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Research Article

LINEAR AND NON-LINEAR OPTICAL PROPERTIES OF MTC SINGLE CRYSTALS DOPED WITH $ZNCL_2$

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ABSTRACT

Non-linear optics is playing a major role in the emerging photonic and optoelectronic technologies. Organic compounds possess a high degree of optical non-linearity than inorganic compounds, but they are thermally unstable. The need to make them thermally stable resulted in a new class of materials called semi organics. In the present study, $Zncl_2$ doped Magnesium Thiourea Chloride (MTC) semi organic single crystals were grown by slow evaporation method. The grown crystals were characterized optically by recording UV-Vis spectrum. The optical band gap energy was determined using Tauc plot. The optical parameters like extinction co-efficient, complex optical dielectric constants and conductivity were determined by available methods. The grown crystals were examined by Kurtz-perry powder SHG method. The band gap energy values show that the grown crystals are dielectrics, and the SHG output of 532 nm was detected.

Keywords: Solution method, optical, Dielectric studies, SHG

1. INTRODUCTION

The invention of high intensity laser has opened up many innovative ways to explore the nature of matter and its interaction with light. Nonlinear optics (NLO) is one of the most interacting research fields that has revealed a host of optical phenomena, such as second and third harmonic generations, sum and difference frequency generations and optical parametric generations [1]. Non-linear optical materials (NLO) exhibiting second harmonic generation have been in great demand over the last few decades due to technological importance in the fields of optical communication, signal processing , instrumentation[2-5]. Non-linear optics is the main focus of many researches going on around the world. It is most attracting due to their potential applications in the field of optical data storage and sensor applications [6-8].

The new grown NLO materials are semi organic crystals known for their large nonlinearity and high resistance to laser induced damage. Metal organic complexes offer higher environmental stability combined with greater diversity of tunable electronic properties by virtue of the co ordinated metal centre. The thiourea molecules are coordinating with several metal ions to form stable co-ordinate complexes.

The NLO properties of some complexes of thiourea have attracted significant attention because both organic and inorganic components in it contribute specifically to the process of SHG [9-11]. Thiourea, which is otherwise centrosymmetric, yields excellent noncentrosymmetric materials. Metal complex of thiourea commonly called semi-organics, include the advantages of both organic and inorganic part of the complex[12] In these view, the attempt has been made to combine magnesium chloride with Thiourea to form a new semi organic NLO materials known as Magnesium thiourea chloride (MTC).

2. EXPERIMENTAL

MTC was synthesized using AR Grade magnesium chloride and Thiourea in the molar ratio 1:3 from the following reaction.

$$MgCl_2+3CS\,(NH_2)_2 \rightarrow Mg\,[CS\,(NH_2)_2]_3Cl_2$$

The synthesized salt was used to grow pure and zinc chloride doped MTC single crystals by slow evaporation technique. The dopant ratio taken in the present study are 1:0.01, 1:0.02, 1:0.03, 1:0.04 and 1:0.05.Totally six crystals were grown in an identical conditions. The optical properties of the grown crystals were examined by recording UV-Vis spectrum using Cary 5000 in the wavelength range 200-800nm.The optical band gap energy (E_g) was determined from the Tauc plot drawn by taking $h\nu$ along x-axis and $(\alpha h\nu)^2$ along y-axis. The x intercept of the line of best fit of the above curve gives the E_g value. The type of transition and optical band gap energy can be determined by Tauc law [13] by plotting equation

$$\alpha h\nu = A(h\nu - E_g)^n$$

where, $h\nu$- Incident photon energy

α- Absorption coefficient

E_g-band gap energy of the material

A-constant that depends on the electronic transition probability

n-an exponent that characterizes the type of electronic transition responsible.

A graph is drawn by taking 'λ' along x-axis and 'n' along y-axis. It is found that the dependence of 'n' is linear at longer wavelength ($\lambda \to \infty$). The value of static refractive index (n_0) was determined from the intersection of straight line with vertical axis at $\lambda = 0$.

The extinction coefficient 'K' was calculated using the formula [14, 15]

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

Where α is the absorption coefficient.

The real and imaginary parts of the complex optical dielectric constant ε_r and ε_i respectively were calculated using the relation [16]

$$\varepsilon r = n^2 - k^2$$

$$\varepsilon i = 2nk$$

The optical conductivity is a measure of the frequency response of the material when irradiated with light. The optical conductivity can be determined from absorption coefficient (α) and refractive index (n) using the relation

$$\sigma_{op} = \frac{\alpha n c}{4\pi}$$

Where 'c' is the velocity of light.

3. RESULTS AND DISCUSSION

The UV-Vis absorption and transmittance curves of the 1:0.01Zn MTC grown crystal are shown in the figs 1&2. It shows wide transmission window in the range 300-700 nm. This reveals that the grown crystals in the present study are potential candidates for opto-electronic applications. In the present case, the high optical transmission and low absorption in the spectral range 200-400 nm indicate that the grown crystals have good NLO property. [17]

The Tauc plot drawn between $(\alpha h\nu)^2$ vs $h\nu$ for 1:0.01Zn MTC grown crystal is shown in the fig.3

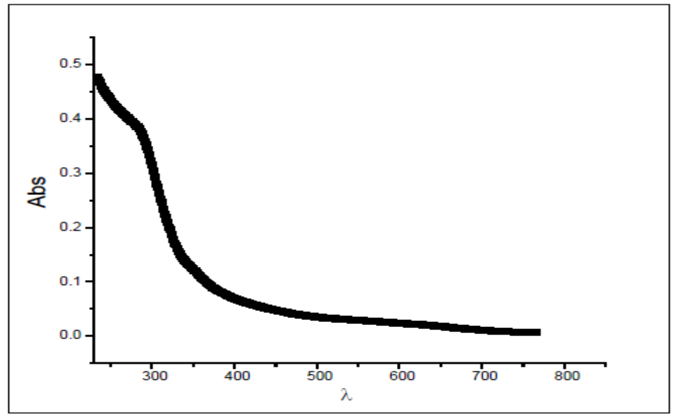

Fig. 1: UV-Vis absorption spectrum of 1:0.01Zn doped MTC single crystal

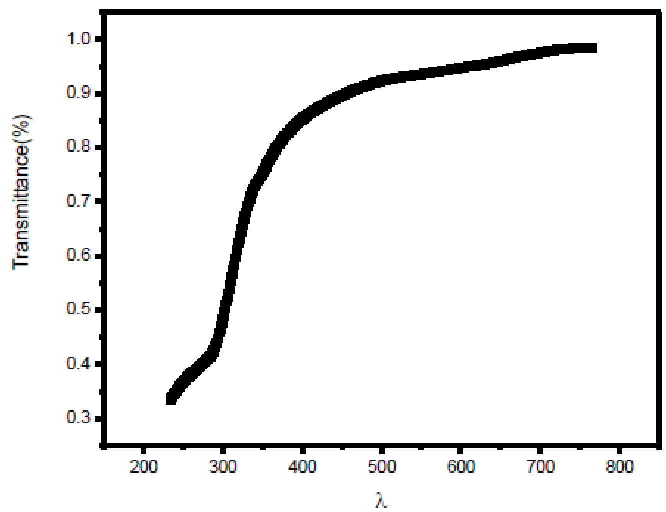

Fig. 2: UV-Vis transmittance spectrum of 1:0.01Zn doped MTC crystal

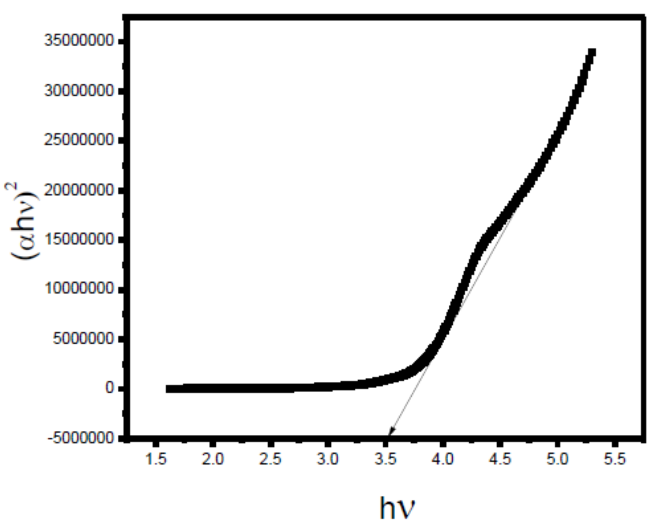

Fig. 3: Tauc plot for 1:0.01 Zn doped MTC single crystal

The Tauc plot shows that the UV-Vis transition in the present case is direct allowed [18]. The optical band gap energy values for all the grown crystals are given in the table.1.

Table 1: Band gap energy values for all the grown crystals

System	Band gap energy (eV)
MTC Pure	3.4161
Zn0.01MTC	3.5085
Zn0.02MTC	3.5262
Zn0.03MTC	3.5427
Zn0.04MTC	4.2286
Zn0.05MTC	4.2494

In the present case, the band gap energy of doped crystals are higher than that of pure MTC, but this increase is non-linear with dopant concentration. The band gap of the NLO materials decides the optical absorption edge. The higher the band gap, the lower is the absorption edge. So, it is clear that the dopant addition has decreased the absorption edge of UV-Vis spectrum. It could be seen that no overtones and absorbance peaks are detected; this is an essential parameter for frequency doubling process, so frequency doubling can be expected for the MTC crystals grown in the present case.

The photon energy dependence of extinction coefficient (K) for 1:0.01Zn MTC grown crystal is shown in the fig.4.

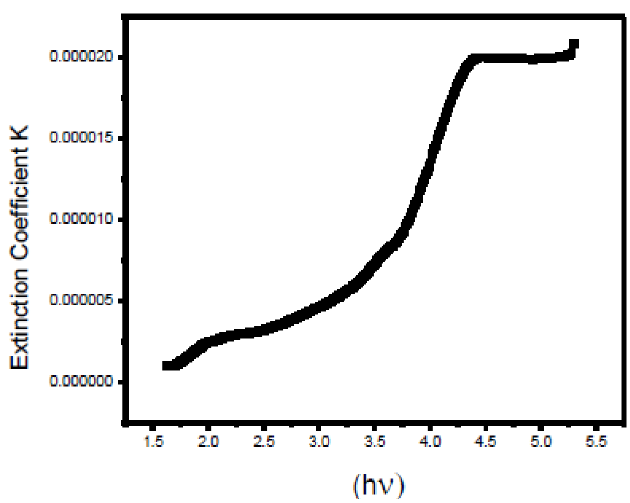

Fig. 4: Variation of extinction coefficient (K) with photon energy for 1:0.01Zn doped MTC crystal

It is found that it increases with photon energy and hence decreases with wavelength. The lower value of extinction coefficient in the visible region reveals that the grown crystals should have high conversion efficiency. The wavelength dependent of refractive index for 1:0.01Zn doped MTC grown crystal is shown in the fig.5.

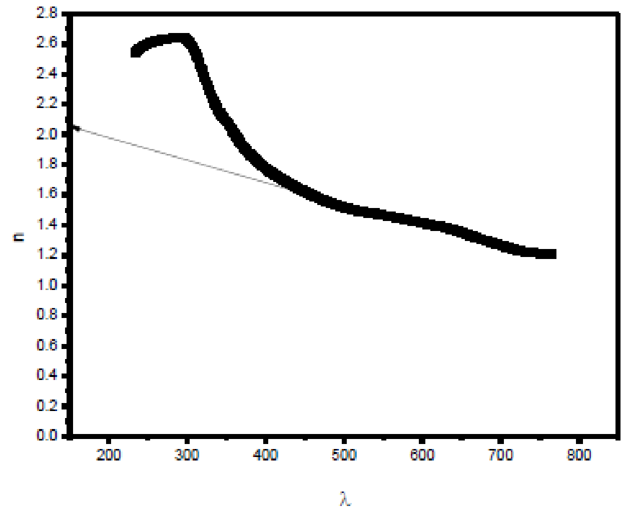

Fig. 5: Variation of refractive index with wavelength for 1:0.01 Zn doped MTC single crystal

Table 2: Static refractive index values for all the grown crystals

System	Static refractive index(n_0)
MTC Pure	2.1465
Zn0.01MTC	2.0573
Zn0.02MTC	2.0829
Zn0.03MTC	1.9434
Zn0.04MTC	2.0577
Zn0.05MTC	2.1721

The refractive index and extinction coefficient are strongly wavelength dependent. It can be seen from the figures that the grown crystals have high transmittance and low refractive index values. So we can say that the crystals grown in the present case can be used as an antireflection coating materials in solar thermal devices [19]. The refractive index values of grown crystals are low and vary nonlinearly with dopant concentration. The static refractive index determined from the graph drawn between 'n' and 'λ' are given in table.2. The variation of real (ε_r) and imaginary (ε_i) dielectric constants with Energy for 1:0.01Zn doped MTC single crystal is shown in fig.6.

It reaches the maximum at Eg and after Eg the values of ε_i and ε_r become equal. The real dielectric constant (εr) values are found to be greater than imaginary dielectric constants. The variation of ln σ with photon energy for

1:0.01Zn doped MTC single crystal is shown in the figure .7

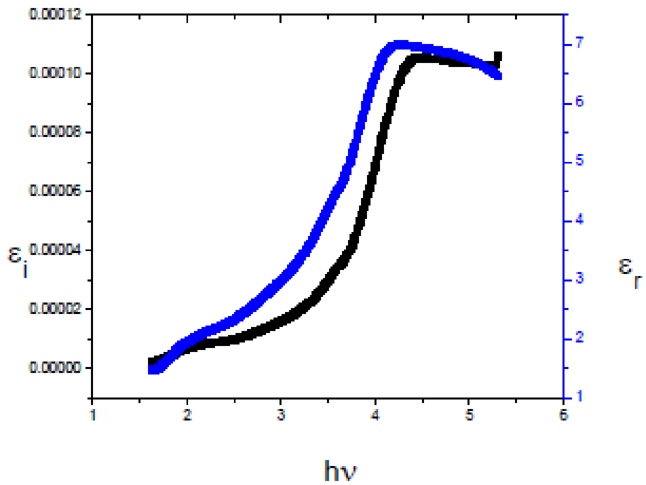

Fig. 6: Variation of real (ε_r) and imaginary (ε_i) dielectric constants with Energy for 1:0.01Zn doped MTC single crystal

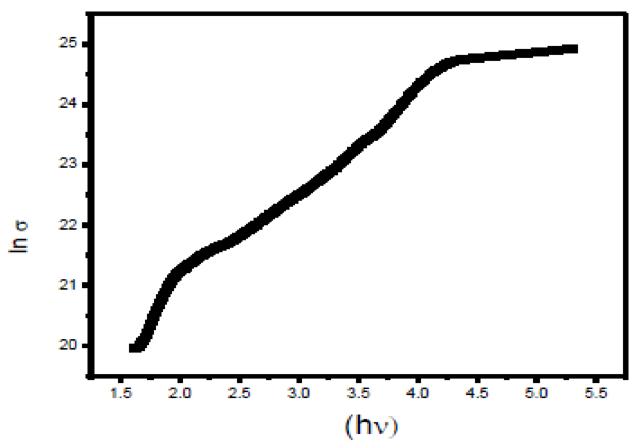

Fig. 7: Variation of ln σ with photon energy for 1:0.01Zn doped MTC single crystal

4. CONCLUSION

The crystals grown in the present study are stable, transparent and optically good quality crystals. The Tauc plot shows that the transition is direct allowed transition. The optical band gap energy varies non-linearly with dopant concentration and it is high for doped crystals than pure crystals. The conductivity increases with increasing photon energy and it shows sudden increase after Eg. Like Eg, conductivity also vary non-linearly with dopant concentration. The ε_r and ε_i values increases with photon energy and reaches maximum. The high transmission, low absorbance, low reflectance and low refractive index of MTC in the UV-Vis region make the material a prominent one for antireflection coating in solar thermal devices. MTC has a lower cutoff wavelength and a wide transparency which makes it suitable for frequency doubling process.

5. REFERENCES

1. Sagadevan Suresh. *Optik,* 2014; **125:**1223-1226.
2. Nagarajan K, Kumara Raman S, Sundaram R, et al. *Cryst. Res. Technol*., 2009; **44:**421-424.
3. Boyd RW. *Non linear optics, Academic Press, San Diego*, 1992; p.155
4. Saleh BE, Teich MC. *Fundamentals of Photonics, Wiley, New York,* 1991;p.113
5. Chemla DS, Zyss J. *Non linear optical properties of organic and crystals, Vol. I and Vol. II Academic Press, New York,* 1987; p.71 & 123
6. Pabitha G, Dhanasekaran R. *Optics and & Laser Technology*, 2013; **50**:150-154.
7. Vijayan N, Ramesh Babu R, Gopalakrishnan R, Ramasamy P, et al. *Journal of Crystal Growth*, 2004;**262:**490-498.
8. Mohan Kumar R, Rajan Babu D, Jayaraman D, Jayavel R, Kitamura. K, et al. *Journal of Crystal Growth,* 2005; **275**:e1935-e1939.
9. Rajasekaran R, Ushashree P M, Jayavel R, Ramasamy P, et al. *J. Cryst. Growth*, 2001; **229:**563-567.
10. Ushashree PM, Jayavel R, Subramanian C, Ramasamy P, et al. *J.Cryst. Growth,* 1999; **197:**216-220.
11. Anie Roshan S, Joseph Cyriac, Ittyachen M A, et al. *Mater.Lett*., 2001; **249:**99-302
12. Venkataramanan V, Maheswaran S, Sherwood JN, Bhat HL,et al. *J.Cryst Growth*,1997; **179:**605-610.
13. Ibrahim A, Al-Ani SK, *Journal of Physics*, 1994; **44**:785-797.
14. Henikhena PA. *African Phys.,* 2000; Rev. 2, 68.
15. Pankove JI. *Optical Processes in Semiconductors, Prentice Hall, New York,* 1971.
16. Das R, Pandy. et al. *JJIMS,* 2011;**1(1):**35-40.
17. Fur YL, Masse R, Cherkaoui MZ, Nicoud JF, et al., Z. *Kristallographie-Crystalline materials,* 1995; **210**:856-860.
18. Tauc J. *North-Holland, Publ. Co. Amsterdam*, 1972; 277.
19. Sabari Girisun TC, Dhsnuskodi S, et al. *Cryst. Res. Technol.,* 2009; **44**:1297-1302.