INTERNATIONAL JOURNAL
FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Growth and Studies on Aluminium Ammonium Sulphate Single Crystal

N. Dharani Rajan[1], S. Jayakumar[2], S. Krishnan[3], G. M. Rajesh[4], Sylaja[5], R. Sambasivam[6], G.S. Gayathri[7], S. Alwar[8]

[1, 2, 3, 4]*Department of Physics, RKM Vivekananda College, Mylapore, Chennai*

[5]*Department of Physics, D.G. Vaishnav College, Chennai*

[6]*Department of Physics, Urumu Dhanalakshmi College, Trichy*

[7, 8]*Department of Chemistry, D.G. Vaishnav College, Chennai*

Abstract: Single crystals of aluminium ammonium sulphate dodecahydrate have been grown by slow evaporation solution growth technique at room temperature. The grown crystals were subjected to X-ray diffraction analysis in order to find the lattice parameter and crystal structure. Structural analysis by single crystal XRD analysis reveals the crystal belongs to cubic system. The cell parameters of the crystal is a = b = c = 24.56 A^o, $\alpha = \beta = \gamma = 90^o$. The X-ray diffraction reveals the crystalline perfection of the grown crystal. An increase in dielectric constant at all frequencies is observed. The grown crystal is characterized by FTIR, FT-Raman, XRD and Dielectric studies. Optical Absorption studies reveal very low absorption in the entire visible region. The functional groups have been determined by FTIR and FT-Raman analysis. Dielectric constant at various frequencies is observed. The UV spectra reveal the material/crystal has band gap of 5.87eV.

Keywords: Crystal growth; XRD; Dielectric studies; Aluminium Ammonium Sulphate dodecahydrate; Solution growth; Assignment.

I. INTRODUCTION

Crystal growth technique holds an important role in electronics, optical, communication, sensors, medical and pharmaceutical materials. Crystal exists as single and polycrystals. Single crystal is used in various biological and chemical fields due to its optical, electrical and mechanical properties. In the present study, single crystal of Aluminium ammonium sulphate dodecahydrate Al (NH_4) $(SO_4)_2 .12H_2O$ is grown by slow evaporation solution growth method. It is also named as ammonium alum. The molecular weight of the alum is 453.33 g/mol. The melting point and density of Aluminium ammonium sulphate is 93.5°C and 1.64 g/cm^3 respectively. It is highly soluble in water and non volatile in nature. The alum under study is prepared using aluminium hydroxide, sulfuric acid and ammonium sulphate. Ammonium alum is used in fertilizers, porcelain cements, animal repellant sprays, water purification in vegetable glues, cosmetics, fire retardant in textiles, dyeing, paints, tanning, mordants, water repellants and deodorants.

Aluminium ammonium sulphate grown by solution growth technique measured using X-ray diffraction analysis, reveals that, crystal belongs to cubic system cell parameters, a = 24.56 A^0, b = 24.56 A°, c = 24.56 A°, $\alpha = \beta = \gamma = 90^o$, volume 14815A^{03}. The grown crystal is characterized by FTIR, FT- Raman and XRD.

Literature survey reveals that the Single crystals grown by slow growth evaporation technique is characterized using X-ray and Neutron diffraction method by many researchers [1]. Grimes NM (1963) made a research on ammonium nickel sulphate hexahydrate [2]. He Y, Chen J, Su G,Zhuang X, Lee G, Jiang R (2001) studied potassium nickel sulphate hexahydrate [3]. Su G, Zhuang X,He Y, Zheng G(2008) studied ammonium cobalt nickel sulphate hexahydrate for uv light band pass filter by X-ray diffraction method [4]. Duraikkan V, Bhadur SA, Athimoolam S(2012) done an experiment on manganese nickel sulphate hexahydrate. Crystal grown by this method and optimum conditions for their growth are reported [5].

II. EXPERIMENTAL METHODS

A. Crystal Growth

Crystals can be grown from melt, solid, liquid and solution. Crystals formed as a result of super saturation, nucleation and growth of nuclei. There are many methods to prepare the crystal like slow cooling, gel growth, solution evaporation, hydrothermal, etc.

In the present investigation, an aqueous solution of Aluminium Ammonium Sulphate analar Grade and double distilled water of 1 molar concentration to obtain homogeneous solution was magnetically stirred for 5 hours at room temperature. A small portion of the solution was used to get the seed crystals by slow evaporation of the solvent the crystallization took place within 20 to 25 days. Fig. l displays the photograph of the grown Aluminium Ammonium Sulphate crystal; Fig.2 and Table 1. represents the structure and properties of the grown crystal respectively. The crystal is used in device applications because of its good thermal stability.
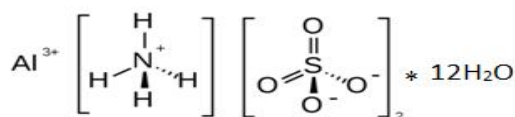
Fig. 1 Photograph of grown Crystal

Fig. 2 Structure of Aluminium ammonium sulphate

Table 1. Properties of Aluminium ammonium sulphate

Crystal	Method and optimum condition	Crystal forms	Crystal System	Colour
Aluminium Ammonium Sulphate dodecahydrate	Solution/1M Aluminium Ammonium Sulphate	Cubes and dendrites	Cubic	Colourless

III. RESULTS AND DISCUSSION

A. Characterization

The grown crystals of Aluminium ammonium sulphate dodecahydrate is characterized using the following methods: FT-IR, FT-Raman, XRD, uv-vis and Dielectric studies. The physico chemical properties is analysed applying ultrasonic techniques.

The FT-IR and FT-Raman spectrum was recorded at SAIF (IIT Madras) by KBr pellet technique in the range of 400-4000 cm^{-1}. The uv-vis spectrum had been obtained. The obtained unit cell parameters, a = 24.56A^0, b = 24.56A^0, c = 24.56A^0, $\alpha = \beta = \gamma = 90°$ are in good agreement with the reported values of vibration assignments.

Aluminium ammonium sulphate is used to minimize the fluoride content in drinking water as defluoridation agent in earthenware and developed by new defluoridation method [6]. Mohamed *et. al*., [7] explains how industrial waste aluminium dross tailings can be used to produce two types of alums namely aluminium sulphate and ammonium aluminium sulphate alums.

The structure of Aluminium Ammonium Sulphate is shown in Fig. 2. ; Fig. 3 and Fig.4 represent the FT-IR and FT-Raman spectra of Aluminium ammonium sulphate. The FT-IR spectrum was recorded using Perkin Elmer Spectrum 1, FT-IR Spectrometer in the range 400-4000cm^{-1}. The sample was prepared using the KBr pellet technique. FT-Raman spectrum was recorded using BRUKER RFS 27 stand alone FT-Raman Spectrometer in the range 0-4000 cm^{-1}. Both the spectra are recorded at SAIF, IIT Chennai. Table 1 shows FTIR and FT Raman wave number, intensity and vibrational assignments. The variation of dielectric constant is plotted with frequency is shown in Fig. 5. UV spectra are shown in Fig. 6.
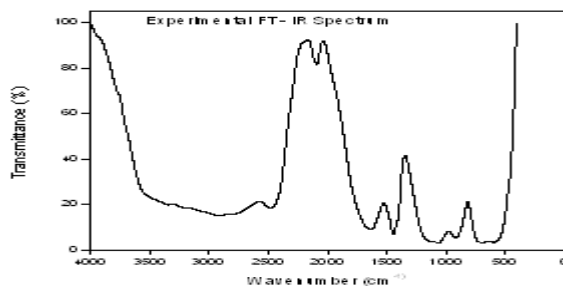

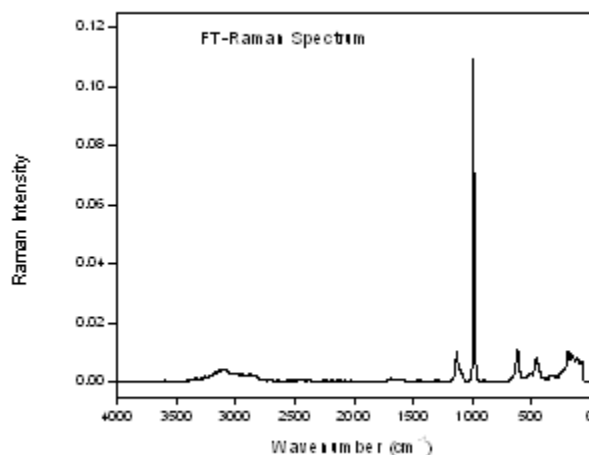Fig. 3 FT-IR spectrum of Aluminium ammonium sulphate

Fig. 4 FT-Raman spectrum of Aluminium ammonium sulphate

Table 2. FTIR and FT-Raman Wave number, Intensity and Vibrational Assignments of Aluminium Ammonium Sulphate

| S.No | FT - IR | | FT Raman | | |
	Experimental Wavenumber	Intensity	Experimental Wavenumber	Raman Intensity	Vibrational Assignments
1	3098	17.2623	3093	0.0042	ν_{ss} OH + ν_{as} NH
2	2476	18.5022	-	-	ν_{as} AlO
3	1638	9.2832	1635	0.00067	β HNH
4	1123	3.6962	1131	0.01049	$\nu_{as}SO_4$
5	1058	3.3378	1060	0.00046	β HNH +$\nu_{ss}SO_4$
6	920	5.4422	990	0.10934	$\nu_{ss}SO_4$
7	689	3.1634			β_s O-H-O
8	601	3.286	616	0.01076	β_{as} SO$_4$
9	477	25.252	460	0.00815	β_{as} SO$_4$

ν_{as} : Asymmetric Stretching; ν_{ss} : Symmetric Stretching; β_{as} : Asymmetric bending;

β_s : Symmetric bending;

1) *Vibrational Assignments*

The FT-IR and FT-Raman analysis of Aluminium Ammonium Sulphate was carried out to investigate the presence of functional groups and their vibrational modes.

a) *SO$_4$ Stretching Vibration:* According to Periasamy et. al. [8], the bands at 1123 cm^{-1}(Na$_2$SO$_4$), 1172.4 cm^{-1} (K$_2$SO$_4$) and 1120 cm^{-1} (NaHSO$_4$) ,1170 cm^{-1} (KHSO$_4$) are assigned to asymmetric stretching of SO$_4$ groups. Thus in this study the FTIR and FT-Raman bands at 1123 and 1131 cm^{-1} are due to asymmetric stretching vibration of SO$_4$ groups. According to Periasamy et. al., [3]. Symmetric stretching of SO$_4$ groups appeared at 1100.0cm^{-1}, 1085.9cm^{-1}, 1070 cm^{-1} (K$_2$SO$_4$), 1060 cm^{-1} , 1000 cm^{-1} (KHSO$_4$). The Raman spectrum of basic aluminium sulphate shows two broad bands, which are assigned to the ν_2 and ν_4 sulphate triplets at 446,459 and 496 cm^{-1} and 572, 614 and 630 cm $^{-1}$ [9,10,11]. In the present investigation the bands at 990 and 1060 cm^{-1}in FT-Raman spectrum are due to symmetric stretching vibration of SO$_4$ group which agrees well with that of Goyprian et.al., [12]. The bands at 1058 and 920 cm^{-1}in FT-IR spectrums are due to symmetric stretching vibration of SO$_4$ group.

b) *SO$_4$ Bending Vibration:* The bands appeared below 700 cm^{-1}are assigned to the symmetric and asymmetric bending of SO$_4$ groups. According to Periasamy et. al., [8], the frequency 575 cm^{-1}, 477.8 cm^{-1} (K$_2$SO$_4$) 390 cm^{-1}, 380 cm^{-1} (NaHSO$_4$) 430 cm^{-1}, 400 cm^{-1} (KHSO$_4$) to symmetric bending of the SO$_4$ groups. The frequency bands observed at 637.7 cm^{-1}, 615.6 cm^{-1} (Na$_2$SO$_4$) 612.8 cm^{-1} (K$_2$SO$_4$) 610 cm^{-1} (NaHSO$_4$) 605 cm^{-1} (KHSO$_4$) are assigned as asymmetric bending of the SO$_4$ groups. Symmetric bending of SO$_4$ group is observed at the frequency range 314.4 cm^{-1} (Na$_2$SO$_4$), 405.1 cm^{-1}(KHSO$_4$). Hence in this investigation the bands at 477 cm^{-1} in FT-IR and 460 cm^{-1} in FT-Raman are due to symmetric bending vibration of SO$_4$ group. The bands at 601 and 616 cm^{-1} in FT-IR and FT-Raman respectively are due to Asymmetric bending vibration of SO$_4$ group. The band at 317 cm^{-1} in FT-Raman spectrum is due to symmetric bending vibration of SO$_4$ group.

c) *N-H and O-H Stretching:* The N-H stretching vibrations occur in the region 3500-3100 cm^{-1}. A study by Mariappan et. al., [13] shows the band at 3362 cm^{-1} was due to N-H stretching. The same observed in the present study, the bands at 3098 cm^{-1} in FT-IR and 3093cm^{-1} in FT-Raman spectra are due to N-H and O-H stretching vibration. The observed wave number at 689 cm^{-1} was due to O-H bending vibration modes. These values agree well with literature [14, 15].

d) *Deformation:* Mariappan et.al. [13] observed the bending vibration at 1531cm^{-1}. In the current investigation, the in-plane bending vibration of HNH is observed at1638 and 1635 cm^{-1} in FTIR and FT-Raman spectrum respectively [16-17].

2) *X-ray Diffraction Analysis:* X-ray diffraction analysis is a key tool in the fields like pharmaceutical, forensic science, glass industry, geological department and microelectronics industry**.** The grown crystals is studied using X-ray diffraction (Saif IIT**,** Chennai) analysis in order to find the lattice parameter and crystal structure. Structural analysis by single crystal XRD analysis reveals the crystal belongs to cubic system. The cell parameters of the crystal is a = b = c = 24.56A^o, $\alpha = \beta = \gamma = 90^o$ .The X-ray diffraction reveals the crystalline perfection of the grown crystal.

3) *Dielectric Studies:* Dielectric measurements were carried out using the parallel plate capacitor method as a function of frequency. Dielectric measurements show that dielectric constant is inversely proportional to frequency. Dielectric loss with high frequency indicates crystal has good optical quality and such material has potential applications. The fluctuation in dielectric constant attributes the change in space charge contributions. At low frequency, the value of dielectric constant is low [18-19].
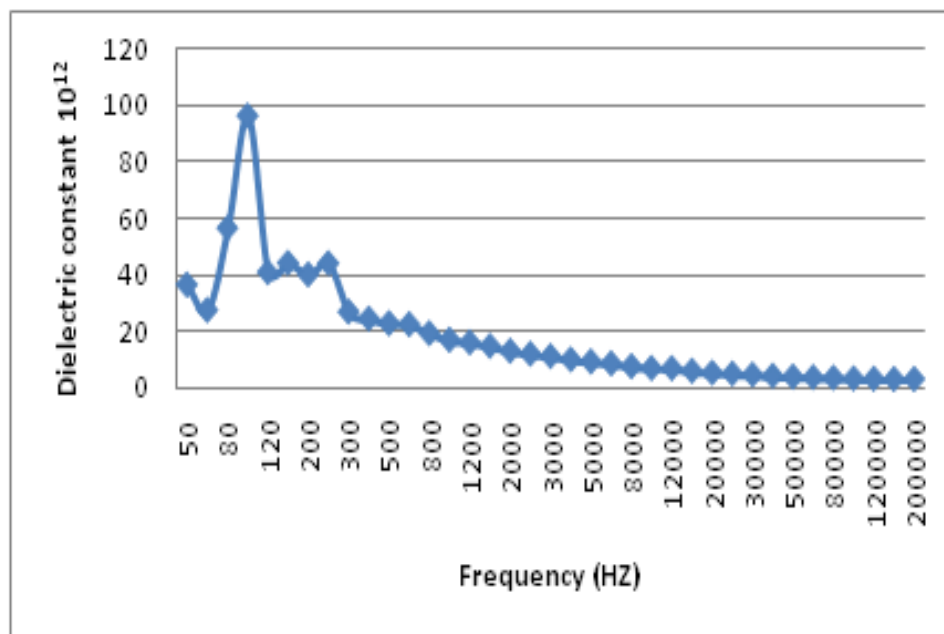

Fig. 5 Variation of Dielectric constant with frequency of single crystal of Aluminium Ammonium Sulphate

4) *UV – Vis Spectral Studies:* The UV-Vis spectral analysis of Aluminium Ammonium Sulphate was carried out using varian5E spectrophotometer in the wavelength range 200 to 900 nm. The spectrum is shown in Fig. 6. The cut off wavelength as observed from the spectrum for Aluminium Ammonium Sulphate crystal is 210 nm. The dependence of optical absorption coefficient with the photon energy helps to study the band gap energy. The band gap formed is found to be 5.87 eV from uv spectrum were calculated using the formula,

Band gap Energy (E) = hγ, E = hc/λ .

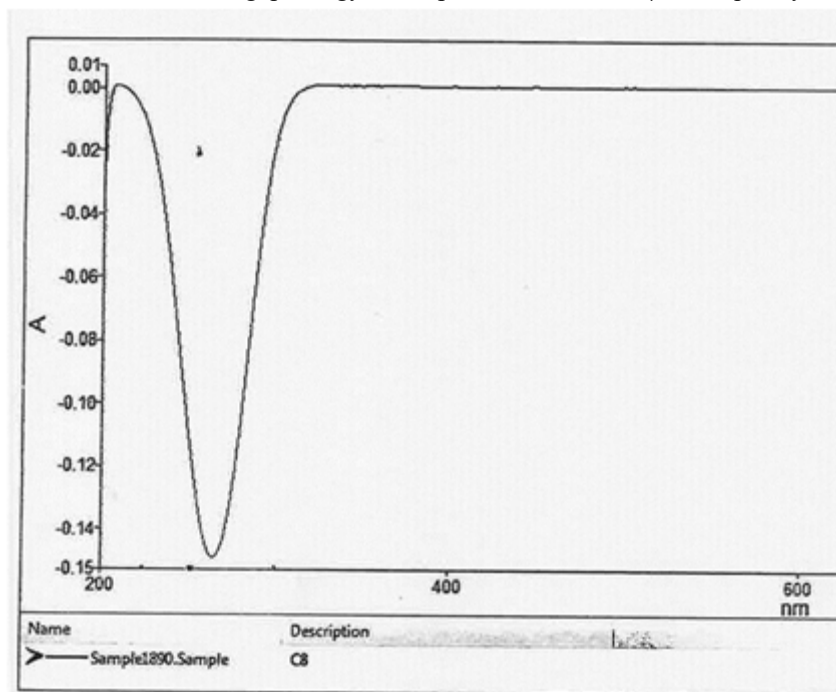where 'E' is band gap energy, 'h' is planck's constant, 'γ' is frequency

Fig. 6. UV – Vis Studies of Aluminium Ammonium Sulphate Variation of Absorption with Wavelength

5) Internal Pressure Studies: Internal pressure is an acoustic parameter obtained using ultrasonic interferometer instrument (Mittal enterprises) of frequency 2 Mhz with thermostated water bath maintained at room temperature accuracy (0.1%). AR Grade samples were used. High precision instruments were used for measuring velocity, viscosity and density.

For computing internal pressure (π_i) given by Suryanarayana,

$$\text{Internal pressure } (\pi_i) = bRT \left| \frac{k\eta}{u} \right|^{1/2} \frac{\rho^{2/3}}{M^{7/6}}$$

where b stands for cubic packing factor, k temperature independent constant, R gas constant, T absolute temperature, η viscosity in Nsm^{-2}, U ultrasonic velocity in ms^{-1} and ρ density in kgm^{-3}, M molecular weight respectively.

Internal pressure thus calculated is obtained in atmosphere [20]. The concentration   of the Aluminium Ammonium Sulphate is varied from 0.25gm/ml to 0.453gm/ml hence varying the internal pressure of the system. The results have been reported in Table 3.

Table 3.Variations of Concentration versus Internal Pressure

S.No	Concentration C- gm/ml	Internal pressure π_i (atmos)x10^5
1	0.025	1.6
2	0.05	0.06
3	0.25	5.3
4	0.45	0.22

IV. CONCLUSIONS

Single crystals, of Aluminium Ammonium Sulphate dodechydrate (15 x 5 x 3nm) is grown by slow evaporation technique. XRD-analysis reveals the crystal belongs to cubic system. The grown crystal is characterized by FTIR and FT Raman. Dielectric studies reveal good optical quality crystals are grown. The band gap is found to be 5.87 eV from uv spectral measurements. Internal pressure decreases at crystal growth concentration, because of its excellent thermal stability, and is used in device application.

V. ACKNOWLEDGMENT

REFERENCES

[1]   Cromer D T, Kay M I , Allen C. Larson. Refinement of the Alum Structures. II. X-Ray and Neutron Diffraction of NaAI(SO4)z. 12H20, y Alum*. Acta Cryst., 1967;22:p. 182 – 187.

[2]   Grimes N W, Kay H F and Webb MW. Acta Cryst. 1963;16: p.823 – 829.

[3]   Youping Hea, Jianrong Chenb , Genbo Sua , Xinxin Zhuanga , Guohui Leea and Rihong Jianga. Journal of Crystal Growth, 2001; 233: p.809–812.

[4]   Genbo Su, Xinxin Zhuang, Youping He and Guozong Zheng .Optical Materials, 2008;30: p.916–919.

[5]   Vanitha Duraikkan , Sultan Asath Bahadur and Shunmuganarayanan Athimoolam.. Journal of Minerals and Materials Characterization and Engineering, 2012; 11: p.1121-1125.5.

[6]   Yadav R N, Singh O P and Rajdeep Yadav.Arch. Apll. Sci. Res. 2010; 2 (3): p.11-22.

[7]   MohamedM A, KassimM E and El-KatatnyE A.J. Mater. Res. 1998; 13 (4): p.1075-1083.

[8]   Periasamy A, Muruganand S, Palaniswamy M,Rasayan.J. Chem.. 2009; 2 (4):p. 981-989.

[9]   Kloprogge J T, Frost R L. J. Mater. Sci. Lett. 2001; 19: p.229–231.

[10] KloproggeJ T, Frost R L. J. Mater. Sci. 1999; 34: p.4367–4374.

[11] Kloprogge J T, Frost R L. J. Mater. Sci. 1999;34:p.4199–4202.

[12] Goypiran Aet. al., J.Raman Spectroscopy 1980; 9: p.297

[13] Mariappan M, Madhurambal G, Ravindran B, Mojumdar S C.J. Therm. Anal. Calorim., 2011;104: p.915-921.

[14] Alia J M, Edwards H G M, Stoev M D. Spectrochimica Acta, Part A, 1999; 55: p.2423-2435.

[15] El-Bahy G M S, El-Sayed B A, AShabana A.Vibrational Spectroscopy, 2003;31:p.101-107.

[16] Brezina B and Havrankova M. Mater. Res. Bull 1971; 6: p.537.

[17] Henisch HK. Crystal Growth in Gels . Pennsylvania state university press. 1970.

[18] Singh NB and Partlow WD. Crystals for ultraviolet light filters, US patent No.5778765,1998.

[19] Baviskar SJ, Bhavsar DS. Arch Appl Sci Res. 2011; 3:p.279-81.

[20] Suryanarayana CV, Indian J. pure Appl. Phys. 1989; 27:p.751.

INTERNATIONAL JOURNAL
FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Call : 08813907089 ⊙ (24*7 Support on Whatsapp)