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Low power optical limiting studies of copper doped lithium tetraborate nanoparticles

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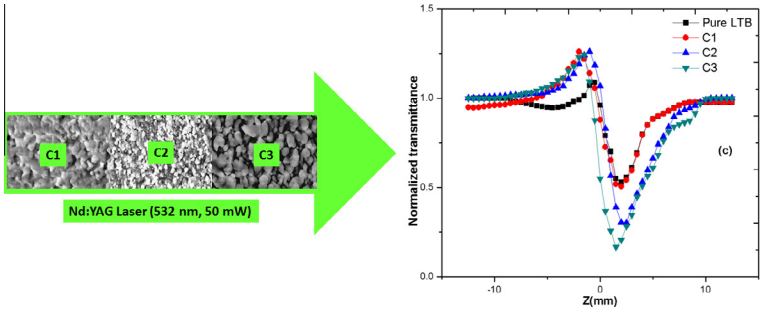
HIGHLIGHTS

- Sol–gel method was followed to prepare pure and LTB:Cu nanoparticles.
- Linear optical studies shows that the samples are transparent in visible region.
- Second harmonic generation efficiency of the samples are equivalent to KDP.
- 0.01 M LTB:Cu shows good low optical power limiting threshold.

GRAPHICAL ABSTRACT



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ABSTRACT

The copper doped lithium tetraborate (LTB:Cu) nanoparticles were synthesized by sol–gel method and characterized by XRD (tetragonal structure) and by FESEM (sphere-like nanoparticle). UV–Vis studies show that there is no strong absorption in the visible region. In the luminescence spectrum, the emission peak at 370 nm reveals the presence of Cu^{+} in LTB lattice. The relative powder second harmonic generation efficiency of pure and doped LTB is equal to the standard NLO material, KDP. The nonlinear optical parameters of LTB:Cu nanoparticles say, nonlinear refractive index, nonlinear absorption coefficient and third order nonlinear optical susceptibility were determined to be of the order of 10^{-8} cm^2/W, 10^{-2} cm/W and 10^{-5} esu, respectively. The optical power limiting behavior of the samples were studied by Z-scan technique with (532 nm, 50 mW) Nd:YAG laser and the limiting threshold values are found to be 22.7 mW for 0.01 M and 24.9 mW for 0.03 and 0.05 M LTB:Cu nanoparticles.

Introduction

Lithium tetraborate (LTB) has the basic structural unit of cradle-like B_4O_7 group which possesses the space group $I4_1cd$ and point group C_{4v}. It has a covalent═B—O—B≡ network consisting of an alternating oxygen-bonded BO_4 and BO_3 oxyanions frame and stabilized by Li^{+} ions within this network [1]. The excessive negative charge distributed over the BO_4 tetrahedrons are compensated by the closely located lithium cations [2]. Among the borates, a remarkable advantage of the title compound is its wide transparency window ranging from 160 to 6000 nm and a wide bandgap (9 eV) which provides a structural flexibility to incorporate dopants [3]. Addition of copper in lithium tetraborate lattice influences the optical properties like deeper absorption band around 240 nm with short wavelength cut-off at 200 nm [4] and shows most intense luminescence emission [5]. Minimum doping level of Cu makes LTB a scintillator for the neutron detection and can be used as a tissue-equivalent thermoluminescent dosimeter [6]. One of the fascinating applications of nonlinear optical materials

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is the optical power limiters. Such materials allow the transmitted output light intensity at very low input powers but opaque for higher incident light intensities. Any of the mechanisms such as reverse saturable absorption, excited-state absorption, free carrier absorption, multiphoton absorption, thermal defocusing, photo refraction, nonlinear refraction and induced scattering is responsible for the optical limiting behavior [7]. From the literature, optical limiting behavior in many number of inorganic clusters are due to the strong nonlinear refraction [8]. Wang et al. reported that the hollow Cu clusters exhibit high nonlinear optical susceptibility by Z-scan technique with increase in annealing temperature [9]. The role of copper concentration on the enhancement of nonlinear refractive index and optical limiting behavior was observed in the Ag–Cu nanoclusters co-doped in SiO_2 sol–gel film [10].

In the present work, copper doped lithium tetraborate nanoparticles, a nonlinear optical material, was synthesized following sol–gel method and its optical properties were investigated. Based on the nonlinear optical parameters such as nonlinear refractive index, nonlinear absorption, the material is found to be a potential candidate for optical limiting application and so the low power optical limiting property was studied extensively for different doping levels using the second harmonic of continuous wave Nd:YAG laser (1064 nm, 50 mW).

Experimental details

Preparation of Cu doped $Li_2B_4O_7$ nanoparticles

Copper doped LTB nanoparticles were prepared following sol–gel method. Lithium hydroxide monohydrate and cupric acetate were mixed in 100 ml double distilled water and stirred well to get a clear solution. Immediately the boric acid was added to the resultant solution. The ratio of lithium and boron was maintained at 1:2 with the dopant concentration of 0.01 M (Sample C1), 0.03 M (Sample C2) and 0.05 M (Sample C3). The reaction was carried out at 323 K in a water bath for 1 h. The resultant product was dried at 423 K for 1 h in a hot air oven. Then the dried samples were sintered at 773 K for one hour in a SiC furnace.

Instrumentation

PANalytical X'Pert Pro Powder X-ray Diffractometer Cu-Kα (λ = 1.5406 Å) was used for the structural analysis. Surface morphological study was carried out using field emission scanning electron microscope (FESEM-Carl Zeiss-Σigma). Using Shimadzu 1800 UV–Vis double beam spectrophotometer (200–800 nm), optical absorption was recorded by dispersing 2 mg of the sample in 5 ml of ethanol and sonicated for 20 min. The luminescence study was done using Horiba FluroMax – 4 spectrofluorometer. Second harmonic generation efficiency test was carried out using Q-switched Nd: YAG laser (1064 nm, 9 ns, 10 Hz).

Z-scan measurement

The Z-scan experiment was carried out with the second harmonics (532 nm) of a diode-pumped Nd: YAG laser with the fundamental wavelength of 1064 nm. 1 mM solution was taken in a 1 mm cuvette and the Gaussian profile laser beam was focused by a lens of focal length 3.5 cm which produced a beam waist ω_0 = 14.99 μm. The diffraction length was calculated as 1.51 mm. Here, the sample thickness L is 1 mm which is less than the diffraction length $z_0 = \pi\omega_0^2/\lambda$ (1.349 mm). Therefore, the condition, diffraction length > L was satisfied and so the sample can be considered as a thin medium. The sample experienced various incident intensities by keeping z = 0 at the focus of the lens and was translated from −20 mm to 20 mm. The corresponding output transmittance of the beam with (closed) and without (open) aperture in the far field was measured using a photodetector fed to the digital power meter.

Result and discussion

Structural and morphological analysis

From the powder X-ray diffraction pattern (Fig. 1), the lattice constants were estimated and all the major peaks were indexed for the three dopant concentrations. The cell parameters are $a = b$ = 9.49 Å, c = 10.24 Å for sample C1, $a = b$ = 9.47 Å, c = 10.27 Å for C2 and $a = b$ = 9.46 Å, c = 10.31 Å for C3 (JCPDS No. 79-0963). There is a slight variation of the cell constants from the pure sample ($a = b$ = 9.44 Å, c = 10.28 Å) which may be due to the inclusion of Cu ion into Li site. The peak broadening was observed from XRD pattern. FE-SEM image (Fig. 2) analysis shows that the nanoparticles are formed with spherical morphology and aggregate with the neighbor. The particle size of sample C1, C2 and C3 is found to be approximately 60 nm, 120 nm and 150 nm, respectively.

UV–Vis spectrum

From the UV–Vis spectra (Fig. 3), it is clear that there is no absorption in the visible region and the samples have a wide transparency window. However the material shows some absorption peaks in the spectrum till 340 nm which lies in the UV region. It is to be noted that the short wavelength cut-off for the bulk LTB is 167 nm. After the addition of Copper ion, strong absorption at 237 nm and other absorption peaks at 281, 320 nm were observed.

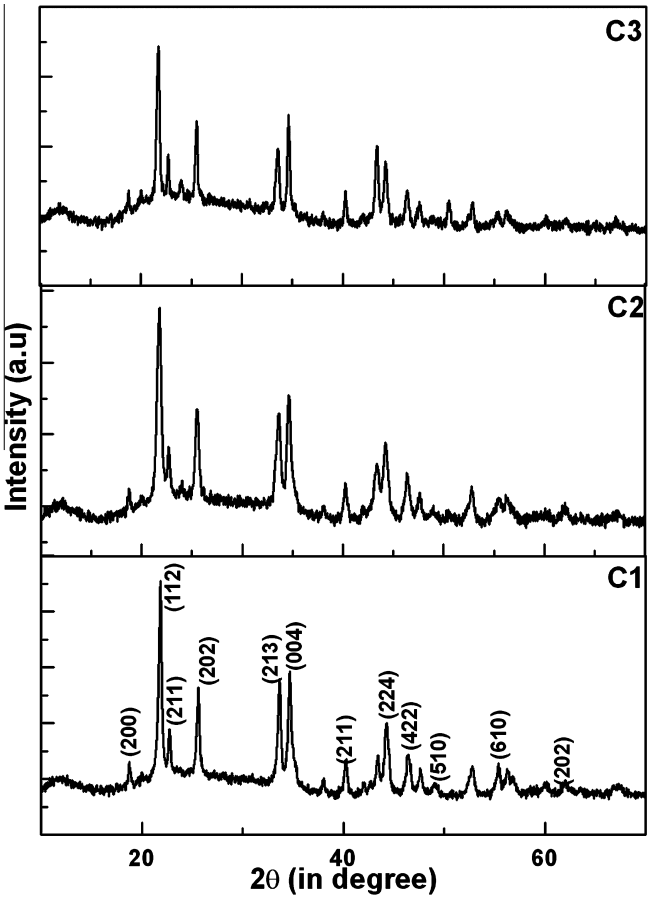

Fig. 1. Powder XRD pattern of LTB:Cu nanoparticles.