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Research paper

Ultrafast nonlinear optical studies of equiaxed $CuNbO_3$ microstructures

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ABSTRACT

Diverse microstructures of monoclinic copper niobate (m-$CuNbO_3$) were synthesized by solid-state reaction (900 °C, 3–12 h). FESEM data demonstrated that agglomerated clusters grew as an elongated grains which migrated to form web-shaped equiaxed structure and dissected to form individual equiaxed microstructure. With femtosecond laser excitation (800 nm, 150 fs), open aperture Z-scan data revealed the presence of two-photon absorption. The nonlinear refractive index (n_2) toggled between positive and negative nonlinearity for different microstructures. Web-shaped equiaxed structure kindled both the nonlinear absorption ($\beta_{eff} = 2.0 \times 10^{-12}$ m/W), nonlinear refraction ($n_2 = 3.16 \times 10^{-17}$ m^2/W) and a strong optical limiting action (onset limiting threshold of 22.24 μJ/cm^2).

1. Introduction

Ultrashort pulse (femtosecond) lasers with high repetition rate (megahertz and gigahertz) have significant applications in the field of nonlinear optics, fibre optic communication, material processing and frequency comb because of its unique properties like high gain coefficient, wide operating wavelength range, excellent heat dissipation and robust mode confinement [1]. Under intense laser excitation, the electric field **E** of the light induces material nonlinear polarization and causes irradiance dependent refraction, absorption, scattering. The attained nonlinear optical (NLO) coefficients such as nonlinear absorption and nonlinear refractive index strongly depend on the excitation parameters like wavelength, nature of laser, energy etc.. Static NLO properties (thermo-optic) are most conveniently studied with continuous wave lasers while dynamic NLO properties (electro-optic) can be explored by pulsed (nanosecond, picosecond and femtosecond) lasers. With ultrashort pulses at high repetition rate, the contributions cannot be purely electronic and the contributions from Kerr and thermal components should be considered during investigation [2]. Hence, understanding the origin of nonlinearity in these domains will be an interesting subject, for example ultrafast thermal nonlinearity has remarkable applications in the production of temperature, chemical sensors and soliton pulse propagation in waveguides [3]. The light induced nonlinear absorption gives interesting effects such as reverse saturable absorption (RSA), saturable absorption (SA) and two photon absorption (TPA)and nonlinear refraction creates effects such as laser induced grating, self-focusing, self-defocusing, self-phase modulation, self-diffraction [4]. Out of these effects, optical limiting arising from energy-absorbing and energy spreading optical nonlinearity have attracted recent attraction towards the safety of photosensitive components from intense laser beam. Unlike nonlinear absorption which occurs instantaneously and requires specific criteria for energy conservation, nonlinear refraction occurs at any wavelength and sometimes may be accompanied with temporal dynamics depending on its physical origin. It is expected that with high-repetition rate ultrashort pulse laser, nonlinear refraction will be more dominating and hence it can yield interesting optical limiting materials. In this sense, the Z-scan technique developed by Sheik-Bahae et al. [5] has been widely applied to study the third-order nonlinear properties and optical limiting in solid and liquid materials.

In recent years, the third-order NLO behaviour of semiconductors have received much attention in the field of photonics due to the possibility of attaining large NLO coefficients arising from optical stark effect and surface trapped states. Zinc oxide, zinc sulphide [6], lead sulphide [7], copper oxide [8] and cuprous oxide [9] are some of the well-known semiconductor NLO materials which demonstrated high third-order nonlinear susceptibility and low limiting threshold. In this series, copper containing niobate systems have gained considerable attention for photonic applications due to its tunable band gap from UV to visible region with respect to its elemental composition. Also, mixing of copper with Group V elements (Nb) have increased the optical and thermal stability of the system [10]. Some of these multi-metal oxide systems include $CuNb_2O_6$,

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$CuNbO_3$, $CuNb_3O_8$, $Cu_2Nb_3O_8$ whose structural and optical properties can be altered by varying their composition and sintering [11]. Enhanced nonlinear absorption coefficient and strong optical limiting action of monoclinic and orthorhombic copper niobate ($CuNb_2O_6$) than benchmark material like CNT under femtosecond (fs) excitation (800 nm, 150 fs) was recently reported [12,13]. Among this series of compounds, ABO_3 system with the presence of BO_6 octahedra and faster charge transport, due to the reduced bond length, can possess favourable properties like large electro-optic coefficients, high thermal stability and strong photo-stability. Impressed by these facts, this article reports the third order NLO properties of $CuNbO_3$ by Z-scan technique achieved using high-repetition rate femtosecond excitation (800 nm, ~150 fs, 80 MHz).

2. Experimental details

Solid state reaction was employed to synthesize perovskite structure ABO_3 molecule as it is as eco-friendly and simple one-step process. Unlike the previous synthesis procedure [12,13] adopted for synthesis of $CuNb_2O_6$, here cuprous oxide was used as a starting precursor. The preparation of $CuNbO_3$ involved the reaction $Cu_2O + Nb_2O_5 \rightarrow 2CuNbO_3$. In a typical procedure, precursor of cuprous oxide and niobium pentoxide was taken in the molar ratio of 1:1 and homogeneously grinded for an hour using agate mortar. To ensure the formation of monoclinic phase of $CuNbO_3$, the mixed powder was sintered at 900 °C [11]. To study the morphological transformation and corresponding NLO properties, the sample was sintered at various sintering time of 3, 6, 9 and 12 h. The phase confirmation of the sample was achieved by PAN Analytical X-Ray powder diffractometer. The investigation on morphological structure and elemental analysis on varying sintering time was accomplished by using FEI Quanta FEG 200 scanning electron microscope. The linear optical properties of the prepared sample were studied by using UV–Vis spectrophotometer (JASCO V-570) and by dispersing in diethylene glycol (1 mg/1 ml). The tremendous increase in the utilization of ultrafast infrared (800 nm) laser with high repetition has kindled the need for investigation of nonlinearity leading to realization of laser safety devices through optical limiting and even beyond for the investigations of shock waves and spatial soliton propagation. Also $CuNbO_3$ possesses negligible absorption in the chosen excitation (800 nm), high linear transmittance which is the essential criteria for optical limiting is fulfilled. Thus the third-order NLO properties of $CuNbO_3$ were studied by Z-scan experiment using high-repetition rate femtosecond excitation (800 nm, ~150 fs, 80 MHz). For Z-scan studies, $CuNbO_3$ dispersed in diethylene glycol (5 mg of the sample in 5 ml diethylene glycol with linear transmission of ~70%) was used because liquid media can easily dissipate high incident intensities through solvent heating and bubbling. Furthermore, dispersion allowed the samples to retain its microstructure and the liquid state can generate nonlinearity through reorientation of the dipoles (induced or permanent molecular dipoles). $CuNbO_3$ prepared by solid state reaction at 900 °C was individually sintered at different sintering time (3, 6, 9 and 12 h) and each sample in dispersed state was subjected to Z-scan experiment separately to understand the influence of sintering time on NLO properties. Here the observed nonlinearity and the responsible NLO phenomena were explained by Sheik-Bahae formalism [14–15]. Complete details of the experimental setup can be found in our earlier works [12].

3. Structural characterization

The recorded powder XRD pattern revealed the formation of crystalline $CuNbO_3$ from Cu_2O and Nb_2O_5.All the diffraction peaks were indexed with JCPDS card No: 01-084-0971 and the prepared material was found to be $CuNbO_3$which crystallized in monoclinic phase (presented as supplementary data, S1). The lattice parameters were found to be a = 9.525(1) Å, b = 8.459(2) Å and c = 6.793 (1) Å. No other characteristic peaks of precursor and other phases of copper niobate were seen [16]. The literature reveals (2 2 0) plane to be a predominant and as sintering time increases (3 to 12 h), the intensity of predominant peak along with other notable peaks increases which confirms the improved crystalline nature of the sample with raise in sintering time. Literature also shows that $CuNbO_3$ of ABO_3 perovskite structure comprised of niobate octahedra where the corrugated niobate layer contain squares of four vertex-shared NbO_6 octahedra which bridge to neighbouring squares via edges. The NbO_6 octahedra compressed to form Nb_4O_{16} group which was aligned in a parallel manner. Further the bridges through its corner oxygen atoms to the neighbouring group form a staircase model. The copper atoms are located between the two layers and linearly coordinated between the two oxygen atoms of Nb_4O_{16} group [10]. The peculiarity of this structure is that these octahedral system is expected to demonstrate strong NLO behaviour because of faster charge transport between niobium and oxygen octahedra due to the reduced bond length.

The morphotypes and elemental composition of $CuNbO_3$ is depicted in Fig. 1. During initial sintering (3 h), cluster of agglomerated microstructure with irregular morphology were formed. The aggregation creates a strong inter-particle bond due to necking between neighbouring particles. The sintering time has highly influenced the morphological structure and at 6 h of sintering, it tries to form as an irregular microstructure with less agglomeration. At 9 h of sintering clusters separate themselves and forms as a defined equiaxed microstructure linked as a chain. Furthermore, a continuous web shaped structure by connecting the grain boundaries was encountered. In Fig. 1d (12 h) the material expounds into individual equiaxed microstructure after breaking of bonds in a chain. Hence the growth mechanism involves the grain elongation at lower time of sintering. Slowly the grain boundary migration allows the restoration of equiaxed shape depending on the mobility of grains [17,18]. And the elongated grain dissected at 12 h of sintering resulting in the breakdown of individual equiaxed structure of copper niobate in shape preferred orientation. The inset shows the enlarged portion of the FESEM image of the samples which clearly pictures the transformation of the agglomerated clusters into equiaxed microstructures due to increase in sintering time.

4. Nonlinear refraction and nonlinear absorption

Closed aperture Z-scan experiments were performed to extract the nonlinear refractive index of the material. Fig. 2 illustrates the closed aperture pattern of monoclinic phase $CuNbO_3$.As the Z-scan experiment was carried out in the fs regime with the high repetition rate of 80 MHz, thermal nonlinearity plays a vital role in deciding nonlinear refraction of the material. The experimental data fitted well with the theoretical values estimated using the standard nonlinear transmittance equation for closed aperture mode [19]. The nonlinear refraction value was extracted using the relation $n_2 = \Delta\phi/2\pi L_{eff} I_0$ and the estimated values are given in the Table 1.In the closed aperture pattern the circles represent the experimental data and the lines correspond to the theoretical fits.

In the photorefractive systems like niobates, the modulation in refractive index arises due to electro-optic effect and charge transport [20]. It is interesting to observe that closed aperture data switched its pattern (Fig. 2) with rise in sintering time: sample sin-

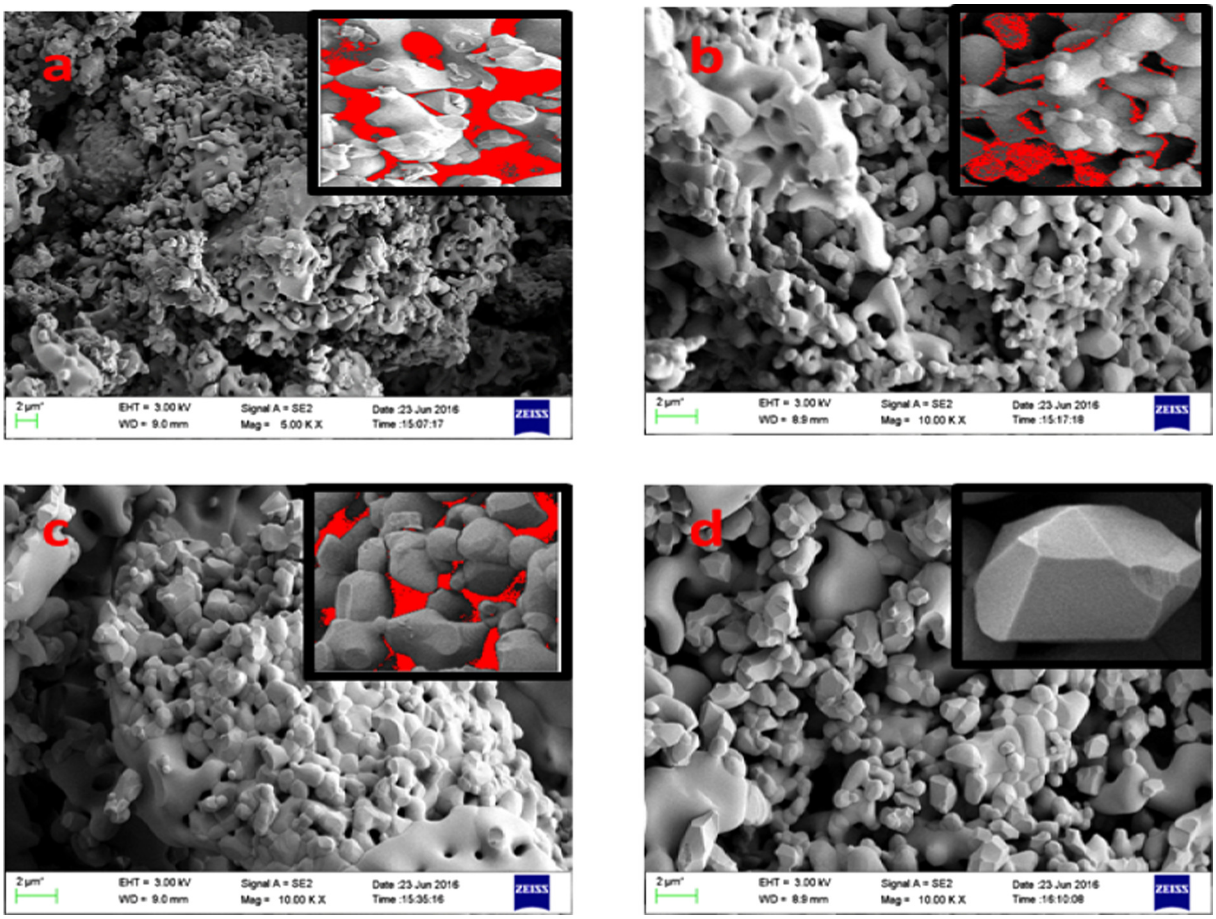

Fig. 1. SEM images representing the formation of equiaxed microstructure in copper niobate due to differing sintering time (a. 3 h, b. 6 h, c. 9 h and d. 12 h). Insets depict the corresponding enlarged view of the morphology.

tered at 3 and 6 h depicted valley-peak pattern, 9 h sample switched to peak-valley pattern and 12 h toggled back to valley-peak pattern. The sign of $n_2$was reversed from positive nonlinearity (convex lens, self-focusing) to negative nonlinearity (concave lens, self-defocusing) and back to positive nonlinearity (convex lens, self-focusing) as the sintering time increased. This toggling of n_2 can be explained as follows: In general nonlinear refraction arises due to self-focusing or self-defocusing depending on whether the material act themselves like a convex lens (refractive index maximum at centre) or concave lens (refractive index minimum at centre). The focused Gaussian beam has spatially varying irradiance; the induced refractive index change varies across the beam profile causing the beam to be strongly distorted. In the FESEM (Fig. 1) it can be witnessed that samples sintered at 9 h have a well-connected structure while all other samples have island like morphology. Although samples sintered at 3 and 6 h have agglomerated and cluster like structure, they are rich in porosity enabling them to behave like islands. Furthermore, the samples sintered at 12 h have well-distinct individual equiaxed structure. We consider the morphological variation played a prominent role in thermodynamical properties of the material. Thus, web shaped equiaxed structure possible favoured temperature distribution to be minimum at centre and maximum towards the wing of Gaussian profile due to strong heat propagation resulting in concave lens like structure (self-defocusing). However, the above discussion is a more generalized scenario and further detailed studies are necessary to completely understand this behaviour. The obtained nonlinear refractive index values are summarized in Table 1 and $CuNbO_3$ was found to possess the same order of magnitude as that of other NLO systems such as β-BaB_2O_4 [21], $CuNb_2O_6$ [13], $BaMgF_4$ [22] and graphene oxide [23].

In the open aperture Z-scan data presented in Fig. 3, all the samples demonstrated strong valley pattern (RSA) where the transmission of the samples gradually decreased towards the focal point for all the prepared samples. There is a noticeable change in the depth profile pattern where the nonlinear absorption gets altered with sintering time. Under fs laser excitation, the observed nonlinearity may arise due to NLO mechanisms like saturable absorption, reverse saturable absorption (RSA), two-photon absorption (2PA), three-photon absorption (3PA) and excited state absorption (ESA). In the case of semiconductors, with near resonant excitation, excited state absorption can take place due to the existence of high density of states near the lower excited state of the atom. Also in semiconductors, one photon absorption or two photon absorption can generate carriers and these electron-hole pairs can be excited to higher states or lower states in conduction band under high intensities through free carrier absorption (FCA). In FCA, four possible transitions are possible: linear absorption, TPA, one photon induced FCA and two-photon induced FCA. Fig. 3 indicates the open aperture data of $CuNbO_3$ sintered at four different hours. The open circle indicates the recorded experimental data and the solid lines correspond to the theoretical fit. The experimental data was fitted using the standard nonlinear transmittance equation for open aperture mode to identify the possible nonlinear absorption mechanism involved [24].

To understand the observed nonlinear absorption mechanism, we studied the UV–Visible absorption spectra. Ground state absorption pattern clearly portraits the strong absorption in the

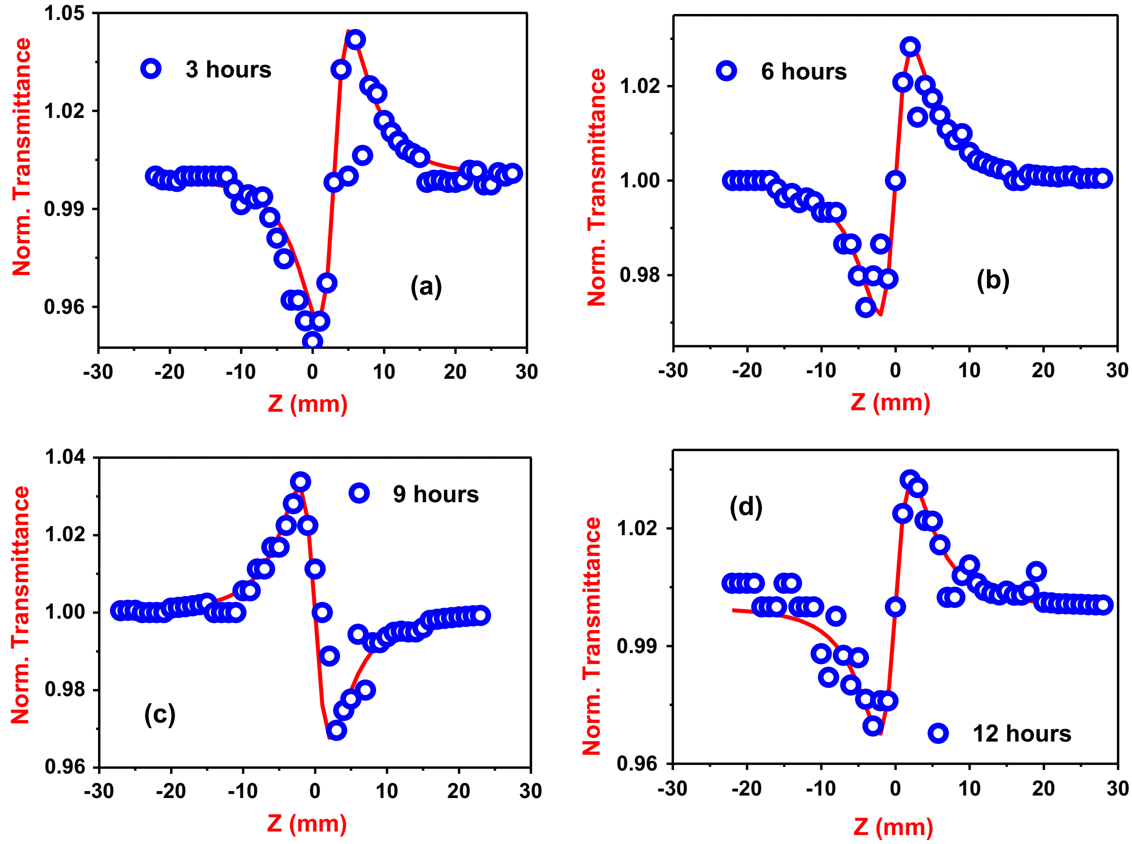

Fig. 2. Closed aperture data of (a) 3 h (b) 6 h (c) 9 h and (d) 12 h sintered copper niobate samples. Open cirlces (blue) are the experimental data points while the solid (red, black) lines are the theoretical fits to the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Third-order NLO coefficients of $CuNbO_3$.

Third-order NLO parameters	3 h	6 h	9 h	12 h
Nonlinear absorption coefficient ($\beta \times 10^{-12}$ m/W)	0.57	0.74	2.00	0.51
Nonlinear refractive index ($n_2 \times 10^{-17}$ m^2/W)	+8.04	+3.26	−3.16	+3.10
Third-order NLO susceptibility ($\chi^3 \times 10^{-11}$ esu)	3.97	1.61	1.56	1.53
Onset of optical limiting (μJ/cm^2)	38.26	26.25	22.24	47.49

UV region and gradual increase in absorption throughout the visible and NIR region (350–800 nm). Furthermore, the Tauc's plot drawn out from the absorption edge shows the band gap of $CuNbO_3$ to be ~2 eV [10]. Hence, under laser excitation, the electrons get optically pumped from the ground state and transit to the excited state (400 nm, 3.1 eV) by absorbing two photons simultaneously which may result in genuine 2PA process [25–26]. The other possibility is that $CuNbO_3$ being a semiconductor the excited state electrons (carriers) can absorb one more photon through free carrier absorption (FCA) to transit them to higher excited state (350 nm, 3.55 eV) resulting in sequential 2PA (1PA + FCA) process [27]. However, since the pulse energy is 1.55 eV and the energy required to raise the electrons to conduction band is 2.0 eV, this mechanism can be ruled out (the possible energy level diagram is given in supplementary data, S2). Thus material sintered at 9 h with well-defined and connected boundaries has higher nonlinear absorption (β_{eff}) co-efficient of 2×10^{-12} m/W. Literature shows $CuNbO_3$ possesses higher order than known materials like azobenzene (10^{-13} m/W) [28], CS_2 (10^{-13} m/W) [29], amino acids (10^{-14} m/W) [30], carbyne (10^{-13} m/W) [31].

Inset of Fig. 3 depicts the onset limiting behaviour of copper niobate that is drawn between normalized transmittance and the input laser fluence extracted from the recorded open aperture data using the standard equation, $F(z) = 4\sqrt{In2}(\frac{E_{in}}{\pi^{3/2}.\omega(z)^2})$ where E_{in} is the input energy incident on the material [32]. The presence of nonlinearity in the material was confirmed from the decrease in output with an increase in input intensity. The observed optical limiting can be ascribed due to 2PA process and as high repetition lasers are used, the contribution due to nonlinear refraction also play an important role. The onset limiting threshold was found to be lower for 9 h sintered sample and here web shaped equiaxed structure kindles the NLO behaviour. Copper niobate possessed onset limiting threshold of 22.24 μJ/cm^2 which was found to be higher than the systems like bismuth nanospheres (2.16 mJ/cm^2) [34] [33], zinc oxide thin film (128 μJ/cm^2) [34], Ag particles (40 GW/cm^2) [35], lead tellurite (5 J/cm^2) [36] excited under similar conditions. Here $CuNbO_3$ (9 h) shows stronger limiting action due to the combined contribution of 2PA and self-defocusing effects.

The third order NLO susceptibility $\chi^{(3)}$of copper niobate ($CuNbO_3$) were estimated from the nonlinear absorption co-efficient and nonlinear refractive index [13]. In the present case, the real part of $\chi^{(3)}$ was higher (10^{-19} m^2/V^2) compared to imaginary $\chi^{(3)}$ (10^{-22} m^2/V^2) suggesting the dominance of nonlinear

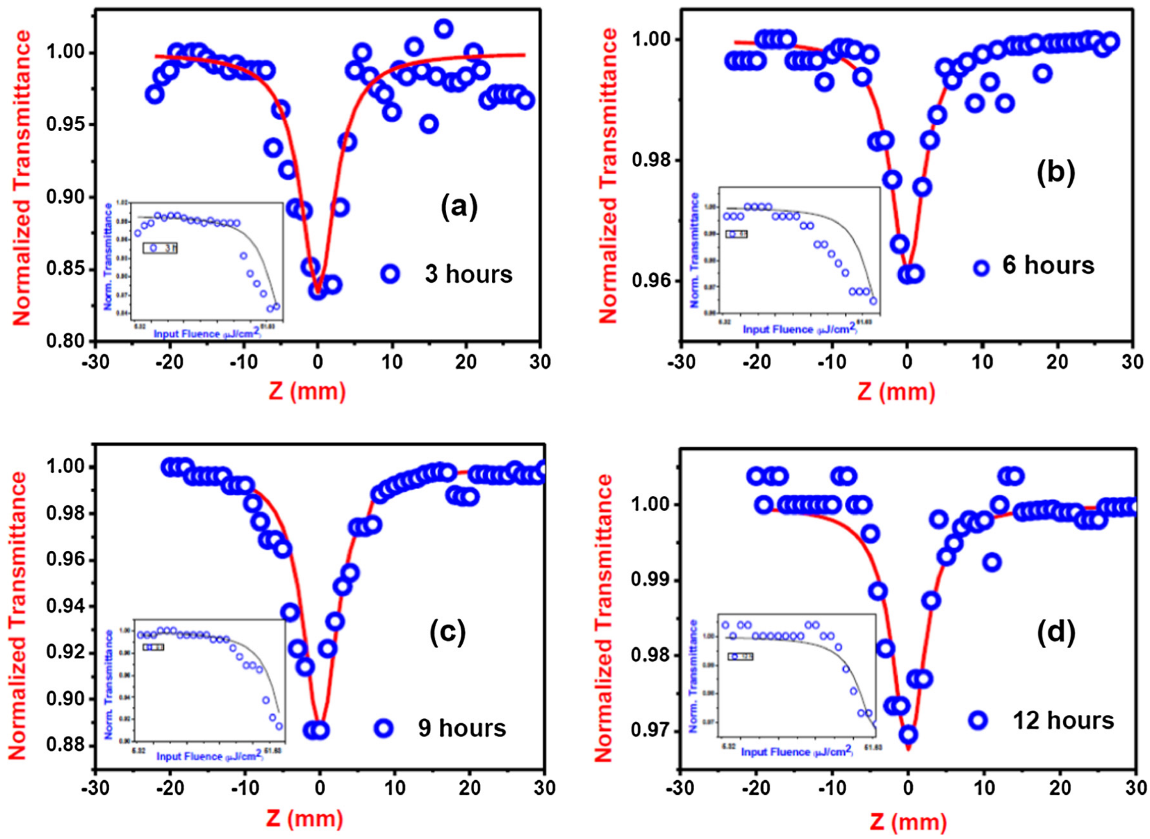

Fig. 3. RSA behaviour observed from open aperture Z-scan data of (a) 3 h (b) 6 h (c) 9 h and (d) 12 h sintered copper niobate samples. Insets depict the optical limiting data retrieved from the open aperture data. Open cirlces (blue) are the experimental data points while the solid (red, black) lines are the theoretical fits to the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

refraction over nonlinear absorption due to the high repetition rate of laser excitation. The estimated third order NLO susceptibility was found to be in the order of 10^{-11}esu (Table 1) and it was found to be higher than other copper based systems and bench mark semiconducting materials like CuO, Cu_2O and CdS. According to Miller rule, higher the refractive index, higher will be the NLO susceptibility and hence samples sintered at 3 h possess higher value. Here, the observed higher NLO coefficient is due to the presence of metal-oxygen bond in the Nb-O_6 octahedra. In transition metals the third order nonlinear susceptibility will be generally higher because electrons in the transition metal oxides are localized at the metals and nearest neighbouring oxygen atoms [37]. The oxygen octahedra with perovskite structure (ABO_3) possessing large electro-optic coefficient and strong refractive index are the reason for the use of niobate systems in NLO applications. The observed change in the nonlinearity arises mainly due to the morphological variation originating from the change in sintering time during the synthesis. The large value of NLO coefficient of $CuNbO_3$ (all the four cases) than other NLO systems originate due to Nb-O_6 arrangement which arises from the local crystal structured arrangements. Apart from the local crystal structure, the morphology plays a vital role in altering the NLO properties. Particularly the web-shaped well connected morphology (9 h) has favouring thermal properties (quick heat conduction) and electronic states (favouring 2PA) which facilitate the peculiar and enhanced NLO behaviour. Recently Benoy Anand et al. reported that grain boundary plays a key role in affecting the linear and nonlinear optical properties of the material [41]. Thus, change in grain boundary along with morphology will likely affect the NLO properties of the material [39–40].

Consequently, it can be inferred that sintering time influences the morphology and NLO properties of copper niobate. Transition of agglomerated clusters into equiaxed microstructure has strongly dominated the nonlinear absorption and refraction behaviour. Toggling of nonlinear refractive index (dominant phenomenon under chosen excitation) with morphology clearly portraits the role of sintering time. Here web shaped equiaxed microstructure has effectively propagated thermal energy arising due to high repetition rate ultra-short pulse excitation resulting in stronger nonlinearity. Additionally, in semiconducting materials surface trap states will occur due to surface reconstruction which significantly contributes to the third-order NLO properties by reorienting the dipoles on the surface [38–40]. Generally aging can alter the surface of the material and literature data shows that higher temperature annealing results in the reduction of surface states due to merging of individual crystal grains. Here in the present case, higher sintering temperature and time employed in preparation of $CuNbO_3$ could have resulted in the reduction of the surface state due to merging of the individual grains which is evident from the FESEM data presented in Fig. 1c. This change in surface trap states may also contribute to the observed nonlinearity, which requires much more detailed investigation to understand its role. Thus, $CuNbO_3$ with web shaped equiaxed microstructure can be effectively utilized for optical limiting applications against high-repetition ultra-short infrared pulse laser.

5. Conclusions

In summary, the third order NLO behaviour of perovskite $CuNbO_3$ and limiting action for the high repetition rate ultra-short pulse laser at 800 nm was studied. Change in morphotype with sintering time was studied through FESEM analysis which exposed the growth mechanism of $CuNbO_3$ as agglomerated clusters (3 h); elongated clusters (6 h); web shaped equiaxed structures (9 h); well-defined equiaxed microstructures (12 h). The peculiar toggling of nonlinear refraction between positive and negative refractive index was observed. The observed RSA pattern fits to two photon absorption and the mechanism was accorded to be instantaneous 2PA. The web shaped equiaxed structure has well connected geometry resulting in strong NLO behaviour compared to other structures. Strong limiting action with limiting threshold of 22.24 $\mu J/cm^2$ arises due to the contribution of both 2PA and self-defocusing process. Accordingly, perovskites copper niobate with web shaped equiaxed structure possessing high NLO coefficients and low onset limiting threshold is an aspirant material for limiting application in the IR region.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2017.05.054.

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