ChemTech

International Journal of ChemTech Research

CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555

Vol.11 No.08, pp 283-288, 2018

Studies on the Thermal, Mechanical, Dielectric and Photoconductivity Properties of Ammonium Hydrogen Oxalate Hemihydrate Single Crystal for NLO Applications

A. Zamara, V. Thayanithi, P. Praveen Kumar*

Department of Physics, Presidency College, Chennai – 5, Tamilnadu, India.

Abstract : Good quality single crystals of nonlinear optical material Ammonium hydrogen oxalate hemihydrate which crystallizes in Orthorhombic crystal system and belonging to space group Pnma were successfully grown from an aqueous solution by slow evaporation method. The grown crystals were characterised by single crystal X-ray diffraction, Thermal studies, Vickers microhardness test, dielectric studies and photoconductivity study. The Nonlinear optical (NLO) property of the crystal was confirmed by the Kurtz-Perry powder second harmonic generation test.

Keywords : X-ray diffraction**,** Nonlinear crystals, dielectric studies, single crystals, organic compounds.

1. Introduction

A challenging endeavour for material science is the growth of high quality single crystals.All basic solid materials are made up of single crystals and they are the backbone of modern technology [1]. Crystals of good quality and structural perfection are required for fundamental research and practical implementation in photonic and optoelectronic technology. Nonlinear optical crystals have been given much importance because of their potential applications such as telecommunications, optical information process, frequency conversion and optical disk data storage [2-4]. Nonlinear optical (NLO) crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible, ultraviolet ranges are required in the field of optoelectronics and photonics [5-7]. In recent years there has been an enormous effort and focus on the design and development of highly efficient organic nonlinear optical materials. Organic NLO crystals show prominent properties due to their fast and nonlinear response and inherent synthetic flexibility and large optical damage threshold [8]. The organic nonlinear optical materials are having good NLO and electro-optical susceptibility in comparison with inorganic counterparts [9]. Organic compounds likeL-histidinium 2 nitrobenzoate [10], caffenium picrate [11], picolinium maleate [12], guanidiniumtrifluoroacetate [13], L-histidinium 2 nitrobenzoate etc have shown higher second harmonic generation efficiency than various inorganic crystals.

P. Praveen Kumar *et al* /International Journal of ChemTech Research, 2018,11(08): 283-288.

DOI= http://dx.doi.org/10.20902/IJCTR.2018.110835

Ammonium hydrogen oxalate hemihydrate (AHOH) is a promising nonlinear optical material and its structure is already reported [14]. The present work focuses on the growth, thermal, mechanical, dielectric and photoconductivity studies of AHOH single crystals. Second harmonic generation study is also done for the grown crystal.

2. Materials and Methods

Ammonium hydrogen oxalate hemihydrate crystals were grown from an aqueous solution by slow evaporation method. Ammonium and oxalic acid were taken in the stoichiometric ratio 1:1 and dissolved in double distilled water. The reaction is as follows,

$$NH_4OH + H_2C_2O_4 \rightarrow NH_4H\,C_2O_4 . \tfrac{1}{2} H_2O \quad (1)$$

The resultant mixture was stirred continuously to obtain a homogenous solution, filtered and kept undisturbed for crystallization. The synthesized material was purified by repeated recrystallisation process. Good quality single crystals were obtained in a period of 3 weeks. The photograph of the as grown crystal is shown in Figure 1.

Figure 1. Photograph of the as grown crystal of AHOH

3. Results and Discussion

3.1 Single crystal X-ray diffraction analysis

The grown crystal of Ammonium hydrogen oxalate hemihydrate was subjected to single crystal XRD analysis to determine the cell parameters by employing ENRAF NONIUS CAD 4, single crystal XRD diffractometer with MoKα radiation (λ = 0.71073 Å). From the XRD data, it is observed that Ammonium hydrogen oxalate hemihydrate crystallizes in Orthorhombic crystal system with space group P_{nma}. The lattice parameter values obtained are a(Å) = 11.225, b(Å) = 12.324, c(Å) = 6.890 which are in good agreement with the reported values [14]. The lattice parameter values are tabulated. (Table 1)

Table 1.Lattice parameter values of AHOH single crystal

Lattice parameters	**AHOH**	**Reported values[14]**
a(Å)	11.225	11.228
b(Å)	12.324	12.329
c(Å)	6.890	6.898
Crystal system	Orthorhombic	Orthorhombic
Space group	P_{nma}	P_{nma}
Volume ($Å^3$)	953.14	954.89 $Å^3$

3.2 Second harmonic generation study

The grown crystal of Ammonium hydrogen oxalate hemihydrate was subjected to Kurtz-Perry powdersecond harmonic generation test (SHG) using the Nd-YAG Q switched laser beam for the nonlinear optical (NLO) property [15]. The sample was illuminated with the laser input pulse of 2.01mJ. The output pulse of 18 mJ was obtained from the grown crystal and it was 24mJ for KDP crystal. The second harmonic generation in the crystal was confirmed by the emission of green radiation from the crystal.The SHGefficiency of Ammonium hydrogen oxalate hemihydratecrystal was found to be 0.75times thatofpotassium dihydrogenphosphate (KDP)crystal.

3.3 Thermal analysis

The TG and DTA spectrum of AHOH single crystal was carried out between 30 ºC and 800 ºC in the nitrogen atmosphere at a heating rate of 10 ºC/min using TGA Q500 thermal analyser and is as shown in Figure 2. There is a sharp weight loss at 200 ºC which indicates the sublimely nature of the crystal. From 200 ºC to 260 ºC there is a major weight loss of 86% which may be due to oxidative decomposition of the crystal. During the decomposition process the material liberates volatile gaseous products like NO_2 and CO_2. The sharp exothermic peak in the DTA at 200 ºC indicates the melting point of the material. The sharpness of this exothermic peak shows good degree of crystalinity and purity of the material. The remaining weight loss of 5% may be due to the residual carbon mass at the end of the decomposition reactions. Hence AHOH single crystal has moderate thermal stability and can be used for NLO applications upto 200 ºC [16].

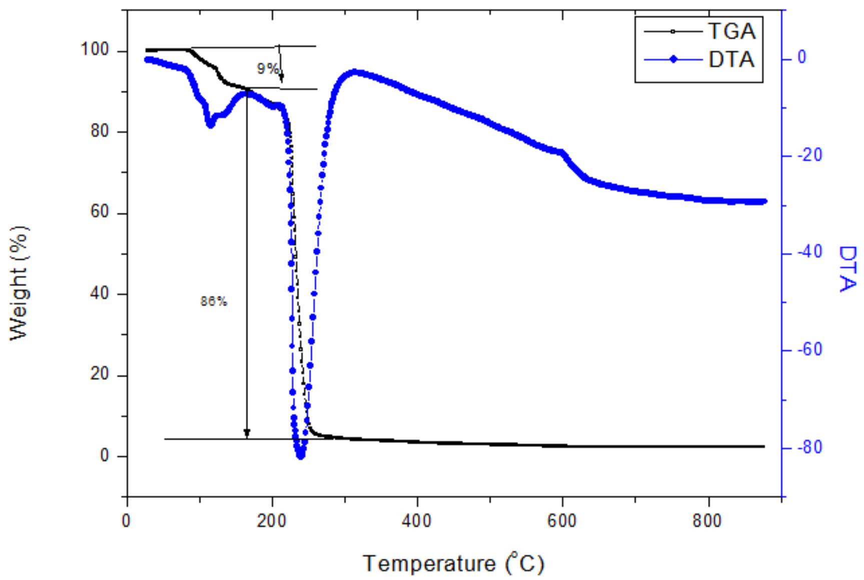


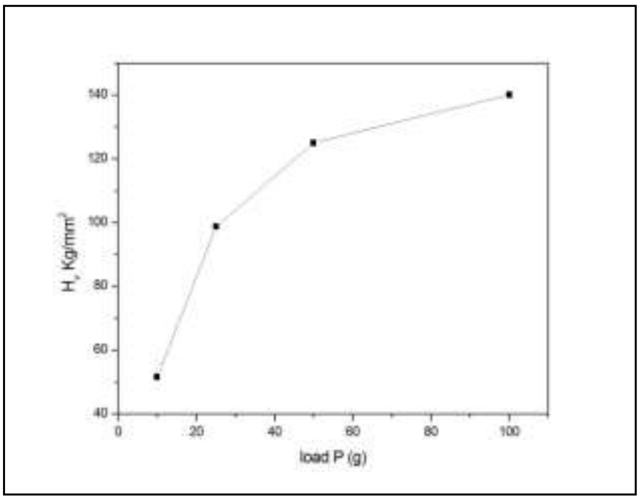
Figure 2. TG-DTA curve of AHOH single crystal

3.4Vickersmicrohardness test

Hardness is a measure of the materials resistance to localized plastic deformation. The microhardness characterisation is very important as far as the device fabrication is concerned.Hardness of the grown crystal has been found by Vickers micro hardness test. The indentations have been made at room temperature on the prominent plane with a constant dwell time of 8 s. The indentation marks have been made on the system for four loads (10 gm, 25 gm, 50 gm, and 100 gm). To get accurate measurements, for each applied load three indentations have been made on the sample and the average diagonal length (d) of the indenter impressions have been measured. The Vickers micro hardness number $H_v$of the grown crystal has been calculated using the equation,

$H_v = 1.8544 \times (P/d^2)$ Kg/mm^2

where P is the applied load, d the average diagonal length of the indenter impression and 1.8544 is a constant of a geometrical factor for the diamond pyramid [17]. It is observed that the hardness value increases upto the applied load of 100 gm due to work hardening of the surface layer. Above 100 gm, cracks have been formed due to release of internal stress generated locally by indentation. The variation of hardness number with load is shown in Fig 3. The work hardening coefficient of the sample has been determined as n= 1.5, from the slope of the log P vs log d graph as in Figure 4. The value of n should lie between 1 to 1.6 for harder materials and above 1.6 for softer materials [18]. The work hardening coefficient of AHOH crystal is 1.5. It shows that the material belongs to the hard material category. The good mechanical hardness contributes to the attractiveness of the sample for various practical applications.



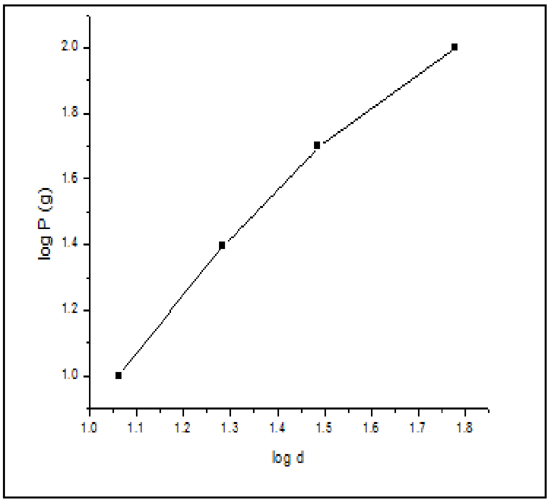


Figure 3. Plot of Load P vs Hardness number H_vFigure 4. Plot of log d vs log P

3.5 Dielectric studies

Single crystals of AHOH was subjected to dielectric studies at temperatures 40°C, 50°C, 75°C, 100°C for various frequencies ranging from 50Hz to 5MHz. The dielectric constant is calculated from the relation

$$\dot{\varepsilon}_r = cd/\mathcal{E}_o A$$

where d is the thickness and A is the area of cross section of the grown crystal. The variation of dielectric constant of AHOH crystal as a function of log f for different temperatures is shown in Figure 5.From the graph it is found that the dielectric constant is found to decrease with increase in frequency. This nature of variation governs the various polarization mechanisms. The high value of dielectric constant at low frequencies is contributed by space charge polarization. It is generally active at low frequencies which indicates the perfection of the grown crystal. In accordance with Miller's rule, the lower value of dielectric constant is a suitable parameter for enhancement of SHG [19]. The dielectric loss of the material strongly depends on the rate of change of time varying field. The variation of dielectric loss with frequency at different temperatures is shown in Figure 6. The curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field. And also the low dielectric loss with high frequency implied that the crystal possesses good optical quality with lesser defects which is an important parameter for NLO materials [20].

Hence the low value of dielectric constant and dielectric loss at higher frequencies is important for the fabrication of materials towards photonic,electro-optic devices and high frequency response devices.

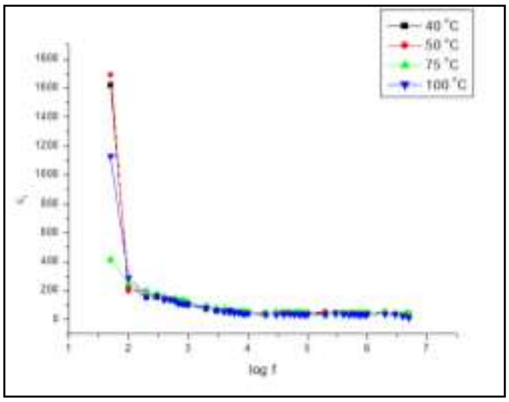


Figure 5. Plot of hardness no:vs log f

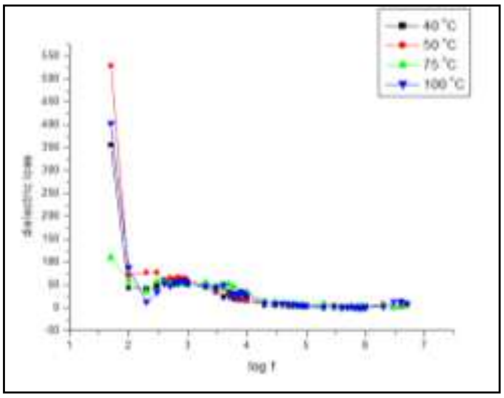


Figure 6. Plot of dielectric loss vs log f

3.6 Photoconductivity study

Photoconductivity studies were carried out at room temperature for the grown crystal using Keithley 485 picoammeter. The dark current was recorded for the sample by keeping it unexposed to any radiation. The light from the halogen lamp (100W) containing iodine vapour is focused on the sample and the photocurrent was measured.

Figure 7 shows the plot of photocurrent and dark current as a function of the applied voltage. It is observed from the plot that dark current (I_d) and photocurrent (I_p) of the sample increase linearly with the applied voltage. It is also seen that the dark current is always greater than the photo current. Hence this material possesses negative photoconductivity.

Negative photoconductivity is explained by Stockmann model[21]. Negative photoconductivity in a solid is due to the decrease in the number of mobile charge carriers or their lifetime, in the presence of radiation[22]. Decrease in lifetime with illumination, could be due to the trapping process and increase in carrier velocity according to the relation, $\tau = (vsN)^{-1}$

where v is the thermal velocity of the carriers, s is the capture cross section of the recombination center and N is the carrier concentration.

For a negative photoconductor, the Fermi gap holds two energy levels in which one is placed between the Fermi level and the conduction band while the other is located close to the valence band. The second level has higher capture cross section for electrons and holes. As it captures electrons from the conduction band and holes from the valence band, the number of charge carriers in the conduction band decreases and current decreases in the presence of radiation.

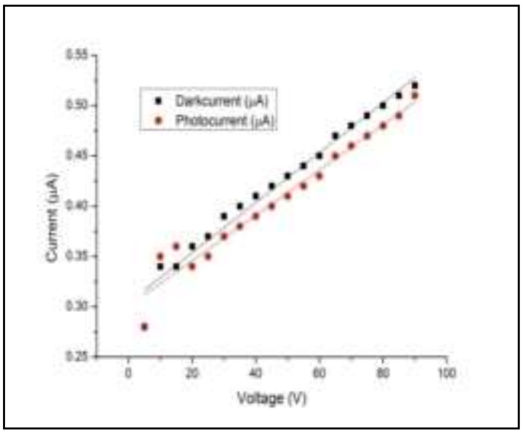


Figure 7. Photoconductivity graph of AHOH

4.Conclusion

Single crystals AHOH were grown by slow evaporation solution growth technique.The lattice parameter values calculated is in good agreement with the reported values. The hardness of the crystals reveal that the AHOHcrystal belong to the hard material category. The dielectric loss with frequency proves that the grown crystal possesses enhanced optical quality with lesser defects.Photoconductivity studies reveal that the crystal has negative photoconductivity. The powder SHG efficiency indicates that the crystal shows efficiency of 0.75 times than that of KDP. Thermal analysis carried out confirms that the crystal is thermally stable uptoa moderate temperature 200 °C. Hence AHOH single crystals can be used as a promising material for non linear device fabrication.

References

1. Scheel H.J, Crystal Growth Technology, John Wiley & Sons Limited, New York (2003).
2. Lin J.T, Wang V.S, Arend. H, Solution growth of new organic nonlinear optical crystal material, SPIE 1104 (1989)1104, 100-132.
3. Duo-rong.U, Dong X.U, Nan Z.L, Ming-guo I.U, Min-hua.J, Organic nonlinear optical crystal MHBA for compact blue-violet laser, Chin. Phys. Lett. (1996) 13, 841-843.
4. Min-hua Jiang, Qi Fang, Organic and semi-organic nonlinear optical materials, Adv. Mater (1999) 11, 1147-1151.
5. Prasad P.N, Williams D.J, Wiley-Interscience, NewYork, 1991.
6. Jaikumar.D, Kalainathan. S, Bhagavannarayana. G, Physica B, Condensed Matter, (2010) 405, 2394.
7. Bright. K.C, Freeda. T.H, Physica B, Condensed matter (2010) 405, 3857.
8. Vijayan. N, Bhagavannarayana. G, Maurya. K.K,Sharma. S.N, Gopalakrishna R, Jayabharathi J, Ramasamy P, Synthesis, growth of single crystals & their characterisation: LAM, Optic(2012) 23,604-608.
9. AnbuchudarAzhagan S, Ganesan S, Effect of ammonium acetate addition on crystal growth, spectral, thermal & optical properties of glycine single crystals. Optik (2012) 123,993-995.
10. Zamara A, Rajesh K, Thirugnanam A, Praveenkumar P, Growth & characterisation of L-Histidinium 2-nitrobenzoate, Optik (2014) 125, 6082-6086.
11. Chandramohan A, Bharathikannan R, Chandrasekaran J, Maadeshwaran P, Renganathan R, Kandavelu V, Synthesis & crystal growth of a new organic NLO material: Caffeinium Picrate (CAFP) – A charge transfer molecular complex salt, Journal of crystal growth, (2008) 310, 5409-5415.
12. Pandi P, Peramaiyan G, Sudhakar S, Chakravarthy G, MohankumarR,Bhagavannarayana G, Jayavel R, Studies on synthesis, growth, structural, thermal, linear and nonlinear optical properties of organic picolinium maleate single crystals, SpectrochemicaActa, Part A Mol&Biomol Spectroscopy (2012) 98, 7-13.
13. Loganayaki M, Sivashankar V, Ramesh P, Ponnuswamy M.N, Murugakoothan P, Growth and characterisation of GuanidiniumTrifluoroacetate, Journal of minerals & materials characterisation and engineering (2011) 10, 843-853.
14. Kuppers H, The crystal structure of Ammonium Hydrogen Oxalate Hemihydrate, ActaCryst., (1973)B29, 318.
15. Kurtz S.K, Perry T.T, A powder technique for the evaluation of nonlinear optical materials, J. Appl. Phys., (1968) 39, 3798-3813.
16. Thirugnanam A, Rajesh K, Madhavan J, Samuel Selvaraj R, Praveen Kumar P, Growth and Characterisation of nonlinear optical L-Bisvalineselenate single crystals, (2013) 5(3), 167-172.
17. Lucia Rose A.S.J, Selvarajan P, Perumal S, SpectrochemicaActa part A 81:270 (2011).
18. Onitsch E.M, Microscope (1950) 12, 95.
19. Miller C, Appl. Phys. Lett., (1964) 5, 17.
20. Balarew C, Duhlew R, J.SolidState Chem., (1984) 55, 1-6.
21. Joshi V.N, Photoconductivity, Marcel Dekker, New York, (1990).
22. Bube R.H, Photoconductivity of Solids, Wiley, New York, (1981).

*****