

Growth and Characterization of Semi Organic Nonlinear Optical Crystal for Electro Optic Modulation

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Abstract: *Crystal growth pervades all aspects of solid-state materials chemistry and the industries that rely upon the functionality of these materials. In the drive toward greener, more efficient processes crystal engineering is an increasingly important requirement in materials such as catalysts; semiconductors; pharmaceuticals; gas-storage materials; opto-electronic crystals; and radio-active waste storage materials. In order to impart this desired functionality it is crucial to control properties such as crystal perfection, crystal size, habit, intergrowths, chirality, and synthesis cost. In this study a semi organic nonlinear optical single crystals of zinc magnesium thiourea acetate (ZMTA) were grown from slow evaporation technique at room temperature. The unit cell parameters were determined from single crystal X-ray diffraction studies. FTIR studies were performed to identify the functional groups present in the compound. The UV-Vis spectrum indicates the grown crystal has good transparency in the entire UV-Vis region spectrum suggesting the suitability of the material for NLO applications. The thermal studies show that the crystal is thermally stable up to 120°C. The relative second harmonic efficiency of the compound is found to be 1.64 times greater than that of KDP.*

Keywords: Solution growth, Single crystal XRD, Optical material, Thermal studies, NLO material

I. INTRODUCTION

In recent development of research in nonlinear optical phenomena are involved in scientific and industrial applications. The property of second harmonic generation are focused in electro optic modulation, optical switching and also it involves in the domain of optoelectronic and photonics. Especially organic and inorganic materials are given increasing attention due to its rapid technological advances in various fields, such as laser technology, fibre optics, telecommunication, optical computing and optical data storage technology [1-3]. To overcome the limitation of these materials, interests have been focused on semi-organic crystals. In which it leads to explore the combined properties of both inorganic and organic crystals like high damage threshold, wide transparency range, less deliquescence, higher mechanical strength and thermal stabilities are obtained for device fabrication [4, 5]. Recently effort has been made on metal complexes of thiourea and analogues. Inorganic matrix of thiourea molecules are an interesting material plays important role due to their large dipole moment and ability to form an extensive network of hydrogen bonds with metals [6, 7]. The NLO properties of some complexes of thiourea, such as bis (thiourea) cadmium sulphate (CTS) [8], potassium thiourea bromide (PTB) [9] and zinc thiourea sulphate (ZTS) have been reported elsewhere [10]. In the present investigation, the effect of Zinc doped MTA crystals have been studied using single crystal XRD, FT-IR, UV-Vis, thermal and microhardness of the grown crystals have been carried out. The NLO property of as grown crystal has been confirmed by Kurtz powder technique.

II. CRYSTAL GROWTH TECHNIQUES

Crystal growth may be a difficult task and therefore the technique followed for crystal growth depends upon the characteristics of the materials below investigation, like its temperature, Volatile nature, solubility in water or different organic solvents and then on the fundamental growth ways on the market for crystal growth area unit loosely.

- Growth from melt.
- Growth from vapor.
- Growth from solution.
- Growth from solid.

The fundamental common principle altogether these ways is that a nucleus is initial shaped and it grows into one crystal by organizing and collection ions or molecules with specific interactions and bonding, so the method is slow and multiple nucleation is decreased.

2.1 Advantage and disadvantage of solution growth

Advantage

- Growth from free surface
- Growth of large oriented single crystal
- Control of atmosphere

Disadvantage

- High vapor pressure materials
- Liquid phase encapsulation
- No reproductivity of the crystal shape

2.2 Single crystal growth

The absence of the defects associated with grain boundaries can give single crystals unique properties, particularly mechanical, optical and electrical. These properties, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics.

A single crystal is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. The absence of the defects associated with grain boundaries can give single crystals unique properties, particularly mechanical, optical and electrical. These properties, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics.

2.3 Nonlinear Optics

Non-linear optics (NLO) is an innovative area of research and development which plays a key role in the field of optoelectronics and photonics.[1] Materials with large second order optical non-linearities find wide applications in the area of laser technology, laser communication and data storage technology.[2] In recent years, several studies dealing with organic, inorganic and semi-organic molecules and materials for non-linear optics are being published due to the increasing demand for processable materials in the photonics applications.[1],[6] The non-linear optical responses induced in various molecules in solution and solids are of great interest in many fields of research.

The interaction of the electromagnetic field of light (normally high intensity laser light) with a nonlinear optical (NLO) material can result in the generation of new electromagnetic fields. As light passes through a species, its electric field interacts with inherent charges in the material causing the original beam to be altered in phase, frequency, amplitude and polarization. Basically, all materials exhibit optical phenomena. This includes all forms of matter (i.e) gases, liquids, and solids. The power of the optical fields require to observe these effects varies over many orders of magnitude, depending on the detailed nature of the electronic structure of the atomic and molecular constituents of the medium, their dynamical behavior, as well as the symmetry and details of their geometrical arrangement in the medium. The important nonlinear optical materials from the device point of view are generally in solid formats and must meet a wide variety of ancillary

material requirements for optical use. In general, they will require extraordinary stability with respect to ambient conditions and in high intensity light sources.

Some materials change light passing through them, depending upon orientation, temperature, light wavelength etc. (red light, lower wavelength) releasing one photon of accumulated higher energy (blue and green light, higher wavelength). NLO materials typically have a distinct crystal structure, which is anisotropic with respect to electromagnetic radiation. The importance of nonlinear optics is to understand the nonlinear behavior in the induced polarization and to analyze and to control its impact on the propagation of light in the matter.

2.3.1 Organic NLO Crystal

The organic non-linear materials show the non-linear behavior of light due to presence of conjugated π - π^* electrons. All these crystals have a good dynamic structure and transparent in nature. These are second order frequency generator organic non-linear materials. The materials are non-centrosymmetric in nature and applicable in optical modulators, optical devices, laser frequency modulators. UV- Spectroscopy shows transparent nature in the entire visible region and near infrared region. On the contrary, precise processing technologies for organic crystals have hardly been developed. Since organic materials are very brittle, having hygroscopic properties, low melting temperatures and particular cleavage planes owing to weak intermolecular bonding, conventional processing technologies used for inorganic materials cannot be extrapolated to obtain arbitrary shape crystals and fine optical surfaces. A disadvantage of organic nonlinear optical (NLO) materials is often their low physico-chemical stability.

2.3.2 Inorganic NLO Crystal

New inorganic nonlinear-optical (NLO) materials are necessary for solid-state lasers to generate coherent radiation in the ultraviolet (UV) and deep-UV regions. Inorganic materials are defined as chemical compounds that contain no carbon (C). However, elementary carbon (C) (as graphite or diamond) and compounds of carbon and, for example, nitrogen, oxygen, or silicon are also classified as inorganic. Examples of such inorganic compounds include carbon monoxide (CO), silicon carbide (SiC), and carbonic acid (H₂CO₃), and salts thereof. All other types of carbon-containing compounds are called organic materials. Inorganic materials, exhibiting second order nonlinear optical properties have attracted in the recent past due to their ability to process into crystals, wide optical transparency domain, large nonlinear figure of merit for frequency conversion, fast optical response time and wide phase matchable angle. Molecular hyperpolarizability of inorganic nonlinear optical crystal are used in optical switching (modulation), frequency conversion (SHG, wave mixing) and electro-optic applications especially in EO modulation. Historically, inorganic NLO materials have been chronicled more extensively inorganic oxide crystal, LiNbO₃, KNbO₃, KDP and KTP, etc., have been studied for device application like piezoelectric, ferroelectric and Electro-optics.

2.3.3 Semi Organic NLO Material

In semi organic materials, the organic ligand is ionically bonded with inorganic host that resulted in new materials having high optical nonlinearities. Complexes of amino acids with inorganic salts are promising materials for optical applications such as optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reaction, laser remote sensing. The high nonlinearity, high resistance to laser-induced damage, low angular sensitivity and good mechanical hardness of semi-organic crystals combine in the strong NLO properties and chemical flexibility of organic materials with the physical sturdiness and excellent transmittance of inorganic materials

III. SYNTHESIS AND CRYSTAL GROWTH

Single crystal of zinc doped MTA material was synthesized using AR grade of Thiourea, Magnesium acetate and Zinc acetate. Double distilled water was used as a solvent. Calculated amount of (3: 0.9: 0.1) the above materials were dissolved in 100 ml of water and stirred well using magnetic stirrer. Well defined single crystals of good transparency were harvested after a period of 15 days and shown in Fig 1.

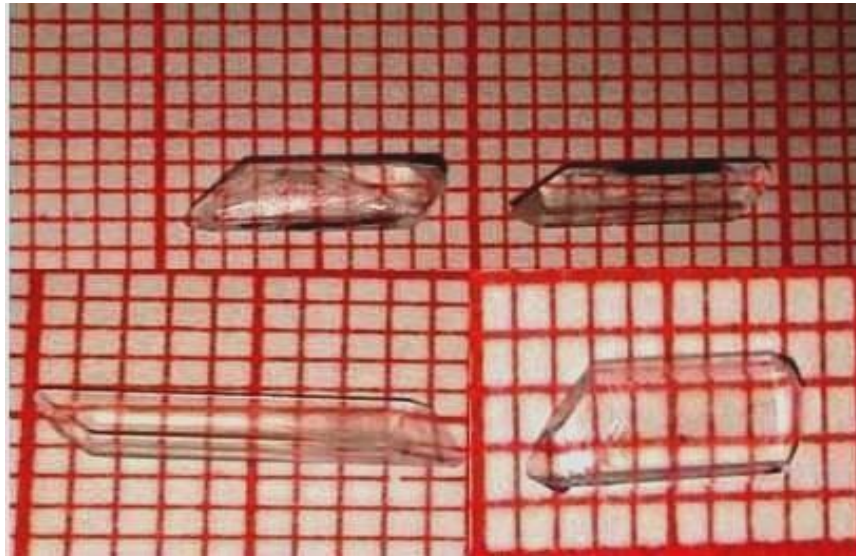


Fig 1:- Photograph of ZMTA crystals

IV. RESULT AND DISCUSSION

4.1 Single crystal XRD studies

The grown crystals were analyzed by single crystal X-ray diffraction to confirm the crystallinity and also to estimate the lattice parameters. From the single crystal X-ray diffraction data, it is observed that the ZMTA crystal is Monoclinic in structure. The morphology of the grown crystal seems to be different when compared with Zinc magnesium tris thiourea sulphate (ZMTS) and Magnesium doped tris thiourea zinc sulphate (TTMZS) [11, 12]. The calculated unit cell parameters are given below in Table 1 and there values are compared with the reported values.

Table 1:- Unit cell parameters of grown and reference crystals

Crystal systems	a(Å)	b(Å)	c(Å)	Volume (Å ³)	Crystal structure
ZMTA	7.113	17.694	11.111	1363.9	Monoclinic
ZMTS	7.74	11.08	15.42	1337	Orthorhombic
TTMZS	15.57	6.315	5.549	545.4	Orthorhombic

Changes in the lattice parameters may be due to incorporation of dopant which causes the increase in volume. However, for ZMTA crystal, changes in the lattice parameters have been observed with respect to ZTMS and TTMZS crystals which confirm that the doped crystal exhibits different structure as that of parent material.

4.2 Optical absorption studies

An optical absorption spectrum of ZMTA crystals were recorded in the wavelength range 200-800 nm using PerkinElmer Lambda 650 UV-Vis spectrometer and is shown in Fig. 2. The UV spectrum shows a wide transparency window with the lower cut off wavelength of grown crystal is 235 nm. Absence of absorption in the region between 260-800 nm is the essential property for the NLO material. The less absorbance behavior in the entire visible region also confirms the colorless nature of the crystal.

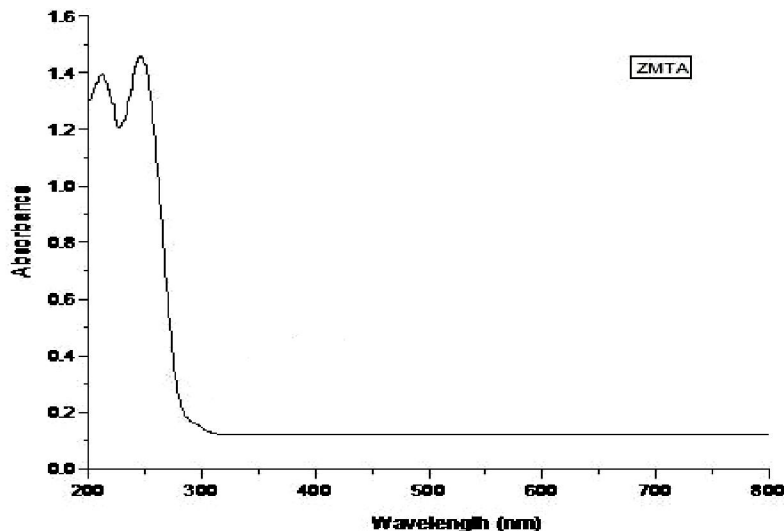


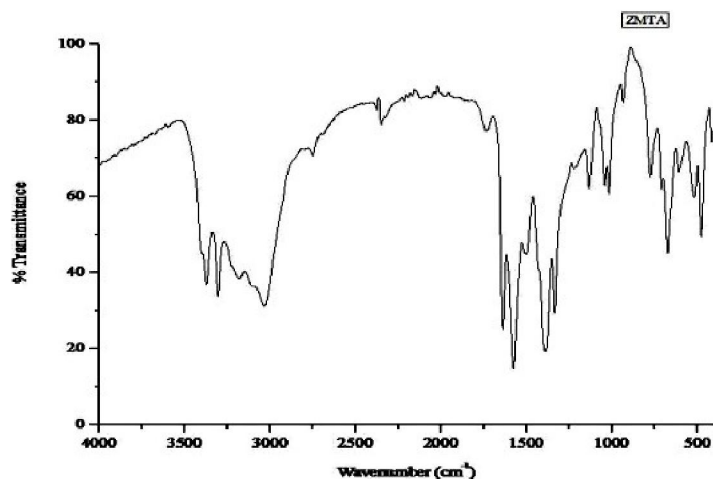
Fig 2:- UV-vis absorption spectrum of ZMTA crystal.

It is observed that the grown crystal has good transparency in the UV-Visible and IR region. While doping Zinc acetate with MTA crystal alter the lower cut off wavelength increase when compared to the reported values [11, 12].

4.3. FTIR studies

The FTIR spectrum of ZMTA crystal displayed in Fig.3 were recorded in the range of 400 – 4000 cm⁻¹. The vibrations at 3378 and 3304 cm⁻¹ are reported as vibrations due to NH₂ asymmetric stretching vibrations and the C-H stretching vibration is observed at 2349 cm⁻¹. The peak at 1635 cm⁻¹ is due to N-H bending vibration [13]. The C=O stretching vibration is observed at 1571 cm⁻¹. The peak at 1389 cm⁻¹ is reported as vibration due to C=S asymmetric stretching vibration [14]. The NH₂ rocking vibration is observed at 1131 cm⁻¹ [11]. The absorptions at 931 and 475 cm⁻¹ are reported as the vibrations due to N-C-N symmetric stretching vibrations [11, 12]. The vibrations around 600 and 1030 cm⁻¹ are reported as clear conformation of presence of zinc acetate in the coordination sphere [15]. Based on the observations, it is confirmed that FTIR spectra indirectly establish the presence of zinc acetate in lattice of MTA crystal.

Fig 3:- FTIR spectrum of ZMTA crystal.



4.4 TG/DTA studies

TG/DTA curves of ZMTA crystal displayed in Fig.4. From the result, the crystal is thermally stable up to 120oC and it is observed that DTA curve show endothermic peak at 210oC for ZMTA crystal. This value can be considered as the decomposition or melting point of the sample. From the result, it is noticed that ZMTA crystal has slightly less thermal stability than reported value of ZMTS crystal and it may due to decrease in bond energy caused by the incorporation of dopant's anion (CH₃ COO)²⁻ in the lattice of the ZMTA crystal. The TG curve of ZMTA crystal show maximum weight loss occurs in the temperature range 120-348oC, which is due to the decomposition of the samples. The sharpness of the endothermic peak shows the good degree of crystallinity and purity of the sample. Further the absence of water in the molecular structure is confirmed by the absence of weight loss around 100oC.

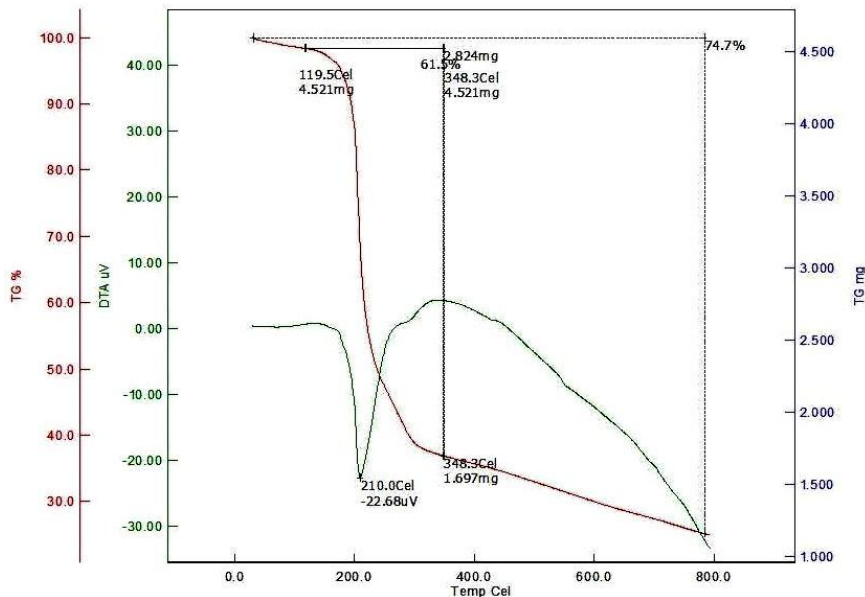


Fig 4:- TG-DTA curves of ZMTA crystal.

4.5 Powder SHG Studies

The second harmonic generation efficiency of grown crystal has been measured by Kurtz-Perry technique [16]. A Q-switched mode- locked Nd: YAG laser was used to generate about 0.68mJ/pulse at 1064 nm fundamental radiation. The second harmonic signal was confirmed from the emission of green radiation by the crystalline powder sample. The result of SHG efficiency of the grown crystal is about 14.42 mV. KDP crystal was used as reference material in the SHG measurement. The ZMTA gives an SHG of 14.42 mV, while the KDP gave an SHG signal of 8.8 mV for the same input beam energy. The SHG relative efficiency of ZMTA crystal was found to be 1.64 times higher than that of KDP.

V. CONCLUSIONS

Optically good quality ZMTA crystals were grown by slow evaporation technique. The presence of small amount of zinc acetate altered the unit cell parameters slightly when compared to reported value. The presence of functional groups was determined by FTIR analysis. The optical absorption studies show that the UV cut-off wavelength of grown crystal is 245 nm making it a suitable candidate for NLO applications. The TG/DTA studies show that the grown crystal is thermally stable up to 120oC. The SHG efficiency of ZMTA crystal is 1.64 times higher than that of KDP and it becomes a promising candidate for optoelectronic and photonic device applications.

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