Indian Journal of Pure & Applied Physics
Vol. 53, June 2015, pp. 404-408

Synthesis, growth and characterization of magnesium sulphamate – A promising non-linear optical crystal

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Received 8 July 2014; revised 10 December 2014; accepted 18 March 2015

Single crystals of magnesium sulphamate, a promising non-linear optical crystal were synthesized and grown from aqueous solution by slow evaporation method at room temperature. The powder X-ray diffraction and single crystal X-ray diffraction analysis confirmed the formation of new crystal. The crystals were characterized by energy dispersive X-ray analysis (EDAX) to reveal their chemical composition. The functional groups were analyzed by FT-IR and FT-Raman techniques. The optical transmission region was analyzed by UV-Vis-NIR studies. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies showed the thermal behaviour of the grown crystal. The non-linear optical (NLO) property of the crystal was tested by Nd-YAG laser as a source.

Keywords: Inorganic compounds, Crystal growth, X-ray diffraction, Raman spectroscopy, Crystal structure

1 Introduction

Non-linear optics (NLO) is an innovative area of research and development which plays a key role in the field of opto-electronics and photonics[1]. Materials with large second order optical non-linearities find wide applications in the area of laser technology, laser communication and data storage technology[2,3]. In recent years, several studies dealing with organic, inorganic and semi-organic molecules and materials for non-linear optics are being reported due to the increasing need for cheap and easily processable materials for photonics applications[1,4]. The non-linear optical responses induced in various molecules in solution and solids are of great interest in many fields of research. As compared to organic crystals, the inorganic crystals have good physio-chemical stabilities, short UV cut-off wavelength and large second order non-linearities. Due to these reasons, the inorganic crystals are gaining popularity in the field of non linear optics[5]. Most recent work has demonstrated that organic crystals can have very large non-linear susceptibilities as compared with inorganic crystals, but their use is impeded by low optical transparencies, poor mechanical properties, low laser damage thresholds and inability to produce and process large crystals[6]. The inorganic materials are widely used in these applications because of their high melting point, high mechanical strength and high degree of chemical inertness[7]. Among the non-linear phenomena, frequency doubling, frequency mixing and electro-optic modulations are important in the field of optical image storage and optical communications[8]. The basic requirements for a NLO crystal to be successfully utilized in frequency conversion are a non-zero NLO coefficient, transparency at the required wavelengths, efficient transfer of energy between the optical waves propagating through the crystal and good physical and optical properties[9]. Mainly solution growth techniques have been applied for growing good quality crystals. The limited thermal stability of many of the compounds examined makes particularly exploratory solution growth as the first technique to be considered[10].

Sulphamic acid (H_2NSO_3H) is the mono-amide of sulphuric acid and is formed as orthorhombic crystal. It is highly stable and can be kept for years without any change in their properties. It is a strong inorganic acid, while mixing it with water it exihibits Zwitterionic form[11]. Owing to these advantages, JIS [Japanese Industrial Standard] has established this reagent as a standard substance for titrimetric analysis and the British analytical methods committee as well as IUPAC have also recommended the acid[12].

The structure of metal ion doped sulphamic acid crystal has been examined by using single and powder

X-ray diffraction studies. The functional groups and the presence of elements were revealed by using FT-IR, FT Raman, UV-Vis-NIR and quantitative energy dispersive X-ray analysis. The thermal analysis showed the exothermic and endothermic behaviour of magnesium sulphamate. The NLO property of the crystal was studied by Kurtz Perry powder test.

2 Material Synthesis and Crystal Growth

The calculated amount of magnesium sulphate hepta hydrate and sulphamic acid were thoroughly dissolved in double distilled water and stirred well using magnetic stirrer to ensure uniform temperature and concentration throughout the entire volume of the solution. The solution was filtered and transferred to crystal growth vessels and crystallization was allowed to take place by slow evaporation under room temperature. The synthesized salt was purified by repeated crystallization. Transparent colourless crystals were harvested after 15-20 days. The photograph of the grown crystal is shown in Fig. 1.

3 Characterization Studies

Powder X-ray diffraction patterns were recorded for the grown crystals at room temperature using EX 2050 powder X-ray diffractometer with Cuk_{α} radiation. Single crystal X-ray diffraction was carried out using Enraf Nonius-CAD 4 diffractometer. To confirm the elements present in the grown crystals, the EDAX analysis was done. FT-IR and FT-Raman spectra were recorded to confirm the presence of dopants using Bruker: RFS 27 spectrometer in the frequency range 400-4000 cm^{-1}. The optical absorption spectrum was recorded by double beam UV-Vis spectrophotometer. Thermal stability of the crystals was tested in the temperature range 0° to 800°C. The NLO property of the crystal was confirmed by Nd-YAG laser.

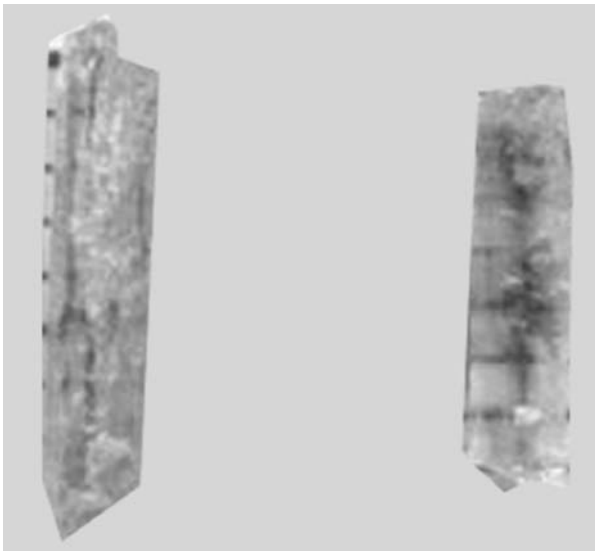

Fig. 1 — Photograph of magnesium sulphamate single crystals

4 Results and Discussion

4.1 Powder X-ray diffraction analysis

Powder X-ray diffraction analysis has been carried out to confirm crystallinity. The sample was scanned over the range 20°-80°C at a rate of 1s. The resulted powder X-ray diffraction pattern with their corresponding d-spacing values is shown in Fig. 2. The prominent well defined Bragg's peak at specific 2θ angle reveals the high crystallinity of magnesium sulphamate crystals.

4.2 Single crystal X-ray diffraction analysis

The single crystal XRD analysis of the grown crystal was carried out using Enraf Nonius – CAD 4 single crystal diffractometer. It was observed that the grown crystal belongs to tetragonal crystal system and the lattice parameters were compared with already reported value of SA crystals[13] in Table 1.

4.3 Energy dispersive X-ray analysis

EDAX is the commonly used method for chemical analysis of materials. In the present investigation, the grown crystal was subjected to EDAX protocol to confirm the presence of elemental composition. The results are presented in Table 2.

It is observed from Table 2 that magnesium ions form about 10 per cent of the total composition of the crystal. This is a strong evidence for the incorporation of the magnesium ions inside the SA lattice. The recorded spectrum is shown in Fig. 3. The distinct peak of magnesium observed in the graph also indicates its presence within the lattice. This confirms the presence of magnesium and sulphonic groups.

4.4 FT-IR analysis

FT-IR spectrum of the grown crystal is shown in Fig. 4. The peak corresponding to 3250 cm^{-1} is due to NH_3^+ stretching vibration and the peak at 2294 cm^{-1} corresponds to N-H stretching[14]. The band observed at 1655 cm^{-1} arises due to symmetric vibration of NH_3^+ group and the band at 1447 cm^{-1} is assigned to asymmetric stretching of NH_3^+ mode. The SO_3^-

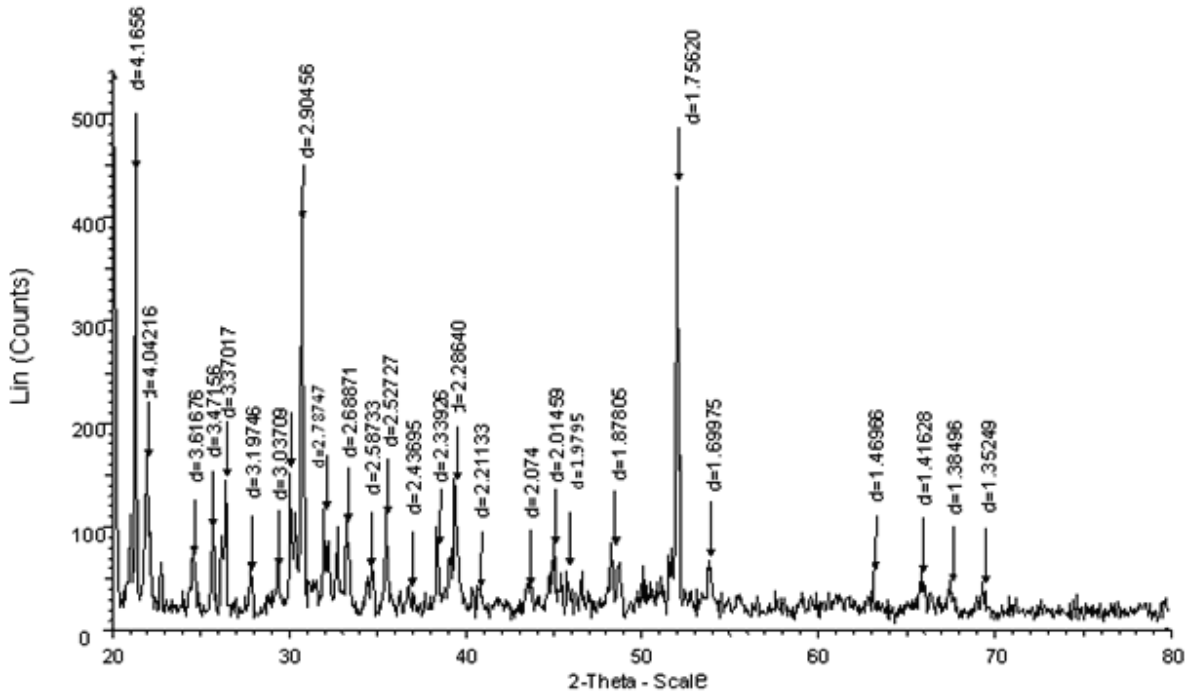

Fig. 2 — Powder X-ray diffraction pattern

Table 1 — Cell parameters of magnesium sulphamate

Sample	a (Å)	b(Å)	c (Å)	α(°)	β(°)	γ(°)	Volume (A^3)	Crystal system
Sulphamic acid	8.078	8.116	9.268	90	90	90	607.61	Orthorhombic
Magnesium Sulphamate	8.05	8.05	9.119	90	90	90	596.6	Tetragonal

Table 2 — Elemental composition of magnesium sulphamate

Element	App Conc	Intensity Corrm	Weight %	Weight % Sigma	Atomic %
O	93.65	1.0829	64.73	0.47	76.68
Mg	12.75	0.7295	13.08	0.29	10.20
S	27.09	0.9140	22.19	0.36	13.12
Totals			100.00		

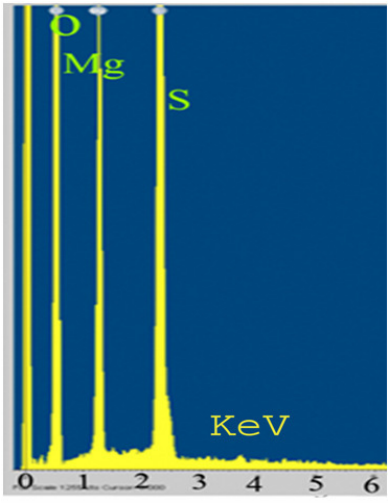

Fig. 3 — EDAX pattern

symmetric stretching is observed at 1093 cm^{-1}. The strong band at 983 cm^{-1} may be due to the rocking mode vibration of NH_3^+ which confirms the Zwitterionic nature[15]. The peak at 618 cm^{-1} indicates the N-S stretching vibration. The vibrational assignments are compared with SA and are tabulated in Table 3.

4.5 FT-Raman analysis

The recorded FT-Raman spectra is shown in Fig. 5. The presence of functional groups was further confirmed by Raman spectrum. The peaks at 3182.12, 3147.46 and 2727.76 cm^{-1} correspond to stretching of NH_3^+. The bands observed at 1546 cm^{-1} and 1508 cm^{-1} are due to NH_3^+ deformation. The peaks obtained at 1304, 1277 and 1146 cm^{-1} are due to SO_3^- stretching and N-H … S bond. The S O_3^- stretching is obtained

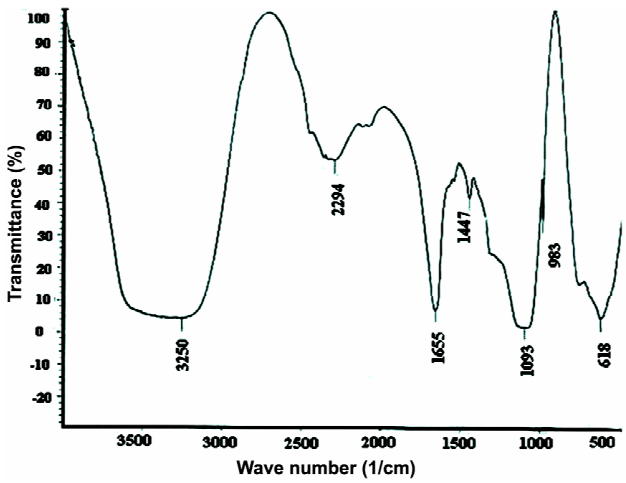

Fig. 4 — Fourier transform infrared spectrum

Table 3 — Characteristic infrared frequencies (cm^{-1}) and assignments for the magnesium sulphamate crystals

Sulphamic acid (cm^{-1})	Magnesium sulphamate (cm^{-1})	Assignments
3211	3250	degenerate NH_3^+ stretching
1635	1655	symmetric vibration of NH_3^+
1455	1447	asymmetric stretching of NH_3^+ mode
1067	1093	SO_3^- stretching vibration
1001	983	NH_3^+ rocking
666	618	N-S stretching vibration

at 1057 cm^{-1} and NH_3^+ rocking is observed at 984 cm^{-1} and the same has also been observed in FT-IR spectrum. It shows that the vibration observed at 984 cm^{-1} is both IR and Raman active. The peaks at 555, 536, 446 cm^{-1} correspond to SO_3^- deformation and peak at 361 cm^{-1} is due to SO_3^- rocking. N-S torsion is observed at 238 cm^{-1}.

4.6 UV-vis-NIR studies

The transmittance spectra of the grown magnesium sulphamate crystals measured by double beam UV-Vis spectrophotometer for the wavelength range 200 to 800 nm is shown in Fig. 6.

The lower cut-off wavelength is 200 nm and there is no remarkable absorption throughout the entire spectra. The crystal is found to be transparent in the region 200-800 nm which makes it valuable for those applications requiring either blue or green light. It is an important requirement for NLO materials having non-linear applications[16,17].

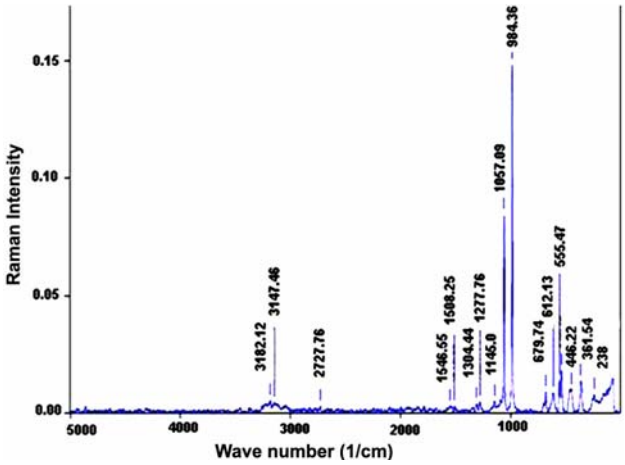

Fig. 5 — Raman spectrum

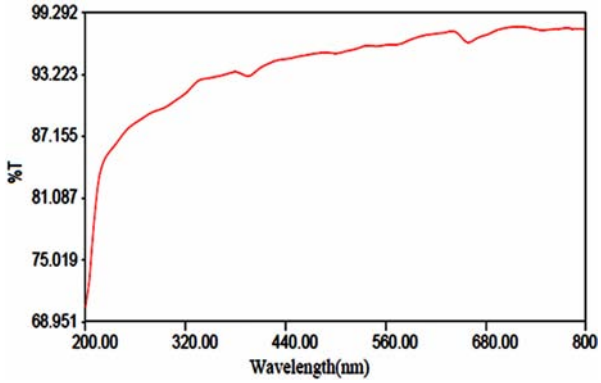

Fig. 6 — Transmittance spectrum

4.7 Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies

Thermal analysis was carried out using NETZSCH STA 409C instrument between room temperature and 700°C in nitrogen atmosphere. Simultaneously recorded TGA and DSC curves of the sample are shown in Fig. 7. From the thermogram, a weight loss at 102°C is attributed due to the loss of water molecules. The same weight loss has been occurred at different stages since they have to be present in the lattice with different binding forces. The exothermic peak observed at 209.5°C corresponds to crystallization peak which takes place after the evaporation of water molecules. The melting and degradation of the molecule occur simultaneously at a temperature of 444.2°C. The weight loss observed at this region may be due to the release of $S0_2$. The decomposition of the studied sample thereafter continues up to 67.8°C and a residual mass of 37.48% were obtained. The TGA and DSC studies reveal that the crystal remains thermally stable till 209.5°C.

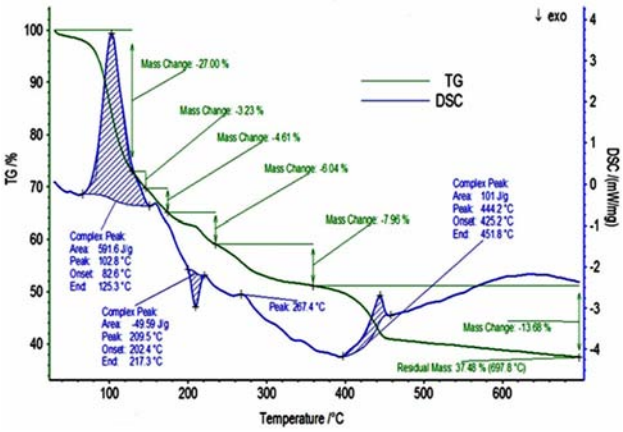

Fig. 7 — TGA and DSC thermogram

4.8 Non-linear optical studies

The second harmonic generation (SHG) property of the grown magnesium sulphamate crystal was examined through Kurtz and Perry powder technique. The sample was subjected to the output of Q-switched Nd:YAG laser emitting a wavelength of 1064 nm with power 0.68 J. A bright green flash emission corresponding to wavelength of 532 nm was generated from the sample. The wavelength of the input radiation has been reduced to half of its initial value. This confirms the frequency doubling which strongly evidences the second harmonic generation of the crystal[18]. The SHG efficiency of the grown crystal has been compared with that of standard KDP crystal and it is found to be 0.77 times that of the standard value.

5 Conclusions

Single crystals of magnesium sulphamate, a promising NLO material have been grown by slow evaporation technique. The sharp well defined Bragg's peaks confirm the crystalline nature of the materials. The single crystal X-ray diffraction studies confirm the newly formed crystal. The elemental composition has been analysed and the presence of magnesium has been confirmed by energy dispersive X-ray analysis. The presence of amine and sulphonic groups has been identified by FT-IR and FT-Raman techniques. The ultraviolet spectrum clearly shows that the lower cut-off wavelength is 200 nm and it has a wide transparency between 200-800 nm which is the desirous property of NLO materials. Thermal stability of the compound up to 209.5°C has been proved from TGA and DSC analysis. The NLO property of the crystal was examined by Kurtz Perry powder test using Nd-YAG laser and the efficiency has been found to be 0.77 times that of the standard KDP crystals.

References

1 Prasad P N & Williams D J, *Introduction to Non linear Optical Effects in Molecules and Polymers* (Wiley Interscience, New York) 1991, p 218.
2 ngelimary P A & Dhanuskodi S, *Cryst Res Technol,* 36 (2001) 1231.
3 Rajasekaran R, Mohan Kumar P, Jayavel R & Ramasamy P, *J Cryst Growth*, 311 (2002) 270.
4 Chemla D S & Zyss J, *Non linear properties of organic molecules and crystals* (Academic Press, New York) 1987.
5 Ramachandra C & Vijayabhaskaran B, *Indian J Pure & Appl Phys*, 49 (2011) 531.
6 Hemalatha P, Veeravazhuthi V & Chandramohan A, *J Cryst Growth*, 311 (2009) 4317.
7 Kirubavathi K, Selvaraju K, Valluvan R, Vijayan N & Kumararaman S, *Spectrochim Acta A, Part A*, 69 (2008) 1283.
8 Sreeramana Aithal P, Nagaraga H S, Mohan Rao P, Avashi D K & Sharma A, *J Appl Phys*, 81 (1997) 7526.
9 de Vries S A, Goedtkindt P, Huisman W J, et al, *J Cryst Growth*, 205 (1999) 202.
10 Kerkoc P & Hulliger J, *J Cryst Growth*, (1990) 1023.
11 Kanda F A & King A J, *J Am Chem Soc,* 73 (1951) 2315.
12 Takayoshi Yoshimori & Tatsuhiko Tanaka, *Anal Chem Acta,* 66 (1973) 85.
13 R.Valluvan, K.Selvaraju & S.Kumararaman *Mater Chem and Phys,* 97 (2006) 81.
14 Muthusubramanian P & Sundara Raj A, *J Molecular Structure*, 84 (1982) 25.15 Ambujam K, Rajarajan K, Selvakumar S, et al, *Indian J Pure & Appl Phys*, 44 (2006) 243.
15 Martin Britto Dhas S A & Natarajan S, *Materials Lett*, 62 (2008) 2633.
16 Vijayabhaskaran B, Arivazhagan M & Ramachandra Raja C, *Indian J Pure & Appl Phys*, 49 (2011) 340.
17 Chandramohan A, Bharathikannan R, Kandavelu, Chandrasekaran J & Kandhaswamy M A, *Spectrochim Acta A Part A,* 71 (2008) 755.