Investigation on dielectric studies and second harmonic generation (SHG) efficiency of bisthiourea cobalt malonate and bisthiourea nickel malonate: A novel semiorganic nonlinear optical materials

N. MALHARI RASTE, K. SATISH PARDESHI[*]
Department of Chemistry, Savitribai Phule Pune University (formerly Pune University), Ganeshkhind, Pune 411007, Maharashtra, India

A new semiorganic NLO materials viz. bisthiourea cobalt malonate (BTCoM) and bisthiourea nickel malonate (BTNiM) have been synthesized by solvent free mechanochemical method. They are characterized by CHNS, FTIR, TG/DTA/DSC, XRD and UV-VIS. spectroscopy. Chemical composition was confirmed by chemical and CHNS analysis. FTIR studies confirmed the presence of various functional groups and coordination of metal ion to thiourea through sulphur atom. Thermal behavior has been investigated by using TG, DTA and DSC showing BTNiM is more stable. The X-ray data suggest that synthesized compounds are polycrystalline in nature. Transmittance spectra reveal that lower cut-off wavelength for BTCoM is 296.52nm and for BTNiM is 297.81nm, thus materials have good optical transmission in entire visible region. Magnetic measurements were carried out by Faraday method. The dielectric measurements of material with varying frequencies at room temperature were studied. The dielectric constant and dielectric loss decreases with increase in frequency for both compounds. These lower values at higher frequency are a desirable property to enhance the second harmonic generation (SHG) efficiency. The SHG conversion efficiency measured by Kurtz-Perry powder technique was found to be higher for BTCoM than BTNiM which defines the nonlinear optical nature of materials and their suitability for NLO applications.

1. Introduction

Nonlinear optical (NLO) materials play an important role in the field of fiber optic communication, optical modulation, laser technology, optical signal processing and opto-electronics since they are capable of producing higher values of the original frequency. They are also used in the area of telecommunication and optical storage devices [1-6]. Recent work shows that organic materials have very large nonlinear susceptibilities compared with inorganic materials but their use is limited by low optical transparency, low laser damage threshold, poor optical quality, and lack of robustness, poor mechanical properties and inability to produce large crystals. In case of inorganic NLO materials, as they have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities due to lack of extended π electron delocalization [7, 8]. Hence recently research is focused on new type of NLO materials which combine the advantages of organic and inorganic materials called semiorganic materials. These materials have high optical nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [9]. Metal complexes of thiourea, commonly called semiorganics;
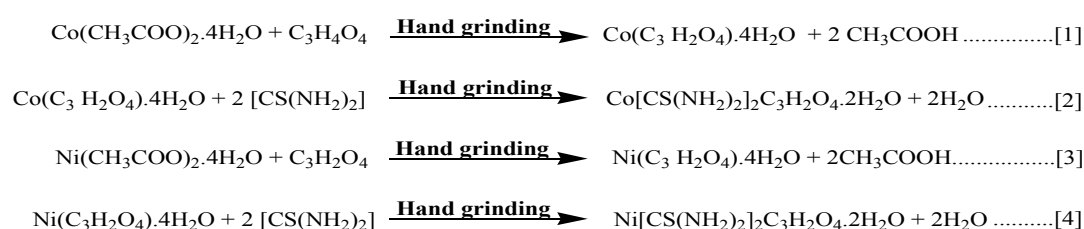
these complexes having lower UV cut-off wavelengths applicable for frequency conversion are of interest because both organic and inorganic components in it contribute specifically to the process of SHG [4, 10-15]. Thiourea is an inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds [16]. Thiourea is a centrosymmetric molecule, when coordinated with metal ions it becomes non- centrosymmetric material to exhibit nonlinear optical property [17]. A variety of molecules of this class have been synthesized by several groups [18-21].

In this paper, we are reporting the synthesis of new semiorganic nonlinear optical materials, bisthiourea cobalt malonate (BTCoM) and bisthiourea nickel malonate (BTNiM) by solvent free mechanochemical method [22]. This method has some advantages like, easy to operate and cheap, environmental friendly method, materials can be prepared in bulk quantity and energy can be saved during synthesis. Characterization of synthesized materials, study of magnetic properties, dielectric measurement and measurement of second harmonic generation (SHG) are also reported.

2. Experimental

2.1 Synthesis

In the present study cobalt acetate (assay 99%), nickel acetate (assay 99%), malonic acid (assay 99%), thiourea (assay 99%) and other required chemicals are of analytical grade, obtained from SISCO Research Laboratories Pvt. Ltd. Mumbai, HIMEDIA Laboratories Pvt. Ltd. Mumbai, S D Fine- Chem. Ltd. Mumbai, Merck Ltd. Mumbai, India respectively and were used without further purification. Syntheses of complexes were carried out by solvent free mechanochemical method. In this method cobalt acetate tetrahydrate/ nickel acetate tetrahydrate, malonic acid and thiourea were taken in stoichiometric ratio (1:1:2). Firstly

cobalt acetate and malonic acid in ratio (1:1) taken in agate mortar and mixture was hand ground for10 minutes at room temperature to obtain semisolid paste of metal malonate hydrate and acetic acid as by-product. Then 2 part thiourea was added and hand grinding process was continued for next 30 minutes. Thiourea coordinates with cobalt malonate to form bisthiourea cobalt malonate. This compound was frequently grinded and dried in air. After one hour, most of acetic acid byproduct goes off from the reaction mixture and semisolid mass gradually turn into fine powder as bisthiourea cobalt malonate. Similarly bisthiourea nickel malonate was synthesized by using same procedure. The BTCoM and BTNiM synthesis is shown in scheme 1.

$$Co(CH_3COO)_2.4H_2O + C_3H_4O_4 \xrightarrow{\textbf{Hand grinding}} Co(C_3H_2O_4).4H_2O + 2 CH_3COOH \text{...............[1]}$$

$$Co(C_3H_2O_4).4H_2O + 2 [CS(NH_2)_2] \xrightarrow{\textbf{Hand grinding}} Co[CS(NH_2)_2]_2C_3H_2O_4.2H_2O + 2H_2O \text{...........[2]}$$

$$Ni(CH_3COO)_2.4H_2O + C_3H_2O_4 \xrightarrow{\textbf{Hand grinding}} Ni(C_3H_2O_4).4H_2O + 2CH_3COOH \text{.................[3]}$$

$$Ni(C_3H_2O_4).4H_2O + 2 [CS(NH_2)_2] \xrightarrow{\textbf{Hand grinding}} Ni[CS(NH_2)_2]_2C_3H_2O_4.2H_2O + 2H_2O \text{...........[4]}$$

Scheme 1. Synthesis of Bis thiourea Co/Ni malonate

2.2 Characterization techniques

The CHN analysis was carried out using CHNS analyzer, Flashea, 1112 series make Thermo-Electron Corporation. Sulphur analysis using VarioEL CHNS analyzer Mode. S. N. 11059102. Metal contents were determined by using known methods [23]. X-ray diffraction studies were carried out using D-8 Advance Brucker AXS, scanning angle ranging from 10° to 80° at a scan rate 1°/min. The FTIR spectroscopy studies are effectively used to identify the functional groups present in the compound and to determine the bonding between metal and thiourea. BTCoM and BTNiM were analyzed using Shimadzu FTIR-8400, Infrared spectrometer, by KBr pellet technique in the range 400-4000 cm^{-1}. The optical transmittance spectrum was recorded in the range of 200-1000 nm using Shimadzu UV-Visible Spectrophotometer, model: UV-1601. Thermogravimetric and differential thermal analysis was carried out using Shimadzu TG/DTA-60H thermal analysis instrument. The thermal analysis was carried out between 20 ^{o}C to 900 ^{o}C at a heating rate 10 ^{o}C/min in the air atmosphere. While, differential scanning calorimetric analysis was done using Shimadzu DSC-60 instrument. Differential scanning calorimetric analysis is between 20 ^{o}C to 450 ^{o}C at same heating rate atmosphere. Magnetic susceptibility was measured by Faraday's method using E-METTLER ZORICH balance obtained by NEO-Pharma Pvt. Ltd. Mumbai. Dielectric study was carried out using instrument, HIOKI HITESTER model 3532-50 LCR mete. Nonlinear optical property was studied by measuring second harmonic generation (SHG) efficiency by modified Kurtz-Perry Powder technique.

3. Results and discussion

3.1 Elemental analysis

The results of elemental analysis (**Table 1**) confirmed the stoichiometry and hence the molecular formula of the synthesized compounds, BTCoM and BTNiM. The observed values are in good agreement with calculated values. The general formula of compound is $M[TU]_2.D.XH_2O$ Where, M = Co and Ni, Tu = Thiourea and D = Dicarboxylate such as malonate.

Table 1. Elemental analysis of bisthiourea divalent transition metal malonates

Complex		BTCoM*	BTNiM#
Metal (M=Co/Ni)	Cal. (%)	16.84	16.82
	Obs. (%)	16.50	16.90
Carbon	Cal. (%)	17.19	17.20
	Obs. (%)	17.07	17.34
Hydrogen	Cal. (%)	4.04	4.04
	Obs. (%)	4.19	4.61
Nitrogen	Cal. (%)	16.04	16.05
	Obs. (%)	15.00	15.74
Sulphur	Cal. (%)	18.36	18.37
	Obs. (%)	18.15	16.96

*Co[CS(NH_2)_2]_2C_3H_2O_4.2H2O, #Ni[CS(NH_2)_2]_2 C_3H_2O_4.2H_2O

3.2 Fourier transform infrared spectral analysis

FTIR spectrums of complexes are shown in Fig.1. In the synthesized complexes, there are two possibilities by which the coordination of metals Co and Ni with thiourea can occur. The coordination with metals may occur either through nitrogen or through sulphur of thiourea [24]. The high frequency N-H absorption bands in the region 3100-

3400cm^{-1} in the spectrum of thiourea have not been shifted to lower frequencies on the formation of metal thiourea complex which indicates that the bonding is only between metal (Co/Ni) and sulphur atoms and not of metal and nitrogen [25].The symmetric and asymmetric C=S stretching vibrations in thiourea at 730cm^{-1} and 1417cm^{-1} are shifted to low frequency region at 725 and 1404cm^{-1} in BTCoM while at 717and 1412cm^{-1} in BTNiM which confirmed the formation of metal sulphur coordination bond. [26].The symmetric C-N stretching vibrations at 1089cm^{-1} in thiourea are shifted to the higher frequencies 1096cm^{-1} in BTCoM and 1090cm-[1] in BTNiM. The increase in frequency may be character of C=N bond on complex formation and a single bond character of C-S bond. The bands observed at 1608cm[1]and 1615cm^{-1} in BTCoM and BTNiM respectively corresponds to NH_2 bending vibrations. The symmetric bending S-C-N at 494cm^{-1}of thiourea shifted to lower frequencies 493cm^{-1} and 479cm^{-1} in BTCoM and BTNiM respectively.
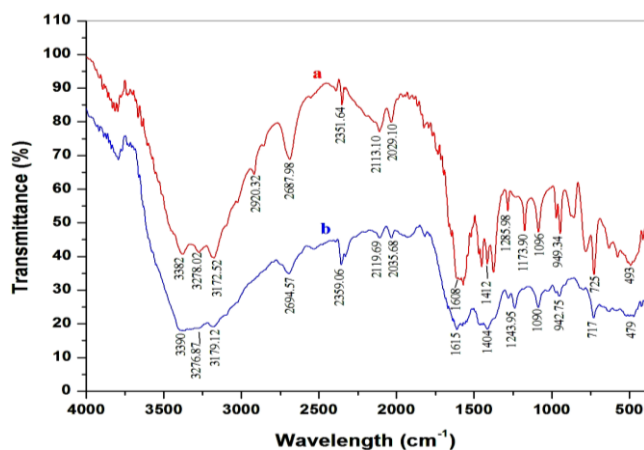
Fig. 1. FTIR spectrum of a) BTCoM and b) BTNiM

3.3 Thermal analysis

Thermogravimetric (TG) analysis, differential thermogram analysis (DTA) and differential scanning calorimetry (DSC) gives information regarding phase transition, water of crystallization and different stages of decomposition of the materials [27].

Fig.2 (a) shows TG and DTA curves of BTCoM. It is seen that the TG curve shows a plateau up to 120.13 °C suggesting that compound is thermally stable up to a temperature of 120.13 °C. Two stage decomposition of BTCoM compound is observed. In the first stage from temperature 120°C dehydration of precursor (BTCoM)

takes place which is followed by decomposition of thiourea upto temperature 267.40°C. In this stage weight loss is 55.63 %. This weight loss is attributed to water of crystallization and release of remaining acetic acid as a byproduct up to 146 °C and after these temperature thiourea molecule decomposes. The CH_3COOH molecules easily volatilized into air during the process of hand grinding. However, it has boiling point of 118 °C, so remaining acetic acid can only be totally removed at a temperature higher than its boiling point. The endothermic effect at 146.17 °C registered on DTA was assigned to the dehydration and removal of acetic acid while that at 212.48 °C temperature decomposition of thiourea molecules. From temperature 120.13 °C to 267.40 °C weight loss is attributed to decomposition of thiourea molecules coordinated to Co into carbon disulphide (CS_2), isothiocynic acid (HNCS), and ammonia (NH_3) [28]. Decomposition of thiourea molecule is also endothermic process which is shown in DTA curve at 212.48°C. In the second stage from temperature 267.40 °C to 728.95 °C decomposition of malonate moiety ($CoC_3H_2O_4$) of BTCoM to cobalt oxide (CoO) takes place. The 23.09% weight loss is observed in TG curve which is attributed to elimination of CO and H_2 gases. This is seen in terms of sharp exothermic peaks at 414.47°C and broad exothermic peak at 548.82°C in DTA curve. The final product CoO is formed at 594.04 °C, but from this temperature there is gain in weight of about 2.12% takes place. This change is due to surrounding oxygen present in furnace that reacts with CO to form CO_2 thus stable CoO is formed at 728.95°C. The probable scheme for the decomposition of BTCoM is shown in Scheme 2.
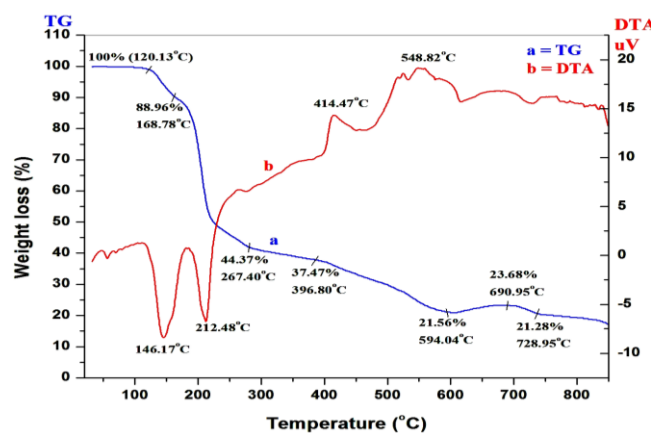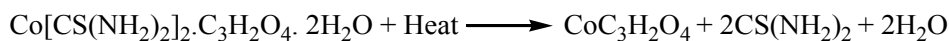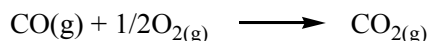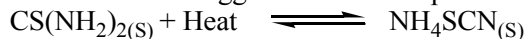

Fig. 2(a). TG- DTA of bisthiourea cobalt malonate.

$$Co[CS(NH_2)_2]_2.C_3H_2O_4. 2H_2O + Heat \longrightarrow CoC_3H_2O_4 + 2CS(NH_2)_2 + 2H_2O$$

Isomeric reaction is suggested for decomposition of thiourea-

$$CS(NH_2)_{2(S)} + Heat \rightleftharpoons NH_4SCN_{(S)}$$

$$2CS(NH_2)_{2(S)} \longrightarrow CS_{2(g)} + H_2NCS_{(g)} + 2NH_{3(g)}$$

$$NH_4SCN_{(S)} \longrightarrow NH_{3(g)} + HNCS_{(g)}$$

$$CoC_3H_2O_4 \longrightarrow CoO + 3CO_{(g)} + H_{2(g)}$$

$$CO(g) + 1/2O_{2(g)} \longrightarrow CO_{2(g)}$$

Scheme 2. Probable scheme for decomposition of BTCoM

The total observed weight loss 78.72% was very close to that of calculated value 78.54% and matches to formula $Co[CS(NH_2)_2]_2.C_3H_2O_4. 2H_2O$. Fig. 2(b) shows DSC of bisthiourea cobalt malonate. The endothermic peak at 124.19 °C in DSC analysis show the dehydration and removal of acetic acid and sharp exothermic peak at 207.01°C, melting point of compound thus thermal stability of BTCoM is relatively good.
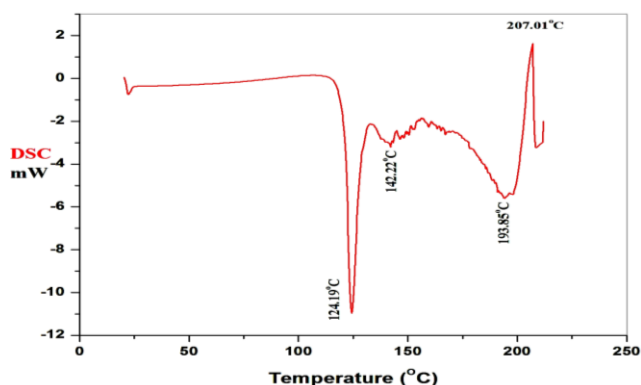

Fig. 2(b). DSC of bisthiourea cobalt malonate.

Fig. 2(c) shows TG-DTA curves of BTNiM. The TG curve shows a plateau up to 126.16°C suggesting that compound is thermally stable up to a temperature of 126.16°C. In BTNiM also two stage decomposition is observed. In the first stage from temperature 126.16°C dehydration of precursor (BTNiM) takes place which is followed by decomposition of thiourea up to temperature 275.37°C. In this stage weight loss is 54.07%. This weight loss is attributed to water of crystallization and release of remaining acetic acid as a by-product up to 160°C and after this temperature thiourea molecules decomposes. The endothermic effect at 160.43°C registered on DTA was assigned to the dehydration and removal of acetic acid.

While that at 204.21°C was attributed to melting point of BTNiM. From temperature 160°C to 275.37°C weight loss is attributed to decomposition of thiourea molecules coordinated to Ni into carbon disulphide (CS_2), isothiocynic acid (HNCS), and ammonia (NH_3). Decomposition of thiourea molecule is exothermic process which is shown in DTA curve at 221.24°C. In the second stage from temperature 275.37°C to 723.36°C decomposition of malonate moiety ($NiC_3H_2O_4$) of BTNiM to nickel oxide (NiO) takes place. The 24.62% weight loss is observed in TG curve which is attributed to elimination of CO and H_2 gases. This is seen in terms of sharp exothermic peaks at 420.87°C and 480.03°C in DTA curves. The final product NiO is formed at 590.97°C but from this temperature there is a gain in weight of about 0.58% takes place. This change is due to surrounding oxygen in furnace react with CO to form CO_2, thus stable NiO is formed at 723°C. The probable scheme for the decomposition of BTNiM is shown in Scheme 3.
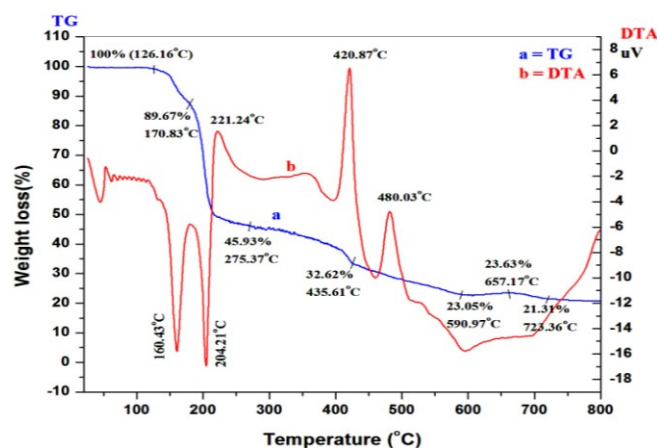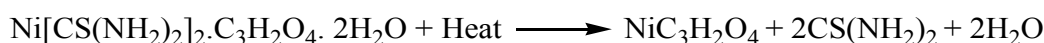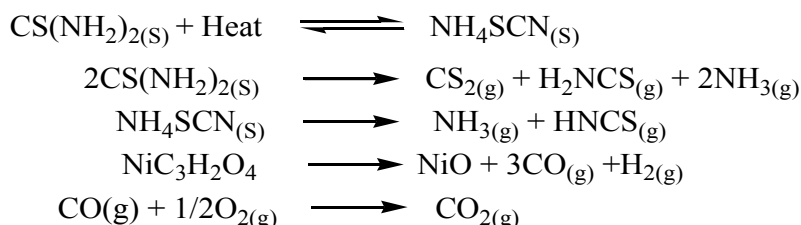

Fig. 2(c). TG-DTA of bisthiourea nickel malonate

$$Ni[CS(NH_2)_2]_2.C_3H_2O_4. 2H_2O + Heat \longrightarrow NiC_3H_2O_4 + 2CS(NH_2)_2 + 2H_2O$$

Isomeric reaction is suggested for decomposition of thiourea-

$$CS(NH_2)_{2(S)} + Heat \rightleftharpoons NH_4SCN_{(S)}$$

$$2CS(NH_2)_{2(S)} \longrightarrow CS_{2(g)} + H_2NCS_{(g)} + 2NH_{3(g)}$$

$$NH_4SCN_{(S)} \longrightarrow NH_{3(g)} + HNCS_{(g)}$$

$$NiC_3H_2O_4 \longrightarrow NiO + 3CO_{(g)} + H_{2(g)}$$

$$CO(g) + 1/2O_{2(g)} \longrightarrow CO_{2(g)}$$

Scheme 3. Probable scheme for decomposition of BTNiM

The total observed weight loss 78.9% was very close to that of calculated value 78.59% and matches to formula $Ni[CS(NH_2)_2]_2.C_3H_2O_4.2H_2O$.

Fig.2 (d) shows DSC of bisthiourea nickel malonate. The endothermic peak at 202°C in DSC analysis shows the

melting point of compound thus thermal stability of BTNIM is relatively good. In both BTCoM and BTNiM decomposition takes place in two stages. BTNiM is thermally somewhat more stable than BTCoM.
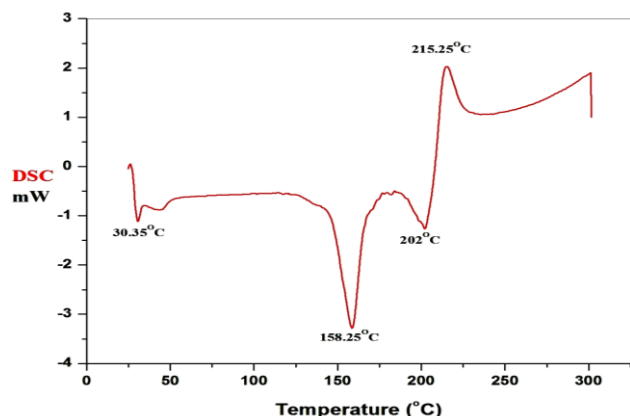
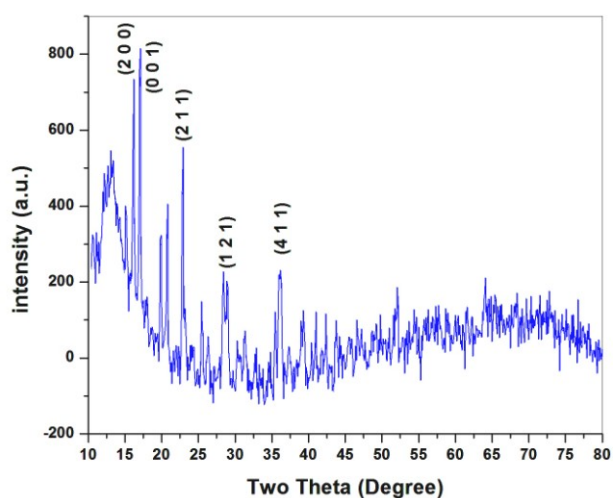*Fig. 2(d). DSC of bisthiourea nickel malonate.*
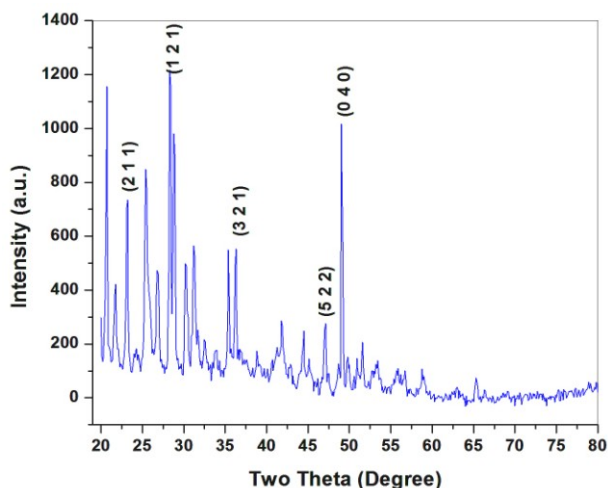

Fig.3 (a) XRD of bisthiourea cobalt malonate

Fig.3 (b) XRD of bisthiourea nickel malonate

3.4 X-ray diffraction studies

The synthesized materials, BTCoM and BTNiM were subjected to powder X-ray diffraction to analyze whether the material is crystalline or amorphous.

The X-ray diffractogram [Fig. 3(a), Fig. 3(b)] shows many diffraction peaks. It is confirmed that the synthesized materials are polycrystalline in nature. The well defined Bragg's peak at specific 2θ angle shows high crystallinity of materials. The d- values of Bragg peaks in the XRD pattern of powdered BTCoM and BTNiM compounds were compared with Cobalt Malonate and Nickel Malonate from the corresponding JCPDS No. 26 – 1647 and JCPDS No. 26 – 1871 respectively. It is observed that d- values of bisthiourea cobalt malonate and bisthiourea nickel malonate compounds are in good agreement with the standard. From this, the monoclinic structure is suggested. The calculated average crystallite size of $Co[CS(NH_2)_2]_2.C_3H_2O_4.2H_2O$ is 62.65nm and that of $Ni[CS(NH_2)_2]_2.C_3H_2O_4.2H_2O$ is 77.21nm.

3.5 Optical transmittance studies

Transmittance spectrum of BTCoM and BTNiM complexes recorded in the UV-Visible region are shown in Fig.4. The lower UV cut-off wavelengths of these complexes are 296.52nm, 297.81nm respectively. The wide transmission range in the entire visible region is essential requirement for non-linear optical materials and it adds advantage in the field of optoelectronic applications [29].
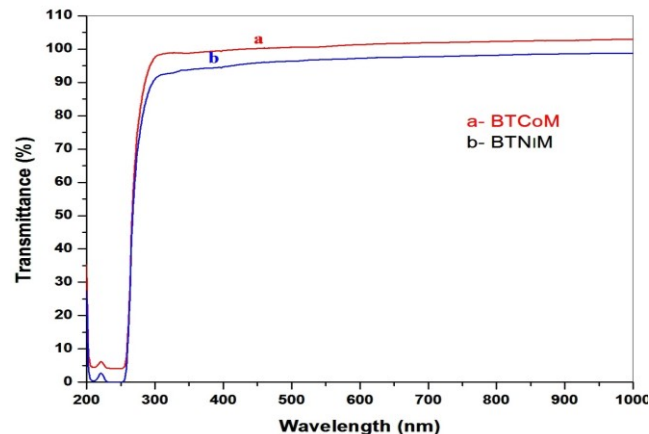

Fig. 4. UV-Visible spectrum of a) BTCoM and b) BTNiM

3.6 Magnetic susceptibility measurement

The room temperature magnetic measurement was carried out by Faraday's method using $Hg[Co(SCN)_4]$ as calibrant. Diamagnetic corrections were applied using Pascal's constant [30]. Magnetic moment data is shown in Table 2. From the magnetic moment data it is observed that BTCoM and BTNiM are paramagnetic in nature.

Sr. No.	Complex	Metal ion	Magnetic moment μ(BM)	No. of unpaired electrons
1	$Co[CS(NH_2)_2]_2.$ $C_3H_2O_4.$ $2H_2O$	Co^{2+} (d^7)	4.31	3
2	$Ni[CS(NH_2)_2]_2.$ $C_3H_2O_4.$ $2H_2O$	Ni^{2+} (d^8)	3.02	2

3.7 Dielectric study

Dielectric constant is one of the basic electrical properties of solids. It is the measure of how easily a material is polarized in an external electric field [31] Dielectric study was carried out using instrument, HIOKI HITESTER model 3532-50 LCR meter. The surface of sample which is in the form of pellet was coated with silver paste for firm electrical contact. The capacitance of sample was measured at room temperature within frequency range 100Hz to 5MHz. The dielectric constant (ε) and dielectric loss (έ) of samples have been calculated using the relations,

$$\varepsilon = cd/A\varepsilon_o \qquad (1)$$

and

$$\acute{\varepsilon} = \varepsilon \tan\delta \qquad (2).$$

Where, c is capacitance, d is the thickness, A is area of cross section of the sample, ε_o is the permittivity of free space.

The variation of dielectric constant and dielectric loss with frequency is shown in figs. 5 and 6 respectively. From the Fig. 5 and Fig. 6, both dielectric constant and dielectric loss of title material decreases with increasing frequency. The decrease of dielectric constant with increasing frequency is a normal dielectric behavior and can be explained on the basis of polarization mechanism. There are four primary mechanism of polarization that exists in materials, i.e., electronic, ionic or atomic, dipolar or orientational and space charge or interfacial polarization. At low frequency, all the mechanisms of polarization contribute to the dielectric constant and with increase in frequency the contributions from different polarization start decreasing [32]. But from the plot it is observed that, as the frequency increases the dielectric constant initially decreases very rapidly and then slowly as the frequency increases. This type of variation suggests higher space charge polarazability at the lower frequency region. This type of behavior is due to the electronic exchange of the number of ions in the crystal giving local displacement of electrons in the direction of applied field,

which gives the polarization. As the frequency increases, a point is reached where the space charge cannot sustain and comply with the external field. This behavior is similar to those of observed in zinc tartarate [33-34] and strontium tartarate [35].
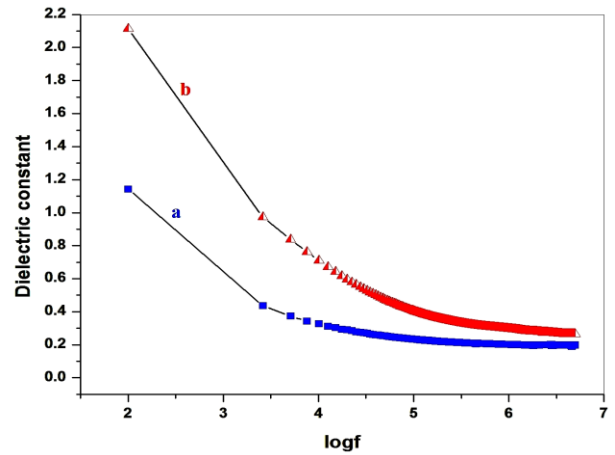

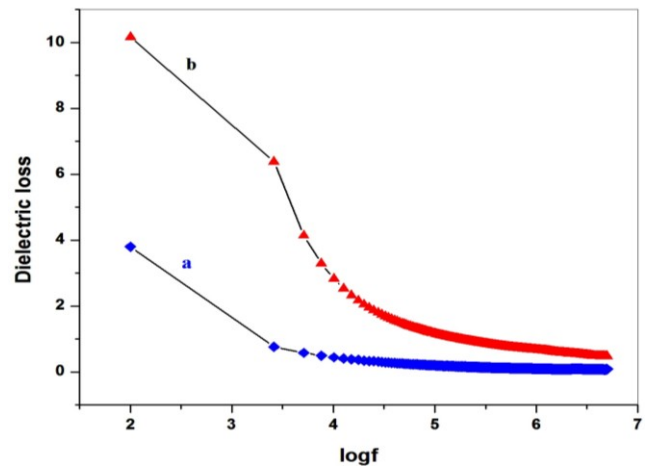*Fig. 5 Variation in Dielectric constant with frequency in a) BTCoM and b) BTNiM.*

Fig. 6 Variation in Dielectric loss with frequency in a) BTCoM and b) BTNiM.

The dielectric constant of both the samples becomes almost constant over from 32600Hz to 5MHz in BTCoM and from 100100Hz to 5MHz in BTNiM. In accordance with the Miller rule, the lower values of dielectric constant are a suitable parameter for the enhancement of SHG coefficient [36]. The dielectric loss was also studied at room temperature with various frequencies. As the frequency increases, the dielectric loss initially decreases very rapidly and then slowly as the frequency increases. The characteristic of low dielectric loss at high frequency for samples BTCoM and BTNiM as evident from Fig.6 suggest that compounds posses good optical quality with lesser defects and this parameter is of vital importance for nonlinear optical applications [37].

3.8 Second harmonic generation (SHG) efficiency

The relative second harmonic generation efficiency was determined by modified Kurtz-Perry powder technique [38] at Indian Institute of Science (IISc), Bangalore, India. It is an important and well accepted tool to evaluate the conversion efficiency of a nonlinear optical material. A Q-Switched Nd: YAG laser having wavelength of 1064nm, with an input power 4.9mJ/Pulse and pulse width 8ns with a repetition rate of 10Hz was used for present experimental study. The input laser beam was incident on powdered form of materials such as BTCoM and BTNiM which was packed in a glass capillary tube. Second harmonic generation was confirmed by emission of green radiation (λ=532nm). SHG efficiency was measured with respect to potassium dihydrogen phosphate (KDP) as reference material is shown in **Table 3**.From the table it is observed that, both the samples exhibits second harmonic generation conversion efficiency which confirmed the nonlinear optical nature of materials. BTCoM shows better efficiency than BTNiM. However, it was found that efficiency of BTCoM was 0.413 times and BTNiM 0.344 times lower than that of KDP as a reference. The SHG activity is due to the non-centrosymmetric structure of compound. The increased SHG efficiency can be taken as better candidate for NLO applications such as Photo cells, solar cells, LED's, LASER diodes, electric eyes, photovoltaic power supplies, various monitoring & control circuit, optical fiber communication systems etc.

Table 3. Second Harmonic Generation (SHG) efficiency.

Complex	Input Energy (mJ/pulse)	SHG output Energy (mV)	SHG Conversion Efficiency (%)
$Co[CS(NH_2)_2]_2$.$C_3H_2O_4$.$2H_2O$	4.9	1.2	24.48
$Ni[CS(NH_2)_2]_2$.$C_3H_2O_4$.$2H_2O$	4.9	1.0	20.40
KDP	4.9	2.9	59.18

4. Conclusions

The complexes such as bisthiourea cobalt malonate and bisthiourea nickel malonates are synthesized by solvent free mechanochemical method.

Molecular formula $M[TU]_2$.$C_3H_2O_4$.XH_2O of complexes was confirmed by elemental analysis.

FT-IR spectrum determines the various functional groups present in BTCoM and BTNiM and it has been found that the symmetric and asymmetric C=S stretching vibrations in thiourea at 730cm^{-1} and 1417cm^{-1} are shifted to low frequency region at 725 and 1404cm^{-1} in BTCoM while at 717 and 1412cm^{-1} in BTNiM which confirmed the formation of metal (Co/Ni) sulphur coordination bond.

XRD data suggest that the synthesized complexes are polycrystalline in nature. Crystallite size of BTCoM is 62.65nm and that of BTNiM is 77.21nm.

Transmission spectrum reveals that the lower UV cut-off wavelengths for BTCoM and BTNiM are 296.52nm and 297.81nm respectively; which indicates good optical transmission in the entire visible region.

Dielectric measurements on the sample exhibit very low dielectric constant and dielectric loss at higher frequencies, indicating good optical quality with less defects in the samples.

Both samples, BTCoM and BTNiM exhibits the second harmonic generation (SHG) conversion efficiency. However, SHG efficiency of BTCoM was found to be 0.413 and BTNiM 0.344 times lower than that of KDP as reference which confirmed the nonlinear optical nature of materials and SHG conversion efficiency makes the samples a potential material for NLO applications.

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[*]Corresponding author: skpar@chem.unipune.ac.in