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Nonlinear absorption and refraction studies of truncated $CuNb_3O_8$ with high-repetition rate femtosecond pulses



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HIGHLIGHTS

- $\bullet\,$ Truncated cubic CuNb_3O_8 was grown by solid-state reaction (750 °C, 12 h).
- CuNb₃O₈ exhibit two-photon absorption with $\beta_{2PA} = 5.4 \times 10^{-10} \text{ m/W}$.
- Nonlinear refractive index arises due to self-defocusing.
- Sample demonstrated optical limiting action under NIR USP laser.
- CuNb₃O₈ shows better nonlinearity than CuNb₂O₆.

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ABSTRACT

Copper niobate with CuNb₃O₈ composition was prepared via one-step solid state reaction (750 °C, 12 h). Powder X-ray diffraction (XRD) confirmed the formation of parental CuNb₂O₆ phase with traces of CuNb₃O₈ on initial sintering (till 9 h), which was then transformed into pure CuNb₃O₈ on higher sintering (12 h). Field emission scanning electron microscope studies (FESEM) illustrates the formation of truncated cubes due to unification of layered structure upon prolonged heating. Third-order nonlinear optical properties of truncated CuNb₃O₈ was studied by Z-scan technique using Ti: Sapphire laser (800 nm, 150 fs, 80 MHz). Pure CuNb₃O₈ possessed strong nonlinear absorption (two-photon absorption coefficient of 5.3×10^{-10} m/W) and nonlinear refractive index n₂ (2.1×10^{-16} m²/W) compared to mixed copper niobate (CuNb₂O₆ - CuNb₃O₈). The third-order nonlinear optical susceptibility of CuNb₃O₈ was ~ 10^{-11} esu and was higher than the known nonlinear optical (NLO) systems such as lithium niobate and solum niobate measured at similar pulse duration. Enhancement in nonlinearity arises due to the influence of morphology and here truncated cubes with the platonic solids offer high polarizability as the charges are concentrated in the edges of the system. The truncated cube CuNb₃O₈ exhibited strong optical limiting action with a low limiting threshold ($34.6 \,\mu$ J/cm²), thus making it appealing for ultrafast optical limiter devices towards photosensitive component protection from Infrared (IR) laser damage.

1. Introduction

In recent years, attempts have been made for searching environmental friendly, cost-effective novel materials which are tailor-made for specific purpose and there has been exponential growth in research activities dealing with nanoparticles for photonic applications such as solar cells, photocatalysis, nonlinear optical (NLO) devices [1–3]. Particularly for NLO applications, inorganic layered transition metal oxides such as niobates have recently garnered huge attraction due to their unique structural arrangement and peculiar semiconducting nature [4]. As high charge and small size of the metal provides great affinity to oxygen, niobates exist in different oxidation states that results in extended oxide structure with tunable optical and electrical properties [5,6]. The structure of niobate is primarily made up of Nb-O octahedral units which are interconnected to form a chain like structure through sharing their edges and corners with neighbouring units [7]. Interestingly variation in structural factors like interlinked layers, specific space arrangement in Nb-O polyhedral and formation of mixed metal niobates alters the optical properties and provides large electro-optic coefficient [8,9]. Specifically combining copper with niobium increases

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the bond length of Cu-O and this covalent bond yields system with greater polarizability [10]. Due to the presence of copper in perovskite structure, the optical and thermal stability of copper niobate is found to be higher compared to other inorganic niobate materials such as lithium niobate, potassium niobate and sodium niobate [10-12]. Also niobium being a photo-carrier in the octahedral system, it disturbs the crystal structure leading to the improvised susceptibility value. Therefore, copper niobate (Cu_xNb_yO_z) is a multifunctional material that constitutes an important class of inorganic solids exhibiting a very wide variety of structures and optoelectronic properties [13]. Hence, attention is focused on the multi metal oxide systems of copper niobate like CuNb₂O₆, CuNbO₃, CuNb₃O₈, Cu₃Nb₂O₈ for intense laser involving photonic applications [14]. These phases of copper niobate can be broadly classified into two categories depending on the monovalent and divalent charge nature of copper present in the system. Here monovalent Cu complexes like CuNbO3 and CuNb3O8, possess completely filled d-orbitals (d₁₀) of copper (Cu⁺) while divalent Cu units like CuNb₂O₆ and Cu₃Nb₂O₈ copper (Cu²⁺) has partially filled d-orbitals (d₉). This induces a variation in the band structure of these copperniobium complex systems which is an interesting pre-requisite for nonlinear absorption. Based on this facts, the influence of crystal and morphological structure of divalent monoclinic-CuNb2O6, orthorhombic-CuNb2O6 and monovalent monoclinic-CuNbO3 on third-order NLO properties under femtosecond laser excitation was reported in detail [15-17]. In ultrafast regime, copper niobate system demonstrated superior third-order NLO properties compared to the wellknown organic and inorganic NLO systems like CNT, graphene oxide, phthalocyanine, Cu₂O and barium borate [15,16]. In the series of copper-niobium-oxygen complexes, CuNb₃O₈ is an interesting candidate due to its stronger photo-intercalation originating from the precluded metal-metal interaction due to the comparatively larger interionic (Cu-Nb) distance in the crystal structure. Also the presence of Nb-O₆ octahedra with faster charge transport properties and the shorter Cu-O distance in the Cu-O-Nb neighbour sharing zigzag chains of CuNb₃O₈ offers favourable properties like large electro-optic coefficients, high thermal stability and strong photo-stability than other copper niobates. So in continuation of the third-order NLO investigation on copper niobates using high-repetition ultrafast IR laser excitation (Ti: Sapphire laser (800 nm, 150 fs, 80 MHz), the objective of the present work was framed to study the influence of stronger photo-intercalation upon optical nonlinearity of other phase of copper niobate, CuNb₃O₈. Apart from the role of crystal structure, it is to be mentioned that the nonlinear optical properties under high repetition rate and short pulse are tactful to the structure and morphology of the material. Experimental evidence demonstrates that polyhedron system provides better nonlinear optical property because of its high charge transferring ability from its edges. Particularly cubes are of specific interest in studying its third-order nonlinearity because their edges can yield a strong nonlinearity. Thus it is expected that CuNb₃O₈ with cubic morphology having large number of edges is expected to provide high third-order nonlinear optical properties in the IR regime. So this article reports the influence of composition and morphology in altering the NLO properties and the probability of using truncated cubic CuNb₃O₈ as an optical limiter for sensor protecting device in the ultrashort pulse laser in detail.

2. Experimental details

Literature reveals that $CuNb_3O_8$ is made up of Cu_3O_8 units which combine themselves to form as copper-oxygen chains and here the niobium atom are sandwiched between the Cu-O layers. Thus the formation of desired composition requires a deficiency in copper and rich supply of niobium and oxygen. So in the preparation of $CuNb_3O_8$, onestep solid state reaction was adopted where the starting materials Cu_2O and Nb_2O_5 (as purchased from Sigma Aldrich) were taken in the ratio of 1:3 ratio. Based on the literature [18] the grinded chemicals were sintered at 750 °C to acquire pure phase of CuNb₃O₈ and sintering was maintained at different time 3-12 h in step of 3 h for achieving different morphology. During the solid-state reaction, Cu and Nb ions were formed from Cu₂O and Nb₂O₅ and they combine themselves in the presence of oxygen to form as CuNb₃O₈. As prepared powders appeared vellow-green colour and were indexed as A1 (3 h), A2 (6 h), A3 (9 h) and A4 (12 h) respectively. The crystallite phase of the material was characterized by XRD measurements using PAN analytical X-Ray powder diffractometer. The surface morphotypes and texture of the samples were studied by Field Emission Scanning Electron Microscope (FESEM) and the elemental composition of the product was analysed from Energy Dispersive Spectroscopy (EDS) using FEI Quanta FEG 200 scanning electron microscope. The linear optical absorption and emission properties were studied by Lamda UV-Visible spectrophotometer and by Jasco FP-8000 spectrofluorometer for the sample dispersed in diethylene glycol. Third-order nonlinear optical properties of the sample were studied by performing Z-scan experiment under ultrashort pulse excitation (mode locked Ti: Sapphire laser-800 nm, 150 fs, 80 MHz). Earlier the samples were sonicated for half-an hour in diethylene glycol for clear dispersion and maintaining the attained morphology. Since the linear transmittance plays an important role in Zscan experiments, all the samples were maintained at a uniform linear transmission of \sim 70% so as to compare the NLO properties of different samples studied. The solution was transferred to 1-mm cuvette and all the Z-scan experiments were performed at low concentrations to avoid any thermal induced scattering. The cuvette, kept at Z-position in a translational stage, was translated along the Z-direction (-Z to + Z) where the light falling on each position was noted using the detector. Nonlinear absorption and nonlinear refraction were studied by the open and closed aperture Z-scan techniques, respectively. In all the Z-scan experiments the input pulses were focused using a 100-mm convex lens providing a beam waist (ω_o) of ~25 µm, corresponding to a Rayleigh range of ~ 2.54 mm.

3. Results and discussion

The recorded XRD patterns of the powders at 750 °C for various sintering time are illustrated in Fig. 1(a). The obtained peaks were indexed and found to be matching with the monoclinic CuNb₂O₆ (JCPDS No. 83-0369) [19] and monoclinic CuNb₃O₈ (JCPDS No. 71-1927) [20]. Literature clearly exposes that two equally intense peaks (131) and $(\overline{1}31)$ represents the characteristic peak of monoclinic CuNb₂O₆ which appears at $2\theta = 29.995^{\circ}$ and 30.542° [14] while for monoclinic $CuNb_3O_8$ the characterization peak shifts to $2\theta = 30.632^{\circ}$ and 30.928° [20] which corresponds to (410) and (202) plane. The 20 value varying from 29° to 32° of the recorded XRD, it can be clearly seen that the samples remained as m-CuNb₂O₆ till 9 h due to the presence of (131) and (131) planes and it transforms as m- CuNb₃O₈ at 12 h which is evident from the observation of (410) and (202) plane. It is to be admitted that the characteristic peak position of m-CuNb₂O₆ at $2\theta = 29.995^{\circ}$ and $2\theta = 30.542^{\circ}$ slowly shifts towards the characteristic peak positions of m-CuNb₃O₈ at $2\theta = 30.251$ and $2\theta = 30.753$. This confirms the presence of traces of m-CuNb₃O₈ at lower sintering time. As sintering time is increased, the dominance of m-CuNb₃O₈ proportionately increases and m-CuNb₂O₆ got suppressed. We believe that the production of the transition from crystal structure of m-CuNb₂O₆ (parental structure) to m-CuNb₃O₈ (superstructure) could be due to thermal expansion arising from higher sintering time [21]. Also thermal expansion coefficient of copper niobate is found to be in the range of 5- 10×10^{-6} /°C which induces a strong thermal expansion upon prolonged heating [22]. It is well-known that, ceramic material possess low thermal expansion co-efficient compared to that of metals due to its stronger bond strength between the atoms. In the present case prolonged imposition of the temperature on the material had made the system to get expanded resulting in the transition of m- CuNb₂O₆ in to m- CuNb₃O₈. Upon prolonged heating of the material, coalescence



Fig. 1. (a) XRD pattern (b) FESEM image copper niobate sintered at different times (A1)-3 h, (A2)-6 h, (A3)-9 h and (A4)-12 h, respectively. A schematic is also presented explaining the formation of truncated cubes from agglomerated clusters.

process occurs (thermal diffusion) between the grain boundaries which results in the change in the d-spacing value of the material [23]. $CuNb_3O_8$ is a superstructure of the parent compound $CuNb_2O_6$ and several shifts in the interatomic distances of Cu, Nb and O occurs due to Cu-deficiency resulting in the formation of $CuNb_3O_8$. Crystal structure of the $CuNb_3O_8$ system consists of distorted Nb-O₆ octahedral layers sharing corners with neighbouring octahedra. The Cu^{2+} ions are interleaved in between the distorted system of niobium octahedra and these two octahedral chains link to form a dense interconnected cage like structure. The recorded EDS spectrum (as given in supplementary data, Fig. S1) in the selected area exposes the formation of $CuNb_2O_6$ (3 h) and $CuNb_3O_8$ (12 h). The pattern confirms the purity of the synthesized materials through the presence of fundamental elements (Cu, Nb and O) alone. Here the estimated elemental composition of the

CuNb₂O₆ and CuNb₃O₈ was Cu-12%, Nb-51%, O-24% and Cu-8%, Nb-68%, O-18%, respectively, which matches well with the predicted theoretical composition. The loss in copper composition further ascertains the change in molecular composition with rise in sintering time. It is evident from the literature [24] that the copper deficiency is encountered in CuNb₃O₈ and a similar reduction is observed in the weight % of copper in pure CuNb₃O₈ sintered at 12 h. The lattice constant of $CuNb_2O_6$ was found to be a = 5.01 Å, b = 14.17 Å, c = 5.76 Å and $CuNb_3O_8$ is a = 15.36 Å, b = 5.07 Å, c = 7.53 Å. Although both the systems belong to monoclinic, crystal packing density of CuNb₃O₈ is higher than CuNb₂O₆. The morphological features and involved growth mechanism in the prepared powders were represented in Fig. 1(b). At initial sintering of 3 h the prepared sample forms an agglomerated or densely packed cluster like structure through interconnection of nanoparticles with lots of junctions formed due to densification. And after further increase in the time to 6 h the nanoparticles fused together connecting one-by-one to form almost uniform layered cluster structure with pores like morphology [23].

On increasing the sintering time to 9 h, a breakage in the bond with a formation of unified structure was observed. On further increase in the sintering time to 12 h not only led to the formation of new crystalline structure but also resulted in the formation of unified truncated cubic like structure. The average width of the truncated cubic structure is almost 150 nm. Similar formation of octahedral cubes is also observed for Cu₂O [25]. This interesting structural arrangement of CuNb₃O₈ makes them a potential material in the nonlinear optical and electro-optic applications [14].

3.1. Linear and nonlinear absorption studies

The linear optical properties of copper niobate arise mainly from the completely filled d-orbitals of copper and empty d-orbitals of niobium. Literature reveals that broad absorption in the visible region arises due to the charge transfer from copper to niobium [16]. Here, it is to be noted that the linear absorption and emission behaviour do not alter much with increase in sintering time as the band gap of CuNb₂O₆ and CuNb₃O₈ is almost same. As expected both mixed and pure CuNb₃O₈ samples shows a broad absorption throughout the UV and visible region. The absorption maximum of pure CuNb3O8 was observed near $255\,\text{nm},$ which is blue shifted when compared to mixed $(\text{CuNb}_2\text{O}_6\text{-}$ CuNb₃O₈) phases. From the absorption edge represented in Fig. 2 (left) the optical band gap of pure $CuNb_3O_8$ is estimated to be ~3.88 eV. Fig. 2 (right) illustrates the emission spectrum of CuNb₃O₈ in which the blue emission peak observed near 430 nm (2.89 eV) is attributed to distorted octahedral charge transfer from the central niobium to oxygen ligand which is commonly observed in octahedral complexes [25]. The peak near 560 nm (2.21 eV) is due to defects related to copper vacancy. The smaller peaks in the vicinity of 650 nm (1.91 eV) are possibly due to the oxygen defects involved in the extrinsic niobate groups. A similar kind of emission was encountered in the zinc and manganese niobate system [26,27]. The predominant reason for the copper and oxygen

vacancies in the copper-niobium-oxygen system is rapid calcination and elemental composition. Here, as the crystal structure of $CuNb_3O_8$ deviates from its parental structural of $CuNb_2O_6$ the distance between the copper and niobium octahedral suffers change that results in copper and oxygen defects.

The nonlinear absorption of the material was studied using open aperture Z-scan experiments wherein the transmitted beam is detected as a whole without any aperture in front of the detector. Under ultrashort laser excitation, the nonlinearity in the material can arises due to any one of the mechanism like saturable absorption (SA), reverse saturable absorption (RSA), two-photon absorption (2PA), three-photon absorption (3PA), excited state absorption (ESA) etc. In this case the interaction of laser with the material provides a valley pattern i.e., the transmittance of the sample slowly gets decreased towards the focal point. This confirms the presence of nonlinear absorption in the samples and the observed nonlinear absorption arises due to reverse saturable absorption process. It can also be clearly witnessed that as sintering time increases, the depth of the valley also increases emphasising the enhancement of nonlinear absorption i.e., truncated cube structured CuNb₃O₈ possess stronger nonlinear absorption than mixed phase (CuNb₂O₆-CuNb₃O₈). While performing Z-scan experiment in liquid media, it is important to understand the NLO contribution of solvent. This is because solvents like CS2 and toluene itself show high nonlinear absorption coefficient ($\sim 10^{-15}$ m/W) [28]. Therefore, an open aperture pattern was also recorded for diethylene glycol and the solvent did not exhibit any nonlinear pattern, confirming the solvent contribution was negligible. Therefore, the observed nonlinear absorption is purely because of the solute (copper niobate) and the solvent (diethylene glycol) plays the role of dispersing agent only. It is to be mentioned that the thermo-optic coefficient of chosen dispersing agent diethylene glycol is $\sim 10^{-4} \text{ K}^{-1}$ which is found to be comparable with solvents like water, ethanol and acetone. However, NLO contributing solvents such as CS₂ and toluene possess high thermo-optic coefficient compared to diethylene glycol and thus display nonlinearity. As the present work aims at studying the nonlinearity of copper niobate with various morphologies, extreme care was taken in choosing the solvent for dispersion.

Fig. 3 depicts the recorded experimental data as circular points and the solid lines represent the theoretical fit. The normalized transmittance of the recorded data was fitted using the relation [29],

$$T_{nPA} = \frac{1}{\left[1 + (n-1)a_n L\left(\frac{I_o}{1 + \left(\frac{z}{z_o}\right)^2}\right)^{n-1}\right]^{\frac{1}{n-1}}}$$

where α_n is the nonlinear absorption co-efficient with n = 2, 3 for twophoton absorption and three-photon absorption (2PA and 3PA) respectively, L is the effective thickness of the sample, Z is sample position $Z_0 = \pi \omega_o^2 / \lambda$ is Rayleigh length and I_o is the input intensity of the laser at focus. The experimental data was fitted for both two and three



Fig. 2. Absorption (left) and emission spectra (right) of (A4)-CuNb₃O₈.



Fig. 3. Open aperture pattern of 3, 6, 9 h (A1-A3) (CuNb₂O₆- CuNb₃O₈) and 12 h (A4) (CuNb₃O₈) sintered samples. Open circles are the experimental points while the solid lines are theoretical fits.

photon absorption process and is found to be best fitting for 2PA.

The existence of nonlinear absorption can be further claimed to be 2PA, as the excitation photons energy (800 nm, 1.55 eV) is less than the half of the bandgap of the material (3.88 eV) favours 2PA [30,31]. The possible electronic transition responsible for 2PA can be explained with the energy level diagram provided in Fig. 4. Under 800 nm (1.55 eV) laser excitation, an electron in the ground state absorb two photons either simultaneously or sequentially to excite themselves to virtual higher state (400 nm, 3.1 eV). And from the excited state, they release the excess of energy as non-radiative process and moves to blue emission state (430 nm, 2.89 eV) arising from distorted octahedral charge transfer. As Z-scan cannot exactly distinguish genuine and sequential 2PA, the observed nonlinear absorption is claimed to be effective 2PA. The electrons are typically short-lived in the intermediate state and there is very little scope for excited state absorption (since the pulse duration is ~150 fs), though it cannot be completely ruled out. Furthermore, it is to be taken account that thermal contribution in the nonlinear absorption is more compared to electronic transition due to the high repetition rate of fs laser excitation source. The estimated nonlinear absorption coefficient β obtained from the fit is given in Table 1. The value of the nonlinear absorption coefficient increases eventually as sintering time increases. The change in phase to CuNb₃O₈ and morphology to truncated cubic structure influenced the change in



Fig. 4. Energy level diagram of the 2PA process in ${\rm CuNb_3O_8}$ under femtosecond laser excitation.

nonlinear absorption of the material. This is because in cubes the heat transfer from the samples to solvents will be higher which in turn increase the bubble growth in solvents resulting in higher nonlinearity [32]. The nonlinear absorption coefficient of $CuNb_3O_8$ is 5.4×10^{-10} m/W, which is higher compared to orthorhombic- $CuNb_2O_6$ and monoclinic- $CuNbO_3$ which were in the order of 10^{-12} m/W. The values are also comparable with the well-known system like LiNbO₃ (1.25×10^{-10} m/W) [33], CdFe₂O₃ (9.3×10^{-12} m/W), CdFe₂O₃-rGO (3.8×10^{-12} m/W) [34], selenium/polypyrrole nano-composite (0.2303 cm/GW) [35], Ag nanocubes (2.2 cm/GW) [36] which were investigated under similar experimental condition.

3.2. Nonlinear refraction studies

The nonlinear refractive index (n₂) of the samples was extracted from the closed aperture Z-scan experiment by keeping the aperture infront of the detector. The closed aperture was performed with the low peak intensities and the obtained nonlinear transmittance was divided by open aperture data to avoid the contribution of nonlinear absorption. Fig. 5 illustrates the recorded closed aperture behaviour of the samples. The medium shows negative nonlinear refraction with defocusing effect due to the intense pump beam and change in the nonlinear refraction arises due to the contribution from the solute [37]. All the samples exhibit peak-valley pattern which indicates the negative nonlinearity that associates to self-defocusing nature of the material. Earlier reports on copper niobate [15-17] also shows that both m-CuNb₂O₆ and O-CuNb₂O₆ exhibit self-defocusing nature (except micro-rods of m-CuNb₂O₆) under IR ultrashort pulse excitation. These self-actions in the nonlinear refraction are highly dependent on the nonlinear polarization induced by the femtosecond laser beam because of the thermal contribution [38]. The experiment was carried out in the femtosecond regime with the high repetition rate and hence the thermal contribution will be higher in deciding the type of nonlinear refraction in the material. When the repetition rate is greater than kilohertz, the sample will not return to the equilibrium temperature in the time between the pulses and this temperature effects are due to continuous or cumulative heating which causes higher effects in nonlinear refractive index greater than the acoustic effects [39]. In Fig. 3, the experimental data is represented as circle and the theoretical fit is given as solid lines were extracted using the below equation [40,41].

Table 1 Summary of the third-order NLO co-efficient of the $CuNb_3O_8$.

Sample	$\beta \times 10^{-10} \text{ (m/W)}$	$n_2 \times 10^{-16} \ \text{(m}^2\text{/W)}$	Im $[\chi\ ^{(3)}]\times 10^{-19}\ (m^2/V^2)$	Re $[\chi\ ^{(3)}]\times 10^{-19}\ (m^2/V^2)$	$[\chi\ ^{(3)}]\times 10^{-18}\ (m^2/V^2)$	Onset Limiting Threshold (μ J/cm ²)
A1	2.4	1.41	1.06	9.73	0.97	77.25
A2	3.1	1.45	1.36	10.03	1.01	88.45
A3	3.3	1.58	1.45	10.92	1.09	39.06
A4	5.4	2.15	2.37	14.83	1.48	34.60

$$T_{CA=1\pm} \frac{4\Delta \Phi\left(\frac{z}{z_o}\right)}{\left[1+\left(\frac{z}{z_o}\right)^2\right]\left[9+\left(\frac{z}{z_o}\right)^2\right]}$$

Where $\Delta \phi$ is the change in phase of the laser beam after interaction with the material. After fitting the experimental data, $\Delta \phi$ value were acquired from the fit for all the cases and it is ensured to be less than π . Numerical calculations shows that the relation is accurate within 3% for the above condition. The nonlinear refractive index was extracted using the relation $n_2 = \Delta \phi / 2\pi L I_0$ and the estimated values are summarized in Table 1. The nonlinear refractive index of pure CuNb₃O₈ is found to be higher than mixed (CuNb₂O₆- CuNb₃O₈) phase. Enhancement in truncated cubic CuNb₃O₈ can be attributed to the peculiar distorted octahedral along with the morphological structure. The nonlinear refractive index is in the order of 10⁻¹⁶ m²/W and comparable with the eminent NLO systems like β-BaB₂O₄ [42], graphene oxide [43], phthalocyanine film [44], ZnO/CTAB composite nanoparticles [45].

3.3. Third-order NLO susceptibility

The third order NLO susceptibilities (χ ⁽³⁾) of the samples were calculated using nonlinear refractive index and nonlinear absorption co-efficient [46].

$$Im [\chi^{(3)}] = 10^{-2} \frac{\varepsilon_0 n_0^2 c^2 \lambda}{4\pi^2} \beta (cm/W)$$
$$Re [\chi^{(3)}] = 10^{-4} \frac{\varepsilon_0 c^2 n_0^2}{\pi} n_2 (cm^2/W)$$

Here Re $[\chi(3)]$ values are found to be higher than Im $[\chi(3)]$ indicating the nonlinear refraction dominance in the observed nonlinearity than nonlinear absorption. Dominance of nonlinear refraction is expected, as the high repetition rate (80 MHz) involved in the experiment contributes thermal nonlinearity that induces thermal lensing behaviour in the sample. As discussed in earlier reports [17], high repetition rate lasers have plenty of applications in the field of nonlinear optics, material processing and in synthesis of frequency comb etc., because of its high gain coefficient, excellent heat dissipation and robust mode confinement. When excited using ultrashort pulses with high repetition rate the contribution to the overall nonlinearity is predominantly mainly thermo-optic in origin. This thermal nonlinearity is due to high repetition rate laser excitation, which induces dominant nonlinear refraction behaviour (Re $[\gamma(3)] > \text{Im} [\gamma(3)]$). The estimated third-order nonlinear susceptibility is provided in Table 1. As expected $\chi^{(3)}$ is found to be higher for pure CuNb₃O₈ than its mixed phases. The higher nonlinearity arises due to the structural coordination in the octahedral systems like niobates, tantalates and vandalates. The metaloxygen bonds lengths play key role in deciding the nonlinearity of the material [47]. As was discussed in our previous works [17] intrinsic defects in the Nb-O octahedral due to the arrangement of Nb atom in the crystal structure disturbs the nonlinear optical susceptibility which probably leads to the improvement in the susceptibility value. The observed optical nonlinearity in the niobate based systems frequently is driven by the polarizability of octahedron system of the distorted niobium [47]. The value of nonlinearity of the system is around 10^{-11} esu and the variation is mainly because of the two factors i) Change in phase of the system and ii) Change in morphological structure of the system due to sintering time. The third-order nonlinear optical susceptibility of truncated cubes were found to be higher compared than well-known NLO systems like $CS_2 (10^{-22} m^2/V^2)$ [48], CdS $(10^{-18} m^2/V^2)$ [48], CdS (10^{-18} m^2/V^2) [48], CdS (10^{-18} m^2/V^2) [48], CdS (10^{-18} m^2/V^2) [48], CdS (10^{-18} m^2/V^2) V^2) [49], Cu₂O (10⁻²⁷m²/V²) [50], β-BaB₂O₄ (10⁻²²m²/V²) [51] studied at similar experimental conditions. Earlier reports demonstrate that copper niobate possesses high thermal conductivity (2W/m.K)



Fig. 5. Closed aperture pattern of 3, 6, 9 h (A1-A4) (CuNb₂O₆- CuNb₃O₈) and 12 h (A4) (CuNb₃O₈) sintered sample. Open circles are the experimental points while the solid lines are theoretical fits.

than many of the known semiconducting systems such as CuO (0.1552W/mK), Nb₂O₅ (1 W/mK) and ZnO (1 W/mK) which in turn high nonlinearity [22,52–54]. Also the presence of niobium which acts as photo-carrier in octahedral system and the edges of cubical morphology contributes to the high nonlinear optical susceptibility of CuNb₃O₈. The values of NLO coefficients presented in this work have an error of \pm 10% mainly due to uncertainties in the estimation of beam waist at focus, input laser fluctuations, fitting errors etc.

3.4. Optical limiting

Lower thermal and mechanical stresses combined with high spatial resolution resulted in topical attraction towards the ultrashort pulsed lasers in the fields of medicine, industry and micromachining when compared to the CW lasers. Therefore, increased demand for the production of the femtosecond lasers with high energy density leads to higher risks of handling these sensitive ultrashort pulse lasers. To address the potential safety issue the scientific community is working on the smart materials that can be used as an optical limiter to secure the photosensitive components. The limiting action of copper niobate in the femtosecond regime was investigated. The optical limiting action of the material was derived from the open aperture pattern. For every position, the laser fluence was calculated from the equation $F(z) = 4\sqrt{In2} \left(\frac{E_{in}}{\pi^{3/2} \cdot \omega(z)^2}\right)$ where E_{in} is the input energy of the laser [55]. Fig. 6 is the optical limiting pattern of copper niobate extracted from the OA drawn between the normalized transmittance and the input fluence. The point of deviation from linearity proportional to the input fluence beyond certain point is the onset limiting threshold. All the four prepared copper niobate samples demonstrated a strong limiting behaviour with a sound variation in the limiting threshold $(77.25-34.6 \,\mu\text{J/cm}^2)$. In the present case, the sample exhibited twophoton absorption behaviour and self-defocusing nature which are the prime responsible for the limiting action. The well-known materials like Olevlamine-Capped Gold Nanoparticles (26.0 J/cm²) [56], Ag-PVA (0.19 J/cm²) [57], CuNbO₃ (47.49 µJ/cm²) [17], Magnesium ferrite (1 J/cm²) [58], BFO-NaNbO₃ (1.9 J/cm²) [59], ZnO TF (128 µJ/cm²) [60], ZnSe/PVP (0.048 J/m²) [61] shows higher limiting value than the

Table 2Comparison of NLO coefficients of the known NLO systems.

Sample	$\beta \times 10^{-10}\text{m/W}$	$n_2 \times 10^{-16}m^2/W$	$\begin{array}{l} \chi {}^{(3)} \times 10^{-18} \\ m^2 / V^2 \end{array}$
CuNb ₃ O ₈	5.4	2.15	1.48
M-CuNb ₂ O ₆ [15]	85.0	-	9.35
M-CuNb ₂ O ₆ /O- CuNb ₂ O ₆ [16]	0.004	0.0023	0.1
M-CuNbO ₃ [17]	0.02	0.32	0.21
Phthalocyanine film [43]	1.5	0.23	0.29
CdFe ₂ O ₃ [33]	0.09	6.77	0.004
CdFe ₂ O ₃ -rGO [33]	0.11	1.49	0.133
Selenium/polypyrrole [34]	0.0023	-	-
Au nanocube [35]	0.024	-	-
β-BaB ₂ O ₄ [41]	-	0.13	-
Graphene oxide [42]	0.12	0.15	0.0007
ZnFe ₂ O ₃ [42]	0.05	0.03	0.00001
ZnO/CTAB [44]	0.05	5.2	0.53
BaMgF ₄ [62]	-	0.025	0.17
Cu ₂ O [63]	0.066	5.00	-

present samples that are examined under similar experimental condition. Thus, CuNb_3O_8 with low limiting threshold (34.6 μ J/cm²) can be preferred as a better optical limiter in the IR regime. Also, the limiting capacity in microjoule scale makes the material interesting candidate for biomedical application like target drug delivery and photo-cancer therapy.

Thus, it is evident that the nonlinearity of the material slowly increases as the prepared samples move towards the pure CuNb_3O_8 from mixed (CuNb_2O_6 - CuNb_3O_8) phase. Literature reveals that platonic solids with large number of edges (cube-12) probably increase the polarizability of the material as the charges are concentrated in the edges of the system. Table 2 presents the NLO coefficients of some of the well-known third order NLO materials investigated under similar experimental condition (800 nm, ~100 fs, ~80 MHz). It can be clearly witnessed that third order NLO coefficients of CuNb_3O_8 are superior to other super structures of copper niobate like mixed-CuNb_2O_6



Fig. 6. Optical limiting behaviour of the copper niobate, mixed CuNb₂O₆-CuNb₃O₈ (A1-A3) and pure CuNb₃O₈ (A4). Open circles are the experimental points while the solid lines are theoretical fits.

(monoclinic and orthorhombic), monoclinic-CuNbO₃. However, NLO coefficients of CuNb₃O₈ are smaller in magnitude than parental structure CuNb₂O₆. It is worthy to be noted that the nonlinear refractive index and nonlinear optical susceptibility of CuNb₃O₈ are higher than already reported ultrashort pulse optical limiters. Therefore, truncated cubes of CuNb₃O₈ with high NLO coefficients and low limiting threshold can be proposed to be an efficient limiter that provides safety from damages induced by high energy IR lasers.

4. Conclusions

A comparative study on the nonlinear optical absorption, nonlinear refraction and limiting behaviour of mixed and pure phase of CuNb₃O₈ was made. Sintering time transformed the crystal structure from parent CuNb₂O₆ into CuNb₃O₈ which was confirmed from the shift in characteristic XRD peak. Morphotypes of the copper niobate turns from agglomerated clusters into most preferential truncated cubes due to densification process. The observed nonlinear absorption is reverse saturable behaviour and can be attributed due to 2PA process. And the nonlinear refraction is self-defocusing arising from the negative nonlinear refractive index of the sample. Among the prepared samples truncated cubic CuNb3O8 possess higher 2PA coefficient $(5.4 \times 10^{-10} \text{ m/W})$ nonlinear refractive index $(10^{-16} \text{ m}^2/\text{W})$ and nonlinear optical susceptibility (10.6×10^{-11} esu). This arises due to factors such as i) niobium in the distorted octahedral chain forming a dense interconnected cage, ii) truncated cubic platonic morphotype with edge structure and iii) perovskite structure providing better thermal stability. Pure CuNb₃O₈ with low limiting threshold (34.6 μ J/ cm²) is identified to be better optical limiting material against ultrashort pulse IR laser than other copper niobate systems like O- CuNb₂O₆, mixed (m-CuNb₂O₆- O-CuNb₂O₆) and m-CuNbO₃.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.matchemphys.2018.09.013.

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