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Third order nonlinearity and optical limiting behaviors of Yb:YAG nanoparticles by Z-scan technique

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HIGHLIGHTS

- First time investigation of third-order NLO of Yb:YAG nanoparticles by Z-scan method.
- Exhibit reverse-saturable absorption, optical-limiting for eye protection and sensor system.
- Giant enhancement in nonlinear refractive index ($n_2 = 8.649 \times 10^{-8}\ cm^2/W$).
- High thermo-optic coefficient ($dn/dT = 6.864 \times 10^{-6}\ K^{-1}$).
- High figure-of-merit ($n_2/2\beta\lambda = 74.50$) indicates effective optical switching application.

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ABSTRACT

The present report explores third order nonlinear optical behavior of phase pure Yb^{3+}:YAG nanoparticles for the first time by Z-scan technique. The measurement was carried out using diode pumped continuous wave (CW) Nd:YAG laser at 532 nm. The Yb:YAG nanoparticles exhibit characteristic near-infrared (NIR) emission at 1030 nm under 940 nm excitation. The nanoparticles exhibit high nonlinear refractive index ($n_2 = 8.649 \times 10^{-8}\ cm^2/W$) and low nonlinear absorption coefficient ($\beta = 0.109 \times 10^{-4}$ cm/W) giving an appreciable figure of merit (FOM) of ∼74.50. The excitation power (8.2–10.5 $W\ cm^{-2}$) dependent emission spectra were recorded to study exchange energy interaction of Yb^{3+} ions with YAG host lattice. By utilizing the nonlinear refractive index 'n_2' from Z-scan measurement, thermo-optic coefficient (dn/dt) was calculated to demonstrate Yb^{3+}:YAG nanomaterial for high power compact solid state laser gain amplifier systems.

1. Introduction

In recent decades, search for photonic materials for novel optical waveguide [1], frequency conversion, optical amplification, Q-switching, optical switching [2,3], optical computing devices based on nonlinear optical principles [4] is getting fascinated. Materials with high optical nonlinearities and superior third-order nonlinear response are essential for optical limiting and can be investigated by a simple Z-scan technique. It is the most versatile and sensitive method proposed by Sheik-Bahae et al. [5], to determine nonlinear optical (NLO) parameters such as nonlinear refractive index (n_2), nonlinear absorption coefficient (β), nonlinear optical susceptibility ($\chi^{(3)}$) and figure of merit (FOM) of photonic materials for optical limiting applications. High nonlinear optical efficiency and large magnitude of third-order nonlinear susceptibility is highly demanded for optical communication and fiber amplification applications. An efficient NLO material should possess high optical homogeneity, large nonlinear refractive index, small nonlinear absorption coefficient, large birefringence, high molecular polarizability, physico-chemical stability and high laser damage threshold [6]. A combination of these properties can be achieved generally in single crystalline materials for nonlinear optical applications [7–9]. With the advent of nanotechnology, in recent years there is widespread interest in exploring third order nonlinear optical properties in nanomaterials such as plasmonic silver and gold nanocolloids [10,11], semiconductor quantum dots [12,13], carbon nanotubes [14,15], graphene [16] and metal-oxide nanoparticles [17–20] by single beam Z-scan method. The non-linearity can be attained by two-photon absorption, multi-photon absorption and particulate induced scattering in nanomaterials. Investigation of nonlinear properties in rare earth doped nanophosphors [21,22] and ferroelectrics [23,24] are recent attraction to obtain better NLO characteristics. Ytterbium doped yttrium aluminum garnet (Yb:YAG) nanoparticles are nowadays getting

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attraction to prepare laser ceramics for compact diode pumped solid state disk laser [25]. The trivalent Yb ion possesses low-phonon energy, absence of upconversion mechanism, broad multiplet absorption and longer excited state lifetime [26,27]. The infrared lasing and second harmonic emission respectively at 1030 and 515 nm in Yb:YAG makes it a potential media to replace traditional Nd:YAG laser system. Therefore, Yb:YAG has also gained interest in the development of diode pumped mode locked femto-second (fs) oscillators [28] and in ultra-short laser generation [29] because of its superior nonlinear optical performances. The irradiance dependent nonlinear refractive index (n_2) variation with absorption wavelength is one of the significant nonlinear behaviors studied by Z-scan method in Yb based lasers. Major et al. [28] performed the Z-scan measurements on rare earth Yb doped $Ca_4GdO(BO_3)_3$, $Ca_4YO(BO_3)_3$ and $Sr_3Y(BO_3)_3$ borate crystal using Ti:Sapphire laser at the lasing wavelength of 1300 nm and observed larger nonlinear refractive index (n_2) value of about 11.4×10^{-7} cm^2/GW for Kerr-lens mode lock lasing system. Although the effect of nanosecond, picoseconds and femto-second laser interaction on third-order nonlinearity of materials for optical switching applications are of recent interest, highly efficient solid state laser developed by Geusic, Marcos, and Van Uitere [30], the most popular Nd:YAG solid state laser is still largely being used by Z-scan technique for the instant exploration of nonlinear optical properties of materials. Because it possesses high gain, narrow line width and low threshold properties which make it the most versatile laser for variety of photonic applications [31]. It can be used for exploring the nonlinear optical properties of nanomaterials [19,32–34] as continuous wave (CW) Nd:YAG laser interaction with nanoparticles can minimize thermal induced stress compared to fiber coupled ultra-short and acousto-optically modulated lasers [35]. In addition, second harmonic frequency-doubling from near infra-red (1064 nm) wavelength to visible green at 532 nm stimulates research interest to explore nonlinear optical property and optical limiting behaviors. The world's first gas laser invented by Ali Javan, Benner and Herriott, the most popular He-Ne gas laser [36] is also still largely being used by Z-scan technique for the exploration of nonlinear optical properties. Basically, Nd^{3+} and Yb^{3+} doped YAG crystals are popular in laser physics and have been largely used for laser operation in pulsed modes. In this aspect, fundamental physics of rare earth doped YAG for lasing action is well reported in literatures, but nonlinear change of refractive index and third-order nonlinearity in Yb:YAG is not addressed in the published reports. To the best of our knowledge, the nonlinear optical property of Yb:YAG nanoparticles is not investigated using Z-scan technique and its third order nonlinear refractive index and absorption coefficient is not yet determined for opto-electronic device applications. In the present work, for the first time, third-order nonlinear properties in Yb:YAG nanoparticles by single beam Z-scan experimental technique is reported. The estimated nonlinear optical parameters are higher than that achieved in other nanomaterials and therefore, Yb:YAG nanoparticles can be useful for optical limiting applications.

2. Experimental technique

The nonlinear optical properties of Yb:YAG nanoparticles with low 1.0 at% and high 5.0 at% Yb^{3+} doping concentrations were prepared by simple reverse strike co-precipitation method. High purity yttrium nitrate ($Y(NO_3)_3{\cdot}4H_2O$; Alfa Aesar, 99.99%), aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$; Alfa Aesar, 99.99%), ytterbium nitrate ($Yb(NO_3)_3{\cdot}4H_2O$; Alfa Aesar, 99.99%) and ammonium hydrogen carbonate (AHC, Alfa Aesar) were used as starting materials. Aqueous solution of metal-cations were made by dissolving yttrium nitrate and aluminum nitrate in 3:5 mol ratio with ytterbium nitrate (low 1.0 and high 5.0 at%; here after stated as Yb:YAG-1 and Yb:YAG-5) in 100 ml distilled water under stirring for 30 min. To initiate precipitation, the metal-cation precursor solution was added drop-wise at 3 ml min^{-1} into 1.5 M of aqueous ammonium hydrogen carbonate solution until the pH reaches 5–7. The resultant suspension was filtered and dried at 70 °C. The air dried powder was calcined at 900 °C in a microwave furnace for 10 min to obtain Yb:YAG nanoparticles.

2.1. Characterization techniques

Structural parameters of Yb:YAG nanoparticles at different Yb^{3+} doping concentrations were determined by powder X-ray diffractometer (XRD, GE-3003-TT) using $CuK_{\alpha1}$ radiation (λ = 1.5406 Å) at a scanning rate of 0.04° s^{-1} in 2θ range from 10° to 70°. The surface morphology, elemental composition and inter-planar spacing's of the nanopowders were examined using field emission scanning electron microscopy (FESEM, FEI QUANTA 200 FEG) and high resolution transmission electron microscopy (HR-TEM, JEM 2100 PLUS). The optical absorption, refractive index (n) and absorption coefficient (α) of the nanopowders were measured using ultra-violet visible-diffuse reflectance spectrophotometer (DRS, UV–Vis 2600). The characteristic near-infra-red emission and excitation powder dependent emission profile of Yb:YAG nanoparticles were analyzed by spectrofluorometer (JOBIN-YVON) excited at 940 nm.

3. Results and discussion

3.1. Structural and morphological studies

The stoichiometry of Yb:YAG nanoparticles were made by varying Yb^{3+} doping concentrations in order to investigate the structural and optical behavior. The Yb^{3+} ions are doped into YAG host lattice to replace Y^{3+} ions in dodecahedral site. XRD pattern (Fig. 1) of Yb:YAG-1 and Yb:YAG-5 samples microwave calcined at a temperature of 900 °C resulted in formation of YAG cubic phase (JCPDS No: 33-0040) with the space group $Ia{-}3\bar{d}$ [37]. No impurity and secondary phases such as Y_2O_3, $YAlO_3$ and Y_3AlO_4 were evolved. From powdercell structural refinement analysis, lattice constants of Yb:YAG-1 and Yb:YAG-5 samples are calculated to be 12.056 ± 0.004 Å and 12.024 ± 0.008 Å, respectively. Since, the ionic radius of Yb^{3+} ion (r = 0.985 Å for CN = 8) is smaller than Y^{3+} ion (r = 1.019 Å for CN = 8), the Yb^{3+} ions can easily substitute Y^{3+} ions in dodecahedral site of $Y_3Al_5O_{12}$ host lattice and resulted in decrement of unit cell lattice parameters [38]. The crystallite size (D) is estimated from full-width at half maximum (FWHM) of X-ray line broadening by implying Scherrer formula $D = 0.9\lambda/\beta \cos\theta$; where, λ is the wavelength of X-ray ($CuK\alpha_1$), β is the FWHM of diffraction peaks and θ is the diffraction angle. The crystallite

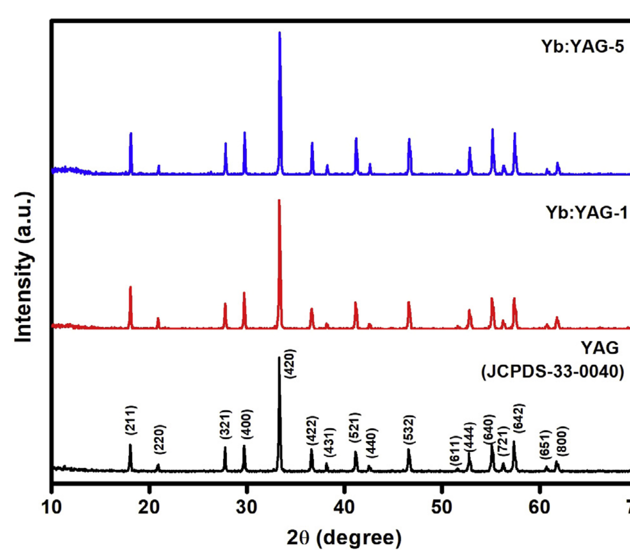

Fig. 1. XRD pattern of Yb:YAG-1 and Yb:YAG-5 nanoparticles calcined at 900 °C.