



Full length article

Third order nonlinear optical properties of Mn doped CeO₂ nanostructuresK. Mani Rahulan^{a,*}, N. Angeline Little Flower^a, R. Annie Sujatha^a, P. Mohana Priya^b, C. Gopalakrishnan^c^a Department of Physics & Nanotechnology, SRM University, Kattankulathur, Chennai 603203, India^b Department of Physics, Indian Institute of Technology Tirupathi, Tirupathi 517 506, India^c Nanotechnology Research Center, SRM University, Kattankulathur, Chennai 603203, India

ARTICLE INFO

Article history:

Received 27 July 2017

Received in revised form 20 September 2017

Accepted 24 November 2017

Keywords:

Nanoparticles

Hydrothermal method

Z-scan

Optical limiting

ABSTRACT

Mn doped CeO₂ nanoparticles with different ratios of Mn were synthesized by hydrothermal method and their structural properties were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). XRD patterns revealed that the peaks are highly crystalline structure with no segregation of Mn. The surface morphology from SEM reveals that particle size decreases with increase in Mn concentration. Nonlinear optical studies of the samples were measured by single-beam open aperture Z-scan technique using 5 ns laser pulses at 532 nm. The measured optical nonlinearity of all the samples exhibit typical third order nonlinear optical behavior including two-photon absorption (2 PA) and reverse saturable absorption (RSA). The experimental results show that the presence of RSA in these nanoparticles makes them a promising material for the fabrication of optical limiting devices.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Over the past few decades, the search of new and highly efficient materials in nonlinear optical (NLO) area has become a very interesting field of research. Investigation on various materials with excellent third order NLO properties has been studied for various photonic applications such as optical switching and optical limiting [1]. Due to tremendous increase in the usage of lasers in day today life, the need of protective devices for the protection of optical components from powerful lasers has become one of the greatest concerns. Such protective devices are called as optical limiters which can be explained on the basis of NLO absorption through the interaction of laser in the nonlinear medium. By knowing the magnitude of nonlinearity such as refractive index, nonlinear absorption and optical susceptibility of a material, the efficiency of power limiters can be identified.

Cerium dioxide, an important functional rare earth oxides exists in the cubic form, having fluorite type structure play an important role in various applications such as polishing materials [2,3], solar cells [4], high temperature resistance coatings [5] ultraviolet blocking materials [6] and catalysis [7]. Besides, CeO₂ possess large nonlinear refractive indices and small energy gaps due to their highly

polarizable oxide ions and cations. This leads to a high polarizability of the whole molecule and easy distortion of the electron density in a strong electric field [8].

Pure CeO₂, an n-type semiconductor has a bandgap (3.2 eV) which absorbs light in the near UV and have good transparency in the visible range. It is well known that doping influences the mechanical, electrical, optical, electronic and surface morphology depending on the nature of host material and the dopant. Doping of trivalent rare earth ions into CeO₂ lattice is a simplest way to enhance their physical and chemical properties for various industrial applications. Insertion of trivalent rare earth ions into the CeO₂ matrix can be done easily compared with other metal oxide host, such as ZnO and TiO₂, due to their close ionic radius to that of Ce⁴⁺ ion. Rare earth elements such as Nd, Yt and Yb into the CeO₂ lattice has been studied to improve both stability and also can tune the optical emission of the host matrix [9–11]. Several applications based on CeO₂ hybrids nanostructures has been studied for several applications however, there are no reports on the nonlinear optical studies of such nanocomposites have been investigated. In this work, we studied the NLO properties of Mn doped CeO₂ with the help of the Z-Scan technique in nanosecond (5 ns, 532 nm) excitation regimes. To investigate the NLA mechanism present in these products, the measured data is numerically modeled to the appropriate nonlinear transmission equations. Based on the measured data and the numerically calculated values of the

* Corresponding author.

E-mail address: krahul.au@gmail.com (K. Mani Rahulan).

nonlinear optical parameters, we demonstrate that two-photon absorption (2 PA) in combination with reverse saturable absorption (RSA) are responsible for the nonlinear optical absorption (NLA) behavior observed in these materials

2. Experiment

Mn-doped CeO₂ nanoparticles were synthesized using a modified hydrothermal method. In a typical synthetic procedure, 0.5 M of cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O) was prepared using deionized water. Subsequently, to this solution 1 gram of tri-sodium citrate dihydrate (C₆H₅Na₃O₇·2H₂O) dissolved in deionized water was added. The mixture was stirred homogeneously for about 1 h. Various amount of manganese nitrate (Mn(NO₃)₂·4H₂O (in mol%) prepared at room temperature was added to the above mixture drop wise at 1 ml/min, and the mixture was stirred for 30 min. The mixed solution was then sealed in a 100 ml Teflon lined autoclave and heated at 120 °C for 39 h. After the autoclave was cooled naturally to room temperature, the precipitate was collected and washed several times with distilled water. The final product was then dried overnight in a vacuum at 80 °C.

2.1. Nonlinear optical measurements

The nonlinear absorption characteristic of the samples was measured using an open aperture Z-scan technique in the nanosecond regime as described by Bahae et al. [12]. A Q-switched Nd:YAG laser was used to generate 5 ns pulses at 532 nm. The samples were taken in the form of dispersed solution in ethylene glycol with the linear transmittance of about 60%. The path length of the sample cell (quartz cuvette) is of 1 mm. The sample was moved in the direction of light incidence near the focal spot of the lens with a focal length of 20 cm. The pulsed beam was split into two parts by a beam splitter: the transmitted part was focused onto samples by lens and the reflected part was used as reference. At each position *z*, the sample experienced different laser intensity, and the position dependent (i.e., intensity-dependent) transmission was measured using an energy meter placed after the sample. Laser pulses were excited at a repetition rate of 10 Hz, and the data acquisition was automated. The low repetition rate was chosen for avoiding thermal effects in the samples during measurement. The pulse energy reaching the sample was approximately 150 mJ.

3. Results and discussion

X-ray diffraction (XRD) analysis was carried out to investigate the crystal phase and purity of samples obtained with different Mn-doped concentrations. Typical XRD patterns are shown in Fig. 1, it is apparent that the diffraction patterns contain characteristic peaks corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes which could be indexed to the phase of ceria with a cubic fluorite structure (Space group: Fm3m), being in good agreement with the standard data reported in JCPDS card (No. 78-0694) [13,14]. The sharp diffraction peaks from all samples suggest a high degree of crystallinity of synthesized samples and no impurity peaks appeared, indicating that the concentration of the dopant has no effect on crystalline phase purity of the products. No additional diffraction peaks due to Mn was seen, indicating well incorporation of Mn ions into the CeO₂ lattice sites. The significant features in the characteristic diffraction peaks upon Mn doping are the reduction of peak intensity and increase in the full width at half maximum (FWHM), indicating decreased crystallite size and degree of crystallinity. Decreased crystal size on doping indicates inhibition of crystal growth. The decrease in the grain size is caused by relaxation of strain induced by substitution of Ce⁴⁺

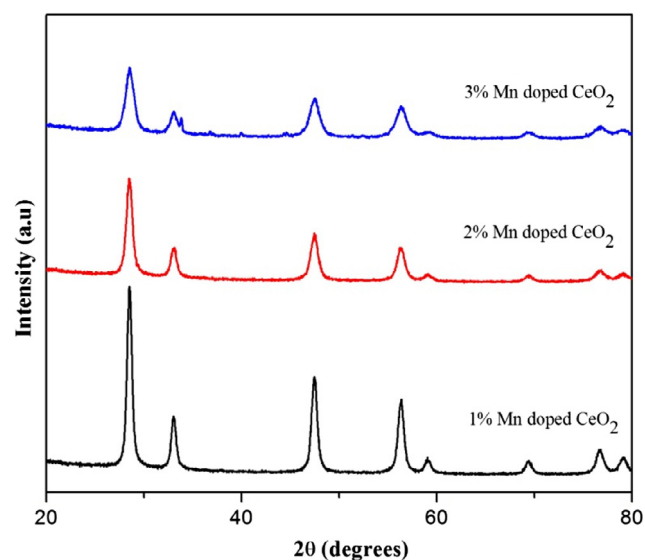


Fig. 1. XRD pattern of Mn doped CeO₂ nanoparticles.

ions of radius 0.097 nm by Mn⁴⁺ ions of smaller radius 0.056 nm [15].

The morphology of CeO₂ with different Mn concentrations was investigated by FE-SEM. It is evident from Fig. 2a that the grains of 1% Mn doped CeO₂ nanostructures are large and the size of these particles are homogeneous. The maximum particle size may reach 500 nm while the smallest diameter is only about 350 nm. On doping 2 and 3% Mn in CeO₂, the grain size continues to reduce and the average size lies in the range of 150 and 70 nm as shown in Fig. 2b & c. The morphology of the samples does not change remarkably after doping and the same shape is maintained. Only changes in the average diameter are observed. These results suggest that Mn has entered the lattice structure of CeO₂ and that doping is successful.

FTIR spectra of Mn doped CeO₂ nanostructures are shown in the Fig. 3. The spectra shows the characterization absorption bands at 3426 and 1625 cm⁻¹ corresponds to ν(O–H) mode of (H-bonded) water molecules and δ(OH) respectively. A strong peak at 1461 cm⁻¹ is attributed to stretching vibrations of Ce–O. The band below 700 cm⁻¹ is due to the envelope of phonon band of metal oxide (Ce–O–Mn) network [16,17]. The absence of other functional groups such as C–H, C=C confirms the phase purity of prepared nanoparticles

3.1. Nonlinear optical properties

The nonlinear absorption measurements of the Mn doped CeO₂ nanostructures studied by open aperture Z-scan technique for an irradiation wavelength of 532 nm is shown in Fig. 4. The open-aperture curve exhibits a symmetric valley in the normalized transmittance about the focal point (*z* = 0) and the transmission of the samples decreases as they move into the beam focus. The presence of normalized transmittance valley on both sides to the focal point implies typical nonlinear absorption behavior and it is evident from these optical responses that the samples exhibits the occurrence of optical limiting behavior in the nanocomposites [18]. The depth of the valley from the curve gives the direct measurement of the extent of optical limiting. This nonlinear absorption behavior is primarily caused by RSA. To identify the mechanism of optical limiting in the nanostructures, the experimentally obtained Z-scan data were fitted theoretically for different nonlinear transmission equations, including RSA and 2PA of the third-order nonlinear absorption process [19]. By simulating

Download English Version:

<https://daneshyari.com/en/article/7129481>

Download Persian Version:

<https://daneshyari.com/article/7129481>

[Daneshyari.com](https://daneshyari.com)