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GROWTH, CHARACTERIZATION OF AMMONIUM CHLORIDE INORGANIC CRYSTALS MODIFIED BY THIOUREA: BAND GAP MEASUREMENT AND STRUCTURAL PARAMETERS STUDY FOR FUTURE SCOPE IN PHOTONICS AND OPTOELECTRONICS

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Abstract

A slow evaporation method is used to get Thiourea Ammonium Chloride (TAC) single crystals. The extinction of various molecular groups was reported by FTIR analysis. The optical properties of absorption, transmission and optical constants measurement of the crystal are analyzed by ultraviolet-visible-near infrared spectroscopy. At the cut-off wavelength of 290nm, the optical band gap resolution of the TAC crystal was calculated as 4.427eV. The XRD results show the intensity peaks of the titled crystal. The crystal structure is depicted as orthorhombic

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from powder XRD analysis, and its lattice parameters are, $a = 5.502A^{\circ}$, $b = 7.685A^{\circ}$, $c = 8.573A^{\circ}$ and it is located from JCPDS. The thermal property of the named crystal was investigated therefore, mass loss, endothermic and exothermic events are recorded at various temperatures by thermo gravimetric analysis. The morphological study was done to examine its crystal perfection; the (NLO) function of TAC crystals has been confirmed through the second harmonic generation (SHG).

1. Introduction

Natural NLO materials are more reasonable than inorganic NLO crystals because their instantaneous moment arrangement is nonlinear susceptibility and their potential applications have been confirmed [1-3]. During the expansion process, the molecular weights of the two natural compounds exceeded their original components [4-5]. These crystals have extraordinary physical qualities and have a reliable record of long-term device robustness [6-10]. In optoelectronics, fitting the hole in the semiconductor material may be a key strategy [11]. Estimate the optical constants of the material, such as the whole and terminal coefficients in the optical strip [12]. The notch in the frequency band strongly affects the electrical characteristics of the semiconductor [13-14]. The development of crystals may be the front of materials science and nanotechnology, which is essential for photonic innovation [15-18]. Continuous innovation and development are essential to find novel and highly useful nonlinear optical devices. In terms of expansion to HIV treatment and labeling preparation, these materials perhaps exercised for optical computing, optical communication, motion and optical information functions to promote mechanical development in IT communication [19-21]. NLO materials that have been doped are claimed to have more advantages than materials that have not been doped. [22]. some organic electronic devices have recently included DNA with the hexa decyltrimethylammonium chloride (CTMA) complex [23]. The wide range of uses for crystalline salts of amino acid complexes has recently piqued the curiosity of researchers. One such substance is urea *L*-malic acid (ULMA), and there are only a few studies on ULMA crystal in the literature [24].

2. Synthesis and Crystal growth of TAC

Molecular weight of Thiourea is 7.612g and molecular weight of ammonium chloride is 5.349g. This substance has a total molecular weight of 12.961g (after sample preparation in 100 ml of water). The solution was prepared by room temperature. The essential chemicals are purchased from SPECTRUM Chemicals in India. Thiourea with ammonium chloride are mixed in a 1:1 ratio in constant temperature bath (CTB) at room temperature, and then transformed into good propellant to formalize it. The crystal was developed by approach of slow evaporative solution mode. A many number of seeds were collected and suspended in a supersaturated solution, they were recrystallized and the TAC crystal formed in 25 days.

3. Characterization Techniques

The sample undergone the XRD, FTIR, UV, TGA and SEM characterization techniques for the analysis

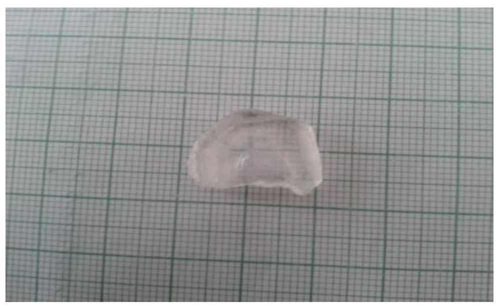

Figure 1. Grown TAC Seed crystal.

4. Results and Discussion

4.1. XRD analysis of TAC crystal

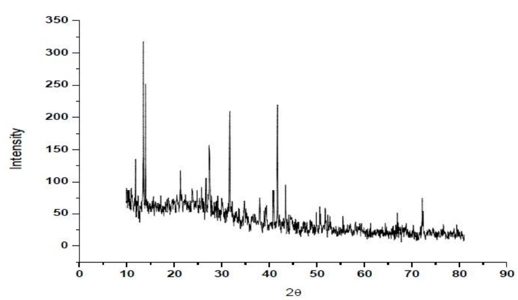

Figure 2. XRD analysis of TAC crystal.

The figure 2 shows that the powder XRD in TAC crystal. CuKISα1 radiation with a wavelength of $1.54056\,A^{\circ}$ is used to records the spectrum of the sample at an angle of 2θ° in the range of 0° to 80°. The diffraction pattern is used to determine the inter planner distance d and value of (hkl) each diffraction peak in the sample spectrum. The orthorhombic crystal equation is used to report the lattice parameters of the identified crystal by JCPDS (43-0648). The lattice parameters are $a = 5.502A^{\circ}$, $b = 7.685A^{\circ}$, $c = 8.573A^{\circ}$ [25-26].

4.2 Optical studies of TAC crystal

4.2.1 Optical absorption studies

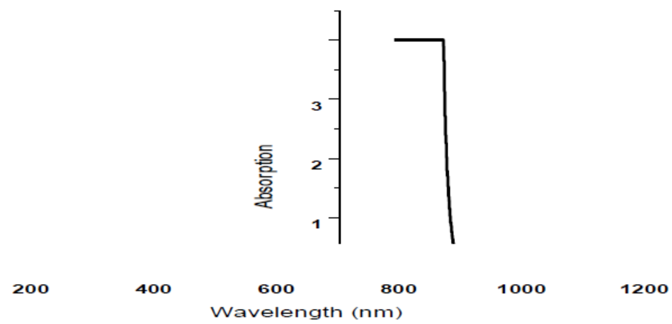

Figure 3. Optical absorption spectrum of TAC crystal.

The Lambda 35 Spectrophotometer is utilized as instrumental tool to confine the optical absorption spectrum in the wavelength range of 190-1100nm Figure 3. The specimen is transparent in the UV-Vis-IR spectrum. Due to the crystal transparency it is accessible for its photonics and optoelectronic equipment. The cut of region of the TAC crystal is 290nm [27]. It is well known the transmission frequency of low wavelengths of improved NLO crystals is between 200nm and 400nm.

4.2.2 Optical transmission studies

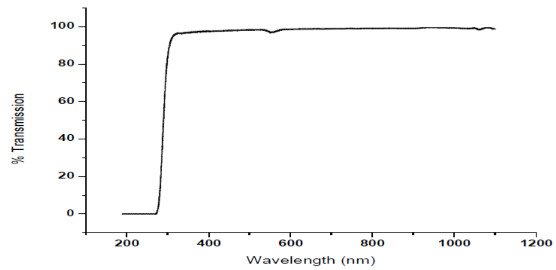

Figure 4. Optical transmittance spectrum of TAC crystal.

The figure 4 shows that the optical transmission spectrum of a titled single crystal in the wavelength ranges of 190nm-1200nm. The crystal is highly transparent in the wavelength range of 290nm [28]. The crystal's high transmission in the visible region suggested that it is well suitable to efficiency of second harmonic generation.

4.2.3 Optical band gap measurement of TAC crystal

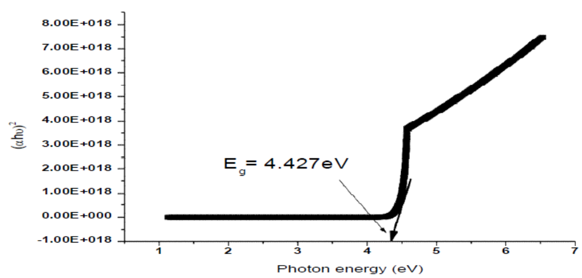

Figure 5. Optical band gap of TAC crystal.

The figure 5 shows that the relationship between $(\alpha h v)^2$ and photon energy. TAC crystal band gap energy is 4.427eV. By result of the huge band gap, the formed crystal has a high visual transmittance [29].

4.3 Fourier transform infrared spectroscopic studies of TAC crystal

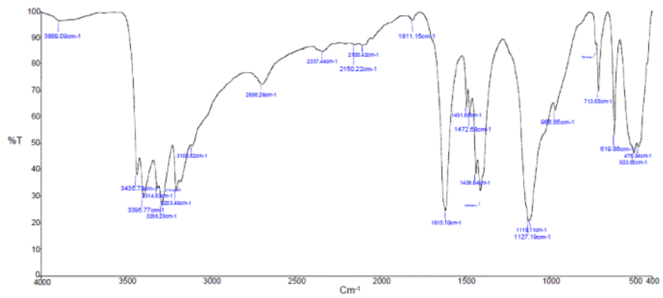

Figure 6. Fourier transform infrared spectrum of TAC crystal.

The FTIR spectrum recorded by make of Perkin-Elmer spectrophotometer in the 400-4000cm^{-1} wavelength range as shown in Figure 6. The intensified absorption bands in the range 3288, 3395cm^{-1} correspond to OH group stretching vibrations, both symmetric and asymmetric. Wave numbers 1119cm^{-1} and 1127cm^{-1} were used to observe the $C–N$ stretching vibrations. In-plane and out-plane vibrations of the $C–H$ group are 966 cm-1and 713cm-1, respectively [30]. A significant peak at 1615cm^{-1} was occurred because of NH_2 stretching of the benzene ring. A bright and strong band due to the $C = N$ of TAC crystal was seen at 1436cm^{-1} [31]. The asymmetric and symmetric stretching vibrations of methyl groups are located at 3108 cm-1and 2698 cm^{-1}, respectively, in the TAC crystal. At 1491cm^{-1} and 1472cm^{-1}, respectively methyl groups display asymmetric and symmetric $C–H$ deformation modes [32].

4.4 Optical constants measurement of TAC crystal

4.4.1 Optical Absorption coefficient measurement of TAC crystal

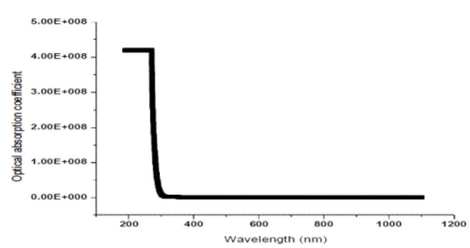

Figure 7. Optical absorption coefficient versus wavelength of TAC crystal.

It is interpreted from the Figure 7 that the optical absorption coefficient increases with increasing wavelength.

4.4.2 Optical Extinction coefficient measurement of TAC crystal

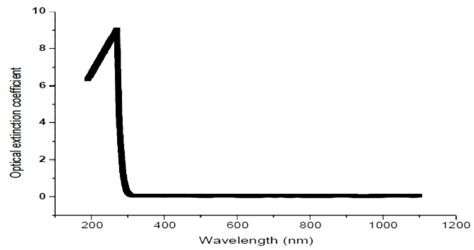

Figure 8. Optical Extinction coefficients versus wavelength of TAC crystal.

Figure 8 shows the optical extinction coefficient value is 9 at a wavelength of 290nm; it is good agreement with the reported value for Thiourea Ammonium Chloride (TAC) crystal. Beyond 300nm the optical extinction coefficient remains constant at zero value.

4.4.3 Optical Refractive index measurement of TAC crystal

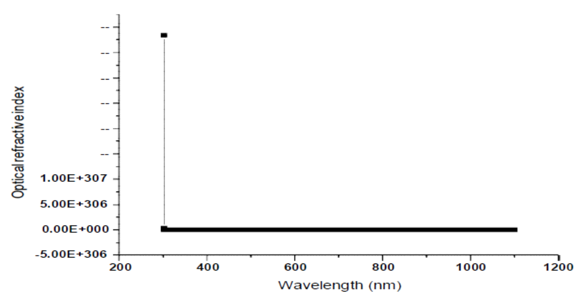

Figure 9. Optical refractive index versus wavelength of TAC crystal.

It shows from figure 9 that the optical refractive index has two values, namely: two corresponding to a wavelength of 290nm and 300nm. This region is the optical wavelength region.

4.4.3.1 Optical Reflectance measurement of TAC crystal

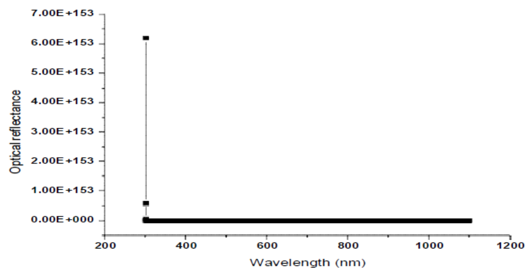

Figure 10. Optical reflectance versus wavelength of TAC crystal.

The figure 10 depicts the modulation of optical reflectance with respect to wavelength in TAC crystal. It shoots up corresponding to a wavelength of290nm and then drops down suddenly and finally remains constant for higher wavelengths.

4.5. TGA and DTA analysis of TAC crystal

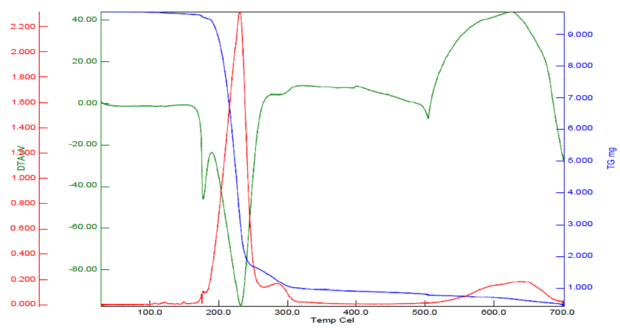

Figure 11. TG/DTA analysis of TAC crystal.

The thermal behavior of Thiourea ammonium chloride crystal was investigated using a CNETZSCH STA 409C/CD system at temperatures ranging from 100°C to 700°C. The primary application of thermal analysis is to aid in understanding the thermal properties depicted in figure 11. Thermo Gravimetric (TG) and Differential Thermal Analysis (DTA) measurements were made in a nitrogen atmosphere using a TG/DTA analyzer (Perkin Elmer make) at a heating rate of 20o/min. Because initial mass loss occurs at 180oC, the TAC specimen is firm. At 240oC, the first exothermic peak was observed [33]. The first endothermic peak at 270oC is caused by the expulsion of water molecules in the sample. The decomposition of the sample causes the endothermic peak at 218oC, and there is a significant mass loss at this temperature. The liberation of gaseous molecules from the sample causes further fewer mass in the temperature range 250-500oC. At 300oC, the total weight loss occurs.

4.5.1 Morphological analysis of TAC crystal

The images recorded by scanning electron microscope the morphology and size distribution of Thiourea Ammonium chloride samples are analysed from the CAREL ZEISS model EVO18 demonstrated in Figure11 (a), (b), (c), and (d). Crystals are obviously varied in size and shape. The close inspection of a SEM micrograph from a selected section of Thiourea Ammonium Chloride (TAC) reveals that the crystals are unevenly formed by their morphological surface evidences, as well as the presence of microscopic micro crystals on the surface.

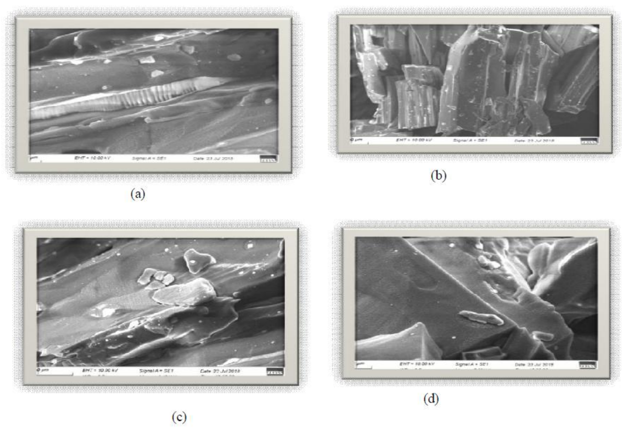

Figure 11. Morphology images of TAC crystal (a), (b), (c) and (d).

4.6 Second Harmonic Generation (SHG) of TAC crystal

The Kurtz and Perry's powder techniques was used to determine the second harmonic generation of Thiourea Ammonium Chloride (TAC) crystal, which uses a Nd-YAG 10ns laser with a pulse repetition rate of 10Hz and a wavelength of 1064nm. The sample was finely powdered and packed securely in a micro-capillary tube. By splitting the original laser beam, a 9.6-mJ pulse intensity laser beam was implanted in its path. The emission of green light at 532nm confirmed the efficient creation of the second harmonic generation [34].

5. Conclusion

The Thiourea ammonium chloride crystal developed by the mode of slow evaporation. The modes of powder X-ray, FTIR and UV-Vis-NIR spectrums are incorporated for this research to identify their significant results like presence of organic molecules and the transmittance of light investigations and the crystalline nature. Photonic and optoelectronic applications are ideal for the crystal in question. By incorporating powder X-ray diffraction analyses from the JCPDS (43-0648) it is found that $a = 5.502A^{\circ}$, $b = 7.685A^{\circ}$, $cc = 8.573A^{\circ}$ are their lattice parameter values and TAC crystal belongs the structure of orthorhombic and space group of primitive. The TAC crystal optical transition confirms the transparency, the optical constants and energy band gap of the titled crystal was 4.427. The mss loss present in the crystal are reported from the analysis of TGA/DTA, the crystal perfection and prescience of microcrystal's are interpreted from surface morphological evidences, and this was revealed in great detail in this article.

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