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Effect of Cerium doping on NiO, Co_3O_4 Nanoparticles and their Properties

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Abstract: Cerium doped NiO and Co_3O_4 nanoparticles were prepared via microwave assisted route. These samples were characterized by X-ray diffraction, Fourier transform Infrared, Scanning electron microscopy, Raman and Photoluminescence spectrometry. Cubic phase of NiO and Co_3O_4 nanoparticles have been ascertained from X-ray diffraction. XRD pattern reveals the decreased nanosized particles formation for NiO and Co_3O_4 due to the incorporation of cerium ion. FTIR analysis has been performed to identify the vibration peaks of metal oxygen. The energy dispersive X-ray spectroscopic analysis (EDX) confirmed the stoichiometric compositions of the cerium, Ni, Co and O elements. Raman spectrum provides superparamagnetic behavior for Ce doped NiO nanoparticles ascertained by increased Raman intensity compared to undoped samples.
Keywords: Microwave; Rare Earth metal; Optical Property; FTIR and Raman.

Introduction

Rare earth doped materials largely enhances the physical properties by control over the size, structural and morphological characteristics of metal oxides [1]. Among different rare earth metals, cerium has attained considerable interest in research due to its remarkable ideal properties such as observation of cerium oxide shift between CeO_2 and Ce_2O_3 due to the formation of redox couple Ce^{3+}/Ce^{4+} based on oxidizing and reducing conditions and it could easily form oxygen vacancies with the relatively high mobility of bulk oxygen species. In the present work, we synthesized cerium doped NiO and Co_3O_4 materials and investigated the benefits of cerium incorporation into NiO and Co_3O_4 lattice sites for controlled growth of crystal structures by microwave reaction method. The present work elucidates, rare earth metal cerium suits well for the preparation of nanostructured NiO and Co_3O_4 materials for promising applications.

Experimental

For the synthesis of cerium doped NiO, required amount of $Ni(NO_3)_2.6H_2O$ and $Ce(NO_3)_2.6H_2O$ with different mol ratio's (Ni:Ce : 1.98:0.02, 1.96:0.04, 1.94:0.06, 1.92:0.08 and 1.90:0.10) were dissolved in 50 ml distilled water separately and vigorously stirred by magnetic stirrer to form a transparent solution. Then 3 ml of ammonia solution was added drop wise to form a clear solution at pH 9. The resulting solution was subjected to microwave radiation with the power of 300 W for 5min duration. After completing the reaction process, the precipitates was separated by centrifugation and rinsed with distilled water and ethanol for several times to remove soluble ions. The precipitate was dried at 80 °C in a hot air oven for 12 h and then the as-prepared powder was calcined under air at 400 °C for 2h to obtain NiO nanostructures from $Ni(OH)_2$. Above synthesis steps were used to prepare Ce doped Co_3O_4 samples with same mol % of Ce ions (1%, 3%, 5% and 10%). In this preparation, initially it forms $Co(OH)_2$ structures and after calcinations at 400 °C, the Co_3O_4 nanostructures were formed.

Results and Discussions

Figure 1 shows the diffraction patterns of Ce doped NiO and Co_3O_4 samples. The structures of these samples are identified as cubic phase [2, 3]. No reflections related to Ce and other impurities such as CeO_2, Ce_2O_3 or other crystalline forms were detected from XRD patterns which confirms that Ce ions were uniformly substituted in Ni and Co lattice sites. **Figure 2 (a-d)** illustrates the morphological images of pure and cerium doped NiO and Co_3O_4 structures. Figure 2b represents the flake shaped with less agglomerated nature obtained for 1% cerium incorporated NiO structures and plate like structure was found for 1% cerium incorporated Co_3O_4 sample. The presence of Ce concentration was confirmed by EDX analysis as shown in the inset of **figure 2**. From these SEM images, it is evidenced that, doping of low level cerium promotes improved morphology of NiO and Co_3O_4 nanostructures with reduced agglomeration and higher uniformity compared to undoped samples. The optical emission profiles for cerium doped NiO and Co_3O_4 samples are shown in **Figure 3A and 3B**. For pure and doped NiO samples, strong emission band at 360.5 nm is attributed to the band gap emission and emissions in visible regions at 410 and 490 nm was undoubtedly due to the presence of defects in the lattice sites [4]. From this optical studies, incorporation of Ce atom produced blue shift due to the confinement of finite size compared to undoped sample. Hence, photoluminescence study emerges that the doping of cerium was used to achieve enhanced optical properties with reduced bandgap than undoped sample.

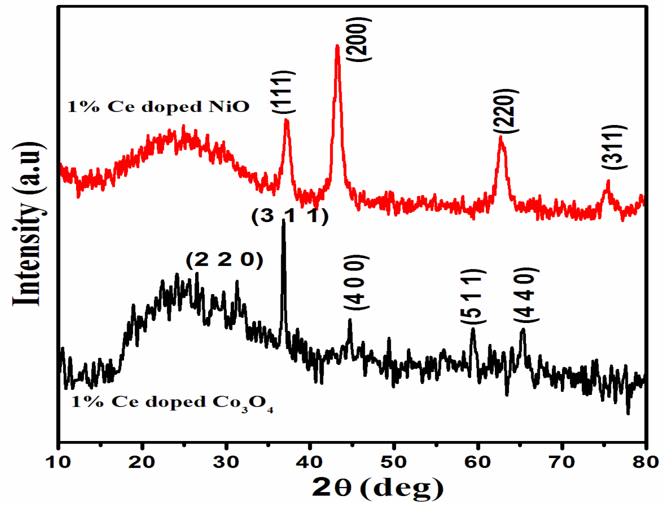

Figure 1 XRD patterns for NiO and Co_3O_4 nanostructures

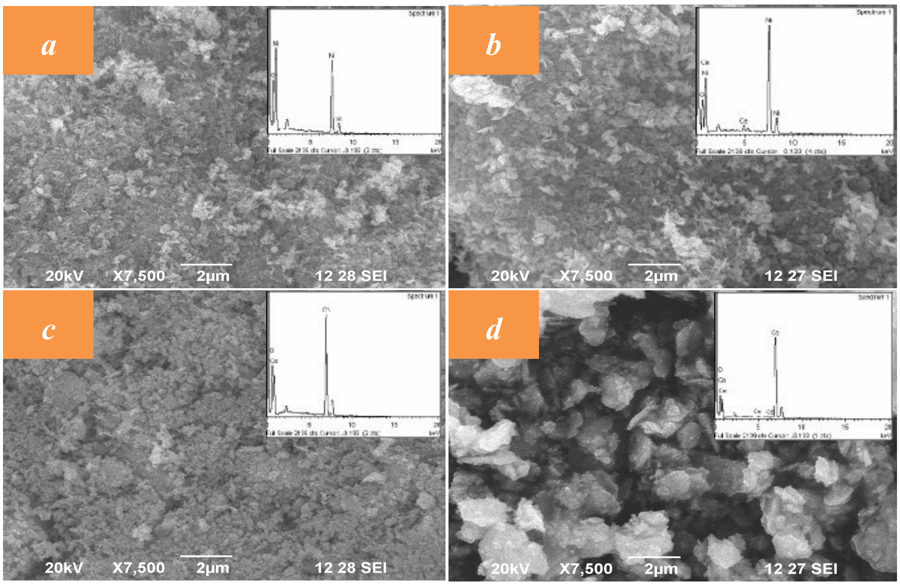

Figure 2 SEM images of undoped(a,c) and Ce doped NiO(b) and Co_3O_4

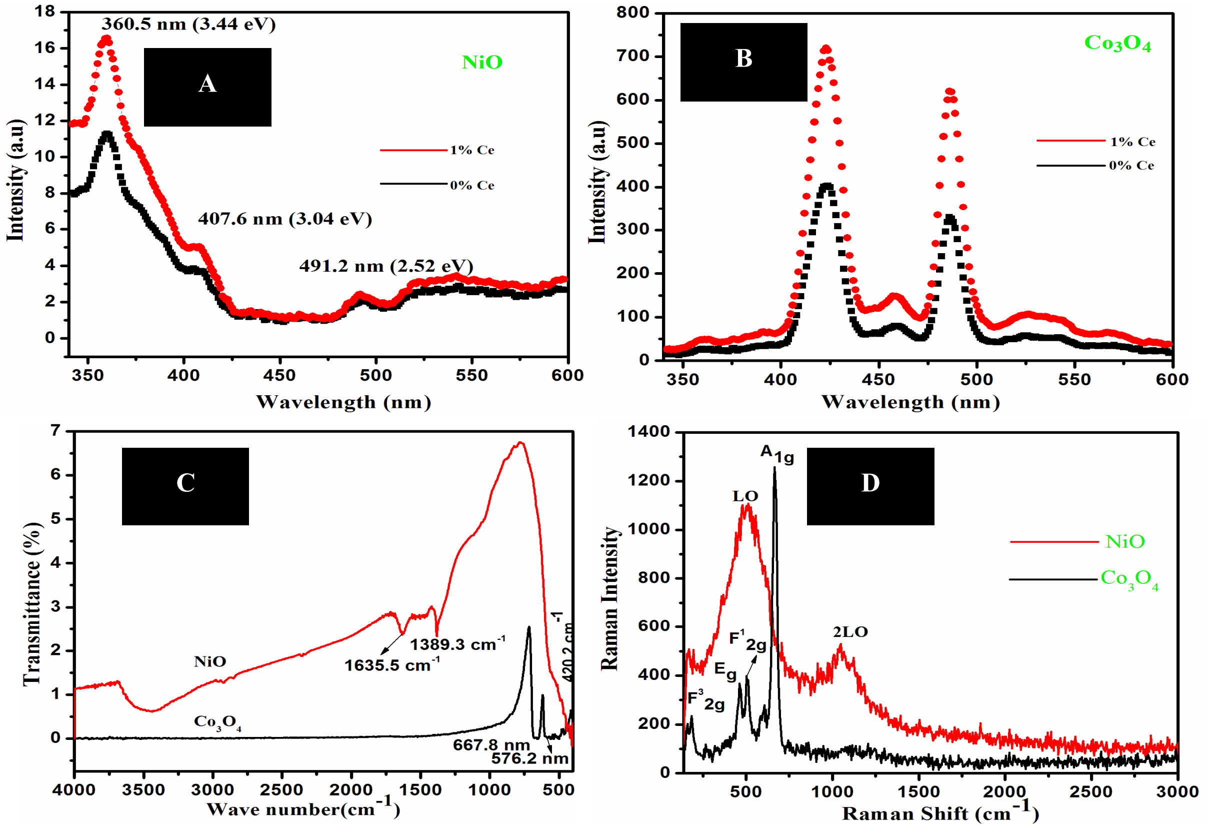

Figure 3 PL, FTIR and Raman spectrum for NiO and Co_3O_4 nanostructures

The investigation of functional characteristics of NiO and Co_3O_4 samples are demonstrated by FTIR analysis shown in **figure 3C**. The metal oxygen peak appeared at 420.2 cm^{-1} for Ce doped NiO and two peaks appeared at 550-580 cm^{-1} and 660-685 cm^{-1} corresponds to metal- oxygen peak for Co_3O_4 sample. **Figure 3D** displays the Raman spectra of NiO and Co_3O_4 nanoparticles. Two peaks were observed at 505 and 1058 cm^{-1} for NiO nanoparticles. The strong peak exhibited at 505 cm^{-1} belongs to longitudinal one phonon (1P) mode and another peak originated at 1058 cm^{-1} due to two phonon (2P) modes of 2LO peak. The absence of magnon peak in the Raman spectrum at 1500 cm^{-1} reveals the transformation of antiferromagnetic to super paramagnetic transition [5]. For Co_3O_4 materials, five obvious Raman peaks are located at 185, 460, 506, 593, and 658 cm^{-1}.They correspond to $3F_{2g}$, $1E_g$ and 1 A_{1g} Raman active modes of Co_3O_4 nanoparticles caused by the lattice vibrations of the spinal structure, in which Co^{2+} and Co^{3+} cations are situated at tetrahedral and octahedral sites in the cubic lattice [6].

Conclusion

In the present investigation, synthesis of Ce doped NiO and Co_3O_4 by microwave route is found to be an efficient, inexpensive and easy method. The structural characterization of the samples explored by XRD shows cubic structure with average crystalline size of 10-15 nm for cerium doped NiO and Co_3O_4 nanoparticles. It is stated that the incorporation of Ce into NiO and Co_3O_4 led to the creation of defects in the lattice sites and the formation of new energy levels in the band gap.

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