Synthesis, growth and characterization of NLO single crystals for Remote Sensing applications

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Abstract. A novel semiorganic optical material, L-alanine doped urea thiourea magnesium chloride (ATUMC) single crystals has been synthesised by evaporating the mixture of solvents slowly at a temperature of 34 °C. XRD data of crystals AUTMC crystals show a slight change in the values of lattice parameters and volume in comparison with the pure urea thiourea magnesium chloride (UTMC) crystal indicating the inclusion of dopant alanine. The various interaction among elements present in the grown sample was elucidated using FT-IR studies. UV studies has confirmed an absorption between 292 –1000 nm region. By adding alanine as dopant the absorption region lies in the same region. NLO property is also analysed for the grown crystal using Kurtz Perry method. The TG/DTA analyses show that the thermal stability is considerably increased with the addition of alanine dopant in the pure TUMC crystal.

1. Introduction

LASER find wide application in computer, information technology, material science, electrical, electronics, communication and remote sensing fields [1-7]. The study of materials serving as laser source is engrossing researchers today. NLO crystals having higher order harmonic conversion are of demand in medical, electronic processing, military, space communication and nonlinear optics [8-13]. Large study has been done to improve NLO property of existing crystals. Research work has been done on thiourea based metallic semi organic NLO single crystals. Our team has worked to improve the efficiency of pure urea thiourea magnesium chloride (UTMC) single crystal and with this research characterization studies it is noted that the addition of alanine enhances the basic properties.

2. Experiment

2.1 Synthesis

A mixture of alanine, urea, thiourea and magnesium chloride in the ratio of 1:1:1:1 was used to synthesise and grow AUTMC crystal. This solvent was stirred completely and filtered in a borosil
glass beaker. This filtered solution was left to slowly evaporate at room temperature. Well shaped single crystals of sufficient dimension was synthesised within 45 days.

The chemical equation of UTMC is as follows:

\[ 2[\text{CS (NH}_2\text{)}_2] + \text{MgCl}_2 \rightarrow \text{Mg}[\text{CS (NH}_2\text{)}_2 \text{Cl}_2 \]

2.2 Solubility

The growth of single crystals can be determined using solubility process. It is essential to determine the supersaturation range for the crystal to be synthesised. Maintaining a steady temperature the mixed chemicals are added to the solvent till no more of the solute can be dissolved at constant temperature. A graph is plotted between solubility in gm/100ml and temperature. This process is repeated for various temperatures and for various weight ranges. A graph is plotted as shown in Fig. 1.

Gravimetric study on the solvent solution was performed for every 5° C increase of temperature.

2.3. Growth
The calculated amount of Merck GR grade alanine, thiourea, urea and magnesium chloride powders were dissolved in double distilled water till homogeneous mixture was obtained. The undissolved bulk powder was filtered using Whatman filter paper and crystallized by evaporating at normal temperature for about 45 days [14-16]. A single crystal with sufficient size and definition was obtained as shown in Fig. 2. The size of AUTMC single crystals were 12× 8× 4 mm³ approximately.
2.4. Single crystal XRD Analysis

Bruker Kappa Apex 2 CCD X-ray diffractometer determines the grown crystals lattice parameters. Characterisation of single crystals is usually done by non-destructive method called X-ray diffraction (XRD). The crystal structure information, texture, size of grain, lattice defects, crystal defects and other minor details of AUTMC crystal is studied through X-ray pattern. AUTMC belongs to triclinic crystallographic system since its lattice parameters are \( a = 12.58 \ \text{Å}, \ b = 8.91 \ \text{Å}, \ c = 5.94 \ \text{Å}, \) with volume \( V = 665.8015 \ \text{Å}^3 \) [17].

2.5. Fourier Transform Infrared Spectral Analysis

Infra-red spectroscopy is an essential tool to determine functional group present in AUTMC crystal sample. Bruker IFS66V spectrophotometer uses KBr pellet technique in the region 4000 – 400 cm\(^{-1}\) [19]. A shift in the spectrum is seen at 730 and 1411 cm\(^{-1}\) respectively. This is due to symmetric and asymmetric \( \text{C}=\text{N} \) stretching vibration of Thiourea. The FTIR spectrum of ATUMC is shown in Fig. 3. The bands at N-H absorption bands 3000 – 2000 cm\(^{-1}\) region indicates the formation of thiourea magnesium formation. Also at 3186 cm\(^{-1}\) bonding of alanine with thiourea is observed.
2.6. UV-Visible Spectral Study

Figure 3. FTIR Spectrum of AUTMC crystal

Figure 4. UV spectrum of AUTMC crystal
The UV absorption spectrum of AUTMC is illustrated in Fig. 4. All electronic applications using light source needs to operate with large transmission range. For AUTMC the cut off wavelengths is found to be at 290 nm which is needed for NLO applications. VARIAN CARY 5E model spectrophotometer is operated in the wavelength range 200 – 1000nm to calibrate the absorption range of AUTMC single crystal [20]. The absorption spectrum at 290 nm was observed for AUTMC crystal. This range is suitable for SHG efficiency.

2.7. Kurtz and Perry SHG test

Non-centrosymmetic crystals needs to possess NLO efficiency which can be tested Kurtz powder technique. When the output frequency is doubled in the grown powdered sample after passing a beam 1064nm from Q-switched Nd: YAG laser the NLO efficiency is tested. This is preliminary study for nonlinear property of [21]. The pure and doped UTMC crystals emit bright green light (λ=532 nm) proving that it possess NLO efficiency.

2.8. Thermal Analysis

Thermogravimetric analysis is used to identify the decomposition temperature of AUTMC crystal. NETSZCH STA 409C/CD instrument is used to study the melting point and decomposition range of AUTMC single crystal. The Fig.5 illustrates the graphical representation of the decomposition process and hence the stability against heat treatment of AUTMC crystal. To begin with at 50˚C - 197.41˚C a weight loss is registered indicating the evaporation of trapped water. Later decomposition starts at 253.20˚C which results in another weight loss. The ample is completely volatilized at 442˚C corresponding to maximum weight loss. An exothermic peak at 240˚C, determines the melting point of AUTMC crystal. From the TG/DTA trace of AUTMC crystal slight weight loss occurs at 240˚C and extreme loss 248˚C as seen in Fig.6. The stability of AUTMC crystal is ensured by this analysis which is an important criteria for device fabrication the melting point of the ATUMC crystal. Hence the melting point of AUTMC crystal lies at 251˚C as seen in DTA curve.

![Figure 5. TGA of AUTMC crystal](image)
3. Conclusion

A novel organometallic material, Thiourea Urea Magnesium Chloride doped with alanine (AUTMC) single crystals was grown by evaporating the saturated solvent slowly at normal temperature for 50 to 60 days. The crystalline composition and Bravais parameters were determined by single crystal X-ray diffraction analysis which detected AUTMC crystal to belong to triclinic system. FT-IR studies confirm the presence of essential grouping of elements in AUTMC crystal. The N-H stretching is observed at 1411 cm\(^{-1}\) which confirms that the dopant has entered into the pure TUMC crystal. Minimum optical absorption is seen for AUTMC in the wavelength region 290 –1000 nm. For the fabrication of NLO devices the above properties discussed play the basic criteria.

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