



# Influence of sintering time on switching of the femtosecond nonlinear optical properties of $\text{CuNb}_2\text{O}_6$



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## ABSTRACT

Transition of mixed phases (monoclinic and orthorhombic) to pure orthorhombic phase was achieved during the synthesis process of  $\text{CuNb}_2\text{O}_6$  by varying the sintering time. The suppression of monoclinic phase and dominant formation of orthorhombic  $\text{CuNb}_2\text{O}_6$  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 self-defocusing behaviour while pure orthorhombic demonstrated reverse saturable absorption and self-focusing process. The switching of nonlinearity along with increase in NLO coefficient of O- $\text{CuNb}_2\text{O}_6$  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 ( $6.0 \times 10^{-17} \text{ m}^2/\text{W}$ ) of O- $\text{CuNb}_2\text{O}_6$  were found to be higher than well-known NLO materials. Orthorhombic  $\text{CuNb}_2\text{O}_6$  exhibited optical limiting action with low limiting threshold of 38.26  $\mu\text{J}/\text{cm}^2$  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 electro-optic 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  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ). 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 ( $\text{CuNb}_2\text{O}_6$ ) 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 ( $\text{CuNb}_2\text{O}_6$ ) can be an interesting subject of investigation for attaining higher NLO performance. This is because, higher sintering temperature can yield pore-free ceramics with low scattering and improved optical transmission which in turn can yield better NLO performance [14]. Impressed by these facts, attempts were made to study the third-order 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  $\text{cm}^{-1}$ . 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 ( $\omega_0$ ) of 25.5  $\mu\text{m}$ . 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  $\text{CuNb}_2\text{O}_6$ . The preliminary difference between the diffraction pattern of these phases is that two equally intense lines (131) and

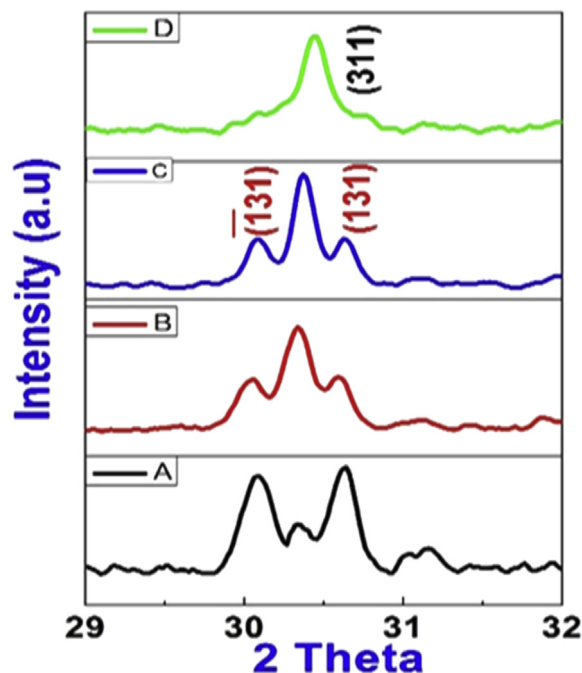


Fig. 1. XRD pattern of  $\text{CuNb}_2\text{O}_6$  obtained at A) 3 h B) 6 h C) 9 h and D) 12 h.

( $\bar{1}31$ ) 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 ( $\bar{1}31$ ) 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 collectively along with a small portion of monoclinic phase. On further increasing the sintering time to 12 h, pure orthorhombic phase of  $\text{CuNb}_2\text{O}_6$  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  $\text{CuNb}_2\text{O}_6$  consists of  $\text{CuO}_6$  and  $\text{NbO}_6$  octahedra in which the site of metal atom was surrounded by distorted octahedron oxygen atoms. Here  $\text{CuO}_6$  octahedra share its four corners with four  $\text{NbO}_6$  while  $\text{NbO}_6$  octahedra share its four corners with two  $\text{NbO}_6$  and two  $\text{CuO}_6$ . Recorded FTIR spectra and band assignments of metal-oxygen vibrations are displayed in

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