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Mechanical, dielectric and thermal analysis of semi-organic NLO materials

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ABSTRACT

Semi organic crystals offer a variety of molecular structures by virtue of the changes brought out in selection of metals, ligand and coordination numbers. The diversity of molecular structure given an opportunity to tune the electronic properties and hence to exploit the linear and non linear optical properties. Efficient non-linear optical crystals bis thiourea manganese sulphate (BMTS), tris thiourea manganese sulphate (TMTS) and urea thiourea manganese sulphate (UTMS) have been grown by slow evaporation technique. All the three crystals belong to orthorhombic system. *In the present work the mechanical, dielectric studies and thermal analysis of BMTS, TMTS and UMTS crystals have been studied and compared. Vicker's micro hardness test was carried out to study the mechanical strength of the crystals. The Meyer's index number (n) was calculated using Vickers's micro hardness number. The change in concentration of thiourea does not have any impact on the mechanical strength of the crystals. The dielectric constant and dielectric loss were found to decrease when the frequency increased. Low dielectric constant and dielectric loss at higher frequency is a desirable property to enhance the SHG efficiency. Thermal strength of the grown crystals has been studied using thermogravimetric (TGA) and differential thermal analysis (DTA). Addition of urea slightly improve the melting point of the crystals.*

Key words: Crystal growth, Optical materials, Hardness, Thermal Analysis, Dielectric studies.

INTRODUCTION

Recent search for new frequency conversion materials is concentrated on semi-organic materials due to their large nonlinearity, high resistance to laser induced damage and good mechanical hardness [1, 2]. Thiourea and its family of crystals have been reported to be of very great interest

for the non linear optical applications [3,4]. We have grown single crystals of bis thiourea manganese sulphate (BMTS), tris thiourea manganese sulphate (TMTS) and urea thiourea manganese sulphate (UMTS). The crystals were grown by the slow evaporation method. In this work the mechanical, thermal and dielectric analysis of the crystals are reported and compared. The Mayer's index number was calculated from Vickers's micro hardness number (Hv).

MATERIALS AND METHODS

The single crystals of BMTS, TMTS and UMTS were grown at room temperature by slow evaporation of their aqueous solution. Care was taken to minimize mechanical and thermal variations. Colourless, bright and transparent crystals were obtained. The crystals were characterized as follows; the mechanical studies of the crystals were made by Vickers's micro hardness test at room temperature. Vickers's micro hardness was measured using MUTUTOYO-MH 112 model (Japan). The dielectric constant and the dielectric loss of the samples were studied using HIOKI 3532-50 LCR HITESTER in the frequency range of 100 Hz to 5 MHz. The thermogravimetric analysis was performed using SDT Q 600 V 8.3 instrument.

RESULTS AND DISCUSSION

1.1 Mechanical test

The mechanical characterization of the crystals was made by Vickers's micro hardness tests at room temperature. Vickers's hardness indentations were made on the flat polished face of the crystals for loads 10, 25 and 50 g for a dwell period of 10 s using Vickers's diamond indenter attached to an incident light microscope. The shape of the impression is structure dependent, face dependent and also material dependent. Several indentations were made for each load and the averages of the entire diagonal (d) of the indented impressions were measured. Vickers's hardness number was determined using the formula $Hv = 1.8544\ P/d^2$, where P is the applied load in Kg, d is in mm and Hv is in $Kgmm^{-2}$. The hardness number was found to increase with load.

The Meyer index number can be calculated from the Meyer's law [5,6] which relates the load and indentation diagonal length $P = kd^n$

$$\text{Log } P = \text{Log } k + n \text{ Log } d.$$

Where k is the materials constant and n is Meyer's index. The above relation indicates that Hv should increase with P, if $n>2$ and decrease with P when $n<2$. In order to calculate the value of 'n', graphs are plotted against log P Vs log d and shown in Figure 1, which give straight lines after least square fit. The slopes of these straight lines give, the values of n and found to be 3.5 for BMTS and TMTS and 11 for UMTS. According to Onitsch [7] and Hannemann [8] 'n' should lie between 1 and 1.6 for hard materials and above 1.6 for softer ones. Hence, we can say that all these crystals belong to soft material category.

It may be noted that change in the concentration (ratio) of thiourea does not change the micro hardness coefficient index. The addition of urea increases the value of 'n' in the case of UTMS.

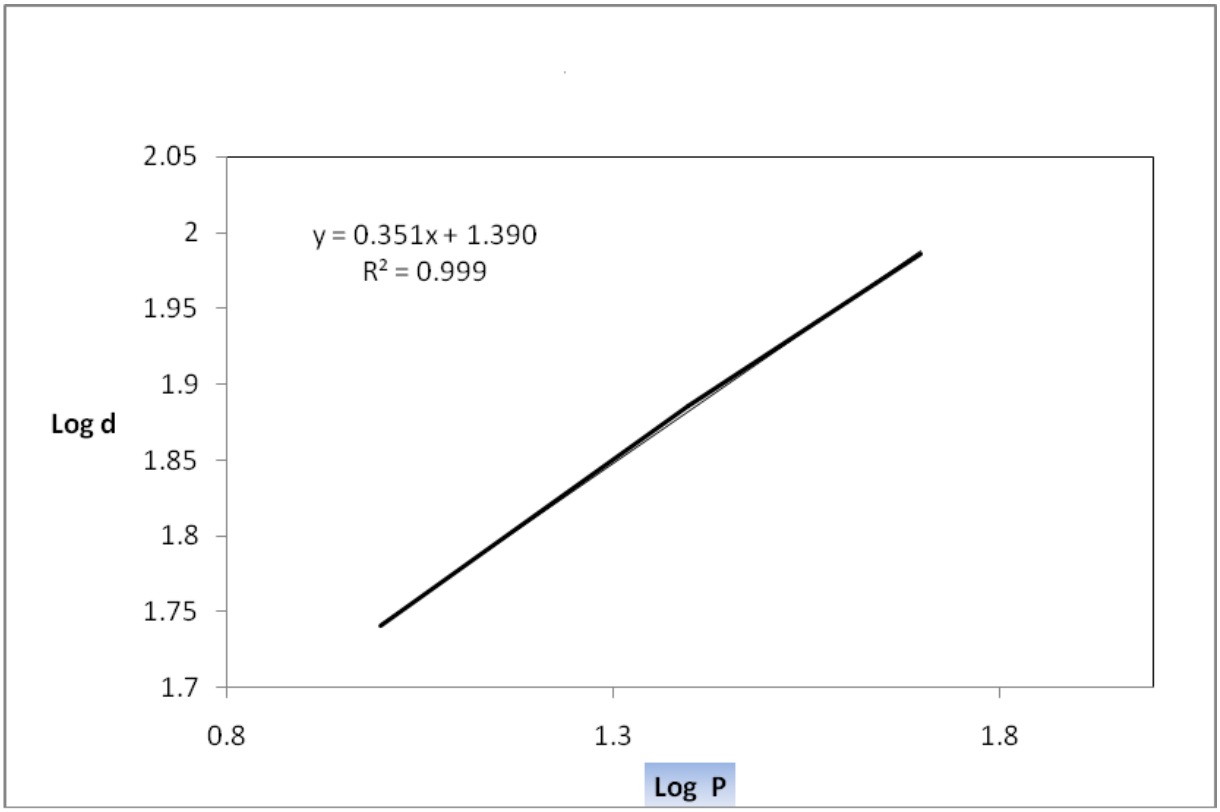

Figure 1Plot of log P Vs log d for BMTS and TMTS

1.2 Dielectric studies

The dielectric constant is one of the basic electrical properties of solids. The dielectric constant is the measure of how easily a material is polarized in an external electric field [9]. The measurement of dielectric constant and loss as a function of frequency and temperature is of interest both from theoretical point of view and from the applied aspects.

The dielectric constant and dielectric loss of the crystals were measured in the frequency range 100 Hz to 5 MHz. It is observed that at low frequencies the higher the temperature, the larger is the dielectric constant. Due to the impedance to the motion of charge carriers at the electrodes, space charge and macroscopic distortion results, which might cause larger values of dielectric constant at lower frequencies [10].As the frequency increases, the dielectric constant values are found to decrease exponentially and attain lower values. The dielectric constant of all the three samples becomes almost a constant over the wide frequency range from 5 KHz to 5MHz. In accordance with the Miller rule, the lower values of dielectric constant are a suitable parameter for the enhancement of SHG coefficient [11].

The dielectric loss was also studied for various frequencies at different temperatures. As the frequency increases, the dielectric loss values also are found to decrease exponentially and attain lower values at different temperatures. The low dielectric loss at higher frequency of the samples indicates that the crystals posses lesser number of electrically active defects [12] and this parameter is of vital importance for non linear optical materials in their application.

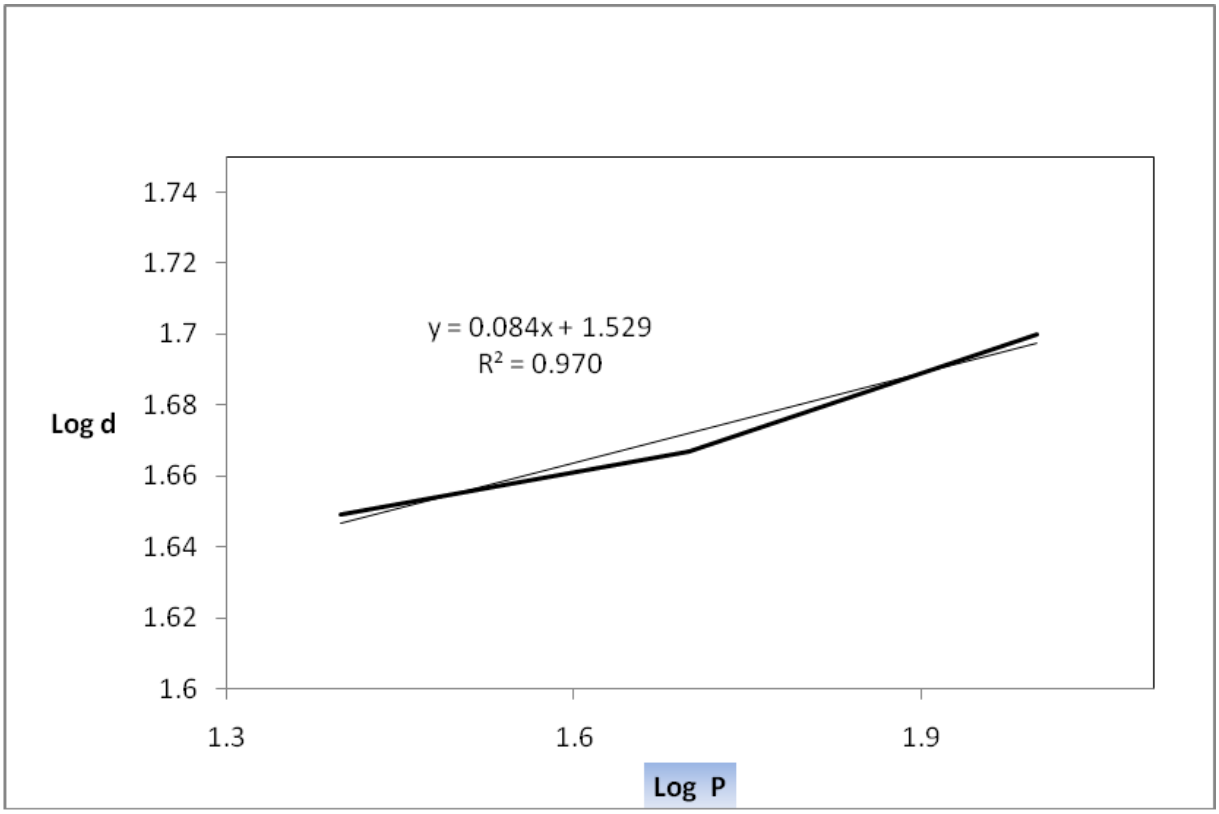

Figure 2Plot of log P Vs log d for UMTS

1.3 Thermal analysis

Differential thermogram analysis (DTA) and thermogravimetric analysis (TGA) give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system. Simultaneous TGA and DTA were carried out for the grown crystals in the temperature range of 30º C to 1000º C with a heating rate of 20K/min in the nitrogen atmosphere. The thermogram and differential thermogram are shown in Figures 2, 3 and 4.

The BMTS crystal decomposes in three stages. The absence of water of crystallization in the molecular structure is indicated by the absence of the weight loss around 100º C. The sharp endothermic peak at 232º C is assigned to the melting point of the crystal. The sharpness of this peak shows the high degree of crystallinity and purity of the sample [13]. From the DTA graph it is observed that the materials are stable up to 181º C. The crystal undergoes two irreversible endothermic transitions at 181º C and 232º C which is followed by one exothermic peak at 401º C indicates major decomposition of the material.

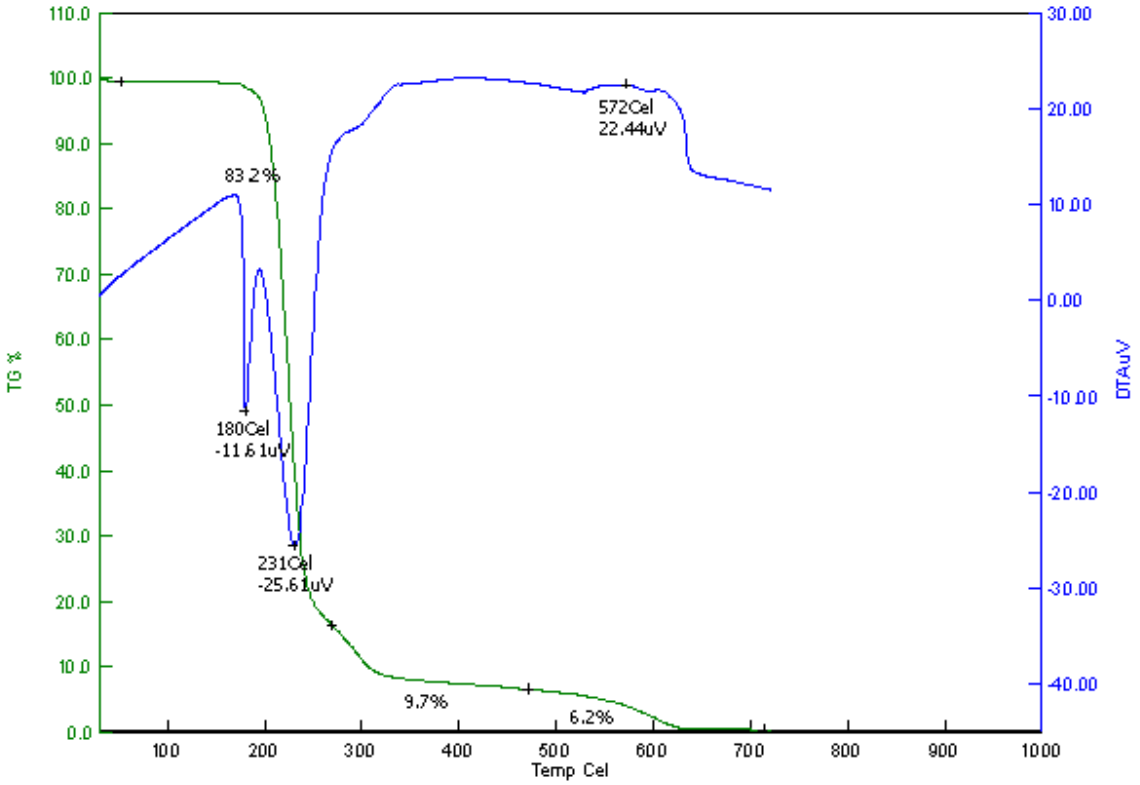

Figure 3Thermogravimetric analysis of BMTS

The TMTS crystal decomposes in a similar way as that of BMTS, TMTS crystals decomposes in three stages at 180º C, 270º C and 480º C. No weight loss is recorded up to 180º C illustrates the absence of physically absorbed or lattice water in the crystal. The melting point of the crystal is assigned at 231º C. The initial mass of the sample was 4.22 mg and at a temperature of about 700º C, almost the entire sample decomposes indicating the bulk decomposition occurring in the sample.

The UMTS crystal decomposes in four stages. The irreversible endothermic transition at 236º C corresponds to the melting point of the crystal. The marginal increase in the melting point may be due to the addition of urea. The decomposition starts at 179º C and major weight loss occurs between 179º C and 270ºC. Heavy mass loss and early decomposition indicates the presence of urea in UMTS. It is seen that different stages, various gaseous fractions like ammonia, carbon monoxide, carbon dioxide, hydrogen are liberated, leading to the bulk decomposition of the compound before 430º C.

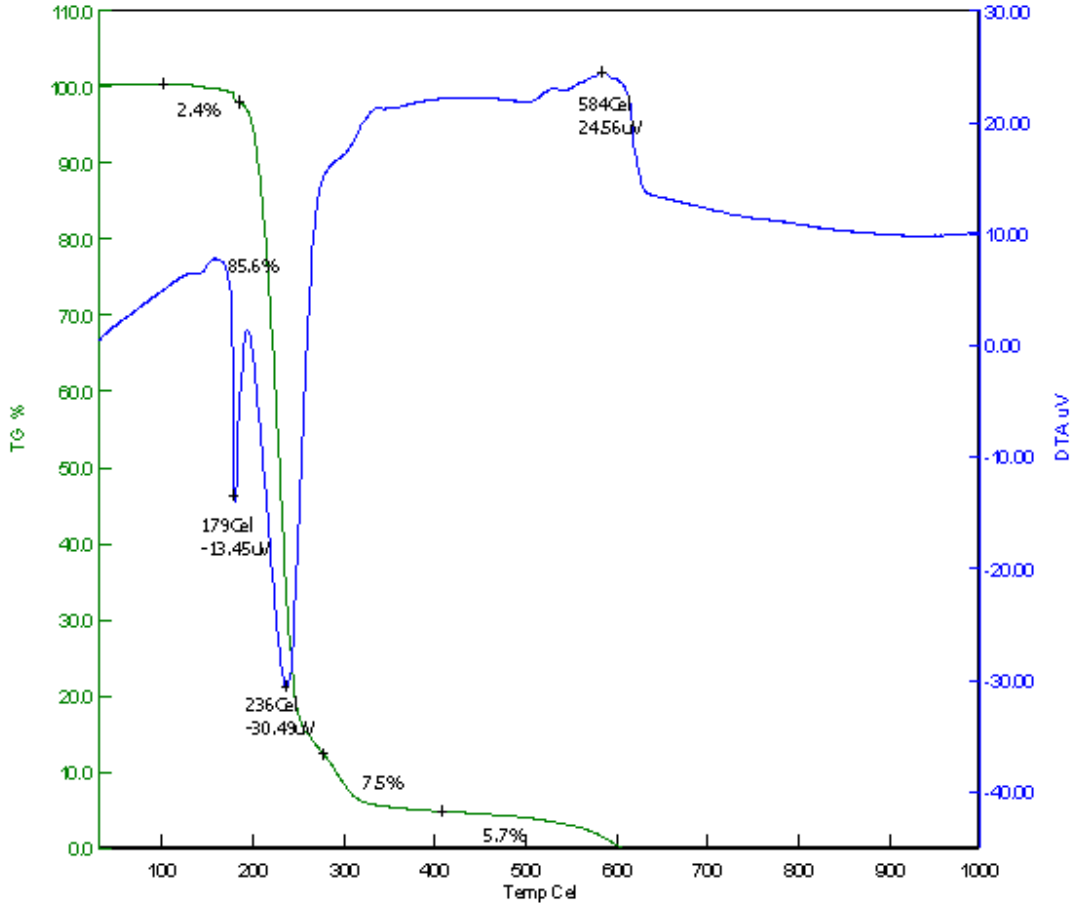

Figure 4 Thermogravimetric analysis of TMTS

CONCLUSION

The Vickers's micro hardness numbers Hv for the crystals were calculated by the application of load in the range 10 – 50 g; Hv increases with increasing load. The value of Meyer's index number was calculated as 3.5 for BMTS, 3.5 for TMTS and 11 for UMTS, which suggests that the crystals belong to soft materials category. The dielectric and thermal properties have been evaluated and reported. The dielectric study reveals that the crystals posses lesser number of defects.

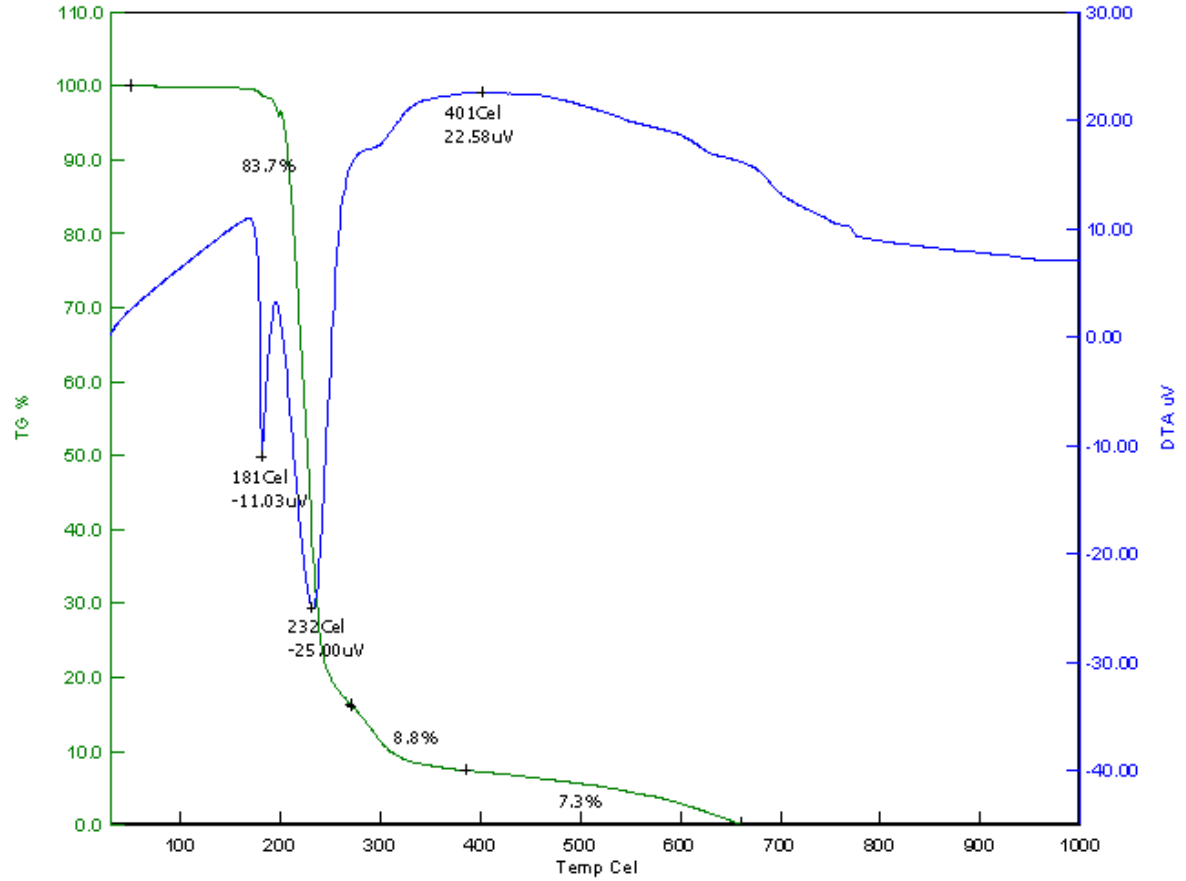

Figure 5 Thermogravimetric analysis of UMTS

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