GROWTH AND CHARACTERIZATION OF AMMONIUM FERROUS SULFATE CRYSTALS DOPED WITH L-THREONINE

C.Stella Rani[1], M.Daniel Sweetlin[2], P.Selvarajan[3]

[1]Research Scholar, Reg.No. 9573 , Research and PG department of Physics, St. John's College, Palayamkottai-627002, Tamil Nadu, India.

(Affiliated to Manonmaniam Sundaranar University, Abishekapatti-627012, Tirunelveli, Tamilnadu, India)

[2]HOD and Associate Professor of Physics, St. John's College, Palayamkottai-627002, Tamil Nadu, India.

[3]Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628216, Tamilnadu, India.

Abstract: ***Single crystals of L-threonine doped ammonium ferrous sulfate (LTAFS) were grown by solution method. Solubility of the grown crystal was measured at different temperatures. The lattice constants of the grown LTAFS crystal were evaluated by single crystal XRD method. The molecular groups of the sample were found by FTIR analysis. Microhardness and work hardening coefficient were estimated for the grown crystal of LTAFS. UV-visible spectral studies were carried out for LTAFS crystal and the linear optical parameters like transmittance, absorbance, band gap, absorption coefficient and extinction coefficient for the crystal of LTAFS were estimated and the results were analyzed.***

Index Terms- Inorganic crystal, doping, crystal growth, characterizatation, hardness, solubility, FTIR, transmittance, extinction coefficient

---

I. INTRODUCTION

Tutton salts are also called as Schönites after the naturally occurring mineral called Schönite and these salts are named after A. E. H. Tutton, who identified and characterized a variety of samples. Tutton's salts are usually the double salts and they contain two different cations crystallized in the same regular crystal lattice. Ammonium ferrous sulfate hexahydrate is also known as the Mohr's salt in chemistry and its molecular formula is $(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O$. It dissolves in water like other Tutton's salts and it gives the aqua ferrous complex which has octahedral molecular geometry [1-3]. Various studies of many undoped Tutton's salts and their crystals have been reported in the literature [4-7]. Metal dopants like iron, chromium, copper, manganese were added into the Tutton's crystals and many studies have been carried out [8-11]. From the background of the work, it is found that dopants like amino acids have not been added into Tutton's salts to alter the various properties and hence in this work, an amino acid like L-threonine is added as dopant into ammonium ferrous sulfate (AFS). L-threonine is an alpha amino acid and it is used in the biosynthesis of proteins. It is protonated to form NH_3^+ and the carboxyl group is deprotonated. It is an essential amino acid and it must be obtained from the diet [12,13]. In this investigation, 1 mole% of L-threonine was added into the lattice of AFS to modify its properties. The results of different studies of the solution grown L-threonine doped AFS crystals are presented and discussed in this paper.

II. CRYSTAL GROWTH

To obtain L-threonine doped ammonium ferrous sulfate (LTAFS), 1 mole% of L-threonine was added into the aqueous solution of ammonium ferrous sulfate. Here double distilled water was used as the solvent. Saturated solution of LTAFS was prepared and it was stirred well for 2 hours to get uniform concentration in the solution. After stirring, the solution was filtered using the good quality filter papers to remove the unwanted materials if any present in the solution. The filtered solution was taken in a cleaned borosil beaker covered with perforated sheet. Due to slow evaporation of solvent, saturated solution was converted into supersaturated solution. After 3 days, small-sized seed nuclei are formed in the solution and then these crystal nuclei are grew into small-sized seed crystals of L-threonine doped ammonium ferrous sulfate **(Fig.1(a))** and then using the seed crystals big-sized crystals are grown. The grown crystals of LTAFS were harvested after a growth period of about 30 days and the single crystal of LTAFS is shown in the **Fig.1 (b).**

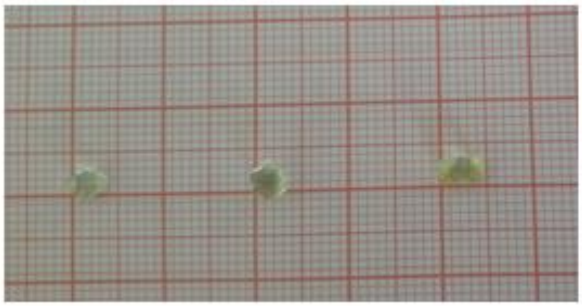

Fig.1(a): Seed crystals of LTAFS

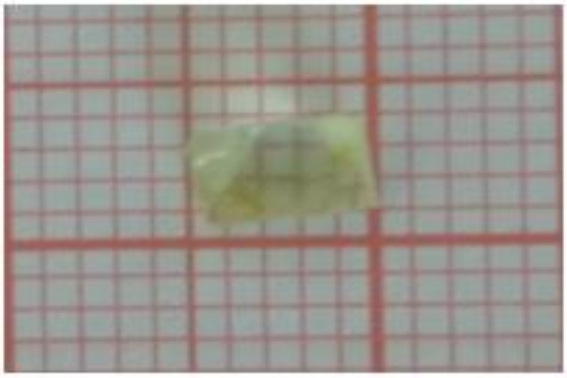

Fig.1(b): Grown single crystal of LTAFS

III. RESULTS AND DISCUSSION

3.1 Single crystal XRD studies

To find the crystal structure and lattice constants, the single crystal of LTAFS was characterized by single crystal XRD study and this study was carried out using an ENRAF NONIUS CAD4 diffractometer with MoK_{α} radiation (λ=0.71073 Å). The principle of the diffractometer is the Bragg's law and it is given by $2d \sin \theta = n\lambda$ where d is the interplanar distance, θ is the Bragg's angle, n is the order of diffraction and λ is the wavelength of X-rays. A good quality crystal of LTAFS was selected from the heap of the grown crystals and it was mounted in the sample holder of the diffractometer. When the monochromatic X-rays fall on the sample, they are diffracted and using the computerized X-ray diffractometer, the single crystal XRD data were collected. The obtained single crystal XRD data for LTAFS crystal are a = 9.319(5) Å, b = 12.663 (4) Å, c = 6.257(3) Å, $\alpha = 90^{o}$, $\beta = 106.48^{o}$ (3) and $\gamma = 90^{o}$, V =708.04 (2) $Å^3$. From the obtained data, it is ascertained that LTAFS crystal has the monoclinic structure. When the lattice constants of LTAFS crystal are compared with those of undoped ammonium ferrous sulfate (AFS) crystal [14], there are slight deviation in the values and this indicates that the L-threonine doped AFS and undoped AFS crystals have the same monoclinic structure.

3.2 Solubility studies

Solubility is defined as the amount of solute in 100 ml of the supersaturated solution and it varies with many factors like temperature, pressure, nature of solvent, pH value of solution, concentration of solute and impurities. When the solubility is measured at different temperatures for a sample, solubility curve can be drawn for the sample. Using the solubility curve, the saturated and supersaturated solutions could be prepared at a particular temperature. The solubility of the sample in particular solvent can be measured by gravimetric method. The values of solubility of the samples are presented in the **Fig. 2.** From the results, it is noticed that the solubility increases with increase of temperature for both undoped and LTAFS crystals. This shows that both the samples have positive temperature coefficient of solubility. It is observed that the solubility is more for L-threonine doped AFS crystal than that of undoped AFS crystal. There are three regions in solubility curves viz., supersaturation region is along the curves, under supersaturation region is below the curves and supersaturation region is above the curves. Thus, using these data, saturated, under saturated and supersaturated solutions of the samples could be prepared easily for further growth of crystals.

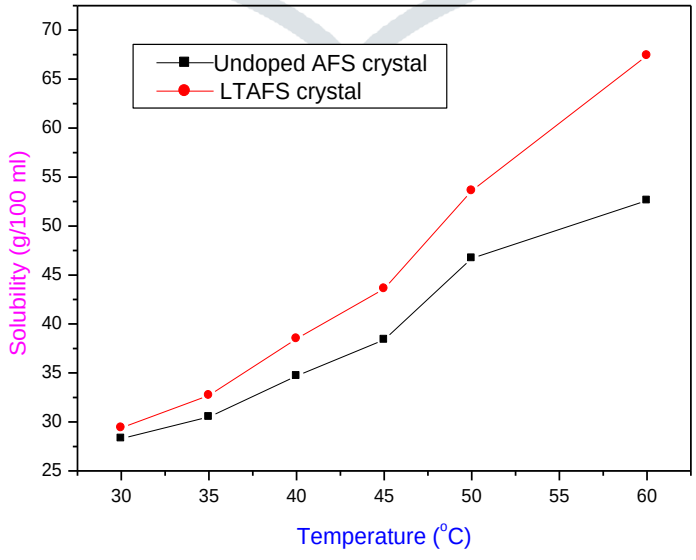

Fig.2. Variation of solubility with temperature for undoped and L-threonine doped AFS crystals

3.3 Finding the functional groups

The functional groups of LTAFS crystal were identified by FTIR method. The FTIR spectrum of the sample was recorded in the range 400-4500 cm^{-1} with a Perkin Elmer Fourier transform infrared spectrometer by KBr pellet technique. The recorded FTIR spectrum of LTAFS crystal is shown in the **Fig.3**. The broad absorption band in the wave number range 3300-2600 cm^{-1} is corresponding to OH stretching and NH stretching vibrations and OH stretching in water molecules present in the sample. The peak at 2049 cm^{-1} is due to vibration of C-H stretching in the dopant. The vibration peak at 1630 cm^{-1} is corresponding to plane bending vibration OH and due to stretching of COO^- ion. The vibration peak at 932 cm^{-1} is due to symmetric mode of SO_4^{2-} and the peak at 1120 cm^{-1} is corresponding to the degenerate asymmetric stretching mode of SO_4^{2-}. The vibration peak at 560 cm^{-1} is due to doubly degenerate symmetric bending mode and the peak at 701 cm^{-1} is corresponding to triply degenerate asymmetric bending mode of the SO_4^{2-}. The other absorption peaks are due to the presence of the dopant L-threonine in AFS crystal. The infrared spectral assignments to the FTIR peaks/bands are allotted as per the data reported in the literature [15].

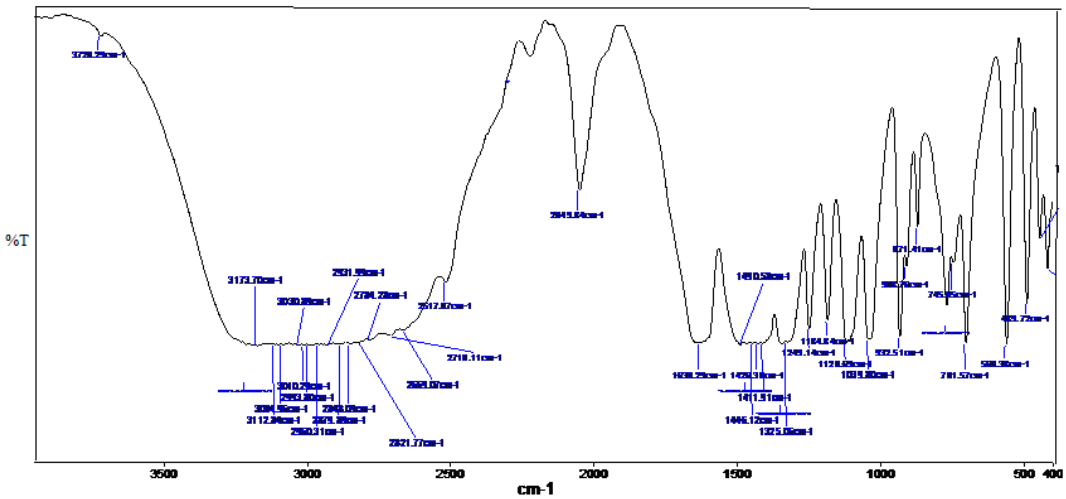

Fig.3. FTIR spectrum of LTAFS crystal

3.4 Hardness measurement

Mechanical hardness is closely related to chemical hardness, which is a measure of chemical bond stability or reactivity. Since hardness depends on bonding in a crystal, hardness is different in different types of bondings. Hence, hardness will vary in various types of crystals like metallic crystals, covalent crystals, ionic crystals, and molecular crystals. Hardness is a measure of the ease with which solids can be plastically deformed. This depends on the mobility of dislocations, their multiplication, and their interactions. The mobility of dislocations is determined by interactions between the atoms or molecules within the cores of the dislocations. In metals, the interactions between groups of adjacent atoms depend very weakly on the configuration of the group, since the cohesive forces depend almost entirely on the local electron density, and are of long range. In covalently bonded crystals, the forces needed to shear atoms are localized and are large compared with metals. Therefore, dislocation motion is intrinsically constrained in them. Ionically bonded crystals contain both long-range and short-range bonding forces because like ions repel each other, while unlike ones attract [16]. If low loads are applied to a crystal, the corresponding hardness is called as microhardness and it is measured using a Leitz Wetzler Vickers pyramidal indenter. Well polished crystals of undoped and L-threonine doped AFS are used in this study. The load (P) is varied between 25 g to 10 g and the time of indentation was maintained constant of 15 seconds. Three or four trials were carried out and the average diagonal indentation length (d) was taken into account for calculation. The variation of average diagonal indentation length with the applied load for the samples is shown in the **Fig. 4.** It is noted that average indentation length (d) increases with increase of load for both the samples and it is found that the value of d decreases when the AFS crystal is doped with L-threonine. The microhardness was calculated using the relation $H_v = 1.8544\ P/d^2$ and the calculated values of hardness are given in the **Fig.5**. It is seen that the hardness increases with increase of the applied load for both undoped and L-threonine doped AFS crystals. This is due to the reverse indentation size effect (RISE). The results indicate that the hardness of AFS crystal increases when it is doped with L-threonine and this is due to increase in the strength of chemical bonding when AFS crystal is doped with L-threonine.

Using Meyer's law $P = a\ d^n$, the work hardening coefficient (n) for the samples were evaluated. Here a is the constant, P is the load and d is the average indentation length. Converting the above equation into a straight line equation, the plots of log(P) versus log(d) are drawn and these plots are shown in the **Figs.6(a) and 6(b).** The slope value of the plot of log(P) versus log(d) gives the work hardening coefficient (n). The obtained values of work hardening coefficient are 2.9391 and 3.1233 respectively for undoped AFS crystal and L-threonine doped AFS crystal. As per findings of hardness, if the work hardening coefficient is more than 1.6, the materials belong to soft materials and hence the grown crystals of this work belong to the category of soft materials.

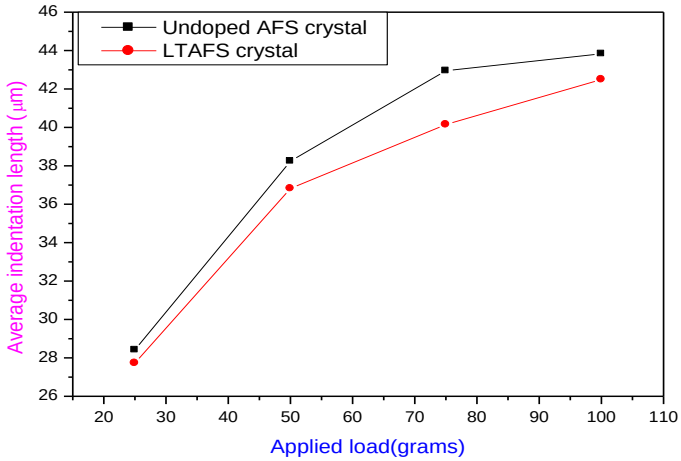

Fig.4. Variation of average indentation length with the applied load for undoped and L-threonine doped AFS crystals

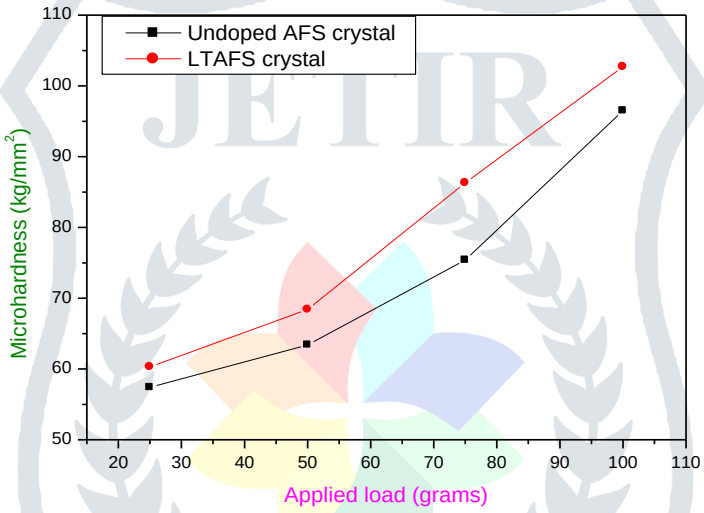

Fig.5. Variation of micorhardness with the applied load for undoped and L-threonine doped AFS crystals

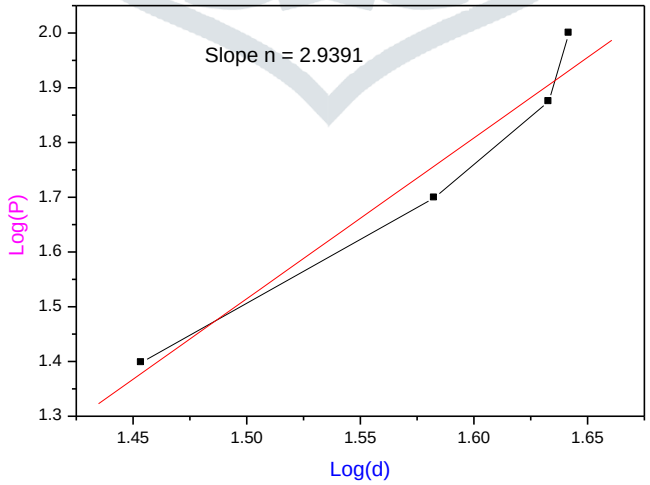

Fig.6(a): Plot of log(P) versus log(d) for undoped AFS crystal

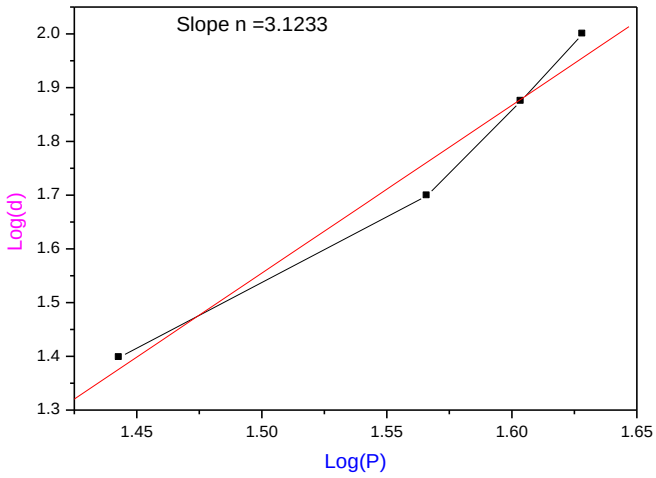

Fig.6(b): Plot of log(P) versus log(d) for LTAFS crystal

3.5 UV-visible spectral characterization

An ultraviolet-visible spectrophotometer is used to record transmittance and absorption spectra of crystalline and liquid samples and this spectrophotometer refers to absorption, reflectance spectroscopy or transmittance spectroscopy in the ultraviolet-visible spectral region. Absorption measures transitions from the ground state to the excited state. This technique is one of the analytical and characterization techniques which are useful in characterizing the absorption, transmission, and reflectivity of a variety of technologically important materials. The quantity of absorption depends on the wavelength of the radiation and the structure of the compound. After the sample absorbs a portion of the incident radiation, the remainder is transmitted on to a detector where it is changed into an electrical signal and displayed after amplificationThe UV-visible spectrophotometer measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I/I_o is called the transmittance, and is usually expressed as a percentage (%T). The absorbance A is based on the transmittance and it is given by $A = \log_{10} (1/T)$. The linear optical parameters of a crystalline material can be obtained by UV-visible spectral studies and these studies can be carried out using a UV-visible spectrophotometer. The recorded transmittance spectrum of LTAFS crystal is shown in the **Fig.7**. It is observed that the transmittance is very high in the visible-NIR region and the UV cut-off wavelength is observed to be at 220 nm and this is the fundamental absorption of the sample. The absorbance spectrum of LTAFS crystal is presented in the **Fig.8** and in this spectrum, it is seen the absorbance is very low in the visible-NIR region. The linear absorption coefficient is determined using the relation $\alpha = (2.303/t)* \log_{10}(1/T)$ where t is thickness of the sample and T is the transmittance. The obtained values of linear absorption coefficient with various values of wavelength are presented in the **Fig.9.** The results indicate that the linear absorption coefficient is low in the visible-NIR region and this spectrum is observed to be same as that of absorbance spectrum.

Tauc' relation is given by $(\alpha h\nu)^2 = A(h\nu - E_g)$ where α is the linear absorption coefficient, h is the Planck's constant, ν is the frequency of light, A is a constant, E_g is the optical band gap [17]. This relation is used to get the exact value of optical band gap of the material. A graph is drawn between $(\alpha h\nu)^2$ and $h\nu$ and this is known as the Tauc's plot and this plot is shown in the **Fig.10.** By extrapolating the linear portion near the onset of absorption edge to the energy axis, the value of band gap is found to be 5.65 eV. The extinction coefficient (k) gives the fraction of the light lost due to the scattering and absorption per unit distance of the penetration medium and it is calculated using the relation $k = (\alpha\lambda) / (4\pi)$ where λ is the wavelength of light. The variation of extinction coefficient with wavelength for LTAFS crystal is shown in the **Fig.11.** From the results, it is observed that the extinction coefficient is very low in the visible-NIR region and it is more at wavelength of fundamental absorption of the sample.

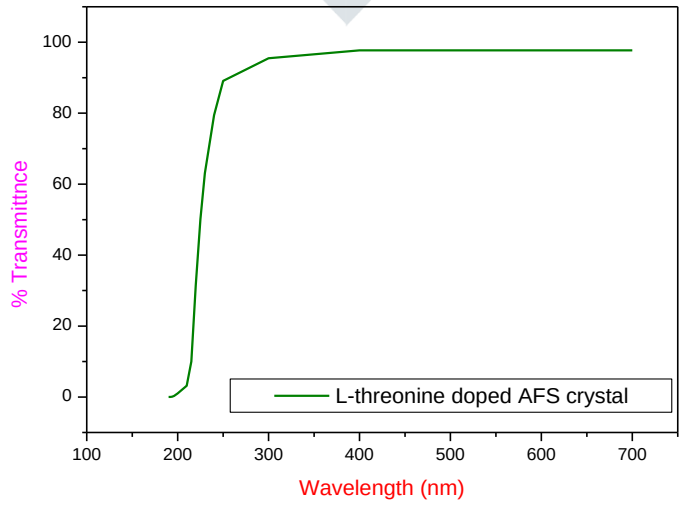

Fig.7. UV-visible transmittance spectrum of L-threonine doped AFS crystal

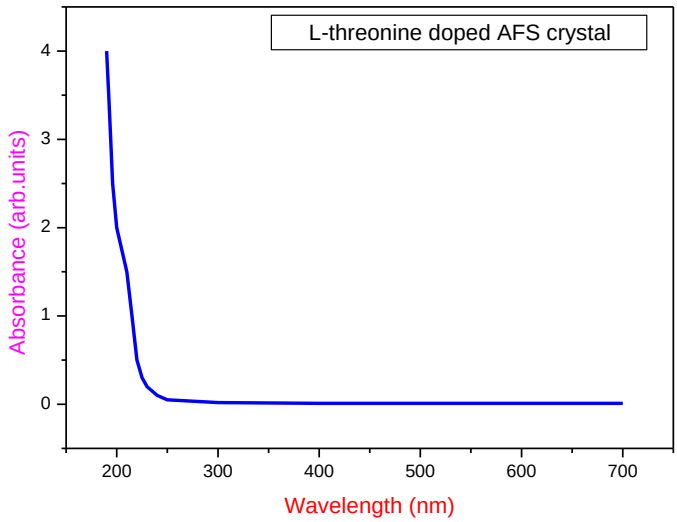

Fig.8. UV-visible absorbance spectrum of LTAFS crystal

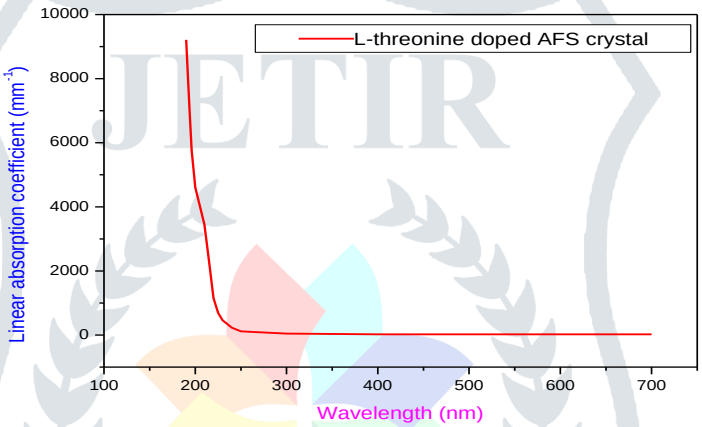

Fig.9. Variation of linear absorption coefficient with wavelength for LTAFS crystal

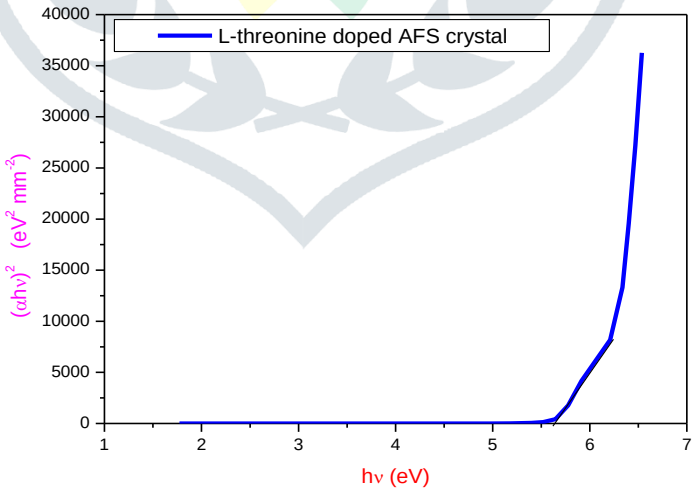

Fig.10. Tauc's plot for LTAFS crystal

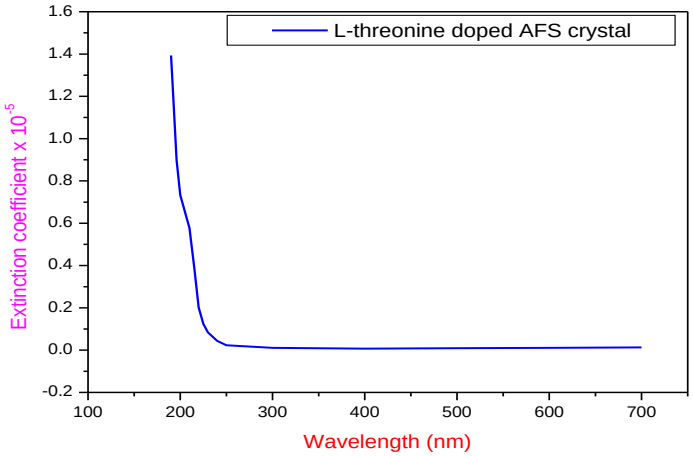

Fig.11.Variation of extinction coefficient with wavelength for LTAFS crystal

IV.CONCLUSION

Single crystals of L-threonine doped ammonium ferrous sulfate (LTAFS) were grown by slow evaporation technique and the colour of the grown crystal is observed to be slight greenish-yellow. Solubility of undoped and L-threonine doped AFS crystals were found by gravimetric method at various temperatures. FTIR spectrum of LTAFS crystal was recorded and functional groups of the sample were confirmed. The lattice parameters of L-threonine doped AFS crystal is found by single crystal XRD method. Microhardness and work hardening coefficient of the undoped and L-threonine doped AFS crystals were determined by Vickers hardness test. It is observed that the cut-off wavelength of LTAFS crystal is at 220 nm and the linear optical parameters were evaluated using transmittance and absorbance spectra of LTAFS crystal.

V.ACKNOWLEDGEMENT

The authors like to thank the staff members of SAIF, Indian Institute of Technology, Chennai, St.Joseph's College, Trichy, VOC college, Tuticorin, STIC, Cochin University to carry out this research work.

REFERENCES

[1]T. Caster Jr., G. S. Newell, W. C. Holton, C. P. Slichter, J. Chem.Phys. 32 (1960)668.
[2]R. W. Kendzie, M. Kesigian, Appl. Phys. Lett. 3 (1963)86.
[3] R. W. Kedzie, D. H. Lyons, M. Kestigian, Phys. Rev. A 138 (1965)918.
[4]H. Montgomery, E.C. Lingafeltee, Acta Crystallographica 17 (1964) 1295.
[5] P. Ballirano, G. Belardi, Acta Crystallographica E 63 (2007) 156.
[6] D. Marinova, M. Geogiev, D. Stoilova, Journal of Molecular Structure 929 (2009) 67.
[7]D. Marinova, M. Geogiev, D. Stoilova, Journal of Molecular Structure 938 (2009) 179.
[8] D. Marinova, M. Geogiev, D. Stoilova, Solid State Science 12 (2010) 765.
[9] P. Sambasiva Rao, Spectrochimica Acta A 52 (1996) 233.
[10] H. Anandalakshmi, P. Neeraja, R. Venkatesan, T.M. Rajendran, P. Sambasiva Rao, EPR in the 21st Century, Elsevier Science B.V, 2000 (225).
[11]H. Anandalakshmi, T.M. Rajendran, R. Venkatesan, P. Sambasiva Rao, Spectrochimica Acta A 56 (2000) 2617–2625.
[12]R.M.C. Dawson et al., Data for Biochemical Research, Oxford, Clarendon Press (1959).
[13] Raïs Badr, Chassagnole Christophe, Lettelier Thierry, Fel, David, Mazat Jean- Pierre, J Biochem., 356 (2001) 425–432.
[14] S.Subramanian, P.Narayana Murty, and C.R.K.Murty, J. Magnetic Resonance 25, (1977) 101-110.
[15]Santunu Ghosh, Michelle Oliveira, Tiago S. Pacheco, Genivaldo J. Perpétuo, Carlos J. Franco, J. Crystal Growth 487 (2018) 104–115.
[16]J. Gong and Y. Li, J. Mater. Sci., 35 (2000) 209.
[17]A. Ashour, N. El-Kadry and S.A. Mahmoud, Thin Solid Films, 269 (1995) 117.