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Growth and Characterization of Thioureasquarate

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ABSTRACT

By slow evaporation solution growth technique an organic NLO material named as Thioureasquarate was grown using ethanol at room temperature. Stirred mixture of squaric acid and thiourea was taken in equimolar ratio and placed in an open area without any disturbances. Various characterization techniques were used to check the suitability of the grown crystal for device fabrication. UV-Vis-NIR, XRD, TG-DSC, SHG and FTIR analyses were used to characterize the grown crystal. Identification of functional group was done by the FTIR analysis. The occurred transparency cut off wavelength 330nm of the crystal is shown in the UV spectrum. The thermal stability was determined by TG-DSC analysis. Kurtz-Perry SHG test confirms that the grown crystal is a promising NLO material. Finally the suitability of the grown crystal for optical device fabrication was confirmed by the observed results.

1. Introduction

Technologists and scientists of last two decades made intense efforts in search of high quality nonlinear optical materials which have a great importance in device applications such as optical communication, signal processing and optical coupling etc., due to its importance in providing major role in modulating optical signal, shifting the frequency optical switching and optical memory. Some organic compounds replaced the classic electronic materials in the field of optical communication due to its very good nonlinear optical and electro optical properties. Because of its large isotopic effect squaric acid plays great role in NLO applications and has a predictable optical behavior [1-9]. The special SHG effect of the squaric acid is due to the displacement of hydrogen atom from its equilibrium position. While adding it with thiourea which is also a very good NLO material induces the optical potential [10-13]. Thioureasquarate a new NLO material has been synthesized and the above said characteristics have been studied by various instrumentation techniques.

2. Experimental

2.1 Synthesis

Thiorueasquarate crystals were grown by using thiourea and squaric acid (AR Grade) as starting materials. A supersaturated solution was prepared by mixing thiourea and squaric acid dissolved in ethanol separately in the ratio 1:1. The prepared solution was double filtered using Wattmann filter paper for quality crystal growth. The beaker contains the saturated solution mixture was kept in a disturbance free environment covered with a polyethylene cover to facilitate the slow evaporation. At room Thioureasquatate crystals were grown by slow evaporation method. The hydrogen bond (NH-O) interaction of thiourea with squaric acid results in a formation of Thioureasquarate. Due to periodical inspection it was noted that on 15th day the crystal starts to grow. Single crystals of Thioureasquarate were harvested as shown in the Fig.1.

Fig. 1 Morphology of Thioureasquarate

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2.2 Measurements

Using perkin Elmer Lambda 35 UV-Vis-NIR Spectrophotometer in the wavelength range 190-1100nm the optical behavior of Thioureasquarate was measured. Bruker IFS 66V model FTIR Spectrometer is used to identify the functional groups using KBr pellet technique in the range from 400 $cm^{-1}$to 4000cm^{-1}. Thioureasquarate crystal's thermal stability was determined by SDTQ600 V8.3 Built 101 thermal analyzer instruments in the region from room temperature to 1100°C at a heating rate of 20° C per minute under the atmosphere of nitrogen. Rich Seifert diffractometer is used to determine the Powder Xrd analysis and hkl values are calculated using Reitveld Index Software. Finally Kurtz Perry method is used to find the NLO behavior of the grown Thioureasquarate crystals.

3. Results and Discussion

3.1 Optical transmission spectrum

The transparency cutoff wavelength and optical transmission is shown in the Fig. 2. It is seen that the grown Thioureasquarate crystal is transparent between the wavelength range 330-1100nm. At 330nm it was observed that the UV transparency cutoff wavelength occurred. The entire observation were made using the UV-Vis-NIR spectrum working under the wavelength range 200-1100nm. The grown Thioureasquarate crystal could be used as a promising material for optical applications due to its high transmittance.

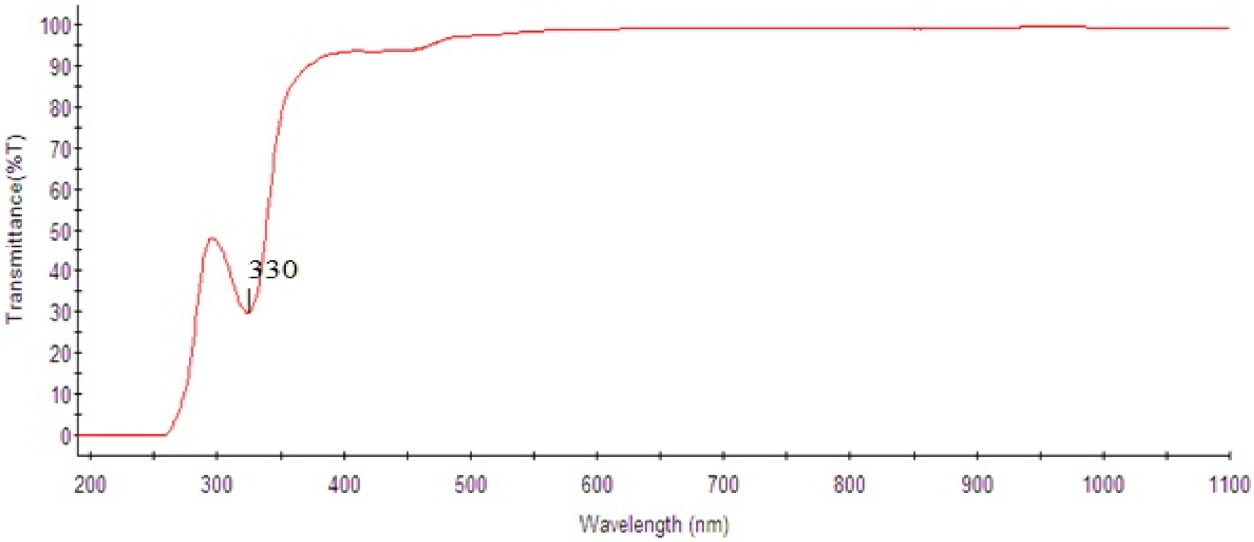

Fig. 2 UV-Vis-NIR spectrum of Thioureasquarate

3.2 FTIR spectral analysis

The most reliable method to identify the functional groups of the grown crystal is Fourier Transform Infra Red spectroscopy (FTIR) using KBr Pellet technique. In Fig. 3, the FTIR spectrum of the Thioureasquarate is shown. A sharp band at 3625 cm^{-1} seen in the FTIR spectrum is assigned -OH stretching vibration. An excellent assignment >C=O stretching vibration mode found at 1650 cm^{-1} confirms the literature value. >C=S stretching vibration of thiourea found at 1563 cm^{-1}. The peak at 920 cm^{-1} shows the wagging vibration of >CH- forms and excellent agreement with expected characteristic value. The observed peaks found in the regions 3299 cm^{-1} and 2406 cm^{-1} is assigned to NH_3^+ asymmetric stretching mode of vibration and NH_3^+ symmetric stretching mode of vibration respectively.Table.1 consists of the observed bands along with their vibration assignments is given below.

Table 1. The observed frequencies and corresponding assignments of Thioureasquarate

The observed FTIR frequencies	Assignments
3625	-OH stretching
3299	NH_3^+ asymmetric stretching
2406	NH_3^+ symmetric stretching
1650	>C=O stretching
1563	>C=S stretching
920	>CH- wagging

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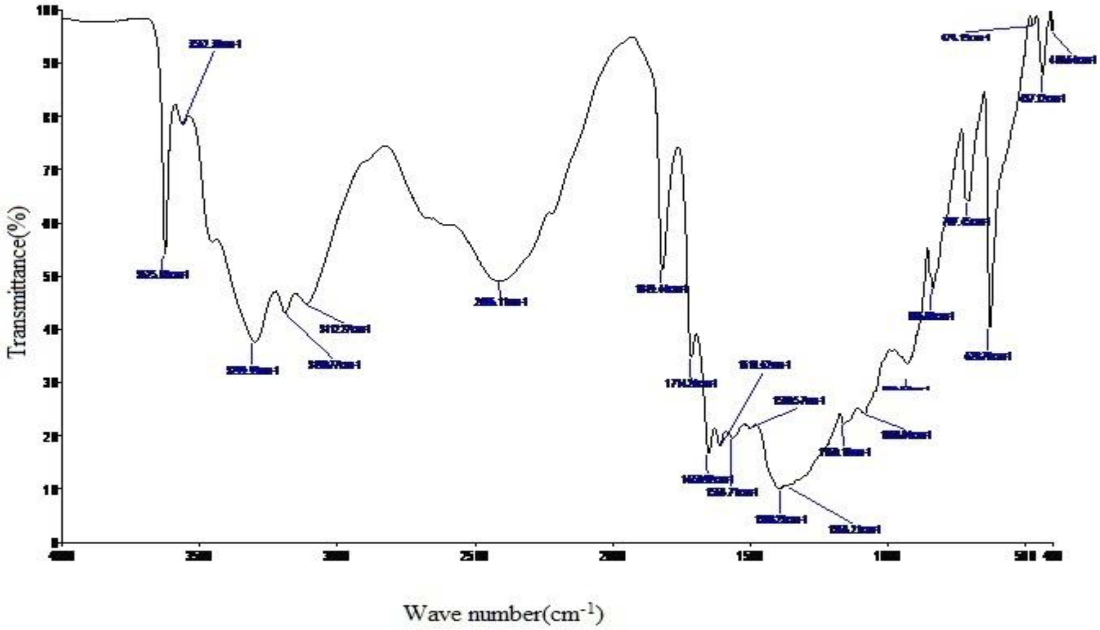

Fig. 3 FTIR spectrum of Thioureasquarate

3.3 Thermal Analysis

An analytical technique of thermo gravimetric analysis of Thioureasquarate was carried out to determine the thermal stability. The occurrence of weight change on heating the crystals was also monitored using the technique. Under inert nitrogen atmosphere the TG-DSC of Thioureasquarate crystal were carried out at a heating rate of 20°C per minute within a range of 30-1000° C. The resultant TG-DSC curves are shown in Fig. 4.

Finally 0.119% of the initial mass was left out while 4.2210 mg is the initial mass loss of the subjected grown crystal to analysis on heating. At 917.65 C the TGA seems to be nearly bent. In DSC the appeared endothermic peak shows the decomposition of Thioureasquarate crystal at 203.72° C. It is confirmed from the TG-DSC analysis that the thermal stability of the grown crystal is up to 155.48°C, which proves that the melting and decomposition takes place simultaneously. The entire compound decomposed around a temperature at 917.65°C. No evidence of entrapped water on the surface of the crystal as there is no weight loss up to 155.48° C. The crystal undergoes a predictable weight loss after the temperature of thermal stability 155.48°C. Hence it can be recommended for device fabrication under the temperature less than 155.48°C.

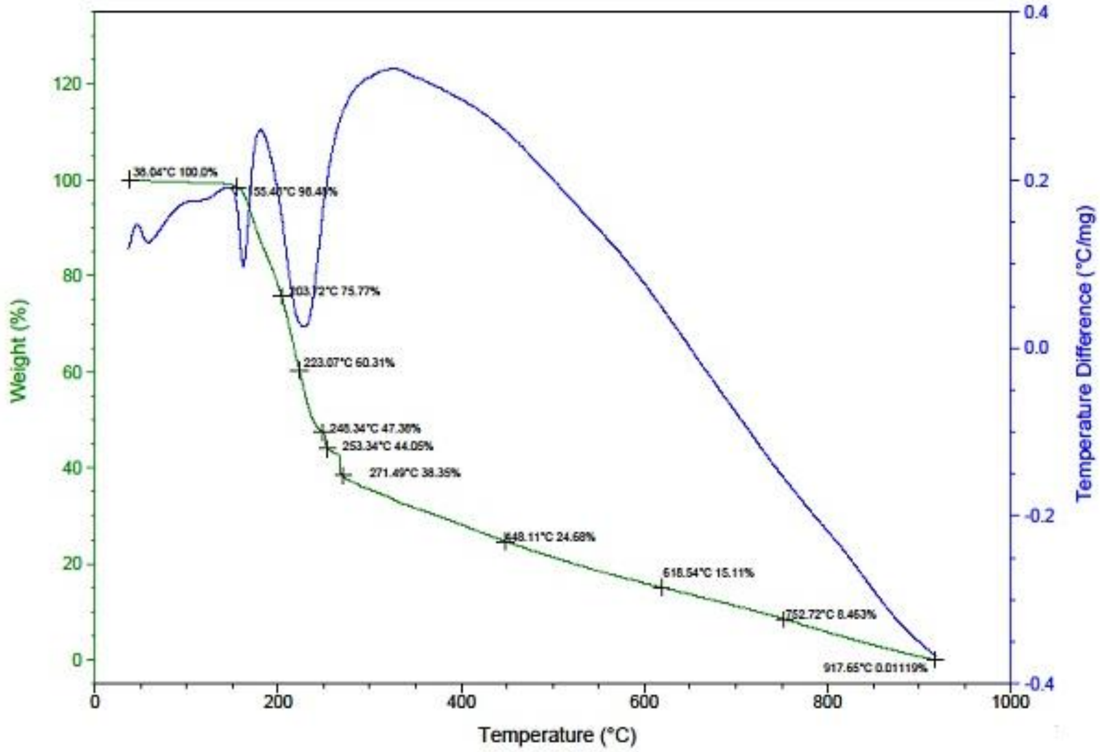

Fig.4 TGA-DSC of Thioureasquarate

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3.4 Powder X-ray Diffraction Analysis

Using Rich Seifert diffractometer with Cu Kα radiation of wavelength λ=1.54060A° the X-ray powder diffraction analysis of the thiourea squarate grown crystals have been carried out and the same is displayed in the Fig. 5. The difference in orientation and grain size attributes the observed peak amplitude difference. The Reitveld index software resolved the diffraction pattern obtained to index the hkl values. Values of hkl and 2θ are enclosed in the table 2which confirms the grown crystal.

Table 2 Powder XRD data for Thioureasquarate

Position 2θ	d-spacing	(hkl)
20.776	4.27407	110
22.121	4.01517	101
23.22	3.82776	220
25.446	3.49493	210
28.395	3.14701	201
28.893	3.08772	121
30.525	2.92691	211
31.336	2.85234	2
33.908	2.64162	2
36.851	2.43714	211
71.312	1.32145	4

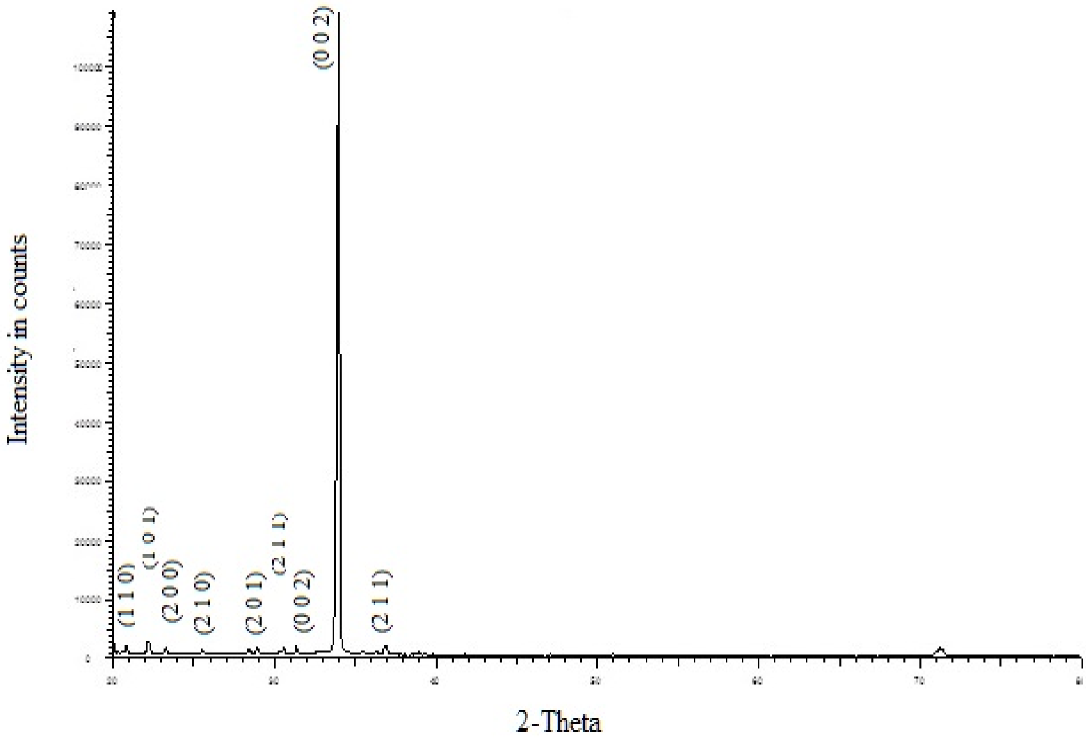

Fig.5 XRD Spectrum of Thioureasquarate

3.5 Second harmonic generation

Q-Switched laser beam of wavelength λ=1064nm with an energy beam of 1.3mj/pulse is used to determine the efficiency of second harmonic generation (SHG) of the grown Thioureasquarate crystals. The penertrating beam has a pulse width 8ns with a repetition rate of 10 Hz was utilized. Fine powder form of grown crystals is made to expose to laser radiation which was crushed using a mortar to determine the SHG in a microcapillary packing.Emission of green light confirms the second harmonic generation behavior of the grown crystal [14-15]. The output of the emitted beam has a value of 13mv which in turn confirms that it is 65% of the KDP crystal and 23% of the Urea.

4. Conclusion

Utilizing the slow evaporation solution growth technique the compound of Thioureasquarate has been conveniently synthesized and grows at room temperature. FTIR analysis shows the presence of functional groups of the grown crystal. XRD measurement confirmed the crystal system along with the Reitveld Software. From UV-Vis-NIR spectrum it was observed that the transparency range of Thioureasquarate ranges in

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between 330-110nm. Positive results of Second Harmonic Generation show that the grown crystal has NLO potential. The thermal stability up to 155.48°C which is in other turn said to be melting point of the grown crystal is confirmed using the TG-DSC curve. All the above said studies may be very useful to suggest for the fabrication of NLO devices lower than 155.48°C.

References

1. U. Korkmaz, A. Bulut, I. Bulut, 3-Phenylpyridinium hydrogen squarate: experimental and computational study of a nonlinear optical material, Spectrochim Acta A Mol Biomol Spectrosc 140, 140-149(2015).
2. X.H. Li, Y.L. Yong, H.L. Cui, R.Z. Zhang, X.Z. Zhang, Theoretical investigation on vibrational spectra, first order hyperpolarizability and NBO analysis of 4-Phenylpyridinium hydrogen squarate, Spectrochim Acta A Mol Biomol Spectrosc,147, 14-19 (2015)
3. U. Korkmaz, A. Bulut, 2-Pyridinium propanol hydrogen squarate: experimental and computational study of a nonlinear optical material, Spectrochim Acta A Mol Biomol Spectrosc, 136, 1058-1068 (2014).
4. U. Korkmaz ,Y. Topcu, M. Tas, A. Bulut, Synthesis, an experimental and quantum chemical computational study: proton sharing in 4-Morpholinium bis(hydrogen squarate), Spectrochim Acta A Mol Biomol Spectrosc, 134, 233-243 (2014).
5. U. Korkmaz, A. Bulut, Synthesis, an experimetal and quantum chemical computational study of a new nonlinear optical material: 2-Picolinium hydrogen squarate, Spectrochim Acta A Mol Biomol Spectrosc 130, 376-385 (2014)
6. C. Ramachandra raja, P. Paramasivam, N. Vijayan, synthesis, growth and characterization of a new nonlinear optical material; 4-phenyl pyridinium hydrogen squarate, Spectrochim Acta A Mol Biomol Spectrosc, 69, 1146-1149 (2008)
7. J. Seliger, V. Zagar, R. Bline, Oxygen 17-NQR study of the phase transition in squaric acid,J. Magn. Reson.58, 359-369 (1984)
8. T. Kolev, R. Worman, M. Spiteller, M. Sheldrick, M. Heller, 4-Phenyl pyridinium hydrogen squarate, Acta. Cryst. E-60, 956-957 (2004)
9. M. Sureshkumar, S. Krishnan, Das, S. Jerome, Growth, optical and thermal studies on novel nonlinear optical crystal: Glycine phthalic acid, Optik, 127(5), 2509-2511(2016).
10. G Madhurambal, B Ravindran, M Mariappan, K Ramamurthi, S.C. Mojumdar, Growth and characterization of cinnamic acid urea single crystal, J. Therm. Anal. Calorim. 104 (3), 875-878 (2011)
11. G Madhurambal, B Ravindran, M Mariappan, SC Mojumdar, Growth and characterization of tristhiourea chromium (III) sulphate, J. Therm. Anal. Calorim. 108 (3), 905-910 (2012)
12. B Ravindran, G Madhurambal, M Mariappan, K Ramamurthi, S.C. Mojumdar, Growth and characterization of mercury cinnamate single crystal, J. Therm. Anal. Calorim. 104 (3), 909-914 (2011)
13. G Madhurambal, B Ravindran, M Mariappan, SC Mojumdar, Investigation on the growth and characterization of nonlinear optical single crystal of bisthiourea iron (II) sulphate, J. Therm. Anal. Calorim. 108 (3), 911-914 (2012)
14. S.K. Kurtz, T.T. Perry, A powder technique for the evolution of nonlinear optical materials, J. Appl. Phys. 39, 3798-3813 (1968)
15. K. Betzler, D. Bauerle, Second harmonic generation in squaric acid, Phy. Lett. 70A (2), 153-154 (1979)

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