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Structural and third order nonlinear optical properties of Gd doped $NiWO_4$ nanostructures

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ABSTRACT

We report the synthesis of Pure and Gd doped $NiWO_4$ nanoparticles by chemical precipitation technique with excellent linear and nonlinear optical properties. The significant effects of Gd doping on optical, structural, morphological and magnetic properties have been investigated by UV–Vis spectroscopy, X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Vibrating sample magnetometer (VSM) techniques. XRD pattern for pure and Gd doped $NiWO_4$ demonstrates the wolframite monoclinic structure and the crystallite size decreases with increase in Gd concentration as confirmed by SEM. Magnetic hysteresis (MH) curves from the VSM measurement have shown excellent ferromagnetic nature of the nanostructures at room temperature. The nonlinear optical properties of $NiWO_4$ nanoparticles investigated using Z-scan technique demonstrate that the nanoparticles with increasing Gd have shown excellent nonlinear optical behavior. The nanoparticles clearly exhibit a negative value of nonlinear refraction, which is attributed to the two photon absorption (2PA) and free carrier absorption.

1. Introduction

The tremendous increasing use of lasers in human interactive sectors from modern defense weaponry to biomedical treatment facilitates the demand for safety devices on laser exposure to avoid undesired laser-induced damage [1]. Hence the proper selection of a material to use it as a protective device are critically required to safeguard delicate optical components from laser induced damage. Such protective devices are called as optical power limiters which can be demonstrated by nonlinear optical (NLO) refraction and nonlinear optical absorption through interaction of intense laser beams in the nonlinear medium. A large number of nanostructured materials have shown to possess farfetched NLO properties, which motivates the design and fabrication of photonic devices. Metal tungstates with formula MWO_4 are technologically important inorganic materials which have been attracting attention from researchers owing to their interesting size and structure dependent optical and electronic properties [2,3]. These materials have found applications in scintillation counters, lasers and optical fibers [4,5]. As a self-activating phosphor, tungstate has some advantages such as high average refractive index and high chemical stability. Among the various mixed metal tungstates, Nickel tungstate is one of the important inorganic materials has many advantages such as low cost and environmental friendliness. Recently, $NiWO_4$ nanoparticles have received much attention because of their large surface area and remarkable quantum size effect. It is well known that optical behavior is particle size dependent and can be tailored by anchoring with suitable metal dopants. The doping of magnetic ions plays a role in controlling their optical properties: (i) the band gap of the compound varies with the concentration of magnetic ions, (ii) the 3d levels of transition-metal ions are located in the band gap and thus d–d transitions alter the spectral characteristics. Materials possessing d and f-electrons have paid much attention for various optical applications. Rare earth metal ions can offer the f-electron, the peripheral 4f electrons are localized, and exchange interactions among 5d or 6s conduction electrons are indirect, and have high orbital momentum [6]. Functionalization with such metal ions changes the optical character of the host material. The most important significance of this functionalization is that these materials offer the tunability of optical bandgap through the

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variation in the concentration of induced defect states leading to the display of unique optical properties.

Crystals containing Mo^{6+} or W^{6+} and cations with non-bonded electron pairs have shown to exhibit interesting second order NLO properties [7–10]. Studies on Two-photon interband absorption in $PbWO_4$ crystals with a scheelite structure and $ZnWO_4$ crystal with a wolframite structure reported that 2PA-induced one-photon absorption is characteristic of tungstate crystals [11]. Different methods have been reported to synthesis $NiWO_4$ nanoparticles with different morphologies. These proposed methods including conventional ceramic method, polymeric precursor method, hydrothermal and precipitation technique [12–15]. Among them chemical precipitation method is most widely used due to their adequate synthetic conditions and cost effective for large scale production. In the present work, we report a systematic study on the effect of both the size and the doping on structural and nonlinear optical properties of Gd-doped $NiWO_4$ nanoparticles synthesized by a simple chemical precipitation method. The third-order NLO properties of the nanostructures were studied using the closed and open aperture z-scan technique with continuous wave laser at 532 nm. The prepared nanostructures exhibited superior NLO properties, making them potential candidates for optical switching applications in continuous wave domain.

2. Experimental section

2.1. Synthesis procedure

Briefly, special grade Nickel II Acetate (Alfa Aaser), Gadolinium III acetate were purchased from Alfa Aaser (99.9%) and used as received without further purification. 0.2 M of Nickel II acetate in double distilled water was prepared. To this, various amount of Gd^{3+}cation solution (1%, 3% and 5%) was mixed under stirring. 0.2 M of disodium Tungstate (Merck) was dissolved in double distilled water separately under constant stirring. As prepared Ni^{2+}/Gd^{3+}mixed metal-ion solution was added dropwise to tungstate solution rapidly and 0.1 M of semisolid polyethylene glycol (PEG-mw 1000) was added to the above mixture as a surfactant. After 3 h stirring followed by 15 h aging, the end product was separated by centrifugation and washed thoroughly with deionized water, ethanol and acetone consecutively. In continuation to drying at ambient temperature for 24 h, the powder was calcined at 500 °C for 6 h in air. For comparison pure $NiWO_4$ nanostructure, also synthesized using the same procedure without the addition of Gd3+cation solution.

3. Results and discussion

3.1. Diffuse reflectance UV–visible spectroscopy

The absorption spectra of the Gd doped $NiWO_4$ nanoparticles are shown in Fig. 1. All the samples show excellent absorption behavior in the UV region with a maximum absorption occurred in the region of 300–400 nm and shoulder peaks at 450 nm. The result reveals that $NiWO_4$ nanostructures have good light absorption properties not only in the UV region but also in the visible light wavelengths The absorption peak appear at UV region is mainly due to excitation from O_{2p} to Wt_{2g} in the ($WO4^{2-}$) group. In the excited state of $WO4^{2-}$group, the hole (on the oxygen) and the electron (on the tungstate) remain together as an exciton because of their strong interaction. The absorption bands at 300–400 nm is attributed to the charge transfer transition in the WO_6 matrix. Bands at 450 nm are assigned to the forbidden electronic transition from $^3A_{2g}$ to ^1E_g and $^1T_{2g}$, respectively [16]. The main absorption band for the samples in the region of 250–350 nm confirms small

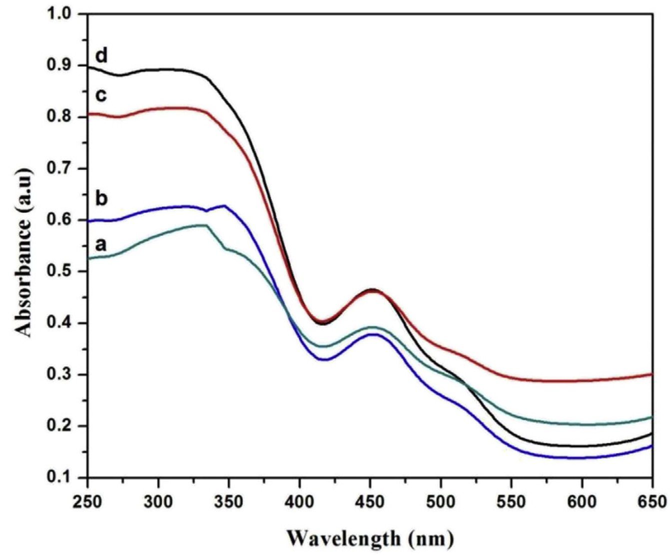

Fig. 1. UV–visible absorption of Gd doped $NiWO_4$ nanoparticles (a)pure (b) 1% (c)3% & (d) 5% Gd.

crystal size, which could be attributed to the strong quantum confinement of the excitonic transition for nano-structures [17].

3.2. X-ray diffraction (XRD) analysis

The phase structure and purity of the samples was investigated by XRD measurements. Fig. 2. Shows sharp diffraction peaks of the synthesized nanostructures indicating that the products are well crystallized. The diffraction peaks of $NiWO_4$ can be indexed to wolframite monoclinic structure in accordance with JCPDS file number-15-0755 [18] and having space group *P*2/*c* (13) which is characterized by altering layers of transition metal and tungstate atom parallel to the (100) plane. No peaks of impurities or other residuals were detected in pure and 1% Gd doped $NiWO_4$, revealing the high purity of the prepared $NiWO_4$. However, XRD reflections recorded for 3 and 5% Gd doped samples, a secondary impurity

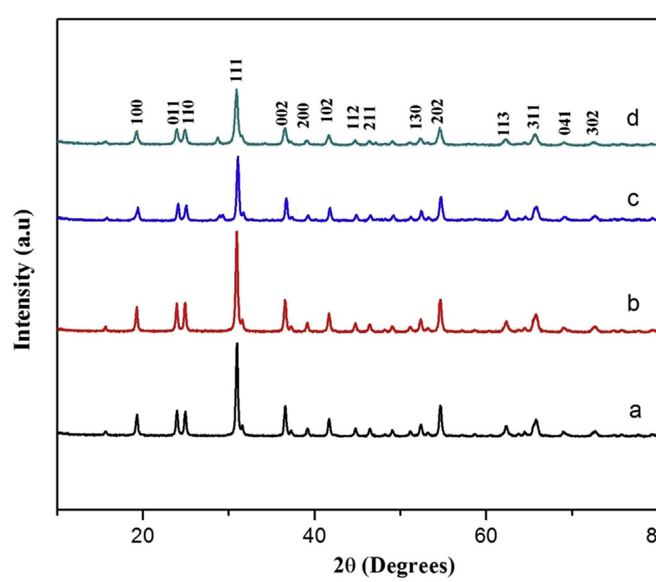

Fig. 2. XRD Pattern of Gd doped $NiWO_4$ nanoparticles (a)pure (b) 1% (c)3% & (d) 5% Gd.