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Growth and characterization of Hexakis(thiourea)nickel(II) nitrate crystals

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ABSTRACT

Single crystals of hexakis(thiourea)nickel(II) nitrate $[Ni(SC(NH_2)_2)_6](NO_3)_2$ are grown by slow evaporation of methanolic solution at room temperature. Structural analysis by single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic system with space group **C2/c** and the cell parameters are $a=22.046(2)$ Å, $b=9.3325(4)$ Å, $c=16.221(2)$ Å, $Z=8$. The metal is coordinated by six thiourea groups with Ni–S–C bond angles ranging from 114.81° to 116.85° and Ni–S bond lengths lying in the range 2.35 to 2.61 Å in a distorted octahedral geometry. The interesting feature observed in this study is that although it crystallizes in centrosymmetric structure, contrary to expectations, it exhibits a positive second harmonic generation (SHG) result, quite likely due to the change in stereochemical arrangement. An Nd:YAG laser with a modulated radiation of 1064 nm directed on the powdered sample leads to local noncentrosymmetry and this could be due to the loss of thiourea ligands resulting in tetrakis(thiourea)nickel(II) complex causing green light emission. The powder X-ray diffraction study reveals the crystallinity of the grown material. The vibrational patterns in FT-IR clearly evidence the complex formation. Thermogravimetric analysis (TG) reveals the purity of the sample and no decomposition is observed up to the melting point. The crystal is further characterized by diffused reflectance spectroscopy, dielectric studies and microhardness analysis.

1. Introduction

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 thiourea molecule is an interesting inorganic matrix modifier due to its large dipolemoment [2] and its ability to form an extensive network of hydrogen bonds [3]. 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. Metal–organic complexes offer higher environmental stability combined with greater diversity of tunable electronic properties by virtue of the co-ordinated metal center. Many metal thiourea complexes possessing second-order NLO activities [4–10] and some of them centrosymmetric in nature [11–13] have been reported. As a part our studies, in the growth of centrosymmetric crystals exhibiting a small SHG efficiency [14], in the present investigation, we are reporting the growth, structure and characterization of hexakis(thiourea)nickel(II) nitrate crystals.

2. Experimental

2.1. Crystal growth

A mixture of stoichiometric amounts of thiourea (E-Merck) and nickel(II) nitrate (Qualigens) (6:1) in n-butyl alcohol was concentrated on a water bath until the presence of solid was noticeable. The light green product separated on cooling. The solid was then collected on a filter, washed with ether and recrystallized using methanol. Single crystals of hexakis(thiourea)nickel(II) were grown at room temperature by slow evaporation of alcoholic solution. The crystallization took place within 7–10 days and the crystals were harvested when they attained an optimal size and shape. Bulk crystals are grown using optimized growth parameters and the photograph of crystal is shown in Fig. 1.

$$Ni(NO_3)_2.6H_2O+6(SC(NH_2)_2)\rightarrow[Ni(SC(NH_2)_2)_6](NO_3)_2$$

2.2. Characterization techniques

The FT-IR spectrum was recorded using an AVATAR 330 FT-IR by KBr pellet technique. The single-crystal X-ray diffraction studies were carried out using an Oxford Diffraction Xcalibur-S CCD system equipped with graphite monochromated MoKα ($\lambda=0.71073$ Å) radiation at 150 K. The molecular structure was

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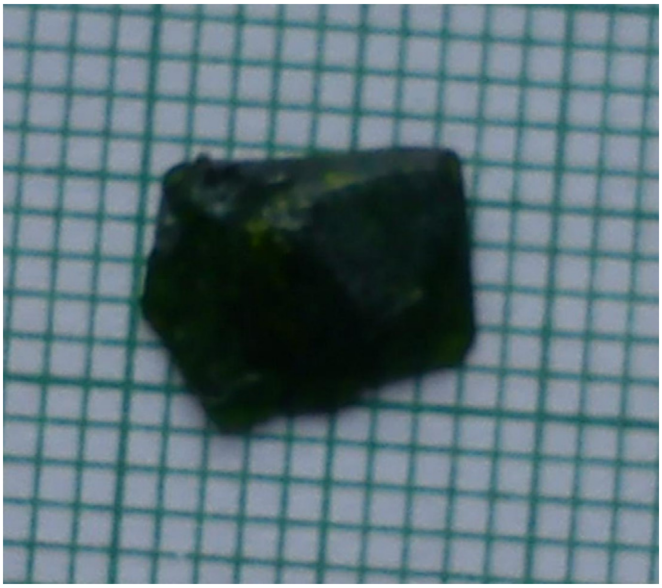

Fig. 1. Photograph of as-grown HTNN crystal.

drawn using ORTEP-3. UV–vis spectrum was recorded using CARY 5E UV–vis spectrophotometer. The powder X-ray diffraction was performed 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°. Thermogravimetric (TG) analysis was carried out using a NETZSCH STA 409C thermal analyzer in nitrogen atmosphere. Vickers microhardness was evaluated for the well polished grown crystal using Reichert 4000E Ultramicrohardness tester. Dielectric measurements were carried out by the parallel plate capacitor method as a function of temperature for various frequencies using a Precision LCR meter (AGILENT 4284A model). The second harmonic generation test on the crystals was performed by the Kurtz powder SHG method [15].

3. Results and discussion

3.1. FT-IR

FT-IR spectrum of HTNN crystal is shown in Fig. 2. Slight shifts in the some of the vibrational frequencies are observed. The broad envelope positioned in between 2750 and 3500 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of $-\mathrm{NH}_2$ group. The $-\mathrm{CN}$ stretching frequencies of thiourea (1089 and 1472 cm^{-1}) are shifted to higher frequencies ($\sim$1102 and $\sim$1490 cm^{-1}). The slight shift in the frequency can be attributed to the greater double bond character of the carbon to nitrogen bond on complex formation. The symmetric and asymmetric stretching frequencies of $-\mathrm{C{=}S}$ (1417 and 740 cm^{-1}) are shifted to lower frequencies (1386 and 712 cm^{-1}). These observations suggest that metal coordinate with thiourea through sulfur atom. The lowering of frequencies can be attributed to the reduced double bond character of the $-\mathrm{C{=}S}$ bond on coordination.

3.2. XRD studies

The X-ray diffractogram (Fig. 3) shows many diffraction peaks. The well defined Bragg's peaks at specific 2θ angles show high crystallinity of HTNN molecule. The XRD of laser irradiated sample is not matching with the XRD before irradiation.

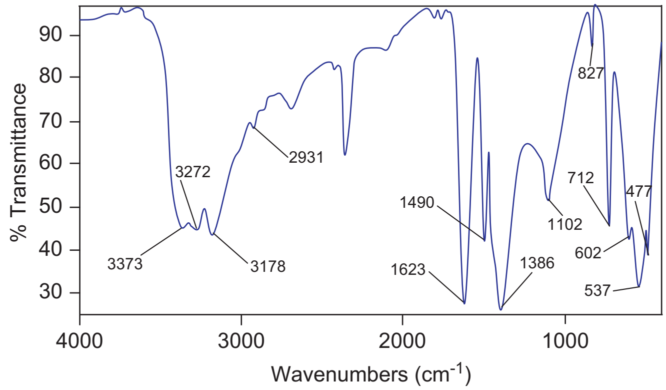

Fig. 2. FT-IR spectrum of HTNN crystal.

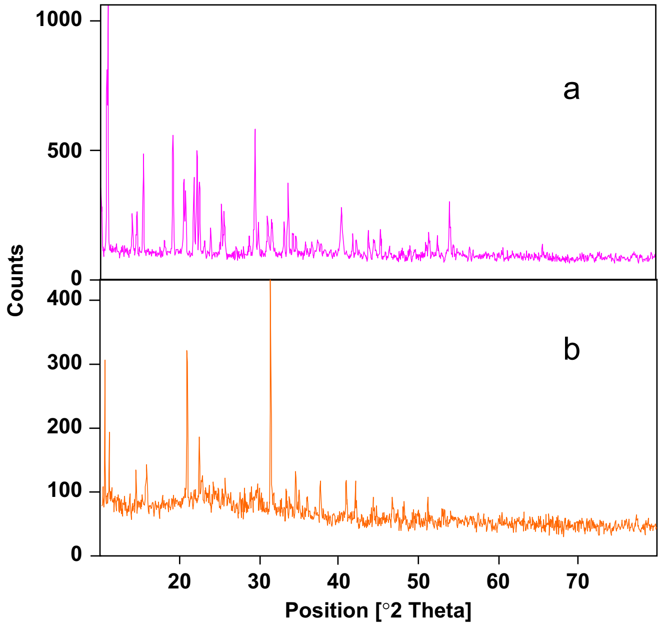

Fig. 3. Powder X-ray diffraction patterns of HTNN crystal (a) before irradiation and (b) after irradiation.

The single crystal XRD analysis shows that the crystal belongs to monoclinic system with space group *C*2/*c*. The unit cell dimensions are $a=22.046$ Å, $b=9.3325$ Å, $c=16.221$ Å, $v=2574.2$ Å^3, $Z=8$. These lattice parameters values closely match the previous studies [16–18] of structure determination of HTNN. The ORTEP diagram of as-grown HTNN single crystal is shown in Fig. 4.

3.3. Diffuse reflectance spectrum

The absorption spectrum obtained between 200 and 1200 nm with high resolution indicates that the absorbance is minimum in the range 400–1200 nm, which is required for the materials exhibiting NLO properties.

3.4. Thermogravimetric analysis

The absence of water of crystallization in the molecular structure is indicated by the absence of weight loss around 100 °C (Fig. 5). A good thermal stability of the material is observed up to $\sim$175 °C. The maximum weight loss (98.89%) observed between 176 to 246 °C may be due to the liberation of volatile substances like ammonia, nitric oxide and sulfur dioxide etc.