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Studies on optical, mechanical, dielectric properties of bisthiourea nickel bromide NLO single crystal

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ABSTRACT

Bisthiourea nickel bromide (BTNB) single crystal has been grown by solution growth technique at room temperature. The crystal structure and lattice parameters were determined for the grown crystal by single crystal X-ray diffraction studies. Optical constants like band gap, refractive index, reflectance, extinction coefficient and electric susceptibility were determined from UV–vis-NIR spectrum. Nonlinear optical property was discussed to confirm the SHG efficiency of the grown crystal. The mechanical strength of the grown crystal was analyzed using Vickers microhardness tester. The dielectric constant and dielectric loss of bisthiourea nickel bromide are measured in the frequency range of 50 Hz to 5 MHz at different temperatures. The ac conductivity studies were carried out on bisthiourea nickel bromide crystals. In order to investigate the growth mechanism and surface features, etching studies are carried out for the crystal. Photoconductivity studies were carried out on bisthiourea nickel bromide crystals.

1. Introduction

Nonlinear optical (NLO) materials play a major role in the promising photonic and optoelectronic technologies. In the recent years, the search for nonlinear optical (NLO) materials find extensive interest among the researchers due to their significant impact on laser technology, fiber optic communication, optical modulation and optical data storage technology [1]. The synthesis of novel and efficient frequency conversion materials has resulted in the development of semi-organic materials, which possess large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical stability [2–4]. Efficient nonlinear optical crystals are required for laser devices due to technological importance in the fields of optoelectronics, signal processing, instrumentation and optical communication [5,6]. In the recent years semi-organic NLO crystals are attracting a great deal of attention due to their high NLO efficiency, high damage threshold and high mechanical strength than organic NLO crystals. Among the semi-organic NLO materials, metal complexes of thiourea, have a low UV cut-off wavelength which is applicable for frequency conversion and second harmonic generation [7,3].

The bulk single crystal of bisthiourea nickel bromide was successfully grown by slow evaporation technique. The cell parameters and crystallinity of the grown crystal were estimated by single crystal XRD. The optical transmittance of the crystal was recorded using the UV–vis-NIR spectrophotometer. The optical bandgap and optical constants of the material were determined by using absorption spectrum. The Vickers microhardness studies were performed to study the mechanical behavior of the crystal. The second harmonic generation efficiency has been determined by Kurtz's powder test. The dielectric loss and dielectric constant were measured as a function of frequency and temperature for the grown crystal. The activation energy is also calculated by ac conductivity studies. Dislocation, surface defects and morphology are characterized by chemical etching followed by etch pit examination using optical microscopy. The photoconductivity studies revealed that the bisthiourea nickel bromide single crystal exhibited negative photoconductivity nature of grown crystal.

2. Experimental procedure

Bisthiourea nickel bromide (BTNB) single crystals were synthesized by dissolving thiourea and nickel bromide in the stoichiometric ratio in distilled water. The solution was stirred continuously using a magnetic stirrer. The prepared solution was filtered and kept undisturbed at room temperature. Tiny seed crystals with good transparency were obtained due to spontaneous nucleation. Among them, a defect free seed crystal was suspended in the mother solution, which was allowed to evaporate at room temperature. Large sized single crystals have been obtained due to

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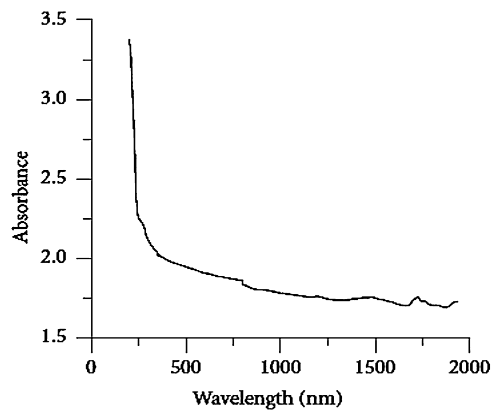

Fig. 1. UV–vis-NIR absorption spectrum.

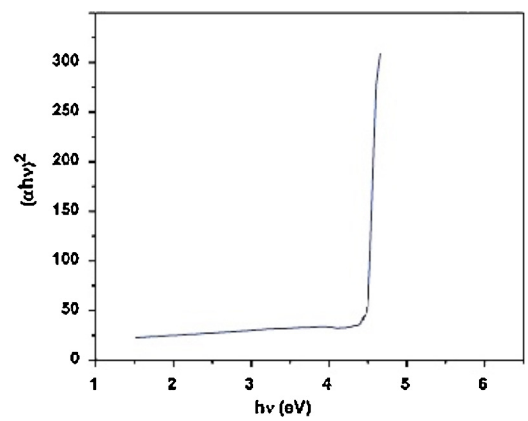

Fig. 2. Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$).

the collection of monomers at the seed crystal sites from the mother solution.

3. Results and discussion

3.1. Single-crystal X-ray diffraction

The single crystal XRD analysis for the grown crystals has been carried out to identify the lattice parameters. The calculated lattice parameters are $a = 6.132$ Å, $b = 8.091$ Å, $c = 9.112$ Å. The crystal belongs to the orthorhombic system and which agree well with the available reported literature values [8].

3.2. UV–vis-NIR spectral analysis

Fig. 1 shows the optical absorption spectrum of the bisthiourea nickel bromide single crystal, recorded in the wavelength region ranging from 200 nm to 2000 nm. The UV cut-off wavelength for the grown crystal was found to be 250 nm. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the relation,

$$\alpha = \frac{2.3026 \log(1/T)}{t} \tag{1}$$

where T is the transmittance and t is the thickness of the crystal. As a direct bandgap of the crystal has absorption coefficient (α) it obeys the following relation:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \tag{2}$$

where E_g is the optical band gap of the crystal and A is a constant. The plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 2. E_g was measured by the extrapolation of the linear part [9]. The bandgap value is found to be 4.35 eV. As a consequence of the wide bandgap, the grown crystal has a large transmittance in the visible region [10].

The high value of band gap indicates that the grown crystal possesses dielectric behavior to induce polarization when powerful radiation is incident on the material. The extinction coefficient (K) can be obtained from the following equation:

$$K = \frac{\lambda\alpha}{4\pi} \tag{3}$$

The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \tag{4}$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation.

Hence,

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t + \exp(\alpha t))}}{1 + \exp(-\alpha t)} \tag{5}$$

Refractive index (n) can be determined from reflectance data using the following equation:

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \tag{6}$$

The refractive index (n) was found to be 1.726 at $\lambda = 2000$ nm. From the optical constants, electric susceptibility (χ_C) can be calculated according to the following relation [11]

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{7}$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \tag{8}$$

where ε_0 is the permittivity of free space. The value of electric susceptibility χ_C is 0.193 at $\lambda = 2000$ nm. Since, the electrical susceptibility of the material can be easily polarized when the incident light is powerful intense. The real part dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the following relations [12]

$$\begin{aligned} \varepsilon_r &= n^2 - k^2 \\ \varepsilon_i &= 2nk \end{aligned} \tag{9}$$

The value of real ε_r and ε_i imaginary dielectric constants at $\lambda = 2000$ nm was estimated at 1.62 and 7.532×10^{-5}, respectively. The moderate values of refractive index and optical band gap suggest that the material has the required transmission range for NLO application. The lower value of dielectric constant and the positive value of the material are capable of producing induced polarization due to intense incident light radiation.

3.3. NLO test – Kurtz powder SHG method

The SHG conversion efficiency of bisthiourea nickel bromide was determined by Kurtz's Perry technique. The crystal was ground into very fine powder and tightly packed in a microcapillary tube. Then it was mounted in the path of Nd:YAG laser beam of energy 1.95 mJ/pulse. When KDP crystal was used as a reference material, it produced 65 mV as output beam of voltage. But it was about 102 mV for the grown sample and hence it is confirmed that the material has NLO efficiency of about 1.6 times that of KDP crystals.