66 cm^{-1} reveals in very small absorption presence of metal oxide bonds. The vibration modes Fe – O and O – Fe – O bands (26).

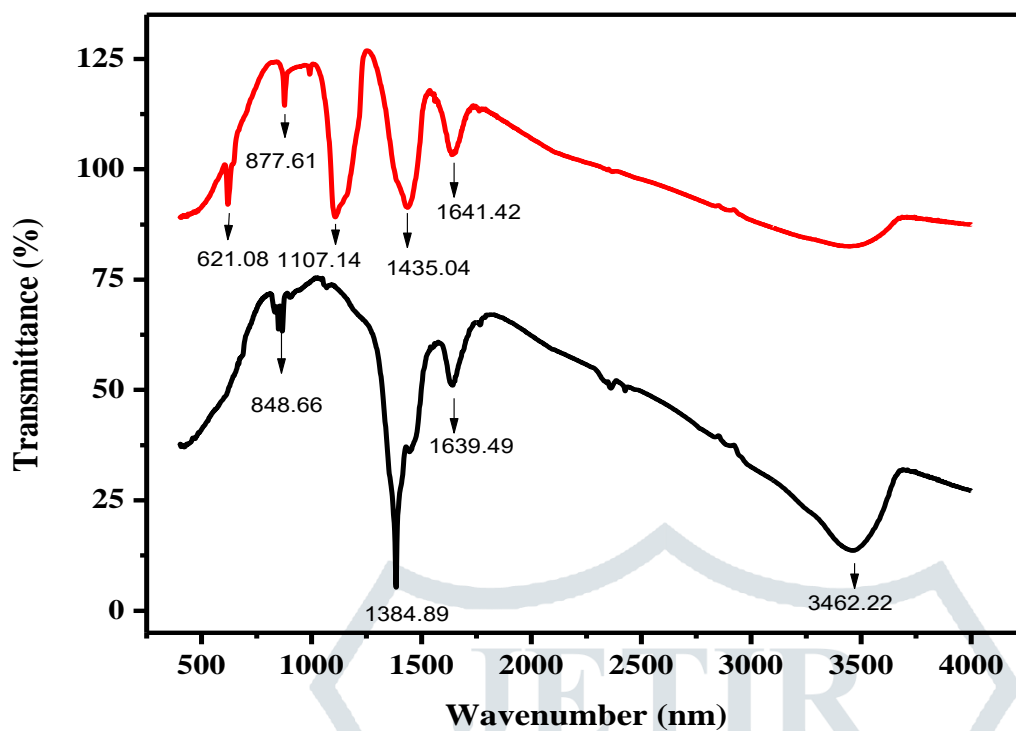


Fig.(2) FTIR spectra of $\text{CeFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0, 0.2$)

3.3 Surface Morphology

Surface morphology and Elemental analysis of nanoparticles are characterized by (SEM) scanning electron microscope and Energy dispersive X-ray (EDX). As much as the shape is concerned $x = 0$ & 0.2 showed the flat plate-like grains. Figure 3 (a) shows the SEM photographs, the particle size around 28.11-28.67 nm grains were found. SEM images of the local morphological of CeFeO_3 and $\text{CeCr}_x\text{Fe}_{1-x}\text{O}_3$ images show good nanocrystalline grains.

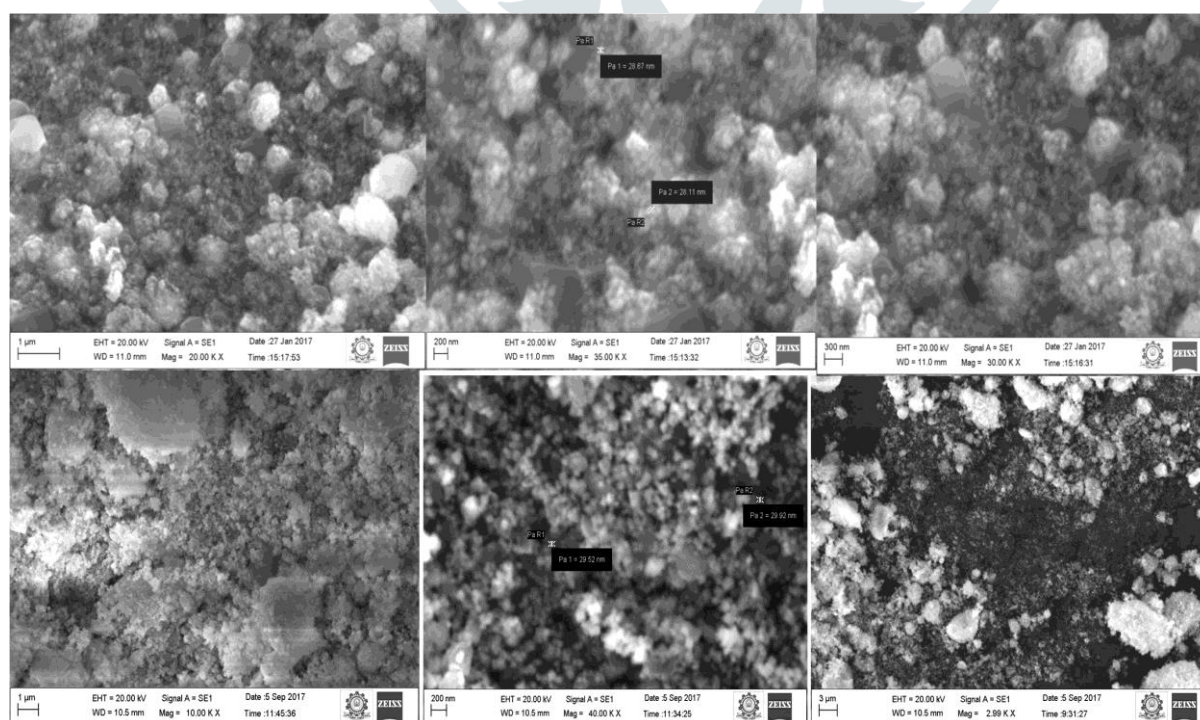


Fig.3 (a) SEM photographs of CeFeO_3 and $\text{CeFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x=0, 0.2$)

The EDX results confirm the elemental pattern of samples as illustration in Figure 3(b). The peaks of Ce, Fe, Cr and O were professed for all samples. We also apparent peaks of Cr for the samples with $x = 0.2$. It is found that the enhanced elements of Cr atomic replies to the reduction of that of Fe atomic as well as the increase of Cr content. It designates that the substitution of Cr ions into Fe site is complete. The presence of Cr, Fe, Ce and O elements including their atomic (At%) and weight (Wt%) percentages are reported.

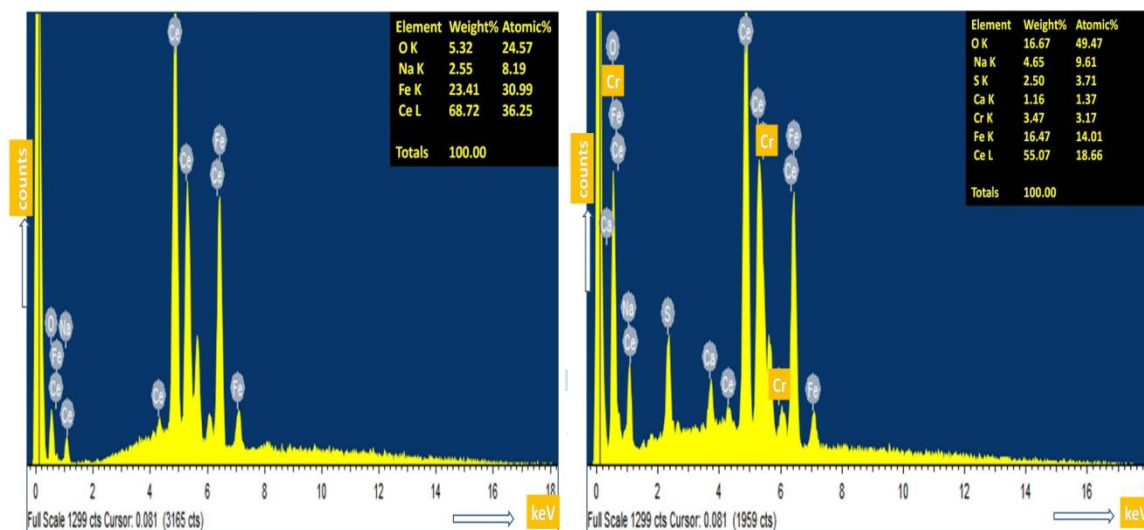


Fig.3 (b) EDAX spectrum CeFeO₃ and CeFe_{1-x}Cr_xO₃ (x=0, 0.2)

3.4 VSM analysis

The magnetic field dependence of specific magnetization (M-H curve) obtained from VSM measurement for CeFeO₃ and CeFe_{1-x}Cr_xO₃ nanoparticle designed at room temperature (RT) varying the applied magnetic field in the range of ± 15 kOe fig (4). From small hysteresis loop behaviour the sample exhibits weak ferromagnetic nature. The magnetic parameters are reported in table 1. It can be seen that magnetization, coercivity, Retentivity are decrease from pure and depend ($x=0-0.2$). The CeFeO₃ is antiferromagnetic behaviour due to the super exchange interaction between these neighbouring Fe³⁺ ions of Fe³⁺ - O²⁻ - Fe³⁺. This behaviour has been observed in the nanoparticle CeFeO₃ samples with in BiFeO₃ and YFeO₃. These loops are not saturated. This indicates that Fe³⁺ spins are not absolutely anti-parallel, but in reality they may be canted. It also indicates that an increase in the Cr content is accompanied by the decrease in the residual magnetization and coercive field. As mentioned before, the ferromagnetism behaviour in our CeFeO₃ samples is due to spin canting of Fe³⁺ as the source of the magnetic moments. The magnetic properties of the rare earth orthoferrites are originated from the super exchange interaction between Fe³⁺ - Fe³⁺, R³⁺ - R³⁺ and R³⁺ - Fe³⁺ via O²⁻ ions.

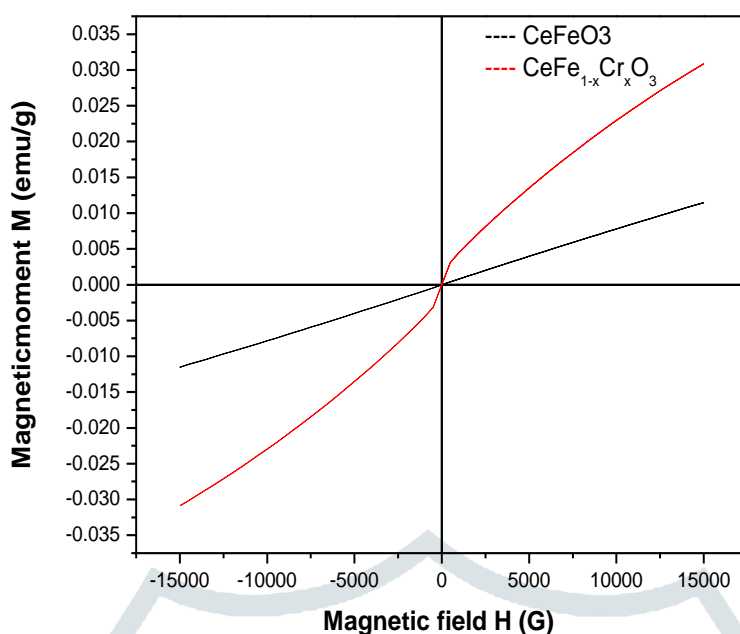


Fig.4 VSM analysis of $\text{CeFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0, 0.2$)

Table:1

X	0	0.2
Coercivity H_c (G)	13.215	13.981
Magnetization M_s (emu)	30.885×10^{-3}	11.50×10^{-3}
Retentivity M_r (emu)	85.01×10^{-6}	11.736×10^{-6}
Squareness (M_r/M_s)	0.00275	0.00102

3.4 CONCLUSION

Nanoparticles of $\text{CeFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0, 0.2$) have been synthesized by Co-precipitation method. The average crystallite size (D_c) is varying between 9nm-24.6nm. The morphology is analysed using scanning electron microscope. The weak ferromagnetic behaviour is observed from hysteresis loop behaviour. Coercivity (H_c), Magnetization and Retentivity are eventually decreasing with 'x' value. At $x = 0.2$ the maximum value of magnetization shows a potential visible – light – driven photocatalyst in the sunlight-induced photocatalytic degradation of wastewater.

Acknowledgment:

We gratefully acknowledge support from Arignar Govt Arts College- Cheyyar, Tamil Nadu, India. We also express our thanks to IIT Chennai for recording VSM analysis of the samples.

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