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A STUDY ON THE GROWTH AND CHARACTERIZATION OF MAGNESIUM SULPHATE DOPED SULPHAMIC ACID SINGLE CRYSTAL

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ABSTRACT

Single crystals of magnesium sulphate doped Sulphamic acid have been grown by slow evaporation technique at room temperature. Single crystal and powder X Ray Diffraction studies were carried out for the structural characterization of grown crystals. FTIR studies and UV-Vis-NIR spectrum were performed to identify the various functional groups and cutoff wavelength of the grown crystal. Thermal stability of the grown crystal was analysed from Thermogravimetric Analysis (TGA) and Differential Thermogravimetric Analysis (DTA). The mechanical strength of the crystal was determined by Vicker's Microhardness Test. Second harmonic generation of the crystal was confirmed by Kurtz powder technique.

Keywords:FTIR, Inorganic Compounds, NLO, Slow Evaporation Method, TGA.

1. INTRODUCTION

The search for new Nonlinear Optical materials and improving the properties of existing NLO material is a continuous process because of its vast application in the field of science and technology. In the developing field of optical communications and laser technology, the production of second harmonics is very essential [1]. For a Nonlinear Optical crystal to be used in frequency conversion, it should have a non zero NLO coefficient, high physical and optical properties and transparency at required wavelengths. When optical waves propagate through Nonlinear Optical crystal, there should be good transfer of energy between the waves [2].

Inorganic crystals have good thermal and mechanical properties, good optical damage threshold and stability, short UV cut off wavelength and high degree of chemical inertness [3-6]. Among the inorganic materials Sulphamate derivatives are most suitable for NLO property with its two planar rings configuration. It's having excellent blue light transmittance and optical nonlinearity [7].

Sulphamic acid (SA) is a highly stable inorganic acid which is soluble in water and exhibits zwitterionic form. Its molecular weight is 97.09. SA has orthorhombic structure [1]. Large single crystals of SA can be grown at

low temperatures [8]. Due to these properties JIS (Japanese Industrial Standard) has accepted SA as a standard substance for titrimetric analysis. IUPAC and British analytical methods committee also recommended SA [9]. It is already reported the growth, structure, UV-Vis-NIR, Raman Studies, dielectric, neutron diffraction and etching of SA single crystal [1, 8, 10-13]. Here we report the growth and characterization of $MgSO_4$ doped SA (SAMS) Nonlinear optical crystal.

2. Experimental Procedure

SAMS was synthesized using commercially available SA (Lobachemie AR grade) and $MgSO_4$ in the ratio 1:1 at room temperature by slow evaporation method. Both SA and $MgSO_4$ are dissolved in 20ml of double distilled water separately. Then both the solutions are mixed together using magnetic stirrer. 40ml of final homogeneous solution was filtered using filter paper to get a clear solution. The filtered solution is taken in a beaker and closed tightly with perforated Aluminium foil to minimize evaporation. Good transparent single crystals are obtained in a month's time. The product is further recrystallized for getting pure single crystal. The photograph of the grown crystal is given in Fig(1).

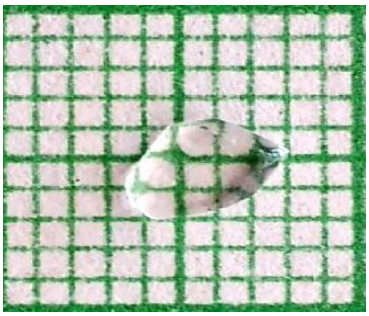

Fig (1) SAMS crystal

3. Characterization Techniques

To determine the lattice parameter values, Single Crystal X-Ray Diffraction is carried out using BRUKER AXS KAPPA APEX II CCD with Shel xtl software. Powder X-Ray Diffraction analysis is done using BRUKER AXS D8 ADVANCE Diffractometer and the 2θ and d values are calculated using Difrac Plus software. FTIR spectrum is recorded in the range 500cm^{-1} to 4000cm^{-1} using THERMO NICOLET AVATAR 370 to identify the incorporation of $MgSO_4$ in to pure SA. The Optical transmission spectra is carried out using VARIAN CARRY 300 SPECTROPHOTOMETER in the wavelength range of 200 nm to 800 nm.The Thermal behaviour of the grown crystal is carried out between 40^{0}C and 730^{0}C in nitrogen atmosphere at a heating rate of 10^{0}C/min using PERKIN ELMER DIAMOND Thermal analysis system. The microhardness measurement is done using Vicker's Hardness Tester. To measure SHG efficiency, Kurtz powder technique was performed on grown crystal.

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4. Results and Discussion

4.1. Single Crystal X-Ray Diffraction

Single Crystal X-Ray Diffraction is carried out using BRUKER AXS KAPPA APEX II CCD with Shel xtl software. Pure SA and Magnesium sulphate crystallizes into orthorhombic structure whereas SAMS crystallizes into tetragonal structure [14, 15]. The lattice parameters are given in Table (1).The change in the crystal structure is due to the incorporation of $MgSO_4$ into the pure SA crystal.

Table (1) Lattice parameters of pure & SAMS

Parameter	Pure SA	SAMS
a A^0	8.100	8.0811
b A^0	8.049	8.0811
c A^0	9.220	9.259
V A^{03}	604.8	604.7

4.2. Powder X-Ray Diffraction Analysis

Powder X-Ray Diffraction analysis of $MgSO_4$ doped SA is done using BRUKER AXS D8 ADVANCE Diffractometer and the 2θ and d values are calculated using Difrac Plus software. The samples are scanned in the range of 3 degrees to 80 degrees. All the observed reflections are indexed. Compared to pure SA, some extra peaks are obtained for SAMS. The extra peaks (013), (005), (004), (025) and change in the intensity of peaks indicates the incorporation of the dopant into the crystal lattice of pure SA and thereby changing the bond length [8]. Definite Bragg peaks confirms the good crystalline nature of the grown crystal [12]. The PXRD of pure and grown crystal is shown in Fig (2) and Fig (3).

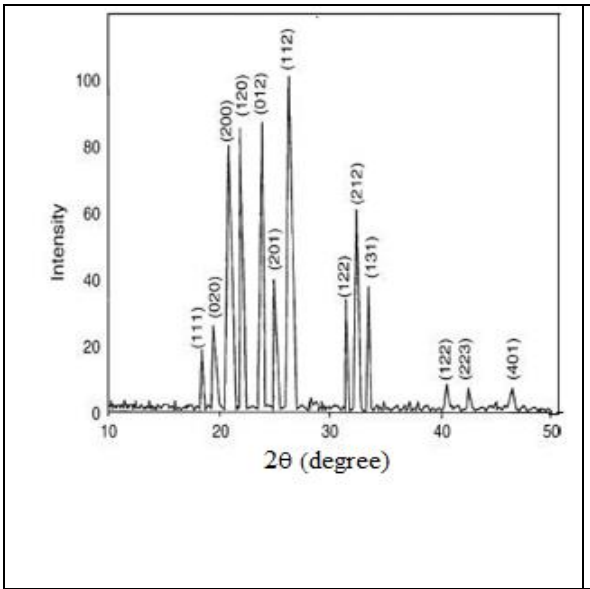

Fig (2) PXRD of pure SA crystal

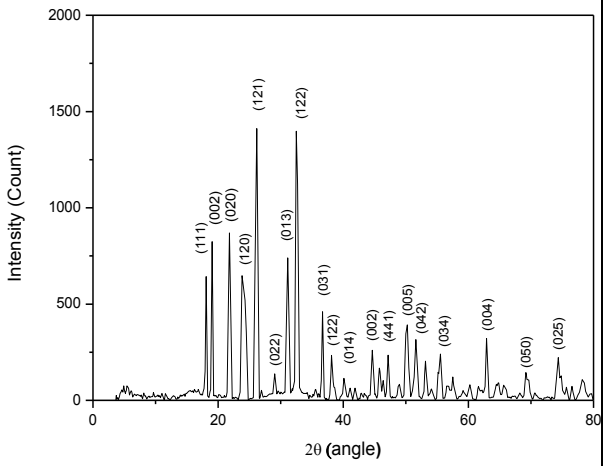

Fig (3) PXRD of SAMS crystal

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4.3. Fourier Transform Infrared Spectroscopy

The functional groups present in the grown sample can be identified using FTIR spectroscopy [12]. Fourier Transform Infrared Absorption spectra of SAMS is recorded in the range 500 cm^{-1} to 4000 cm^{-1} using THERMO NICOLET AVATAR 370 and is given in Fig (4). Doping of $MgSO_4$ into the lattice of pure SA shows some significant change in the absorption pattern. The presence of various functional groups in the grown sample makes the FTIR spectrum complex. The broad envelope in the region 3750 cm^{-1} -2970 cm^{-1} in pure SA is not observed in SAMS [16]. At 1455 cm^{-1}, the frequency of deformation of NH_3^+ is observed for pure SA, where as it is seen at 1446 cm^{-1} for SAMS. The SO_3^- stretching at 1069 cm^{-1} in pure SA is shifted to 1067 cm^{-1} for SAMS. The absorption band in the range 3000 cm^{-1} to 4000 cm^{-1} becomes narrow when compared to the absorption band of pure SA. This is due to the incorporation of the dopant in the grown crystal. The various functional groups present in SAMS are assigned and recorded in the Table (2).

Table (2) Vibrational band assignments for SAMS crystal

Pure SA	SAMS	Assignment
3211	3154	Degen. NH_3^+ stretching
2871	2871	Sym. NH_3^+ stretching
1538	1542	Degen. NH_3^+ deformation
1455	1446	Sym. NH_3^+ deformation
1337	1267	Degen. SO_3^- stretching
1069	1067	Degen. SO_3^- deformation
1001	1005	S - O stretching
687	690	NH_2 and N – H wagging
539	542	Degen. SO_3^- deformation

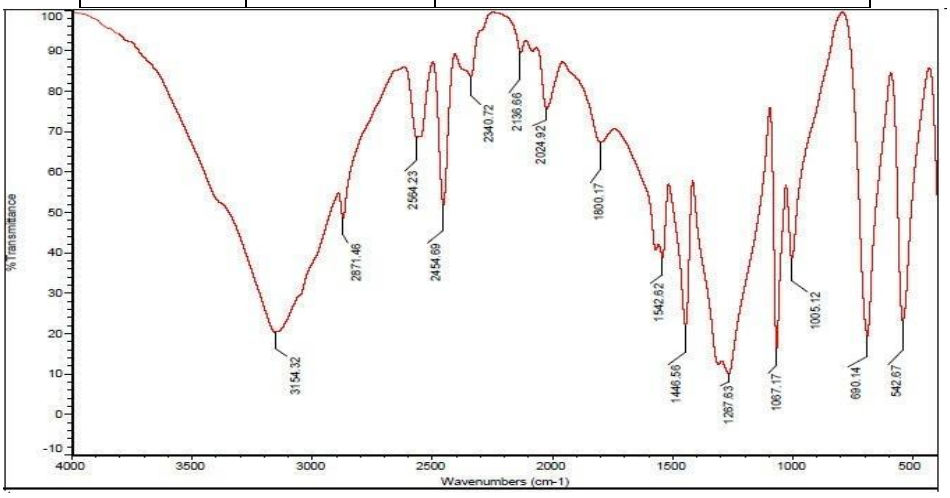

Fig (4) FTIR of SAMS crystal

4.4. UV-Vis-NIR Studies

Optical transmission, absorption and transparency analysis of a crystal is very important which helps it to be used in optoelectronic field [12]. UV-Vis analysis of the grown crystal is carried out using VARIAN CARRY 300 SPECTROPHOTOMETER in the wavelength range of 200 nm to 800 nm. It is observed that the lower cutoff wavelength is 248 nm which is less than that of pure SA. The transparency of SAMS is 84% from 527 nm - 705 nm. This indicates that the dopant has improved the optical transparency of the grown crystal. There is no considerable absorption till 800 nm. So it can be used for optoelectronic application in the visible region. The UV-Vis-NIR spectrum of grown crystal is given in Fig (5) and (6).

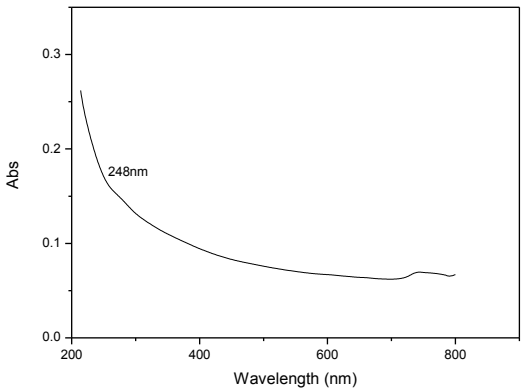

Fig (5) UV-Vis-NIR of SAMS crystal

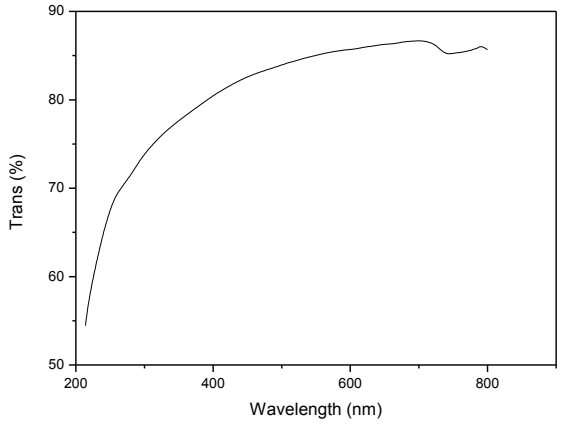

Fig (6) UV-Vis-NIR of SAMS crystal

4.5. TGA/DTA Analysis

TGA/DTA analysis is carried out between 40^0C and 730^0C in nitrogen atmosphere at a heating rate of 10^0C/min using PERKIN ELMER DIAMOND Thermal analysis system. A crystal of weight 7.768 g is used for investigation. The sharpness of the peak indicates the high degree of crystallinity and purity of the grown crystal [7].

From TGA / DTA, it is observed that SAMS undergoes single stage of decomposition. There is no weight loss till 227^0C, which confirms that the crystal is devoid of any physically absorbed water on it. So SAMS crystal can be used for Nonlinear Optical activity till 227^0C where as pure SA decomposes fully at 204^0C which corresponds to its melting point [8]. It shows a sharp endothermic peak at 227°C due to evolution of N_2 gas and stable upto 400°C with the formation of Magnesium oxide as final product. The grown crystal completely decomposes around 410^0C. The TGA/DTA of grown crystal is shown in Fig (7).

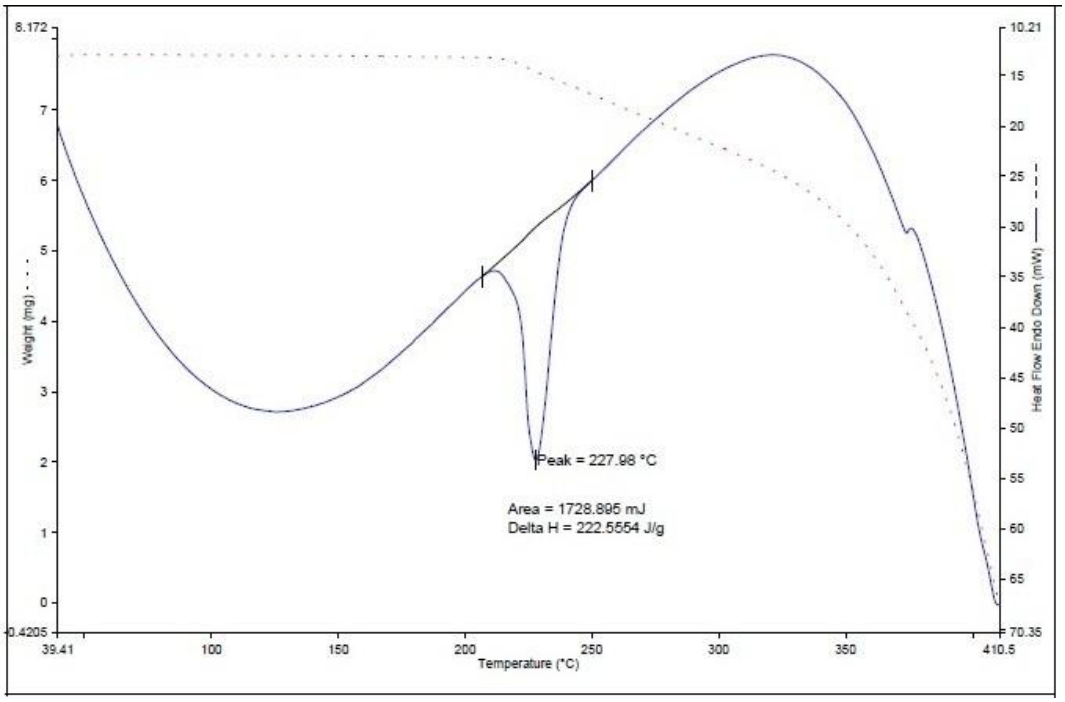

Fig (7) TGA/DTA of SAMS crystal

4.6. Microhardness Study

The mechanical properties like Young's modulus and residual stress of crystals can be explained from Microhardness measurements [17]. The microhardness of SAMS crystal is measured using SHIMADZU MICROHARDNESS TESTER with a diamond intender. Loads of magnitude varying from 25 g to 100 g is applied for a fixed interval of time over a well polished grown crystal. There is an increase in hardness with load due to the work hardening of the surface layer. Beyond 100 g cracking occurs which is due to the release of internal stresses generated locally by indentation. The Vickers Microhardness Number Hv is calculated using the relation $Hv= 1.8544P/d^2$ $kgmm^{-2}$ where P is the applied load in kg and d is the average diagonal length of the indentation in mm. A graph is plotted between Hardness number (Hv) and applied load (P) and is shown in Fig (8). According to Onitsch and Hannemann work hardening coefficient ' n' should lie between 1 and 1.6 for hard materials and above 1.6 for soft materials [18, 19]. A graph is plotted between log P and log d and is shown in Fig (9). From the slope of the graph the work hardening coefficient (n) is found to be 4.504, which shows that the grown crystal is a soft material

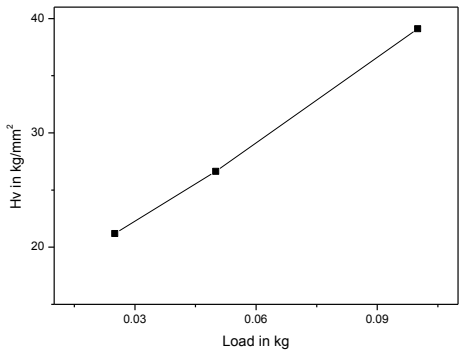

Fig (8) Plot of P Vs Hv of SAMS crystal

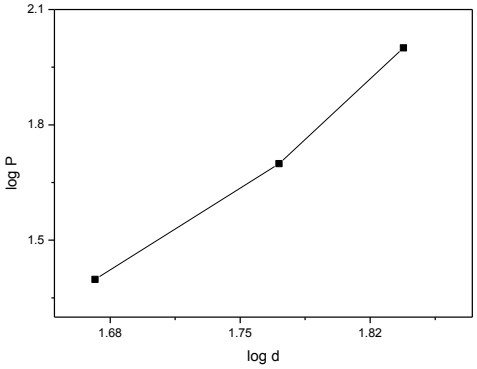

Fig (9) Plot of log P Vs log d of SAMS crystal

4.7. Non Linear Optical study

Kurtz Perry technique is used to test the Second Harmonic Generation of grown crystals. A fundamental beam of 1064nm from a Q-Switched Nd-YAG laser is made to fall on the powdered sample. Pulse energy is 300 mJS^{-1} and pulse width is about 10 nS. The bright green emission from the grown crystal confirms second Harmonic Generation. The NLO efficiency of the SAMS is 1.09 times that of KDP crystal.

5. Conclusion

Single crystals of good optical quality have been grown by doping $MgSO_4$ to SA by slow evaporation method at room temperature. By SCXRD the tetragonal structure of the grown crystal was confirmed. All functional groups in the grown crystals were confirmed by FTIR analysis. Good transmission range and cut off wavelength of 248 nm is detected by UV – Vis – NIR analysis. Thermal studies reveal that $MgSO_4$ has slightly improved the thermal stability of grown crystal. Microhardness studies show that the grown crystal is a soft material. NLO study confirmed the Nonlinear Optical property of the grown crystal.

REFERENCES

1. Dr.Rita A Gharde, Divakar T Chunarkar, Characterization of Sulphamic Acid Single Crystal by Optical Techniques, *International journal of Scientific and Research Publication, 2(6)*, 2012, 1 - 4.
2. de Vries S A, Goedtkindt P, Huisman W J et al, X-ray diffraction studies of potassium dihydrogen phosphate (KDP) crystal surfaces, *Journal of Crystal Growth, 205(1)*, 1999, 202 – 214.
3. M D Agarwal, W S Wang, K Bhat, B G Penn, D O Frazeir, in, Nalwa H S(Ed.), *Handbook of Advanced Electronic Materials And Devices*, (Academic Press, USA), 2001.

4. J Ramajothi, S Dhanushkodi, K Nagarajan, Crystal growth, thermal, optical and microhardness studies of tris (thiourea) zinc sulphate - a semiorganic NLO material ,*Journal of Crysal Research and Technology, 39(5),*2004, 414-420.
5. C Ramachandra & B Vijayabhaskaran B, Synthesis, growth and characterization of a new non –linear-optical crystal :Copper cobalt thiocynate, *Indian Journal of Pure and Applied Physics, 49,* 2011, 531-534.
6. K Kirubavathi, K Selvaraju, R Valluvan, N Vijayan & S Kumararaman, Synthesis, growth, structural, spectroscopic and optical studies of a new semiorganic nonlinear optical crystal: L-Valine hydrochloride, *Spectrochim. Acta Part A, 69(4),* 2008, 1283-1286.
7. S Rafi Ahamed and P Srinivasan, Synthesis, growth and Characterizations of Cesium Sulfamate single crystal by solution growth technique, *Elixir Crystal Growth, 50,* 2012 10628-10631.
8. R Valluvan, K Selvaraju et al , Growth and Characterization Of Sulphamic Acid Single Crystals: A Nonlinear Optical Material, *Material Chemistry and Physics, 97 (1),* 2006, 81-84.
9. TakayoshiYoshimori and Tatsuhiko Tanaka, Preparation of Sulphamic Acid Single Crystals And Their Assay By Precise Coulometric Titration, *Anal Chem Acta, 66*, 1975, 85.
10. RL Sass, The Neutron Diffraction Studies On The Crystal Structure Of Sulphamic Acid Crystal', *Acta 13(4),* 1960, 320-324.
11. T Thaila and S Kumararaman, 'Effect of NaCl and KCl Doping On The Growth Of Sulphamic Acid Crystals', *SpectrochimicaActa Part A. Molecular and Biomolecular Spectroscopy, 82(1),* 2011, 20-24.
12. A S Raj and P Muthusubramanian, Normal Coordinate Analysis Of The Sulphamate Ion, Journal Of Molecular Structure,. *Journal of Molecular structure. The Chem, 89(34),* 1982, 291-296.
13. S J Hickling and R G Woolley, Normal Coordinate Analysis Of The Sulphamate Ion, *Journal Of Molecular Structure. Chemical Physics letters, 66(1),* 1990, 43-48.
14. S Rajyalakshmi, B Brahmaji, et al, Influence of metal ions Mg2+, Fe2+ on the growth of sulphamic acid single crystals, *International Journal of Chem. Tech Research, 8(2)* ,2015, 599 - 604.
15. P J Rentzeperis & C T Soldatos, The crystal structure of anhydrous magnesium sulphate , *Acta crystallographica , ,11(10),* 1958, 686.
16. Gharde R A, Divakar T Chunakar, Unidirectional Seeded Single Crystal Growth From Solution Of Sulphamic Acid And Its Characterization,,*International Journal of Advanced Research in Computer Engineering & Technology, 1(6),* 2012,241-245.
17. P Hemalatha, V Veeravazhuthi & D Mangalraj, Vickers Microhardness Study of Nonlinear Optical Single Crystals of Doped and Undoped S-Benzyl Isothiouronium Chloride',*Journal of Materials Engineering and Performance , 18,* 2009,106-108.
18. E M Onitsch, The present status of testing the hardness of materials, *Mikroscopie, 95,* 1956, 12-14.
19. HannemammM.,*Metall.Manchu 23* ,1941,135.