Studies of L-methionine doped Ammonium Ferrous Sulfate single crystals grown by solution method

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ABSTRACT *Undoped Ammonium Ferrous Sulfate (AFS) and L-methionine doped AFS crystals were grown at room temperature (30 ^{o}C) by solution method with slow evaporation technique. The grown crystals are observed to be stable, non-hygroscopic, transparent and light green-brownish in colour. By XRD method, it is found that the crystal structure of the undoped and L-methionine doped AFS crystals is monoclinic. The microhardness studies were carried out for the samples to ascertain the mechanical strength. The functional groups of L-methionine doped AFS crystal are identified by FTIR spectral method. The different elements present in the doped AFS crystal are identified by EDAX method. Real part and imaginary part of undoped and L-methionine doped AFS crystals are measured at temperatures 30 and 70 ^{o}C and Nyquist plots were drawn. The thermal stability of the doped AFS crystal was checked by TG/DTA studies and it is ascertained that the sample has water molecules in the lattice.*

Keywords: *Tutton's salt; single crystal; doping ; growth from solutions; XRD; hardness; solubility; EDAX; TG/DTA*

1. Introduction

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 with the molecular formula $(NH_4)_2Fe(SO_4)_2{\cdot}6\ H_2O$ is one of the Tutton's salts. It dissolves in water like other Tutton's salts and it gives the aqua ferrous complex which has octahedral molecular geometry. Almost all the Tutton's salts crystallize in monoclinic structure [1,2]. Different kinds of studies of many undoped Tutton's salts and their crystals have been reported in the literature [3-8]. Dopants like iron, chromium, copper, Manganese were added into many Tutton's crystals and various studies have been carried out [9-12]. From the literature survey, 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-methionine has been added as dopant into ammonium ferrous sulfate. L-methionine is one of the two sulfur-containing protein organic amino acids, the other one being cysteine. L-methionine is an alpha amino acid which is used in the bio-synthesis of proteins and it consists of an α-amino group which is in the protonated (NH_3^+ form) and an α-carboxylic acid group which is in the deprotonated (COO^- form) and an S-methyl thio-ether as a side chain and it is classified under a nonpolar and aliphatic amino acid. L-methionine and its metal compounds are the interesting compounds because they serve as catalyst to accurate antiviral properties. It is one of the few amino acids that help in the manufacture of creatinine monohydrate which is a compound essential for energy production and muscle building [13-15]. The aim of this work is to grow the single crystals of undoped and L-methionine doped ammonium ferrous sulfate by solution method and to carry out various studies of the grown crystals.

2. Experimental methods

2.1. Growth of single crystals by solution method

AR grade ammonium ferrous sulfate (AFS) and L-methionine were purchased commercially (99% purity) from Merck India. Saturated solution of AFS was prepared using the double distilled water as the solvent and it was stirred for 3 hours and solution was filtered using a good quality Whatman filter paper. After filtering twice, the solution was taken in a growth vessel covered with a porous polythene sheet. Due to slow evaporation of solvent, formation of nuclei took place after 3 days and these crystal nuclei were grown into big-sized crystals of AFS. To get the L-methionine doped AFS, 1 mole% of L-methionine was added into the aqueous solution of AFS and same growth procedure was followed to harvest the doped crystals of AFS. For the growth of both undoped and L-methionine doped AFS crystals, the growth period

was about 25 days and the harvested crystals are transparent, non-hygroscopic and slightly green-brownish in colour. The photograph of the harvested crystals is shown in the figure 1. It is observed that the morphology of L-methionine doped AFS crystal is different from that of undoped AFS crystal.

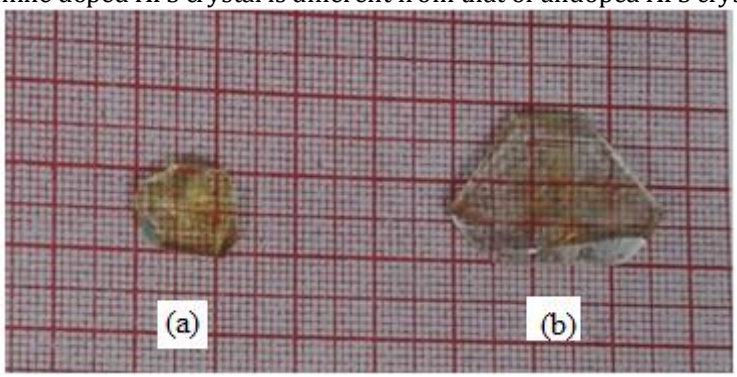


Fig.1. Grown crystals of (a) undoped AFS and L-methionine doped AFS crystal

2.2 Measurement of solubility

Solubility of the samples in water was measured by gravimetric method. A beaker with 10 ml of water was taken and the sample was added in small amount at successive stages and subsequent stirring was continued till the small precipitate was formed at the bottom of beaker. After attaining the saturation, 5 ml of saturated solution was pipetted out and the same was poured in to a dry and petri dish and it was heated slightly to evaporate the solvent. The amount of sample present in 5 ml solution was measured gravimetrically. From this, the amount of the sample present in 100 ml of solution was calculated. The solubility of both undoped and L-methionine doped AFS crystals were measured for various temperatures and the obtained data are given in the figure 2. The results show that the solubility increases with increase of temperature for both the samples and hence they have positive temperature coefficient of solubility. The solubility of L-methionine doped AFS crystal is observed to be more compared to that undoped AFS crystal. The presence of L-methionine in host AFS crystal leads to increase of solubility in water because L-methionine dissolves well in water.

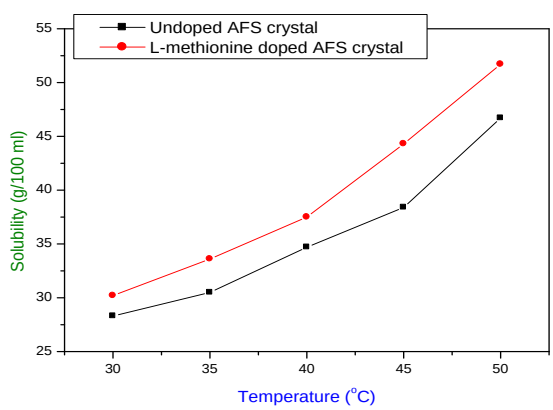


Fig.2: Solubility curves for undoped and L-methionine doped AFS samples

2.3 Analyzing techniques

The grown single crystal of L-methionine doped AFS was subjected to single crystal XRD studies using an ENRAF NONIUS CAD4 diffractometer with MoK_{α} radiation (λ=0.71073 Å) to find the crystal structure and lattice constants. Microhardness hardness study of the grown crystals was carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. Smooth, flat surface was selected and subjected to this study on the plane of the samples. Indentations were made for various loads from 25 g to 100 g. Several trials of indentations were carried out on the prominent face and the average diagonal lengths were measured for an indentation time of 10 seconds. The Fourier transform infrared spectrum of L-methionine added AFS sample was recorded in the range 400-4500 cm^{-1} with a Perkin Elmer Fourier transform infrared spectrometer by KBr pellet technique and this method is used to identify the

functional group present in the sample. The complex impedance of the samples was measured using an impedance analyser at different frequencies and temperatures. TG/DTA studies were carried out in the temperature range 40-700 ^{o}C using a TG/DTA analyser. EDAX spectrum of the sample was recorded using a SEM-EDAX instrument to identify the elements in the sample.

3.Results and discussion

3.1 FTIR studies

FTIR spectrum of L-methionine doped AFS crystal was recorded and it shown in the figure 3. In FTIR spectrum of L-methionine doped AFS crystal, the broad absorption band in the wave number range 3570-2950 cm^{-1} is corresponding to OH stretching and NH stretching vibrations and OH stretching in water molecule present in the sample takes place due to vibrations of two hydrogen bonds together with oxygen atom. The absorption peak at 1676 cm^{-1} is due to in plane bending vibration OH and due to stretching of COO^{-} ion. The vibration peak at 979 cm^{-1} is corresponding to non-degenerate symmetric mode of SO_4^{2-} and the peak at 1100 cm^{-1} is assigned as the degenerate asymmetric stretching mode of SO_4^{2-}. The IR peak at 534 cm^{-1} is due to doubly degenerate symmetric bending mode and the peak at 624 cm^{-1} is corresponding to triply degenerate asymmetric bending mode of the SO_4^{2-}. The FTIR assignments to the absorption peaks/bands are given in accordance with the data reported in the literature [16] and they are tabulated in the table 1.

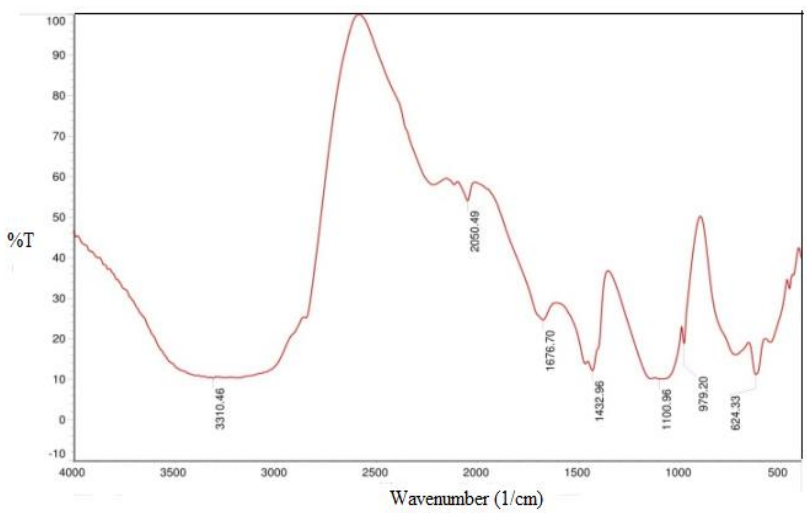


Fig.3. FTIR spectrum of L-methionine doped AFS crystal

Table 1. FTIR spectral assignments for L-methionine doped AFS crystal

Wave number (cm^{-1})	FTIR assignments
3500-2950	OH stretching and NH_3^{+} stretching
2050	CH stretching
1676	OH bending vibration
1432	COO^{-} stretching
1100	Asymmetric stretching mode of SO_4^{2-}
979	Symmetric stretching mode of SO_4^{2-}
624	Asymmetric bending mode of the SO_4^{2-}.
534	Symmetric bending mode of the SO_4^{2-}.

3.2 EDAX analysis

Energy dispersive analysis by X-rays (EDAX) method is also called as EDS or EDX method and it is an n analytical technique used for the detecting various elements present in a sample. In this method, high energetic beam of X-rays is focused into the sample and after interaction the sample emits X-rays. The number and energy of X-ray photons emitted from the sample can be measured by an energy dispersive spectrometer attached with a SEM. The recorded EDAX spectrum of L-methionine doped AFS crystal is shown in the figure 4. The The characteristic peaks of iron, sulphur, oxygen, nitrogen and carbon at 6.398 keV, 2.307 keV, 0.525 keV, 0.392 keV and 0.277 keV respectively are noted in the recorded EDAX spectrum. As from the results, it is confirmed that the impurity has entered into the crystal lattice of AFS.

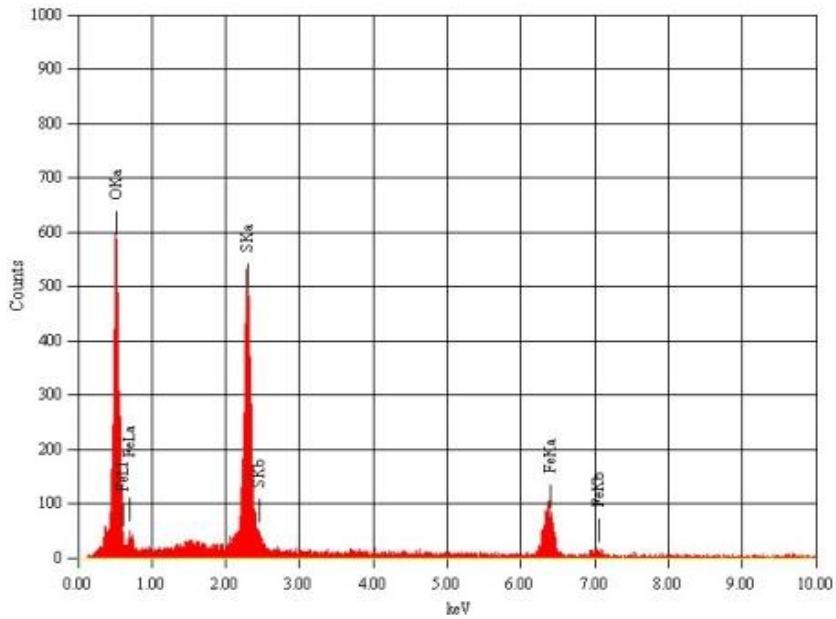


Fig.4. EDAX spectrum of L-methionine doped AFS crystal

3.3 Finding the lattice constants

Single crystal XRD method was used to find the lattice constants of the grown L-methionine doped AFS crystal. A small sized, good quality sample crystal was selected from the harvested heap of crystals and using a single crystal X-ray diffractometer, the lattice constants are obtained. The single crystal XRD data of the sample are provided in the table 2. For the comparison purpose, the lattice constants of undoped AFS crystal are also given in the same table. From the data, it is confirmed that like the undoped AFS crystal, L-methionine doped AFS crystal also crystallizes in monoclinic structure. The lattice constants of L-methionine doped AFS crystal are observed to be slightly different from those of undoped AFS crystal [17].

Sl.No.	Sample	Lattice constants
1.	Undoped AFS crystal [17]	a = 9.32 Å , b = 12.65 Å, c = 6.24 Å, $\alpha = 90^o$, $\beta = 106.8^o$ and $\gamma = 90^o$, V= 704.27 Å^3
2.	L-methionine doped AFS crystal	a = 9.315(3) Å, b = 12.629 (4) Å, c = 6.273(2) Å, $\alpha = 90^o$, β = 105.97^o (3) and $\gamma = 90^o$, V =709.46 (4) Å^3

Table 2. Lattice constants of undoped and L-methionine doped AFS crystals

3.4 TG/DTA studies

Thermogravimetric (TG)/differential thermal analysis (DTA) were carried out for the grown L-methionine doped AFS crystal using a TG/DTA analyser in the temperature range 40-740 ^{o}C and the recorded TG/DTA thermal curves of the sample are shown in the figure 5. From TG curve, it is observed that the sample is stable upto 90 ^{o}C without any weight loss. The first endothermic peak at 120 ^{o}C in the DTA curve corresponds to liberation of four water molecules from crystal lattice of L-methionine doped AFS and at this stage, about 18% of weight of the sample is lost. The small endothermic peak at 163 ^{o}C is due to liberation of further two water molecules from the sample. It is to be mentioned here that the sample has six water molecules in the formula unit of the sample and these water molecules will usually be removed in the temperature range of 100-200 ^{o}C. The endothermic peak at 332 ^{o}C is corresponding to loss one mole sulfate ion and the endothermic peak at 427 ^{o}C is due to loss of the remaining mole of sulfate and two moles of ammonium ions from the sample. The last endothermic peak at 652 ^{o}C is due to further decomposition of the sample. In this sample, it is noticed that at every stage of decomposition there is a loss of weight of the sample and the weight % of the residue found at 700 ^{o}C is about 15%.

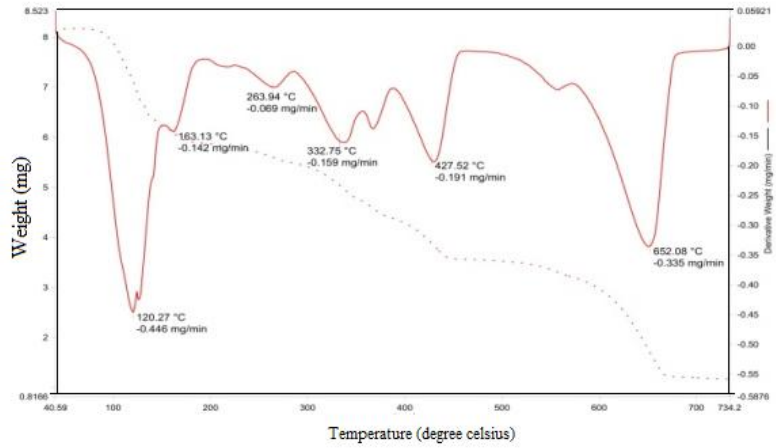


Fig.5. TG/DTA thermal curves of L-methionine doped AFS crystal.

3.5 Microhardness studies

High mechanical strength of a material is necessary for fabrication of devices and it is indicated by the hardness and stiffness of the material. Physically, hardness is the resistance offered by a solid to the movement of dislocation and the major contribution to hardness is attributed to the high stress required for homogeneous nucleation of dislocation in the small dislocation free region indented. If the low load in the order of grams are applied to a material for finding the hardness, it is called as the microhardness. Since dielectric and NLO crystals are soft in nature, microhardness measurement is measured. There are many methods to measure hardness of the material and among them, Vickers microhardness method is an important and accurate method and it is based on an optical measurement system. In Vickers method, square based pyramidal indenter is used to measure the average diagonal indentation formed on the sample. A well polished crystal of undoped AFS was placed on the platform of the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time of 10 seconds. The microhardness number was calculated using the equation $H_v = 1.8544\ P/d^2$ where P is applied load and d is the average diagonal indentation length. Similarly, a well polished crystal of L-methionine doped AFS was subjected to different loads and hardness number was calculated. The variations of hardness number with the applied load for undoped and L-methionine doped AFS crystals are shown in the figure 6. It is observed that for both the samples, hardness increases with increase of applied. When AFS crystal is doped with L-methionine, the hardness increases and this is due to incorporation of L-methionine in the form of ions in the interstitial positions of the host crystal of doped AFS. Since the hardness is observed to be increasing with increase of the applied load for undoped and L-methionine doped AFS crystals, they have reverse indentation size effect [18].

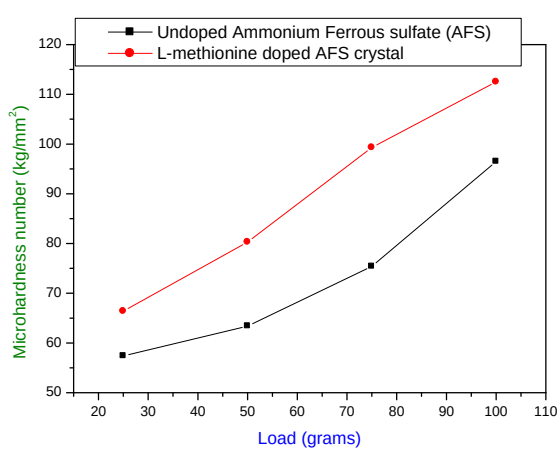
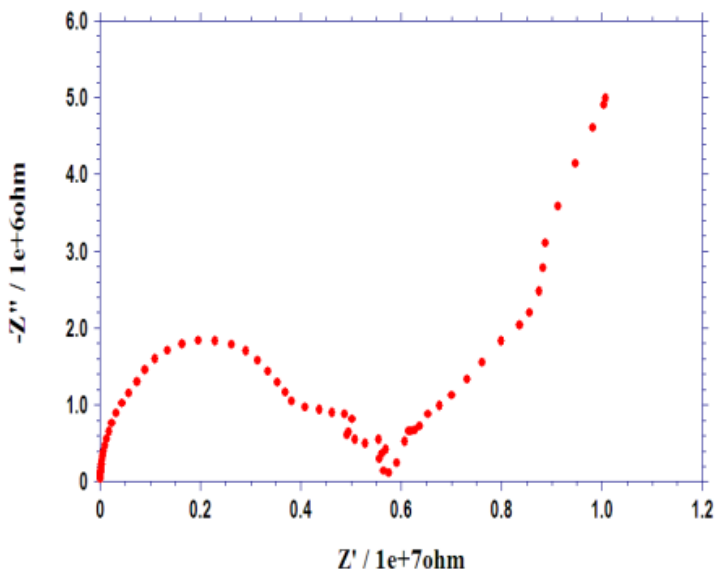


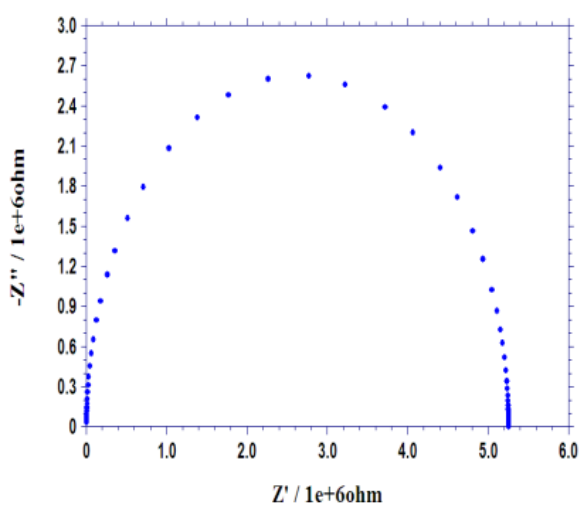
Fig.6. The variations of hardness with the applied load for undoped and L-methionine doped AFS crystals

3.6 Impedance studies

Impedance is a complex quantity and it has real part of impedance (Z′) and imaginary part of impedance (Z″) and it is written as Z* = Z' - jZ''. The complex impedance of a material depends upon frequency and temperature and it was measured using an impedance analyzer at various frequencies and temperatures. From the data of impedance of the sample, bulk resistance, grain boundary resistance, DC conductivity and relaxation time of the sample. Using the data of the real part and imaginary part of impedance of undoped and L-methionine doped AFS crystals, the Nyquist plots were drawn at different temperatures and they are shown in the figures 7 and 8. Nyquist plots of sample reveal the presence of bulk effect and grain boundary effect of the samples. Semicircles at low frequencies are considered due to the grain boundary whereas the semicircles at higher frequencies depict the bulk effect. For both the samples, as the temperature increases the impedance decreases showing the insulating property [19]. The bulk resistance (R_b) at different temperatures has been obtained from the intercept of the semicircular arc on the real axis (Z'-axis). The value of grain boundary resistance (R_{gb}) is obtained from Z' value corresponding to the peak of the semicircle. The obtained values of bulk resistance and grain boundary resistance of undoped and L-methionine doped AFS crystalline samples are given in the table 3. From the data, it is observed that bulk resistance and grain boundary resistance decrease with increase of temperature and hence conductivity increases. When AFS crystal is doped with L-methionine, it seems that the grain boundary resistance and bulk resistance increase at both 30 °C and 70 °C.

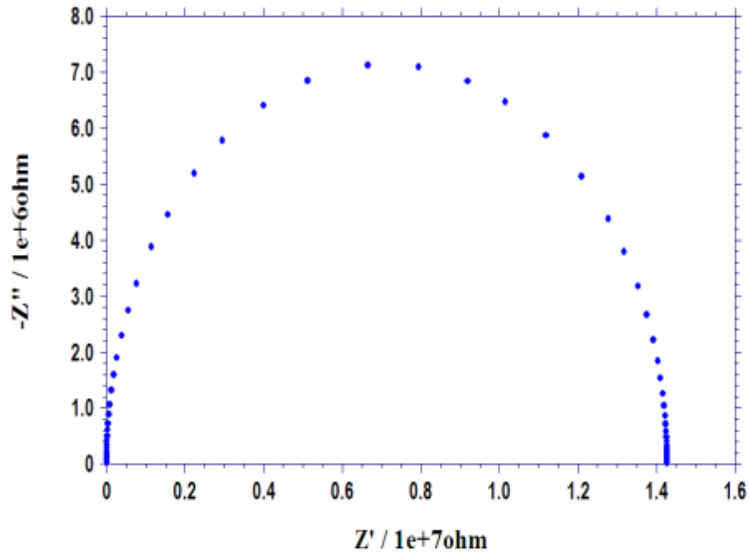


(a)

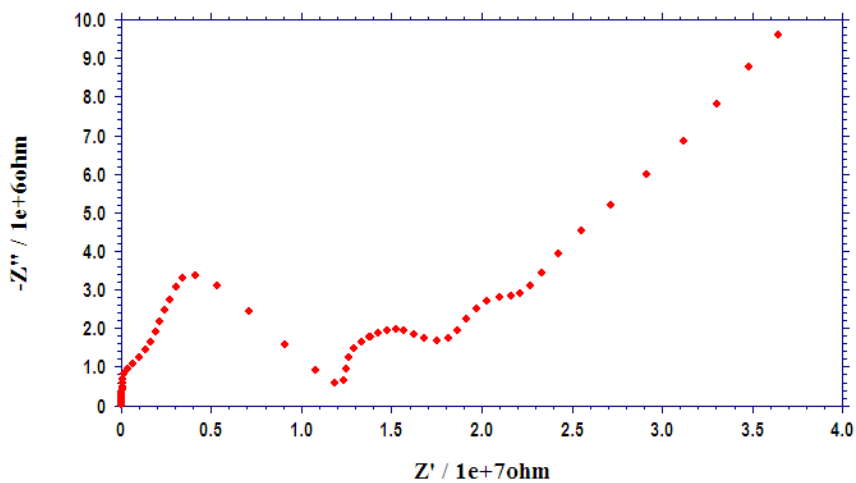


(b)

Fig.7. Nyquist plots of undoped AFS crystal (a) at 30 °C and (b) at 70 °C



(a)



(b)

Fig.8. Nyquist plots of L-methionine doped AFS crystal (a) at 30 °C and (b) at 70 °C

Table 3: Values of grain boundary resistance and bulk resistance for undoped and L-methionine doped AFS crystals

Sl.No.	Sample	Grain boundary resistance (ohms)	Bulk resistance (ohms)
1.	Undoped AFS sample	0.25 x 10^7 at 30 °C 2.85 x 10^6 at 70 °C	0.58 x 10^7 at 30 °C 5.21 x 10^6 at 70 °C
2.	L-methionine doped AFS crystal	0.62 x 10^7 at 30 °C 0.45 x 10^7 at 70 °C	1.41 x 10^7 at 30 °C 1.20 x 10^7 at 70 °C

4. Conclusions

Single crystals of undoped and L-methionine doped AFS were grown by solution method using the double distilled water as the solvent. The presence of the functional groups such as OH, NH, COO^-, SO_4^{2-} is confirmed by FTIR method and the elements such as C, N, O, Fe, S in the L-methionine doped AFS crystal have been identified by EDAX spectral analysis. The crystal structure of both undoped and L-methionine doped AFS crystals is found to be the same. Vickers microhardness was measured for both the samples at different applied loads. TG/DTA studies reveal the presence of water molecules in the sample and it is

confirmed that the sample is thermally stable upto 100 ^{o}C. Bulk resistance and grain boundary resistance of undoped and L-methionine doped AFS crystals were determined by impedance analysis.

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