Synthesis and optical characterization of Nickel doped Thiourea Barium Chloride (TBC) single crystals

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Abstract. Organometallic Thiourea barium chloride (TBC) single crystals were synthesized using solution evaporation process at room temperature. Synthesized thiourea barium chloride crystals were recrystallized and during the recrystallization process 1M%, 2M% and 5M% of nickel (Ni) was added to the solution and kept for crystallization. The variation of intensity peaks and the shift in the XRD peaks were observed due to the incorporation of nickel in the host matrix. Variations in the absorbance and transmittance spectra of the pure and Ni doped crystals further confirms the presence of nickel in TBC single crystal. The optical bandgap of the pure and nickel doped single crystals were calculated using Touc’s relation. The results show that bandgap decreased with the dopant concentration in the thiourea barium chloride crystal. The optical constants such as extinction coefficient and reflectance were also studied using the absorption spectrum. The FTIR absorption also shows minute shift in the absorption peaks due to the presence of nickel in the host matrix. Photoluminescence spectra of pure and doped crystals were studied.

1 Introduction

Organometallic materials are gaining importance because of its potential application towards information technology, frequency conversion, optical signal processing and optical image processing [1–3]. Organic materials posess higher nonlinearity but for the practical usage it lacks thermal and mechanical stabilities. Inorganic materials posess higher thermal and mechanical stabilities but moderate nonlinearity. The solution to overcome these drawbacks by producing a material with nonlinearities of the organic materials and the mechanical and thermal stabilities of the inorganic materials by combining these to obtain a new class of materials called organomettalic single crystals [4]. Thiourea is a organic molecule which has large dipole moment and affinity to form bonds between metal atoms through sulfur [5]. Thiourea belongs to centrocemmetric space group when combines with metal atom the crystal system changes to noncentrocemmetric space group [6]. In the oresent work, organic thiourea is combined with inorganic barium chloride to form thiourea barium chloride single crystals. The synthesized crystals was further doped with nickel in different concentrations and analysed. The crystals were studied using powder XRD, UV-vis, FTIR and photoluminescence analysis.

2 Synthesis of TBC and Ni doped TBC crystals

Organomettallic thiourea barium chloride (TBC) single crystal was synthesized by taking 1 : 1 molecular ratio of thiourea and barium chloride as raw materials. These were then dissolved in deionised water and stirred for 5 hours to obtain a saturated homogenous solution. The suspended particles in the solution was removed by filtering the solution and the solution was then kept for slow evaporation. Defectless crystals could be harvested in 3-4 weeks. In the recrystallization process Ni
was added to the TBC solution in the form of Nickel chloride. Crystals of TBC were formed during the following chemical reaction,

\[ CH_4N_2S + BaCl_2 \rightarrow Ba(CH_4N_2S)Cl_2 \]  

(1)

3 Characterization of crystals

Structural analysis of synthesized pure and nickel (Ni) doped crystals were studied using powder XRD (Rigaku 600) using CuKa (\(\lambda = 1.5405\) Å) scanned range: 10°-50° with a scanning rate of 2° per minute. UV-Vis spectrum was recorded using ocean optics spectrometer USB 4000 in the wavelength range of 200 to 800 nm. The IR transmittance spectrum was recorded and studied using Shimadzu FTIR spectrometer by KBr pellet technique in the range of 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). The photoluminescence (PL) spectra of TBC and ADTBC crystals were recorded using Horiba Scientific-Fluoromax-4 spectrophotometer TCSPC.

3.1 Powder XRD

The synthesized crystals were crushed into fine powders and subjected to powder XRD analysis, which is shown in figure 1(a). The crystals were analyzed using X-Pert Highscore Software and the peaks were indexed. It was observed that the pure and nickel doped crystals belongs to monoclinic crystal structure confirming that doping will not alter the crystal structure of TBC. From the powder crystal XRD it was observed that the pure and Ni doped crystals will not show much variations in the peak positions but small shift is observed which can be attributed as the nickel stays as a interstitial atom or in vacancy cites of TBC matrix shown in figure. 1(b).

![Figure 1](image1.png)

Figure 1. (a) Powder XRD pattern (b) Enlarged powder XRD pattern of Pure, 1 M% Ni doped, 2 M% Ni doped and 5 M% Ni doped TBC crystals.

3.2 Uv-Vis analysis

The absorbance and transmittance spectrum of pure and Ni doped TBC crystals were shown in figure 2. For both pure and Ni doped crystals there is an absorption peak at around 233 nm which can be attributed as the electronic transition of thiourea unit of TBC crystals. In addition to this, 1, 2 M% Ni doped TBC crystal show a small absorption peak at around 278 nm. Moreover, 5 M% Ni doped crystal
shows another absorption peak at around 285 nm corresponding to the Ni addition in the crystal shown in figure 2(a).

Figure 2. (a) Uv-Vis absorption spectra (b) Uv-Vis transmission spectra of Pure, 1 M% Ni doped, 2 M% Ni doped and 5 M% Ni doped TBC crystals.

Figure 2(b), shows the transmittance spectrum for Pure and Ni doped crystals. The pure TBC crystal shows nearly 100% transmission in the visible region where as the Ni is added to the TBC crystal the transmission in the visible region reduces. It may be noted that 1 M% Ni doped crystal shows 97% transmission and 90% transmission was observed for 2 M% Ni doped TBC crystals. Further, 5 M% the crystal shows nearly 85% transmission indicating that the addition of Ni decreases the transparency in the visible region.

3.2.1 Optical constants determination
Optical bandgap of the pure and Ni doped crystals were calculated using the Touc’s relation [7], shown in figure 3.

\[
\alpha = \frac{2.3026 A}{t}
\]  

(2)

We have used Touc’s relation, \((\alpha h\nu)^2 = A(h\nu - E_g)\), where \(\alpha\) is the optical absorption coefficient, \(h\nu\) is the photon energy, and \(A\) is a constant.

The optical bandgap of the crystals was calculated by extrapolating the linear portion of Tauc’s plot. Pure TBC crystal shows bandgap of 4.54 eV and 1, 2 and 5 M% Ni doped TBC crystals shows the bandgap of 4.21 eV, 4.18 eV and 4.11 eV respectively. It was found that band gap of the Ni doped crystal decreases with the increase in the dopant percentage of Nickel in the TBC crystal.

Light loss per unit distance (Extinction coefficient) is calculated using the Eq. 3. [8]

\[
K = \frac{\alpha d}{4\pi}
\]

(3)
Figure 3. Optical bandgap of Pure, 1 M% Ni doped, 2 M% Ni doped and 5 M% Ni doped TBC crystals.

Figure 4(a), shows the extinction coefficient with respect to wavelength.

Figure 4. (a) Extinction coefficient (b) Reflectance spectrum of Pure, 1 M% Ni doped, 2 M% Ni doped and 5 M% Ni doped TBC crystals.

Light loss is minimum for pure TBC crystal, while it is more for Ni doped TBC crystals. As the dopant percentage of the crystal increases the light loss increases in the Ni doped crystals but the light loss for the synthesized crystals are in the order of 10^-6. The lower value of extinction coefficient indicates that the light loss in the crystal is negligible.

Reflectance of the light from the crystal is calculated using the Eq. 4. [7,8], shown in figure 4(b).

\[ R = 1 \pm \frac{\sqrt{1-\exp(-\alpha t)+\exp(\alpha t)}}{1+\exp(-\alpha t)} \]  

where \( t \) is the thickness of the sample and \( \alpha \) is the absorption co-efficient. The crystal reflects nearly 6.2% in the UV region and reflection is minimum in the visible region. Doped crystal shows another peak in the UV region and the reflection is maximum for 5 M% Ni doped TBC crystal. Higher
transmission, lesser reflectance and absorbance suggests that the crystal could be used as antireflecting coatings in solar devices [1].

### 3.3 FTIR analysis

The presence of Nickel in the host lattice was confirmed using the FTIR spectral data. The synthesized pure and Ni doped TBC crystals were powdered and ground with KBr to prepare pellets. IR spectrum of the synthesized crystals were shown in the figure 5. Absorption at 716 cm⁻¹ for pure, 1 and 2 M% Ni doped TBC crystals and 688 cm⁻¹ for 5 M% Ni doped TBC crystal were attributed to the C-S symmetric stretching [9]. The absorption at around 1376 cm⁻¹ for pure TBC crystal was attributed as C-S asymmetric stretching and similar C-S asymmetric stretching was noticed at around 1376 cm⁻¹, 1372 cm⁻¹, 1372 cm⁻¹ for 1, 2, 5 M% Ni doped TBC crystals [10]. Shift in the C-S vibrations confirmed the strain in the crystal lattice due to nickel incorporation in the host lattice. NH₂ bending vibration was observed at around 1640 cm⁻¹ for pure and 1, 2 M% Ni doped TBC crystals [11]. 5 M% Ni doped TBC crystal shows a NH₂ bending vibration at around 1633 cm⁻¹. Compared with pure TBC, there was no extra peak observed in Ni doped TBC but a minute shift was observed due to small amount of added dopant entering into the host lattice.

![FTIR spectrum](image)

**Figure 5.** FTIR spectrum of Pure, 1 M% Ni doped, 2 M% Ni doped and 5 M% Ni doped TBC crystals.

### 3.4 Photoluminescence (PL)

The photoluminescence spectra of synthesized TBC and Ni doped TBC crystals were shown in figure 6. The equimass crystals were dissloved in double distilled water and the molecules were excited and emission spectra were recorded. Crystal show emission at around 402 nm for pure TBC crystal, and at 403 nm for 1, 2 M% Ni doped TBC crystals and at 404 nm for 5 M% Ni doped TBC crystal. It was observed that the emission intensity increases as the dopant percentage increases and the emission is due to sulphur vacancies [12]. Enhancement in the emission peak of the crystal suggests that crystals can have potential applications in optoelectronic device fabrication such as solar cells and LED's [13].

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**Fig. 6.** Photoluminescence (PL) spectrum of Pure, 1 M% Ni doped, 2 M% Ni doped and 5 M% Ni doped TBC crystals.

### 4 Conclusions

Pure and Ni doped TBC crystals were synthesized by solvent evaporation technique. The crystallinity nature of the synthesized crystals were studied using powder XRD studies. There was no extra XRD peak observed for Ni doped TBC crystals. However, shift in the peak positions and change in intensities of peaks are attributed as Ni incorporated in the host lattice. Uv-vis absorption spectra shows that the crystal possesses extra absorption peak at around 285 nm for 5 M% Ni doped TBC crystal and for smaller dopant percentage of Ni it appears as lower intensity peak. Crystal shows good transparency for pure TBC crystals and the transparency decreases as the dopant concentration increases. Doped crystals show two bandgaps corresponding to the UV absorption spectra and the bandgap decreases for the doped crystals as the increase in the dopant concentration. FTIR spectral analysis reveals the dopant incorporation in the host lattice and there was a shift in the transmission peak intensities as the dopant concentration increases. The optical constants such as reflectance and extinction coefficient were studied using the absorption data. The results show promise for their application in optoelectronic device fabrication and information processing devices. Enhancement on photoluminescence spectra was observed for the doped crystals and the maximum intensity was observed for 5 M% Ni doped TBC crystal. The increase in PL intensity as the increase in the Ni dopant suggest that crystals can be used in practical applications such as photonic devices and laser applications.

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