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Influence of sintering time on switching of the femtosecond nonlinear optical properties of CuNb₂O₆



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ABSTRACT

Transition of mixed phases (monoclinic and orthorhombic) to pure orthorhombic phase was achieved during the synthesis process of $CuNb_2O_6$ by varying the sintering time. The suppression of monoclinic phase and dominant formation of orthorhombic CuNb₂O₆ was confirmed from the XRD and FTIR data analysis. FESEM studies demonstrated that due to increase in sintering time, coarsening process initiated the grain growth and trapping of pores leading to pore-free structures. The nonlinear optical (NLO) properties of mixed and pure copper niobate were studied by the Z-scan technique using near-infrared (800 nm, ~150 fs, 80 MHz) laser excitation. Mixed phases exhibited saturable absorption and selfdefocusing behaviour while pure orthorhombic demonstrated reverse saturable absorption and selffocusing process. The switching of nonlinearity along with increase in NLO coefficient of O-CuNb₂O₆ was attributed to the decreased metal-oxygen bond length and pore free structure. The increase in nonlinear absorption coefficient with input irradiance suggests the occurrence of effective 3 PA (2 PA followed by ESA) process. The magnitudes of nonlinear absorption coefficient $(2.14 \times 10^{-23} \text{m}^3/\text{W}^2)$ and nonlinear refractive index (6.0 \times 0⁻¹⁷ m²/W) of O-CuNb₂O₆ were found to be higher than well-known NLO materials. Orthorhombic CuNb₂O₆ exhibited optical limiting action with low limiting threshold of 38.26μ /cm² and favouring NLO properties suggesting that the material to be an entrant candidate for safety devices against ultrashort pulsed lasers.

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1. Introduction

Ultrashort pulse (800 nm) lasers in the infrared find extensive applications in medicine (dentistry, ophthalmology and neurology) and defence sectors (directed energy weapons, jamming electrooptic sensors and damaging light-sensitive targets) due to its capability of greater penetration depth and stronger thermal effects [1–5]. For complete realization of the above mentioned applications, it is very necessary to choose the materials that have strong thermal nonlinearity and stability [6,7]. Though organic material such as phthalocyanines [7], porphyrins [8], triphenylmethane [9] and fullerenes [10] hold good nonlinear optical (NLO) properties, the major concern is their inferior chemical and optical stability. With concern on photo-stability against intense lasers, semiconductors are recently preferred as an alternate for organic materials [11]. Especially metal oxides of copper with Group V transition metals (niobium) can yield systems with high NLO coefficients (due to peculiar octahedral co-ordinated structure) and excellent anti-photo corrosive nature (reduces the oxidation of copper into Cu₂O and CuO). Copper-niobium-oxygen systems generally called as copper niobate can be prepared in many compositions and phases by varying the sintering time which can result in compounds with tunable optical properties. Compared to other inorganic NLO niobate materials such as lithium niobate, potassium niobate and sodium niobate, copper niobate possesses broad spectral range, large electro-optic coefficients, high thermal stability and strong photo-stability due to the presence of copper in the perovskite structure [12,13]. Recently the nonlinear optical (NLO) properties of monoclinic phase of copper niobate (CuNb₂O₆) with low limiting threshold under femtosecond excitation (800 nm, 150 fs) were reported. The significance of that material was that the performance of that material was better than benchmark material like CNT. The origin of thermal nonlinearity under high repetition and short pulse duration are most sensitive to the structure of the







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material. The type of nonlinear absorption and nonlinear refraction strongly relies on the phase and morphology of the material. In this sense, exploring the other phases of copper niobate such as higher temperature sintered materials like orthorhombic (CuNb₂O₆) can be an interesting subject of investigation for attaining higher NLO performance. This is because, higher sintering temperature can vield pore-free ceramics with low scattering and improved optical transmission which in turn can vield better NLO performance [14]. Impressed by these facts, attempts were made to study the thirdorder NLO properties and optical limiting behaviour of high sintered ceramics, orthorhombic phase copper niobate by Z-scan experiment using ultra-short laser pulse (800 nm, 150 fs, 80 MHz). As sintering time was increased, the synthesized material transit from mixed (monoclinic and orthorhombic) phases to pure orthorhombic phase of copper niobate with significant increase in its NLO behaviour. Sign reversal in NLO properties and the influence of phase in switching its NLO behaviour was discussed in detail. These orthorhombic copper niobate may be given attention due to its potential application for protection of eyes and as sensors of ultrashort infrared pulsed lasers.

2. Experimental details

Literature survey revealed that monoclinic and orthorhombic phases of copper niobate can be obtained by solid state reaction at sintering temperature of 700 °C and 900 °C respectively [15]. Based on this, pure monoclinic phase of copper niobate was successfully prepared at 700 °C for 3 h and formation of micro-rods at an elevated reaction time of 12 h was recently reported [16]. In continuation of this work, to attain pure orthorhombic phase, copper oxide and niobium was taken as precursor in the ratio of 1:2. The precursors were grinded together for an hour and transferred into crucible for sintering process. The sample was sintered at prescribed temperature of 900 °C (crucial for orthorhombic phase formation) at various reaction times of 3-12 h. The obtained powders appeared to be yellowish-green rather than the reported black colour which was due to the disposition of the Cu-atoms in the crystal lattice [17]. For preliminary phase confirmation, XRD was taken using PAN analytical X-Ray powder diffractometer. The presence of various vibrations related to metal-oxygen in the molecules was studied using JASCO FTIR spectrophotometer in the region of 1000–400 cm⁻¹. The textural and morphological analysis was done by FESEM studies using FEI Quanta FEG 200 scanning electron microscope. The third-order nonlinear optical properties were determined by Z-scan studies under ultrashort pulse excitation using a Ti:Sapphire laser system (800 nm, 150 fs, 80 MHz). Here copper niobate was dispersed in diethylene glycol with ~70% linear transmittance. The change in far-field transmittance was measured with (closed) and without aperture (open) by navigating the solution placed in 1 mm cuvette along the propagation of laser beam (-Z to Z). The laser was focused onto the sample through 100 mm convex lens having beam waist (ω_0) of 25.5 µm. The change in transmittance of the material for every Z-position was repeatedly captured for its liability. For further discussion, the samples obtained at 3, 6, 9, 12 h were named as A, B, C, D respectively.

3. Results and discussion

Fig. 1 illustrates the recorded XRD pattern of the powders obtained at 900 °C for various sintering time. The obtained peaks were indexed and found to be matching with the monoclinic (JCPDS No. 83-0369) and orthorhombic (JCPDS No. 83-1201) phases of CuNb₂O₆. The preliminary difference between the diffraction pattern of these phases is that two equally intense lines (131) and



Fig. 1. XRD pattern of $CuNb_2O_6$ obtained at A) 3 h B) 6 h C) 9 h and D) 12 h.

 $(\overline{131})$ with d = 2.975 Å and 2.919 Å representing monoclinic while a single intense line (311) with d = 2.939 Å between these lines corresponding to orthorhombic phase [13].

At a sintering time of 3–9 h, presence of both monoclinic and orthorhombic phases was observed. Sample sintered at 3 h possessed, well-defined characteristic peaks (131) and $(\overline{131})$ of monoclinic phase along with minor traces of orthorhombic phase. For sample sintered at 6 h, a sharp intense peak (311) was formed with suppression of monoclinic characteristic lines indicating the dominant formation of orthorhombic phase. At 9 h, the intensity of the orthorhombic peak increased collectedly along with a small portion of monoclinic phase. On further increasing the sintering time to 12 h, pure orthorhombic phase of CuNb₂O₆ with single intense line (311) were formed and the lines corresponding to monoclinic phase were fully vanished. Thus it was identified that change in sintering time has greatly influenced the phase transformation and the material switches from mixed to orthorhombic phase. The proportion of orthorhombic phase was found to be increasing with sintering time and the product turns predominantly orthorhombic from 12 h. Though the crystal structure of orthorhombic phase is very similar to the bonding scheme of monoclinic phase, two important structural differences are that in monoclinic phase copper ions are arranged in a pair wise manner and the geometry of the niobium atom is much distorted [17]. Also the average bond length between niobium and oxygen was found to be shorter in orthorhombic (3.01 Å) than monoclinic (3.19 Å) structure, which may provide an interesting opportunity for the enhancement of NLO coefficients. Also it is to be noted that, the electro-optic and nonlinear optical properties of niobate materials depend strongly on the intrinsic defects present in the crystal structure, due to the role of electron-phonon contribution [18].

The molecular structure of $CuNb_2O_6$ consists of CuO_6 and NbO_6 octahedra in which the site of metal atom was surrounded by distorted octahedron oxygen atoms. Here CuO_6 octahedra share its four corners with four NbO_6 while NbO_6 octahedra share its four corners with two NbO_6 and two CuO_6 . Recorded FTIR spectra and band assignments of metal-oxygen vibrations are displayed in



Fig. 2. FTIR spectrum of $CuNb_2O_6$ obtained at A) 3 h B) 6 h C) 9 h and D) 12 h.

Fig. 2. The bands located around 850 and 700 cm⁻¹ attributes to edge shared Nb-O₆ octahedra while 632 cm⁻¹ band was due to the corner shared Nb-O₆ octahedra. The absorption peak in the vicinity of 500 cm⁻¹ designates the edge and corner shared Cu-O₆ octahedra [19]. No strong variation in the IR peak positions were due to the similar molecular geometry of both phases of copper niobate. However, a small shift in 632 cm⁻¹ (12 cm⁻¹) of Nb-O (corner) was due to the shortened bond length of orthorhombic CuNb₂O₆. Among the samples, orthorhombic system showed a less transmittance spectrum compared with the mixed phases which may be due to IR absorbing nature of the phase.

Fig. 3 demonstrates the typical FESEM images of sintered $CuNb_2O_6$ which showed the homogenous nature of the samples. In

general during solid-state reaction of niobates, morphologies with pore structures are normally expected [20]. Also sintering occurs at the temperature below melting point which allows the atoms to move and fill the spaces between grains. In the present case, as sintering time increased (3–9 h) slightly agglomerated plate like networks with reduction in number of pores was encountered. At elevated sintering time of 12 h. the sample got highly agglomerated with not much noticeable pores in the networks (see inset of Fig. 3). Due to higher sintering temperature, the particle coarsening was initiated which leads to pore free or dense ceramics. Due to mass transport, the grains grow and hence the pores get trapped inside the grains leading to fully dense pore free structures. Thus sintering time not only changes the phase of the system but also its morphological structure. Hence orthorhombic CuNb₂O₆ with high relative density and pore-free structure can results in low scattering and improved optical transmission, which is an important criteria for achieving better NLO performance [14].

The third order NLO properties of orthorhombic phase copper niobate (CuNb₂O₆) were estimated from the recorded open and closed aperture pattern of Z-scan under ultrashort pulse (femtosecond) laser excitation. Fig. 4 indicate the recorded open aperture pattern and it can be observed that the transmission of samples gradually decreases at the focal point as sintering time increases. This resulted in switching of peak (saturable absorption) to valley pattern (reverse saturable absorption) at 12 h. Thus the samples sintered at 3-9 h which has mixed phases (monoclinic and orthorhombic) of CuNb₂O₆ exhibits saturable absorption behaviour (SA). While the sample obtained at 12 h with pure orthorhombic phase shows reverse saturable absorption (RSA). As the dominance of orthorhombic phase in the prepared sample increases, the nonlinear absorption shift towards RSA which might be due to increase in excited state cross section. Under femtosecond excitation, the occurrence of nonlinear absorption maybe due to saturable absorption (SA), reverse saturable absorption (RSA), two photon



Fig. 3. FESEM image of CuNb₂O₆ sintered at A) 3 h B) 6 h C) 9 h and D) 12 h with inset indicating the available pores.



Fig. 4. Open aperture pattern of mixed A) 3 h B) 6 h C) 9 hand pure orthorhombic D) 12 h CuNb₂O_{6.2} PA (dashed line) and 3 PA (solid line) fits are shown in (D). Open circles are experimental data points.

absorption (2 PA), three photon absorption (3 PA) and/or excited state absorption (ESA). To identify the mechanism involved, transmittance of normalized energy for multi-photon absorption was fitted using the following equation [21].

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

Where α_n is the multiphoton absorption co-efficient (n = 2,3, ...),I₀ is the incident irradiance, L is the thickness of the sample and $z_0 = \pi \omega_0^2 / \lambda$ is Rayleigh range. In Fig. 4, open circles indicate the recorded experimental data points and the solid lines correspond to the theoretical fits.

In Fig. 4D, the open aperture Z-scan data for pure orthorhombic $CuNb_2O_6$ (12 h) was found to be fitting well for three photon absorption (3 PA) than two photon absorption (2 PA) equation. The involved mechanism can be explained with the aid of UV–Visible absorption spectrum provided in Fig. 5a. The observed nonlinearity can be ascribed due to genuine 3 PA or effective 3 PA (2 PA + ESA) process. In the linear absorption spectrum (Fig. 5a), a broad absorption peak at 270 nm arises due to transfer of charges from oxygen ligands to central niobium atom in NbO₆ octahedra group. Under IR (800 nm, 1.55 eV) excitation, electrons could have absorbed three photons simultaneously (genuine 3 PA) resulting in the direct transition to the excited state (270 nm, 4.65 eV) of copper niobate. Also from the absorption edge (330 nm), the band gap was estimated to be 3.7 eV. Here as excitation energy (1.55 eV) is less than half of the band gap (3.7 eV) of copper niobte [16], the

observed nonlinearity can also arise from the contribution of twophoton absorption and excited state absorption. So the other possibility (sequential 3 PA) is indirect transition in which electrons are optically excited from the ground state to intermediate states (3.1 eV) by absorbing two photons followed by excited state absorption and then possibly moves to the higher energy (3.7 eV) state. The present Z-scan data cannot distinguish the above two possibilities, hence the observed nonlinearity can be collectively termed as effective 3 PA. For better understanding of the mechanism involved in nonlinear absorption behaviour, the open aperture experiment was carried out at various input power (2–9 mW) of laser pulses. The depth of OA pattern was found to be increasing with input (Fig. 5b), suggesting the strengthening of reverse saturable absorption in the material. We fitted the experimental data to 2 PA initially. The intensity dependent behaviour of estimated 2 PA coefficient is shown in Fig. 5c. It was observed that 2 PA coefficient increased with input intensity (depletion in ground state population) suggesting the occurrence of 3 PA process [22]. Hence, with possible electron transitions discussed above the data suggests the observed nonlinearity to be an effective 3 PA (i.e. two photon absorption followed by excited state absorption (2 + 1 process) rather than genuine 3 PA process) [23]. The estimated nonlinear absorption coefficients are summarized in Table 1 and are found to be higher than well-known recently reported systems such as chal-cogenide glasses $(10^{-27} \text{ m}^3/\text{W}^2)$ [24], CHCl₃ chromophore $(10^{-23} \text{ m}^3/\text{W}^2)$ [25], ZnO $(10^{-24} \text{ m}^3/\text{W}^2)$ and ZnS $(10^{-23} \text{ m}^3/\text{W}^2)$ [26], Lead Telluride $(10^{-29} \text{ m}^3/\text{W}^2)$ [27], Ferrofluids $(10^{-30} \text{ m}^3/\text{W}^2)$ [28], ZnMgO thin films $(10^{-27} \text{ m}^3/\text{W}^2)$ etc. [29].

To estimate the nonlinear refractive index of the material (n_2) closed aperture Z-scan experiment was performed. Fig. 6 illustrates



Fig. 5. a) UV-Vis absorption spectrum of orthorhombic phase copper niobate b) Open aperture pattern and c) estimated nonlinear absorption coefficient as a function of input intensity of orthorhombic copper niobate.

Table 1		
Third-order NLO coe	fficients of mixed and	l pure O- CuNb ₂ O ₆ samples.

Sample Code	Nonlinear absorption coefficient	$n_2 \times 10^{-17}(m^2/W)$	$\text{Re}\;\chi^{(3)}\times10^{-19}(m^2/\text{V}^2)$	$Im \; \chi^{(3)} \times \; 10^{-22} \; (m^2/V^2)$	$\chi^{(3)}\times10^{-11}(esu)$	Limiting Threshold $(\mu J/cm^2)$
Α	$-5.5\times10^{-12}\;m/W(SA)$	-5.4	3.9	24.2	2.8	_
В	$-0.6 \times 10^{-12} \text{ m/W(SA)}$	-2.9	2.1	02.7	1.5	_
С	$-0.4 \times 10^{-12} \text{ m/W(SA)}$	-2.3	1.6	01.9	1.2	_
D	$+2.14\times10^{-23}\ m^3/W^2(3\ PA)$	+6.0	-	-	-	38.26



Fig. 6. Closed aperture pattern of mixed A) 3 h B) 6 h C) 9 hand pure orthorhombic D) 12 hCuNb₂O₆.

the recorded closed aperture (CA) data of the samples. Nonlinear refraction could be a result of electron transition nonlinearity, reorientation effect or thermal lensing effect or mixture of them [30]. As the experiment was carried out in femtosecond regime with high repetition rate of 80 MHz, thermal nonlinearity plays a key role in the observed nonlinear refraction. The experimental values of closed aperture was fitted using the following equation [31].

$$T_{CA} = 1 + \Delta \phi \frac{4x}{(x^2 + 1)(x^2 + 9)}$$
(2)

Where $\Delta \phi$ represents phase shift at the focus and $x(=z/z_o)$ is position of the sample.

The open circles in the data presented in Fig. 6 represents the experimental data and solid line corresponds to the fitted theoretical data. As observed in nonlinear absorption, pure orthorhombic copper niobate (12 h) suffers a sign reversal in nonlinear refractive index when compared with mixed phases (3-9 h). Samples sintered at 3–9 h shows a peak-valley pattern suggesting the defocusing nature (negative nonlinear refraction). While for 12 h sintered sample the pattern switches to valley-peak confirming the self-focusing behaviour (positive nonlinear refraction). Here the switching of nonlinear refraction was due to the modulation of phase equilibrium with respect to distribution of pores due to the local heating induced by light propagation [32]. Also the phase shift is provoked by nonlinear absorption of the sample [33] and the nature of thermal lens effect strongly depends upon the polarization of sample. The nonlinear refractive index was evaluated using the relation, $n_2 = \frac{|\Delta \phi|\lambda}{l_0 L_{eff}}$ and the acquired value was presented in Table 1 which shows an increasing trend with sintering time. A similar order of nonlinear refractive index ($\sim 10^{-17} \text{ m}^2/\text{W}$) was observed for other recently reported potential NLO materials such as phthalocyanine [34], BaMgF₄ [35], Tellurite glass [36], β -BaB₂O₄ [37] and graphene oxide [23].

Fig. 7 depicts the variation of transmittance as a function of input fluence of copper niobate drawn out from open aperture data. For every position, the laser fluence was calculated from the equation $F(z) = 4\sqrt{ln2} \left(\frac{E_{in}}{\pi^{3/2}.\omega(z)^2}\right)$ where E_{in} is the input energy of

the laser [38]. For mixed phase (3–9 h) samples, the output increases with input fluence due to the saturable absorption nature. This depicts that mixed phase copper niobates have potential applications in Q-switching as passive saturable filter, optical isolation

and mode locking devices [39]. While for pure orthorhombic phase (12 h) the output decreases with increase in input intensity confirming the presence of nonlinearity in the material. The material shows limiting behaviour with limiting threshold of $38.26 \ \mu J/cm^2$ which was found to be lower than other optical limiting materials like zinc oxide thin film ($128 \ \mu J/cm^2$) [40] and porphyrin-covalently functionalized multi-walled carbon tubes ($18.3 \ J/cm^2$) [41], graphene decorated Ag particles ($40 \ GW/cm^2$) [42], PbTe ($5 \ J/cm^2$) [27]. As expected, the limiting threshold of 0-CuNb₂O₆ decreased ($38.26-31.43 \ \mu J/cm^2$) with increase in input fluence.

From the nonlinear absorption co-efficient and nonlinear refractive index, third order NLO susceptibility $(\chi^{(3)})$ of the mixed phase copper niobate was calculated using the standard relations [43]. Here, the real part was found to be higher than imaginary part of nonlinear optical susceptibility suggesting the dominance of nonlinear refraction due to the influence of the thermal component arising from high repetition rate. The estimated third order NLO susceptibility of mixed phase copper niobate are summarized in Table 1 and are found to be higher than other copper based systems such as CuO (10^{-18} esu) and Cu₂O (10^{-19} esu) [44], BaMgF₄ (10^{-12} esu) [35], β -BaB₂O₄ (10^{-14} esu) [37] and bench mark system like graphene oxide (10^{-15} esu) [23]. Here the increase in third order optical nonlinearity of the material can be attributed to the change in bond length between the metal and oxygen in transition metal oxides [45]. Among the samples, O-CuNb₂O₆ possessed higher NLO coefficient which was due to decreased metal-oxygen bond length [13]. As discussed earlier, monoclinic phase of copper niobate has highly distorted niobium octahedra compared to orthorhombic phase which in turn increases the bond length between cation and anion. Thus shortening of Nb-O bond length of octahedral coordinated structure of O-CuNb₂O₆ has facilitated the enhancement of NLO coefficients. Further the presence of intrinsic defects result in dilation of Nb-O1 and extension of Nb-O2, thereby playing a significant role in local rearrangement. This local rearrangement of Nb atom in the crystal structure disturbs the nonlinear optical susceptibility which probably leads to the improved NLO properties [46]. As mentioned in our earlier work on monoclinic copper niobate [13], the emission spectrum of orthorhombic copper niobate (provided in supplementary data) has an absorption peak in the vicinity of 430 nm which were due to the self-trapped excitons arising from charge transfer from oxygen ligands to the niobium. Thus due to the presence of intrinsic defects, the prepared copper niobate showed higher nonlinear optical coefficients. Also dense structure of O-CuNb₂O₆ due to pore shrinkage has facilitated the improvement in thermal stability. Therefore



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Fig. 7. Normalized transmittance vs input fluence of mixed A) 3 h B) 6 h C) 9 hand pure orthorhombic D) 12 h CuNb₂O₆ (for various power of input laser).

tunability of NLO coefficients of CuNb₂O₆ with change in sintering time was confirmed. A similar observation of increasing NLO values with change in reaction time was observed for barium borate excited under cw laser (532 nm, 50 mW) [46]. So sintering time plays a very important role in switching the NLO behaviour of CuNb₂O₆. Also the proportion of phase and morphology contributes a major role in deciding the type of nonlinearity in the material. As strength of orthorhombic phase increases, the behaviour switches from saturable to reverse saturable and self-defocusing to selffocusing nature. Thus it can concluded that O-CuNb₂O₆ with its favouring NLO properties can be used as a better optical limiter against ultra-short pulse infrared laser excitation.

4. Conclusions

Mixed and pure orthorhombic phase of CuNb₂O₆ was prepared by solid-state reaction method at various sintering time of 3-12 h. In the recorded XRD, two equally intense lines (131) and $(13\overline{1})$ with d = 2.975 and 2.919 Å represent monoclinic phase while, a single intense line (311) with d = 2.939 Å between these lines corresponds to orthorhombic phase. The proportion of orthorhombic phase was found to be increasing with sintering time and the material switches from mixed (monoclinic and orthorhombic) phase to pure orthorhombic phase. FESEM analysis depicts that sintering initiates the particle coarsening due to mass transport which leads to pore free or dense ceramics. As sintering time increases, the grains grow and hence the pores get trapped inside the grains leading to pore free structures in orthorhombic phase. Open aperture Z-scan shows that mixed phases exhibit saturable absorption while pure orthorhombic phase shows reverse saturable absorption. As the dominance of orthorhombic phase in the prepared sample increases, the nonlinear absorption shift towards RSA which might be due to increase in excited state cross section. Theoretical fit made for the observed nonlinearity was found to be matching for 3 PA process. The increase in nonlinear absorption coefficient with input intensity suggested the occurrence of higher order nonlinearity and was ascribed to be effective 3 PA (two photon absorption followed by excited state absorption (2 + 1)process)). The closed aperture of mixed phase samples show a peak-valley pattern suggesting the defocusing nature (negative nonlinear refraction) and for pure orthorhombic it switches to valley-peak pattern confirming the self-focusing behaviour (positive nonlinear refraction). Third-order nonlinear susceptibility was found to be higher for mixed phase copper niobate than other NLO. Mixed phase copper niobates are identified to be saturable absorber and find applications in Q-switching as passive saturable filter, optical isolation and mode locking devices. Further pure orthorhombic phase exhibited limiting behaviour with limiting threshold of 38.26 µJ/cm2. The decreased Nb-O bond length and pore free structure in orthorhombic system favours the high NLO Coefficient. Proliferation on applications of the ultra-short NIR lasers urges the development of optical limiters and orthorhombic copper niobate with favouring properties (high nonlinear absorption coefficient (2.14 \times 10⁻²³ m³/W²), nonlinear refractive index $(6 \times 10^{-17} \text{ m}^2/\text{W})$ and low limiting threshold (38.26 µJ/cm2)) can be a pick of the bunch among the well-known NLO materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.optmat.2017.02.060.

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