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Enhancement of second harmonic generation efficiency: Growth and characterization of magnesium(II)-doped tetrakis(thiourea)nickel(II) chloride crystals

K. Muthu [a], C.K. Mahadevan [b], SP. Meenakshisundaram [a,*]

[a] Department of Chemistry, Annamalai University, Annamalainagar 608002, India
[b] Physics Research Centre, S.T. Hindu College, Nagercoil 629002, India

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ABSTRACT

The influence of magnesium doping on the properties of tetrakis(thiourea)nickel(II) chloride crystals has been described. The reduction in the intensity observed in powder X-ray diffraction of doped specimen and slight shifts in vibrational frequencies confirm the lattice stress as a result of doping. Surface morphological changes due to doping of the alkaline earth metal are observed by scanning electron microscopy. The incorporation of Mg(II) into the crystal lattice was confirmed by energy dispersive X-ray spectroscopy. Lattice parameters are determined by single crystal XRD analysis. The thermogravimetric and differential thermal analysis studies reveal the purity of the materials and no decomposition is observed up to the melting point. The crystal is further characterized by Kurtz powder technique and dielectric studies.

1. Introduction

Nonlinear optical (NLO) materials have a significant impact on frequency conversion, laser technology, telecommunication, optical computing and optical storage technology. Organometallic compounds have the potential for combining both organic and inorganic properties like high damage threshold, wide transparency range, more stability and high nonlinearity [1]. It is well known that thiourea is capable of forming a number of coordination compounds with various metals. The NLO properties of metal complexes of thiourea have attracted significant attention in the last few years, because both inorganic and organic compounds contribute specifically to the process of second harmonic generation (SHG).

Tetrakis(thiourea)nickel(II) chloride (TTNC) is a promising semi-organic nonlinear optical material. TTNC belongs to the tetragonal system with non-centrosymmetric space group I4 [2]. Few reports are available in the literature for the structure [3], growth and characterization of tetrakis(thiourea)nickel(II) chloride [4–6]. Metal ion doped materials are currently receiving a great deal of attention due to the rapid development of laser diodes [7,8]. Several foreign metallic cations existing in the parent compounds with high valency and small radii will affect the whole growth process and enhance physical properties. Doping influences thermochemical, electrical, optical properties and surface morphology depending upon the nature of the host material and the dopant.

Incorporation of Mg into pure α-$LiIO_3$ [9], SnO_2 nanoparticles [10] and bis(thiourea)cadmium(II) chloride [11,12] crystals significantly enhances the electrical conductivity, optical, microhardness and the dielectric properties. Ultraviolet one-color photo refraction (UV-OPR) is enhanced by Mg doping [13]. The SHG conversion efficiency was enhanced by the presence of Mg in $LiNbO_3$ crystals and the optical damage, which is a serious problem with $LiNbO_3$ crystals, can be reduced by doping with Mg [14]. The Mg concentration in Mg-doped $(Ba_{0.6}Sr_{0.4})_{0.92}K_{0.075}TiO_3$ thin films has a strong influence on surface morphology, dielectric and tunable properties [15]. The effect of Mg-doping on the structural and physical properties of $LuFe_2O_4$ and $Lu_2Fe_3O_7$ was reported [16]. Magnesium and strontium doped octacalcium phosphate thin films by matrix assisted pulsed laser evaporation was studied by Boanini et al. [17] and the morphological transition of ZnO nanostructures was influenced by magnesium doping [18]. Doping studies of TTNC have not been reported so far to the best of our knowledge. Recently, we have investigated the Mg(II)-doping effects on bis(thiourea)zinc(II) chloride [19] and tris(thiourea)zinc(II) sulphate [20]. In the present investigation, we report the growth and characterization of Mg(II)-doped TTNC.

* Corresponding author. Tel.: +91 4144 221670.
E-mail address: aumats2009@gmail.com (SP. Meenakshisundaram).

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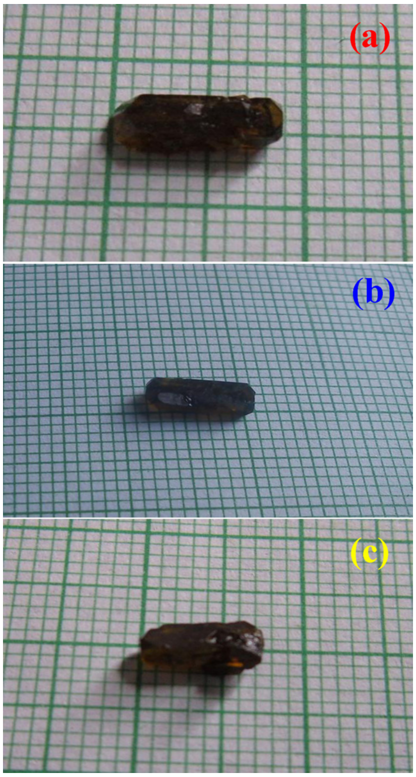

Fig. 1. Photographs of as-grown TTNC crystals. (a) pure (b) 1 mol% Mg(II)-doped (c) 10 mol% Mg(II)-doped.

2. Experimental

2.1. Synthesis and crystal growth

Tetrakis(thiourea)nickel(II) chloride was synthesized according to the reported method [2] using AR grade nickel chloride and thiourea in a stoichimetric ratio 1:4.

$$NiCl_2{\cdot}6H_2O + 4(SC(NH_2)_2) \rightarrow NiCl_2[SC(NH_2)_2]_4$$

The purity of the synthesized material was increased by successive recrystallization processes. Crystals were grown by slow evaporation solution growth technique. Doping of magnesium (1 mol% and 10 mol%) in the form of magnesium chloride (Merck) was done during the crystallization process. The crystallization took place within 30–35 days and the crystals were harvested when they attained suitable size and shape. Photographs of as-grown pure and Mg(II)-doped crystals are shown in Fig. 1.

2.2. Characterization techniques

The FT-IR spectra were recorded using an AVATAR 330 FT-IR by KBr pellet technique in the range 400–4000 cm^{-1}. The grown crystal was subjected to single crystal X-ray diffraction using Bruker AXS (Kappa APEXII) X-ray diffractometer. The powder X-ray diffraction was performed by using Philips Xpert Pro Triple-axis X-ray diffractometer at room temperature at a wavelength of 1.540 Å with a step size of 0.008°. The SEM images were taken using a JEOL JSM 5610 LV scanning electron microscope. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using a NETZSCH STA 409C thermal analyzer in nitrogen atmosphere. Dielectric measurements (capacitance of the crystal, C_{crys} and the dielectric loss factor, tan δ) on the TTNC crystal were carried out by the parallel plate capacitor method as a function of temperature for various frequencies using a Precision LCR meter (AGILENT 4284 A model). The second harmonic generation test on the crystals was performed by the Kurtz powder SHG method [21].

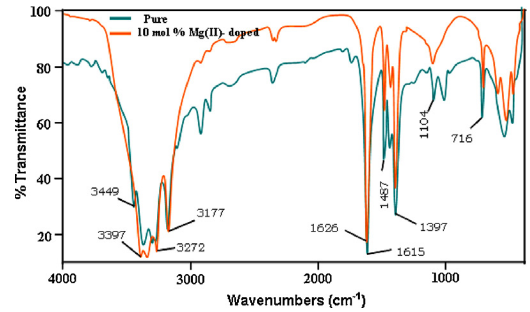

Fig. 2. FT-IR spectra of TTNC.

3. Results and discussion

3.1. FT-IR studies

FT-IR spectra of pure and 10 mol% Mg(II)-doped TTNC crystals are shown in Fig. 2. A close observation of FT-IR spectra of pure and doped specimens reveal that doping generally results in small shifts in some of the characteristic vibrational frequencies. It could be due to lattice strain developed as a result of doping. The broad envelope positioned in between 2750 and 3500 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of —NH_2 group. The absorption band observed at ~1615 cm^{-1} in pure and 1626 cm^{-1} in doped TTNC is assigned to NH_2 bending mode of vibrations. The CN stretching frequencies of thiourea (1089 and 1472 cm^{-1}) are shifted to higher frequencies for pure and Mg(II)-doped TTNC crystals (~1104 and ~1487 cm^{-1}). The CS stretching frequencies (1417 and 740 cm^{-1}) are shifted to lower frequencies (~1397 and ~716 cm^{-1}) for pure and doped samples. The lowering of frequencies can be attributed to the reduced double bond character of the —C═S bond on coordination. These observations suggest that metal coordinate with thiourea through sulfur atom.

3.2. X-ray diffraction studies

The as-grown pure and Mg(II)-doped TTNC crystal was finely powdered and subjected to powder X-ray diffraction analysis. The indexed powder patterns of pure and doped specimen are shown in Fig. 3. The observed peaks are in good agreement with the JCPDS file [22]. No new peaks or phases were observed by doping with alkaline earth metal magnesium but variations in intensities are observed. The well defined Bragg's peaks at specific 2θ angles

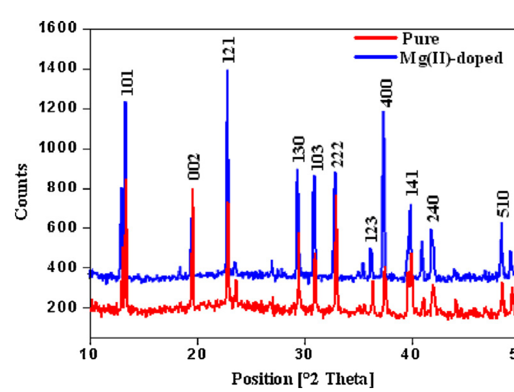

Fig. 3. Powder XRD patterns of TTNC.