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Third order nonlinear optical properties of monoclinic and orthorhombic $CuNb_2O_6$ under CW laser illumination

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ABSTRACT

Third-order nonlinearity of monoclinic and orthorhombic phase of $CuNb_2O_6$ is studied in low power regime of 532 nm by Z-scan technique. In open aperture, monoclinic $CuNb_2O_6$ possess stronger saturable absorption due to the distorted structure arising from unequal arrangement of copper atoms. Closed aperture exposes the self-defocusing nature and orthorhombic phase exhibits stronger nonlinear refraction. Variation in third-order NLO coefficient due to change in phase and morphology of $CuNb_2O_6$ confirms the influence of sintering temperature and time. Microrod monoclinic $CuNb_2O_6$ possess maximum nonlinear absorption coefficient (6.47×10^{-3} cm/W) and pure orthorhombic $CuNb_2O_6$ attains maximum nonlinear refractive index (5.13×10^{-8} cm^2/W) along with higher third-order nonlinear optical susceptibility (1.91×10^{-6} esu). Higher thermal nonlinearity resulted in stronger optical limiting action with pure orthorhombic $CuNb_2O_6$ (5.16 mW, 1.26 mW) compared to other phases. For understanding the material suitability for laser safety device, nonlinearity and limiting action of $CuNb_2O_6$ thin films were demonstrated. Earlier formation of monoclinic phase with morphology change (700 °C) and transition of monoclinic rich mixed orthorhombic phase to pure orthorhombic phase (900 °C) with increase in sintering time (3–12 h) was confirmed by XRD, FTIR and SEM analysis. Thus orthorhombic $CuNb_2O_6$ material with stronger self-defocusing and optical limiting action makes it more preference than monoclinic $CuNb_2O_6$ for third-order NLO applications.

1. Introduction

In recent years plenty of investigations is being made on search for the novel materials with outstanding third-order nonlinear optical properties for application in laser safety devices like optical limiters. Especially with tremendous increase in the usage of continuous wave (CW) lasers, the potential of damage of optical sensors including human eyes is very high due to induced high thermal nonlinearity. This is because under CW laser treatment, the involvement of local heating is very high and thus the induced thermal nonlinearity can easily damage the photosensitive components [1]. For a material to be an excellent optical limiter it must possess distinguished characteristics like high third-order NLO coefficients and strong thermal stability [2,3]. **S**everal organic materials such as tetrathiafulvalence derivatives, porphyrin compounds, metallopthalocyanines, azo-based iminopyridine complexes and graphene systems are found to exhibit strong third-order NLO properties in pulsed laser excitation domain [4–8]. In this continuation, many works on estimating the limiting behaviour under continuous wave laser excitation was made in organic materials, the concern of thermal stability reduces its possibility to be utilized for laser safety device fabrication. Owing primarily to high stability of inorganic materials such as ZnO [9], MgO [10], CdS [11] performance of the third-order inorganic NLO materials stands high compared to those made from organic materials. Binary niobates with general formula AB_2O_6 perovskite structure are one such series of compounds that can have excellent third-order NLO applications. These systems possess metal oxygen bonds that are octahedrally packed to form a columbite structure resulting in strong spontaneous polarization and high optical nonlinearity [12]. $CuNb_2O_6$ is one of the important AB_2O_6 material that exist in two different phases namely monoclinic and orthorhombic which are made up of closely packed copper and niobium octahedral chains [13]. The crystal structure of $CuNb_2O_6$ consist of copper and niobium octahedron that are linked to each other separately to form a chain like arrangement. Further, copper octahedra share its four corners with the neighbouring four niobium octahedra. While, niobium share its four corners with two NbO_6 and two CuO_6

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octahedra. The major difference between the crystal structure of two phases is that in monoclinic phase Cu ions are arranged in a pair-wise manner and the octahedra of niobium is much distorted compared to orthorhombic phase. The distance between Cu-Cu in [1 0 0] are unequal that manifests effects on the optical properties of $CuNb_2O_6$.

Because of the noticeable properties of $CuNb_2O_6$ like high opto-electric coefficients and strong chemical and thermal stability, this class of semiconducting material yield a promising applications in solar cell devices. Beyond its excellent photovoltaic performance, recent report shows that the material exhibit interesting NLO properties due to their strong anti-photocorrosive nature and high thermal stability. Investigation on the third order nonlinear optical properties of $CuNb_2O_6$ under high-repetition rate femtosecond laser excitation exposed that microrod structured monoclinic $CuNb_2O_6$ ($\beta_{2PA} = 85 \times 10^{-10}$ m/W) exhibited high nonlinear optical absorption coefficient. Also the transition of monoclinic to orthorhombic phase suffered a transfer of two-photon (2PA) to three photon (3PA) process due to the change in available electronic states [14]. Strong limiting action with low limiting threshold (0.21 μJ/cm^2) hinted the possible utilization of $CuNb_2O_6$ for ultrafast thermal nonlinearity based laser safety devices. Impressed by the strong thermal nonlinearity in ultrafast domain, attempts were further made to study the thermal nonlinearity of $CuNb_2O_6$ under CW laser excitation. Hence this article reports the third-order NLO properties of pure monoclinic, mixed (monoclinic and orthorhombic) and pure orthorhombic phase of $CuNb_2O_6$ by Z-scan technique using continuous wave mode Nd:YAG (532, 50 mW) laser. Influence of phase and morphological arrangement of $CuNb_2O_6$ in third-order NLO performance is discussed in detail.

2. Preparation and instrumentation

Literature reveals $CuNb_2O_6$ exist in two different phases namely monoclinic and orthorhombic which can be prepared by employing solid state reaction at 700 °C and 900 °C respectively [14,15]. By adopting similar procedure, different phases of $CuNb_2O_6$ was synthesized and the detailed procedure is reported elsewhere [14,16]. The precursors copper oxide (CuO) and niobium pentoxide (Nb_2O_5) were taken in an appropriate ratio (1:1) and grinded for an hour for attaining homogeneity. The grinded portion were sintered at 700 °C and 900 °C at different time (3–12 h) to acquire monoclinic and orthorhombic phase of varying morphology respectively. To understand the influence of sintering temperature and time in NLO properties, the solid-state reaction was attempted at different sintering time of 3–12 h, insteps of 3 h. This is because, earlier report shows that sintering temperature and time play a very crucial role in achieving the desired phase and morphology of the materials. The prepared samples were indexed as A (700 °C, 3 h), B (700 °C, 6 h), C (700 °C, 9 h), D (700 °C, 12 h), E (900 °C, 3 h), F (900 °C, 6 h), G (900 °C, 9 h) and H (900 °C, 12 h) for further characterization.

Preliminary identification of different phases of copper niobate were made by recording XRD using PAN analytical X-Ray powder diffractometer. The vibrations related to metal-oxygen in the molecules was analysed by JASCO FTIR spectrophotometer in the region of 1000–400 cm^{-1}. The morphological analysis was done by FESEM studies with FEI Quanta FEG 200 scanning electron microscope. For Z-scan measurement, the samples were taken in liquid medium to ascertain the influence of morphology in NLO and also to avoid issues like thermal decomposition of sample during excitation, scattering etc.,. Here the solvent like diethylene glycol which do not show any nonlinearity is chosen as a dispersing medium and the prepared samples were dispersed by sonicating the solution for an hour. The concentration of the sample is adjusted such that all the samples show a uniform linear transmittance of ~70%. The third order NLO properties was studied by Z-scan technique using Coherent compass™ 215M-50 Nd:YAG laser (532 nm, 50 mW). Also we agree that the thermal nonlinearity is a slow process (10^{-3} s) and hence cannot be used for ultrafast photonic devices. However these materials can be used as laser safety devices which protects the photosensitive components including human eye from continuous wave laser damages. A converging lens of 3.5 cm was used to focus the laser with beam waist (ω_0) 15.84 μm and Rayleigh length ($Z_0 = \pi\omega_0^2/\lambda$) 1.48 mm. The sample kept at the Z-position was moved along the direction in a translational stage along the Gaussian beam profile through its focal plane. The intensity dependent nonlinear absorption and refraction was measured from the transmittance change using open and closed aperture experiment respectively. To study its optical limiting action, for every input power, the corresponding output power was measured.

3. Phase and morphology

Fig. 1 represents the recorded XRD pattern of the samples sintered at 700 °C (A–D) and 900 °C (E–H) for different sintering time 3(3)12 h respectively. All the peaks observed were indexed using JCPDS card No. 01-086-0348 (Monoclinic) $CuNb_2O_6$ and 00-020-0361 (Orthorhmbic) $CuNb_2O_6$. Literature reveals copper niobate crystallizes in monoclinic phase at 700 °C and orthorhombic phase at 900 °C [15]. Formation of monoclinic and orthorhombic $CuNb_2O_6$ can be confirmed by analyzing the XRD pattern in the range of $2\theta = 29–32°$. Peaks positioned at $2\theta = 29.995°$ and $2\theta = 30.542°$ are the signature peak of monoclinic phase while the peak at $2\theta = 30.326°$ corresponds to orthorhombic phase of $CuNb_2O_6$. As expected the recorded XRD pattern clearly reveals the formation of monoclinic $CuNb_2O_6$ at 700 °C with high crystallinity. At 700 °C sintering, presence of two equally intense peaks of (1 3 1) and $(\bar{1}\ 3\ 1)$ with d = 2.971 Å and 2.921 Å confirms the formation of pure monoclinic phase of copper niobate without any traces of precursors and orthorhombic phase. Here as sintering time increases at 700 °C [Fig. 1A–D], the intensity of characteristic

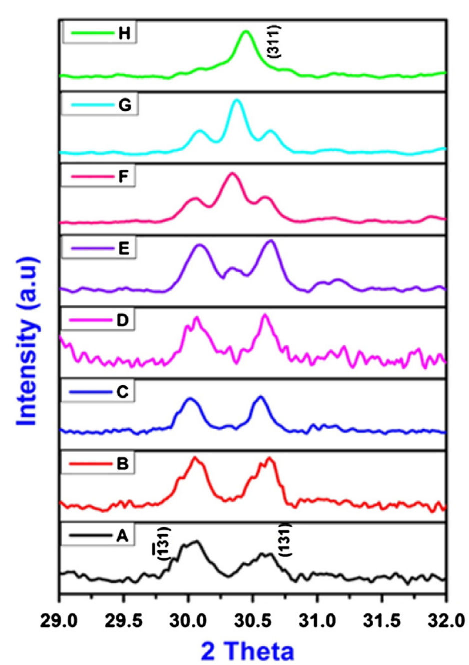

Fig. 1. Represents the XRD pattern of monoclinic (A–D), mixed (E–G) and orthorhombic (H) phase of $CuNb_2O_6$ respectively.