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RESEARCH ARTICLE

INVESTIGATIONS ON THE SYNTHESIS, GROWTH AND CHARACTERIZATION OF THIOSEMICARBAZONE COMPLEX CRYSTAL

R.N. JAYAPRAKASH[1], P. SUNDARAMOORTHI[2]* AND N.DINESH BABU[1]

[1]Department of Physics, Adhiyamaan College of Engineering, Hosur – 635109, Tamilnadu, India.
[2]Department of Physics, Thiruvalluvar Government Arts College, Rasipuram-637401, Tamilnadu, India.

Corresponding Author: prakashnandhi@yahoo.co.in

Abstract

Urea thiosemicarbazide single crystal was grown by low temperature solution growth method from aqueous solution at room temperature. Single crystal and powder X-ray diffraction studies have been carried out for the grown crystals to confirm the crystal structure and crystalline nature. Modes of vibration of various functional groups present in the grown crystal have been identified by FTIR spectroscopy analysis. The UV-Vis spectral analysis was carried out to understand the optical suitability and transparency of the grown crystal for device applications. Non linear optical property of the compound have been confirmed by Kurtz-Perry powder second harmonic generation test using Nd: YAG laser as source. Dielectric studies were performed with respect to temperature at various frequencies (50Hz-5MHz).

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Keywords: Optical, Dielectric, Photoconductivity, Single crystal XRD, Nonlinear.

Introduction

In recent years search of new nonlinear optical (NLO) materials has been of great interest, because of their significant usage in various applications including high speed information communication, wireless optical computing, optical data storage, laser technology, color display and medical diagnostics etc [1-3]. Organic materials are more attractive when compared to inorganic counterparts due to their large nonlinearities, ultra fast response, high laser damage threshold for laser power and structural diversity [4-6]. Many investigations are being carried out in the last few decades, set of new organic materials with large second order optical nonlinearities in order to satisfy technological requirements. Presences of delocalized π electron conjugation systems asymmetrized by the electron donor and acceptor groups are highly polarisable entities for NLO applications of the organic material [7]. Extensive electron delocalization reported in the arylhydrazones structures helps the thiosemicarbazone complexes to acquire second harmonic generation efficiency [8]. However, a variety of crystals in this class have been grown by several groups [9-12]. In continuation of our work on thiosemicarbazone, we are reporting the synthesis of urea thiosemicarbazide material and growth of single crystals by solvent evaporation method. The structural, functional, linear and nonlinear optical properties of the grown crystal were characterized by single crystal XRD, powder XRD, FTIR, UV and Kurtz Perry SHG measurement.

Material synthesis and Crystal growth

Urea thiosemicarbazide single crystal was synthesized by mixing analytical grade urea and thiosemicarbazide in the stoichiometric ratio 1:1 in

triple distilled water. The solution was stirred continuously and to make the solution homogenous, it was slightly heated and then left undisturbed for the precipitation of urea thiosemicarbazide. The purity of the synthesized salts was enhanced by repeated recrystallization process. Slow evaporation method was employed for the growth process. Saturated solution of urea thiosemicarbazide was prepared at 35 °C using triple distilled water and stirred thoroughly for 3 hrs. Then solution was filtered and transferred into 100 ml beaker having perforated holes. The solution beaker was housed in constant temperature bath at 35 °C for solvent evaporation. Well defined morphology with good transparency single crystals were harvested from the mother solution. Good quality crystals were extracted in order to study various characterization studies. As grown single crystals of urea thiosemicarbazide is shown in figure 1.

Structural studies

Finely crushed powder of urea thiosemicarbazide crystal subjected to powder X-ray diffraction using a PANalytical Xpertpro diffractometer (Netherlands) in the 2θ ranging from 10 to 70° by using Kα radiation. From the diffraction pattern, the d spacing for each diffraction peak in the spectrum was identified. The prominent peak appears at 2θ of 28.210° and also includes many low intensity peaks. The sharp and well defined Bragg's peaks confirmed the crystallinity of the grown crystals. Powder X-ray diffraction pattern of the grown crystals was shown in figure 2.

Single crystal XRD analysis

The unit cell parameters are determined by using the single crystal X-ray diffraction data obtained with a four-circle Nonius CAD4/diffractometer (MoKα, λ = 0.710738 Å). The unit cell parameters are a = 4.87 Å , b = 5.95 Å , c = 7.25 Å and α = 77.59º, β = 76.69º, γ = 83.74º and volume = 199 $Å^3$. From the data, the grown crystal is belongs to Triclinic with space group is P system.

Functional study

In order to confirm the functional group and chemical bonding present in the synthesized material, FTIR spectrum was recorded for urea thiosemicarbazide by KBr pellet technique in the range 400 to 4000 cm^{-1}. The band obtained at 1530 cm^{-1} is attributed to the presence of imine group. A absorption at is 2360 cm^{-1} due to C-H stretching and C-S stretch of the thiosemicarbazide is observed at 1160 cm^{-1}. The N-H deformation and C-H deformation vibration is observed at 1620 cm^{-1} and 999 cm^{-1} respectively. The peak at is 3360 cm^{-1} due to NH_2 asymmetric stretching and peak at 3180 cm^{-1} is due to NH symmetric stretching.

Linear optical study

Optical absorption spectrum of the grown urea thiosemicarbazide crystal in solution mode was recorded in the range 200 to 800 nm at room temperature. Strong absorption was observed at 255 nm, which indicates that this material is a potential candidate for generating blue-violet light using a diode laser. As observed in the spectrum figure 4, absence of absorption in the entire visible region, it is a favorable condition for optoelectronics applications and used as SHG material in the visible region [13].

Non-linear optical study

In order to confirm non linear optical behaviour, Kurtz and Perry method [14] employed for the powder sample of urea thiosemicarbazide. Grown crystals were grounded into fine powders and filled in micro capillary tube. A high intensity Nd: YAG laser (1064 nm) was illuminated on the micro capillary tube with a pulse duration of 10 S. Emission of bright green light from the tube confirm the generation of second harmonics in the material. The second harmonic signal of 6.2 mV was obtained for an input energy of –mJ/pulse. For KDP sample, the SHG value gives a signal of 11 mV for the same input energy. The level of charge transfer between the chromophore determines the level of SHG output of the material [15-16].

Dielectric studies

Figure.5 and 6 show the plot of dielectric constant (ε_r) as a function of log frequency and plot of dielectric loss (tanδ) as a function of log frequency. It is observed that both ε_r and tanδ show similar variation with frequency. Broadly speaking the graph exemplifies the fact that the dielectric constant and dielectric loss are both inversely proportional to frequency. This is a normal dielectric behaviour [17] that both ε_r and tanδ decrease with increasing frequency. This can be understood on the basis that the mechanism of polarization is

Figure 1. As grown single crystal of urea thiosemicarbazide

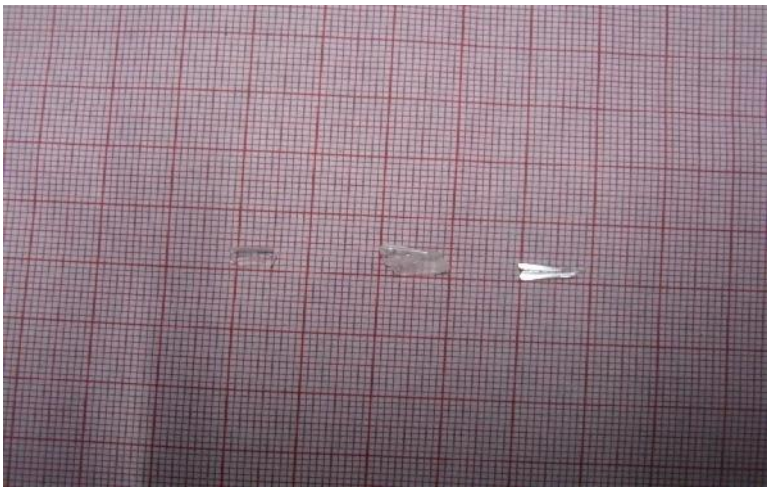


Figure 2. Powder X-ray diffraction pattern

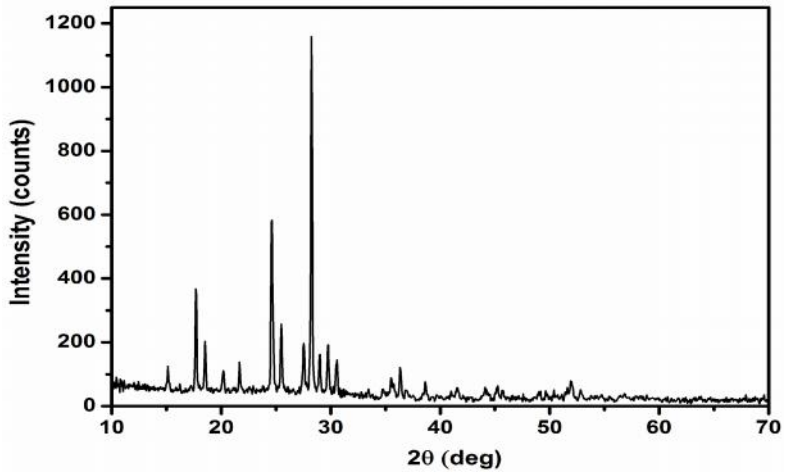


Figure 3. FTIR spectrum

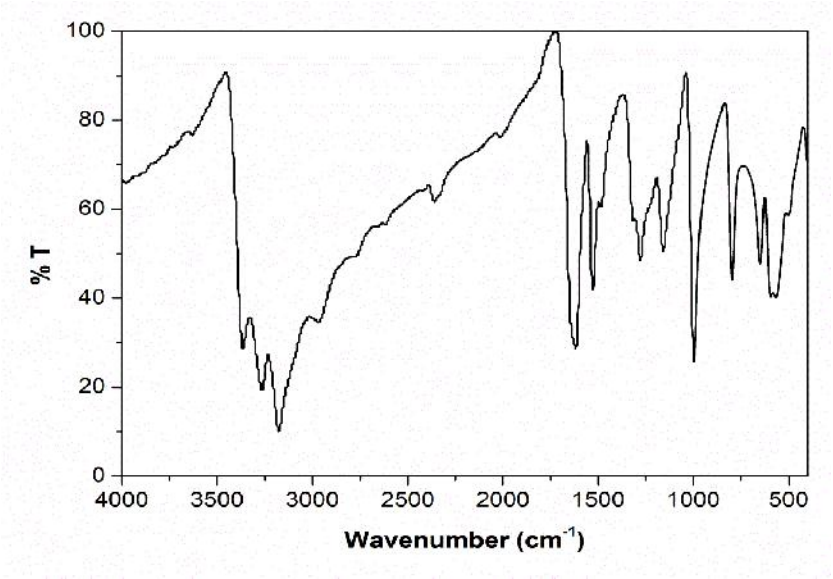


Figure 4. Optical Absorption spectrum

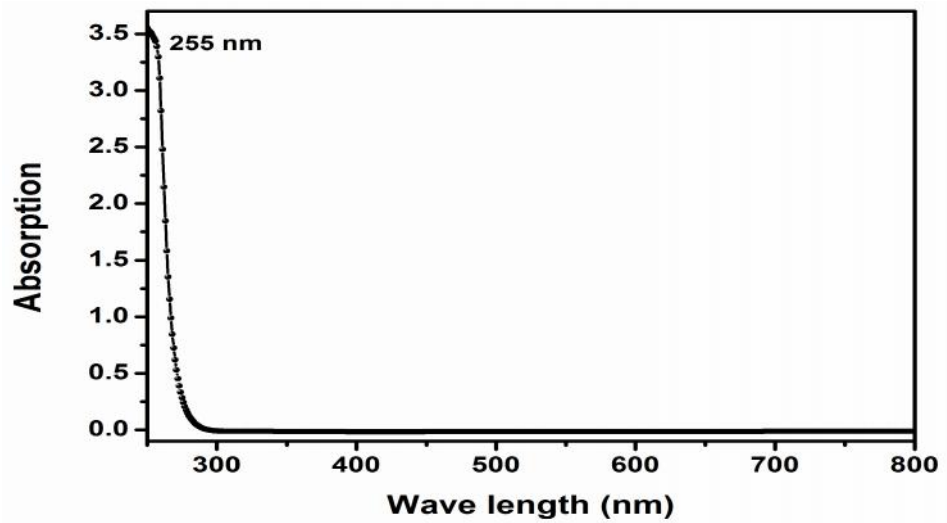


Fig.5 Dielectric constant Vs Log f

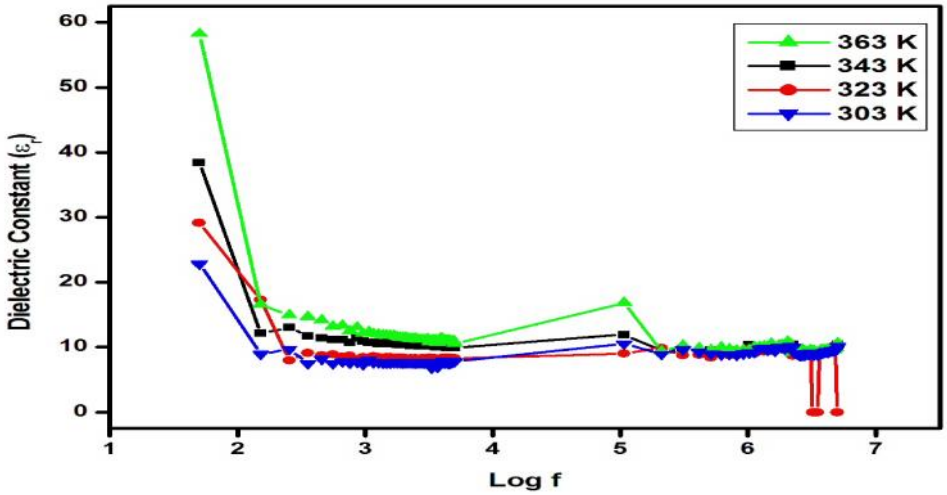


Fig.6 Dielectric loss Vs Log f.

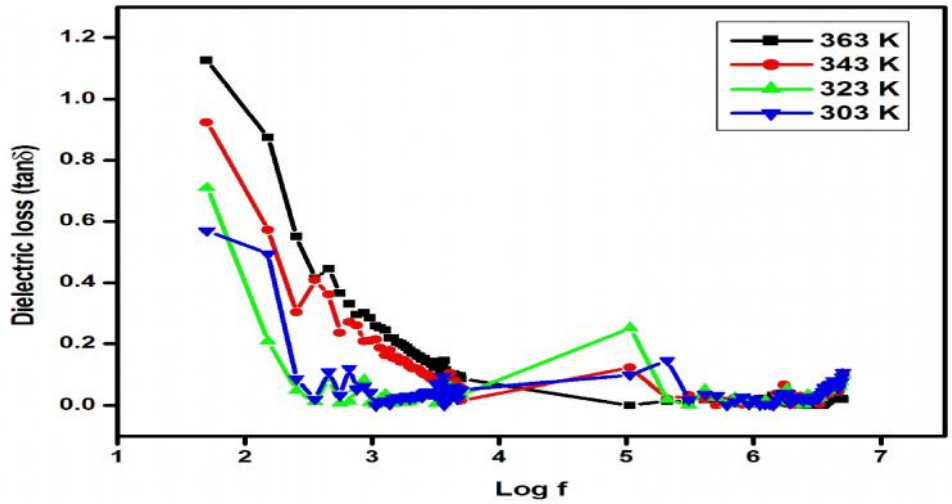
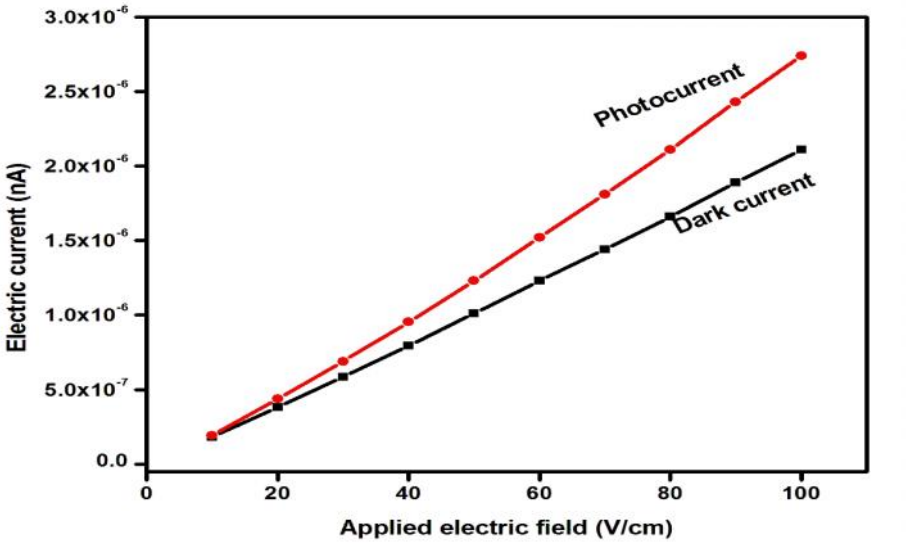


Fig. 7. Photoconductivity response for the crystal.



similar to that of conduction process. The electronic exchange of the number of ions in the crystals gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization. As the frequency increases, the point are reached where the space charge cannot sustain and comply with the external field and hence the polarization decreases, giving rise to diminishing values of ε_r and tanδ. Continuous gradual decrease of ε_r as well as tanδ suggest that Urea thiosemicarbazide crystals are like any normal dielectric may have domains of different sizes and varying relaxation times. The very high value of ε_r at lower frequencies may be due to the presence of all the four polarizations namely, space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually.

Photoconductivity

Photoconductivity studies were carried out at room temperature using Keithley 6512 electrometer. Crystal was silver pasted on opposite faces and thin copper wire was connected both sides on the sample and it is connected in series with electrometer. The sample was protected from all the radiation. The applied input voltage was increased from 10 to 100V and resultant dark current was recorded. Then the samples were exposed to radiation from 100W halogen lamp containing iodine vapour and tungston filament. Phtocurrent was recorded for the same input voltage. Fig.7 shows the photo current and dark current response for the sample. From the figure it is concluded that dark current is higher than photocurrent and this phenomena is called negative photoconductivity.

Conclusion

Thiosemicarbazone complex crystal was grown from aqueous by low temperature solution growth method. The cell parameters and crystalline nature of the crystals were estimated from X-ray diffraction studies. The presence of various functional group in the grown crystals were confirmed by FTIR spectrum. The optical window and low cutoff wavelength are identified from UV analysis. The second harmonic efficiency of the grown crystals was measured by Kurtz-perry powder method. Photoconductivity study reveals the negative photoconductivity nature of the crystal. In dielectrics dielectric constant is very high at low frequency.

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References

[1] B.J. McArdle, J.N. Sherwood, A.C. Damask, J. Cryst. Growth 22 (1974) 193–200.
[2] M. Aravindhan, K. Sankaranarayanan, K. Ramamurthy, C. Sanjeeviraja, P. Ramasamy, Thin Solid Films, 477 (2005) 2–6.

[3] S. Ayers, M.M. Faktor, D. Marr, J.L. Stevensons, J. Mater. Sci. 7 (1972) 31–33.
[4] R.L. Sutherland, Hand Book of Nonlinear Optics, Dekker, New York, 1996.
[5] D.S. Chemla, J. Zyss (Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, vols. 1 and 2, Academic Press, New York, 1997.
[6] M. Prakash, D. Geetha, M. Lydia Caroline, Spectrochimica Acta Part A 81 (2011) 48– 52.
[7] P. Tansuri, K. Tansuree, B. Gabriele, R. Lara, J. Cryst. Growth Des. 4 (2004) 743–747.
[8] H. Beraldo, D. Gambino, Mini Rev. Med. Chem. 4 (2004) 31–39.
[9] R. Santhakumari, K. Ramamurthi, Spectrochimica Acta Part A 78 (2011) 653–659
[10] S. Manivannan, S. Dhanuskodi, Journal of Crystal Growth 257 (2003) 305–308
.
[11] R.Santhakumari, K.Ramamurthi, R.Ramesh Babu, Helen Stoeckli Evans, G.Bhagavannarayana, R.Hema, Spectrochimica Acta Part A (2011)
[12] P. Maadeswaran, J. Chandrasekaran, S. Thirumalairajan, Optik 122 (2011) 259–262
[13] P. Maadeswaran, S. Thirumalairajan, J. Chandrasekaran, Optik 121 (2010) 773–777.
[14] K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798–3813.
[15] J.L. Oudar, J. Chem. Phys. 67 (1977) 446.
[16] J.L. Oudar, J. Zyss, Phys. Rev. A 26 (1982) 2028.
17] J. C. Anderson, Dielectrics, Chapman and Hall, 1964.

