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Nonlinear Optical limiting behavior of Gd^{3+} doped $CoWO_4$ nanostructures

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Abstract: Nanocrystalline pure and Gd^{3+} doped $CoWO_4$ nanostructures were synthesized by single step chemical precipitation technique. The framework substitution of Gd in $CoWO_4$ nanoparticles was established by X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) techniques. XRD pattern reveals the pure and doped $CoWO_4$ nanoparticles belong to the monoclinic structure. The increase in Gd doping enhanced the 'blue-shift' in the UV-Vis absorption spectra. Electron microscopy studies clearly evidence the formation of round edged nanocubes with an average particle size of 60–80 nm, emerges in the polycrystalline nature. UV–Visible absorption spectra of Gd doped $CoWO_4$ nanocrystals shows a strong absorption peak at 278nm. Nonlinear optical transmission studies of the nanocomposites is measured using the open aperture Z-scan technique employing 7 nanosecond laser pulses at 532 nm. Experimental results show that both pure $CoWO_4$ and Gd doped nanoparticles exhibit excellent optical limiting performance.

Keywords: Optical limiting behavior, Gd^{3+} doped $CoWO_4$ nanostructures.

Introduction

Materials with excellent nonlinear optical (NLO) properties have gained much attention due to their potential applications such as optical power limiting, optical switching and 3-D optical memory devices. Of the various NLO behaviors, optical limiting is one of the most promising for practical applications, as it can protect the human eye and optical sensors from the damage caused by intense optical radiation[1]. The selection of optical limiters has lead to the study of various materials[2,3]. Extensive studies of optical nonlinearities of nanosized semiconductor materials have demonstrated interesting physical properties. The reduction in the dimensionality of semiconductor systems from bulk to nanoscale can enhance their nonlinearities due to the quantum size effect and other mesoscopic phenomena of nanoparticles [4,5]. Moreover, semiconductor materials can be tailored by varying the size, shape and composition of constituent nanoscale particles to fit wide range of photonics and optoelectronic.

Cobalt tungstate ($CoWO_4$) is a well-known p-type semiconductor and has many applications, such as in antiknock, pigment additives and photovoltaic electrochemical cell. $CoWO_4$ belongs to the wolframite structure with monoclinic phase. Only limited investigations were reported in early research on rare earth doped transition metal tungstates. We believe that the excellent chemical stability and luminescent nature of $CoWO_4$ nanostructure with suitable rare earth element will make it as a potential candidate for practical application. Various methods are followed to synthesis cobalt tungstates with desired morphology. Most of the reported

synthetic methods are solid state reaction, sol–gel, chemical precipitation, and hydrothermal process. The most inventive and simple way to synthesis the doped metal tungstates is chemical-precipitation method.

Of all the available trivalent rare earth (RE) ions, Er^3, Gd^3 and Yb^3 are the most popular and effective ions for optical pumping. To the best of our knowledge there are no reports published elsewhere on limiting behavior of wolframite $CoWO_4$ with trivalent Gd^3 ion doping. In addition to the host material, foreign impurities also play a key role for obtaining the efficient limiting activity. In this present investigation for the first time we are reporting the optical behavior of Gd doped $CoWO_4$ nanostructures.

Experimental

Materials and Methods

Pure and Gd^{3+} doped $CoWO_4$ wolframite were synthesized by single step chemical precipitation technique. Typical synthetic procedures were discussed briefly; analytical grade cobalt II acetate (Alfa Aaser), Gadolinium III nitrate (Alfa Aaser) of various concentrations (1, 3 and 5 %) and disodium tungstate (Merck), dissolved in double distilled water separately under constant stirring. As prepared Cobalt metal-ion solution was added dropwise to tungstate solution over 15 min, the violet colored precipitates were formed. Immediately, 0.1 M of polyethylene glycol (PEGmw 1000) was added to the above mixture as a surfactant.The stirring was continued until the complete precipitation followed by 15 h aging. Finally, the end product was separated by centrifugation and washed thoroughly with deionized water, ethanol and acetone consecutively. After drying at ambient temperature for 24 h, the powder was calcined at 600℃ for 6 h. For synthesis of a pure $CoWO_4$ nanostructure, the same procedure was followed without Gd^3 cation solution as mentioned above.

Results and Discussion

XRD Pattern

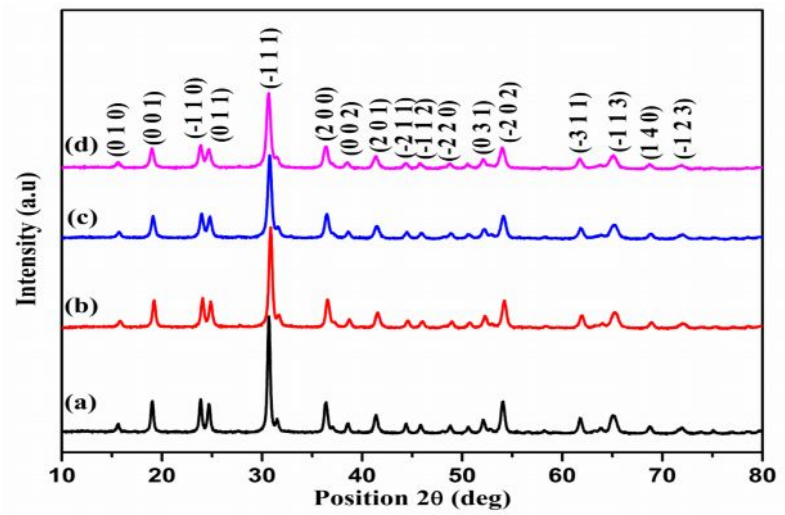


Fig.1 shows XRD Pattern of (a) $CoWO_4$ (b) $CoWO_4$:Gd at 1% (c) $CoWO_4$:Gd at 3% (d) $CoWO_4$:Gd at 5%

Powder XRD pattern of chemically precipitated pure and Gd doped $CoWO_4$ calcined at 600℃ are shown in figure 1. After calcination, the powders reveal the crystallinity confirmation. It clearly indicates the formation of single phase monoclinic $CoWO_4$ nanostructure with the space group of P2/c (13). Further it reveals that there is no ternary oxide phase due to WO_4 and Co_3O_4. All the peak position and their relative intensity were indexed with standard spectrum of [JCPDS#72-0479] wolframite $CoWO_4$ monoclinic phase. With respect to the Gd doping concentration, there is no peak shift was observed but the intensity decreased gradually. This implies the addition of Gd^3 ion in the Co_2 site reduces the crystalline size of the $CoWO_4$. The calculated particles sizes are about in the range of 60–80 nm.

FTIR Spectra

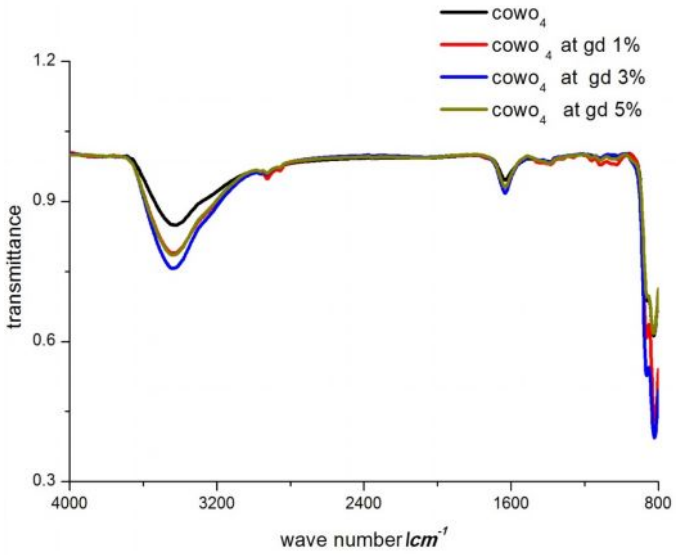


Fig.2 shows FT-IR spectra

The FTIR spectra of Gd^{3+} doped $CoWO_4$ nanoparticles is shown in figure 2. Intense band appeared in the low frequency region of 400–1,000 cm^{-1} which belongs to the characteristic deformation modes of Co–O, W–O and W–O–W. The strong intense band in the region of 3,000–3,800 cm^{-1} corresponds to OH stretching vibration of surface absorbed or internally bonded water molecules. The bending mode of H–O–H is located at about 1,640 cm^{-1}. The absorption of CO_2 from the atmosphere at the $CoWO_4$ surface was identified from the sharp peak positioned at about 2,370 cm^{-1} in FTIR spectra. From the figure it can be seen that the intensity of O–C–O stretching band increases with increasing the concentration of Gd^{3+} .This may be due to the presence of Gd^{3+} in Co_2 site that absorbs more CO_2 from air during calcinations.

UV- Visible Spectra

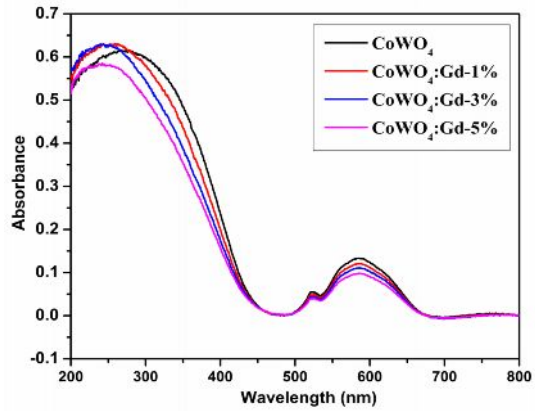


Fig.3 shows UV-Vis spectra

Optical absorption spectra of pure wolframite and Gd doped $CoWO_4$ nanparticles heat treated at 600℃ is shown in figure 3. All samples exhibits the strong absorption maximum at around 270–300 nm, confirms the strong UV absorption of the material. This confirms that the addition of Gd does not change the host $CoWO_4$ matrix. Further it suggests that this absorption may be directly related to the formation of $[WO_6]^{6-}$ complex within the wolframite structure. In addition of Gd into Co_2 site it can be seen that there is peak shift towards lower wavelength with respect to the Gd^3 concentrations. This may be due to the active interaction of trivalent cation with divalent ion which is due to the quantum confinement effect. The strong d–d transition band was observed in the visible region (i.e. 500–700 nm) which also shifted slightly towards high frequency with respect doping concentration. The absorption peak at 278 nm does not change significantly whereas peak broadening increased in magnitude, possibly due to the formation of wide distribution of Gd nanoparticles. When the particle size is decreased or decomposed from each other, the intensity of the absorption spectrum decreases. The sharp defined Plasmon band observed in the case of Gd might be due its narrower size distribution

Scanning Electron Microscopy

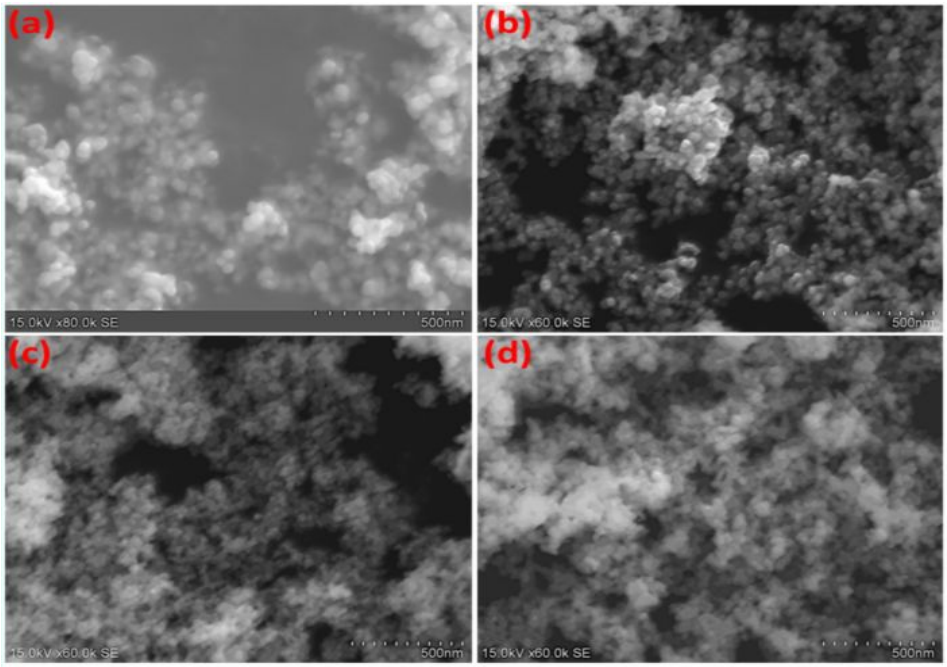
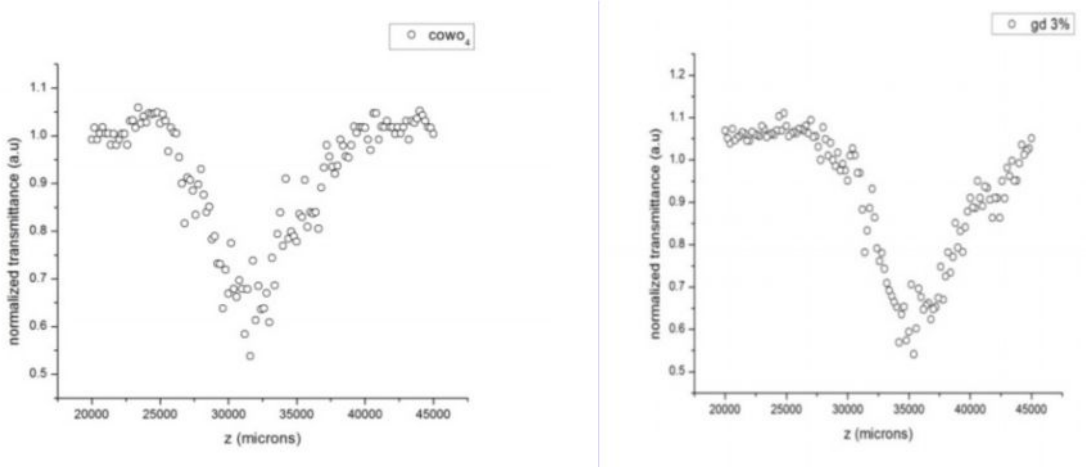


Fig.4 shows SEM images of (a) $CoWO_4$ (b) $CoWO_4$:Gd at 1% (c) $CoWO_4$:Gd at 3% (d) $CoWO_4$:Gd at 5%

The SEM images of the pure $CoWO_4$ and the Gd doped compounds were taken different magnifications. The observed SEM images show the particles are in round edged cubical morphology with uniform distribution. All the samples are showing nearly the same morphological features with an average particle size of 40–60 nm. This infers that the addition of Gd does not affect the crystal structure which confirms the incorporation of Gd on to Co lattice site. While increasing the doping concentration the particle size was considerably reduced and aggregated.

Non Linear Optical Property



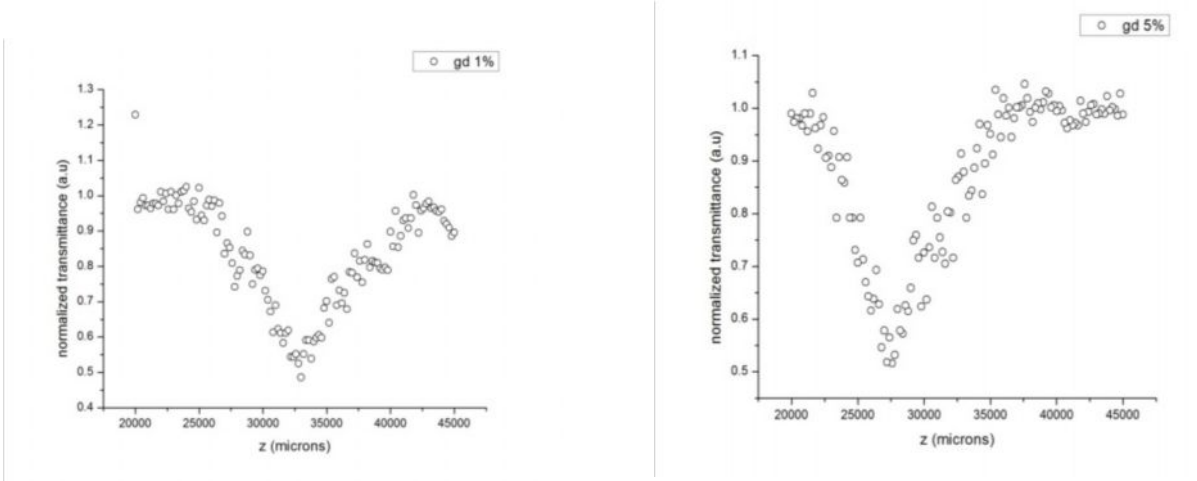


Fig.5 shows the nonlinear transmission curves of pure and Gd^{3+} doped $CoWO_4$

Nonlinear optical absorption reveals the information about photo-excited structure of state and carrier dynamics. The figure shows the open aperture Z-scan traces of $CoWO_4$ nanoparticles at different Gd concentrations for an irradiation wavelength of 532 nm. The traces in the open aperture configuration show a dip at the focus position in all the samples, indicating the existence of a nonlinear absorption process. The nonlinear behaviour is due to reverse saturable absorption (RSA) behaviour. The observed RSA is a result of optical limiting effect. It is seen that, all the nanoparticles show excellent optical limiting behaviour. Generally, metal nanoclusters have close-lying bands on which electrons move quite freely. The free electrons give rise to a surface plasmon absorption band in metal clusters, which depends on both the cluster size and chemical surroundings. In Co_3O_4 films ESA has been reported to occur with 532 nm, nanosecond laser pulse excitation, along with saturable absorption (SA)[6,7].

Nonlinear optical properties of semiconductor nanostructures depend mainly on their size and the excitation wavelength. Factors such as nature of the surface of the nanocluster, particle size and the distribution of particles, influence the response to a great extent. The interaction between the matrix and dopant, thus gives rise to the formation of trap states due to surface defects. When a photon of energy 2.33 eV is excited, the carriers may get excited to this defect level and free carrier absorption from these levels may occur with pulses of nanosecond duration which give rise to the large enhancement of the nonlinearity in the nanoparticles.

Conclusion

In this present investigation, we adopt the single step solution based XRD pattern of the samples shows monoclinic phase with polycrystalline nature. The addition of Gd up to 5 % does not show any secondary phases due to the Gd_2O_3. From SEM observation round edged nanocubical surface morphology was confirmed. UV–Vis absorption analysis of Gd^{3+} doped $CoWO_4$ exhibits the intense UV absorption at 278 nm which confirms the excellent optical behavior of the wolframite structure. The small shift towards high frequency region for the doped samples addressing the interaction of Gd^{3+} ion with $CoWO_4$ structure. Optical power limiting measurements indicates that the obtained nanoparticle exhibits good optical limiting at 532 nm wavelength. All the particles display reverse saturable absorption (RSA) at similar intensity in solutions. It was found that the optical limiting performances of nanoparticles are greatly enhanced with increased volume ratio of Gd. The enhanced third-order nonlinearities of nanoparticles are interesting from the application point of view which could be used as a potential candidate for the application of nonlinear optical device.

References

1. Crane, R., Lewis, K., Van Stryland, E., Khoshnevisan, M., Materials for optical limiting, Mater. Res. Soc. Proc., 1995, 374.
2. Tutt, L. W., Boggess, T. F., A review of optical limiting mechanisms and devices using organics, fullerenes, semiconductors and other materials, Prog. Quantum Electron. 1993, 17, 299.
3. Perry, J. W., Nonlinear Optics of Organic Molecules and Polymers, CRC Press, New York, 1997.
4. Henneberger, F., Schmitt-Rink, S., Gobel, E. O., Optics of Semiconductor Nanostructures. Akademie Verlag, Berlin, 1993.
5. Yoffe, A..D., Low-dimensional systems: quantum size effects and ... and some quasi-two-dimen- sional systems. Adv. Phys., 1993, 42, 173–262.

6. Yamamoto, H., Tanaka, S., Naito, T., Hirao, K., Nonlinear change of refractive index of Co3O4 thin films induced by semiconductor laser (lambda=405 nm) irradiation. Applied Physics Letters, 2002, 81, 999–1001.
7. Ando, M., Kadono, K., Kamada, K., Ohta, K. Third-order nonlinear optical responses of nanoparticulate Co_3O_4 films Thin Solid Films, 2004, 446, 271–276.

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