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GROWTH AND CHARACTERISATION OF L-LEUCINE ADDUCT ADDED WITH SODIUM FLUORO ANTIMONATE SINGLE CRYSTALS

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Abstract. The crystal structure of a newly synthesised molecular adduct of sodium fluoro antimonate with L-Leucine of the composition $NaSbF_4(C_6H_{13}NO_3)$ is determined for the first time. The organo mixed antimony fluoride crystals are grown by slow evaporation technique from the aqueous solution. The grown crystal is confirmed by single crystal x-ray diffraction and powder x-ray diffraction studies. The various functional groups are assigned by FT-IR technique. The transparency of LSFA is confirmed by optical absorption spectrum and the direct band gap energy is found to be 4.0 eV. The thermal stability of the crystal is found to be 212°C. The presence of CH and OH bands are identified by NMR analysis. The percentage of carbon, Hydrogen and Nitrogen in the crystal are confirmed by CHNS analyser and it is reported.

Keywords: L-Leucine, fluoro antimonates, X-ray diffraction, opto electronics, organo metalics.

1. INTRODUCTION

There has been a great deal of interest in the recent years on metal fluoro compounds due to its mildness, versatility, selectivity and its operational simplicity. The unique properties of fluorine possess an unusual reactivity to the metal fluorine bond [14,17]. The development of main metal mediated M-F bond formation process is still an unexplored field virtually [2]. The number of antimony fluoro complexes are still scarce and few studies on their reactivity have been reported. Fluoro complexes of Sodium and Ammonium are gaining more interests due to their electro optic and super ionic Properties [1,9]. The crystal chemistry of water soluble crystals of fluoro antimonates and their relative compounds have been well studied in the literature [3,4,11,16,18]. It was also known that a number of fluoro complexes of antimony (III) with al-

kali fluorides have considerable interests due to their high optical homogenity and other optical characteristics. The structure, electrical and mechanical properties of sodium fluoro antimonate NH_4SbF_4 is reported by Kharitono et al. and Benet Charles et al [5-8]. Amino acids are the organic materials which contain proton donor around (COOH) and the Proton acceptor amine (NH_2) group in them and they are used to prepare the novel derivatives and give the direction for searching new second order and third order NLO materials [12,13]. The crystal structure of amino acids and their complexes have provided interesting information about the effect of other molecular properties. Some complexes of amino acids mixed with inorganic compounds exhibits high non linear optical property [15]. Complexes of amino acids with inorganic acids and salts are promising materials for its optical inheritance and they tend to combine the advantages of organic amino acids with that of inorganic acid [10]. These interests have been intensified by the possibility of using them in technological devices.So the effort have been made on the amino acid mixed complex crystals inorder to make them suitable for various applications. L –Leucine is a branched chain amino acid with molecular formula $C_6H_{13}NO_2$ which is the most important ketogenic amino acid in humans. In the present study, bulk single crystals of L-Leucine Sodium Fluoro Antimonate (LSFA) have been grown by the solution method with optimised growth conditions. The grown crystals are subjected to various characterisation studies and are reported.

2. Experimental Procedure

The starting materials of analytical grade Sodium Fluoride (NaF_2) and Antimony tri Fluoride (SbF_3) are mixed together in the appropriate ratio to synthesise sodium fluoro antimonate (NH_4SbF_4). The calculated amount of L-Leucine was added to the prepared solution slowly with stirring. The mixed solution was stirred well for 8 hours under constant temperature at 40^{o}C. The saturated solution was filtered and crystallisation process was allowed to takes place by slow evaporation under room temperature. The transparent colourless crystals with size 0.6 $\times$ 0.5 $\times$ 0.7 cm^3, are harvested over a period of 15 to 20 days and are shown in Fig.1. The crystals thus grown were analysed by physical and chemical methods.

3. Results and Discussions

3.1. **Single X-ray diffraction studies.** In order to determine the lattice parameters, the single crystal x-ray diffraction data were collected for a well developed single crystal of LSFA using ENRAF NONIUS CAD4 X-ray diffractometer. Reflections from a finite number of planes were collected. The unite cell dimensions are determined based on all reflections. It is observed that the crystal belongs to the Monoclinic system with the cell dimensions a = 8.047$\mathring{A}$, b = 5.5027$\mathring{A}$, c = 8.5424$\mathring{A}$ and V = 377.35$\mathring{A}$ with phase group P21c.

3.2. **Powder X-ray diffraction studies.** Powder X-ray diffraction spectrum of the grown crystal has been recorded in between the 2θ values ranging from 10° to 80°. Powder X-ray diffraction was also used for the determination of diffraction peaks. The reflections from a finite number of planes were collected on SIEFERT X-ray diffractometer using CuKα

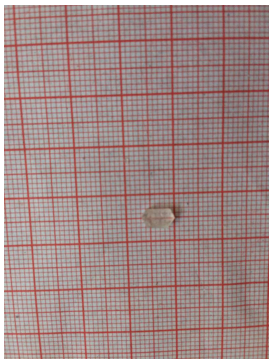

FIGURE 1. Photograph of as grown LSFA single Crystal

(λ - 1.5414$\mathring{A}$) radiation. The powder X-ray dif-fraction spectrum is shown in Fig.2. The lattice parameter values reveals a close agreement with the calculated values of powder X-ray diffraction spectrum confirming the identity of the grown crystals.

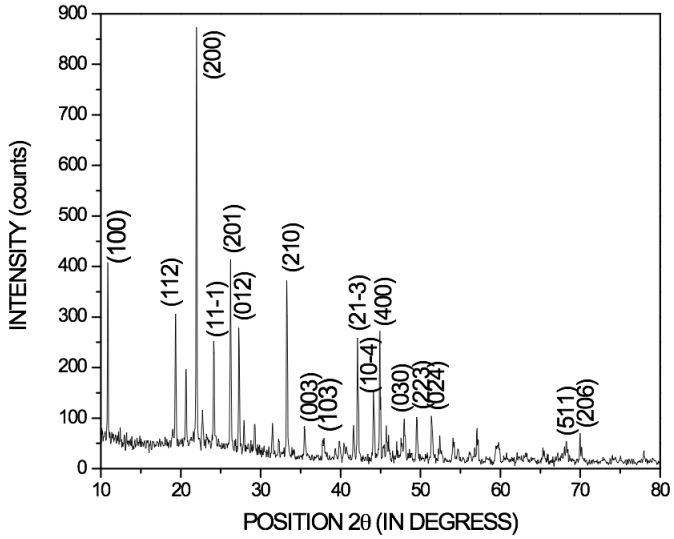

FIGURE 2. Powder X-ray spectra of LSFA single crystals

3.3. **Chemical (CHN) analysis.** The LSFA crystals are characterized by chemical analysis. The chemical composition of the synthesised LSFA was determined by carbon, hydrogen and nitrogen (CHN) analysis using Elementar Vario EL III analyser. The CHN analysis reveals that LSFA has the percentage of elements of C=0.5%,
H = 0.3% and N=0.8%. The calculated values agree well with the experimental values.

TABLE 1. FT-IR assignments of LSFA single crystal

Absorbed IR frequency (cm^{-1})	**Assignments**
3387	OH stretching
2959	CH vibration
2361	NH_3^+ symmetric stretching
1630	O=H bending
1408	COO^- symmetric stretching
1023	C-COO^- stretching
815	NH bending
515	Sb-F bond

3.4. **FT-IR Analysis.** The Infrared spectroscopy is used to identify the functional groups of the synthesized compounds. The FT-IR spectrum of LSFA was recorded by KBr pellet method using Bruker IFS 66V FT-IR spectrometer. Fig.3 shows the IR spectrum of LSFA crystals are recorded in the range of 400 to 4000 cm^{-1}. The observed vibrational frequencies and their assignments are listed in Table 1.

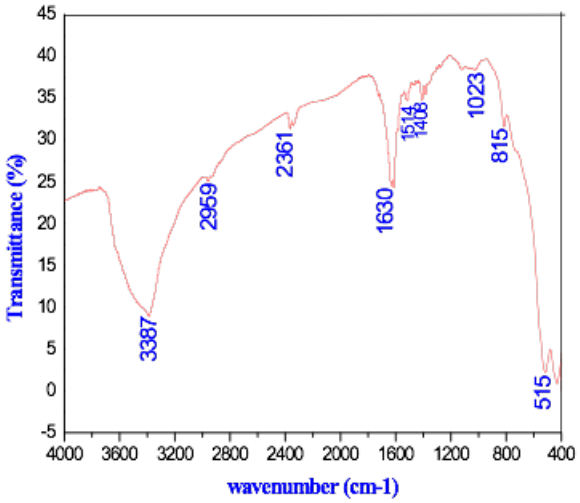

FIGURE 3. FT-IR Spectrum of LSFA single crystal

3.5. **Linear Optical studies.** The UV-Visible spectrum gives information about the structures of molecules due to the absorption of UV and Visible light and the transition of the electron in the π orbital to the high energy π^* orbital. To determine the optical absorption range and hence to know the suitability of LSFA single crystals for optical applications, the UV Vis -NIR spectral transmission was studied using a Varian Cary 5E UV Vis-NIR spectrometer with a single crystal of 3mm thickness in the range of 200 - 800 nm. The lower absorption cut off wavelength of

the LSFA crystal is at 260 nm which makes it a very potential material for blue light emission. The UV absorption of LSFA is shown in Fig. 4. The crystal has a wider transparency range extending into the visible and IR region. The band gap energy of the material is calculated by drawing the Tauc's plot between energy hν and direct energy $(\alpha h\nu)^{\frac{1}{2}}$ as shown in Fig.5. The band gap energy of the material is found to be 4.0 eV. This indicates that the LSFA crystal is a high energy band gap material which has its applications in the fabrication of opto electronic devices.

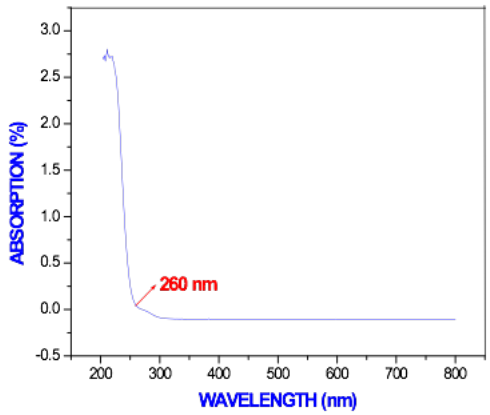

FIGURE 4. Absorbance Spectrum of a LSFA single crystals

3.6. **NMR Analysis.** NMR Spectroscopy is used to determine the molecular structure based on the chemical environment of the magnetic nuclei like H^1, C^{13} , P^{31} etc even at low concentrations. This is one of the most powerful non destructive techniques in elucidating the molecular structure of the chemical and biological compounds. NMR spectra of the grown LSFA crystal

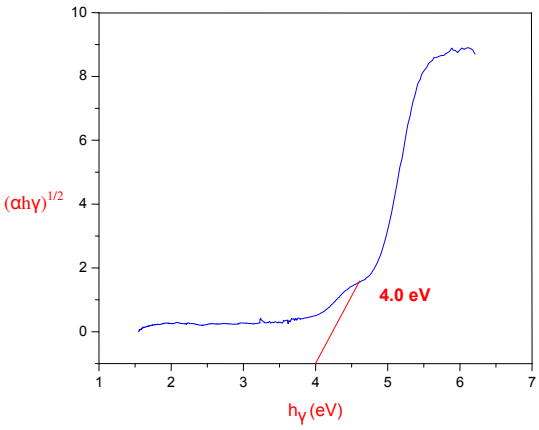

FIGURE 5. Tauc's plot of LSFA single crystal

is recorded using BRUKER 700 MHZ nuclear magnetic resonance spectrometer using D_2O as solvent. Fig. 6 shows the proton NMR spectrum of the grown crystal. In the NMR spectra, the CH_3 bond is observed at 0.8ppm and CH doublet peak at 3.7 to 3.8 ppm. The presence of hydroxyl peak is observed at 1.6 to 1.7 ppm which confirms the existence of organic groups in the LSFA crystal.

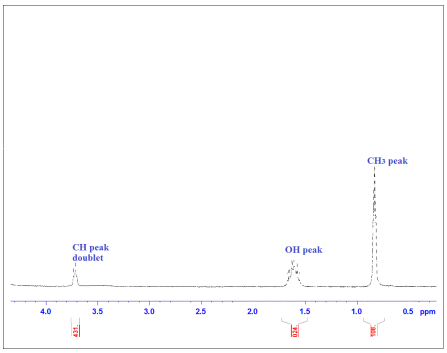

FIGURE 6. Proton NMR of LSFA single crystals

3.7. **Thermal Analysis.** The TG and DTA studies of LSFA crystal is carried out using SDT Q600V8.0 thermal analyser with temperature ranging from 20-800°C at a heating rate of 10°C/min with nitrogen atmosphere is shown in Fig. 7. A careful examination of DTA reveals an endothermic peak at 261.8°C. This confirms the staring state of the decomposition of the crystal at 262°C. The sharpness of this endothermic peak shows the good degree of crystallinity of the sample. There is no phase transition observed till the material melts and this enhances the temperature range for the utility of the crystal for optical applications. The TG curve also reveals that single state weight loss is observed between 262°C and 690°C. The weight loss is occurred due to the evolving volatile decomposition of the crystal due to CO_2, CO and H_2O from the compound. After that this semi organic crystal becomes volatile. It is also seen that 30% of the sample remains stable after 800°C also which is due to the stability of antimony atoms present in the crystal.

4. CONCLUSION

Optically good quality single crystals of LSFA was grown using slow evaporation method using solution growth technique. The grown crystal are characterized by single crystal and powder XRD techniques to deduce the unit cell parameters. The formation of LSFA and its lattice parameter is confirmed by single crystal x-ray diffraction study and the intensity of peaks is verified by Powder x-ray diffraction. The major functional groups and vibrational frequencies are assigned and identified from FT-IR spectral analysis which confirms the presence of major functional groups. In the absorption spectra of UV studies, it is evident that LSFA has its lower cut off wavelength at 260 nm and the energy band gap is about 4.0 eV. The composition of C, H and O are analysed by CHNS analyser. From the TG/DTA curve, the LSFA crystal is highly

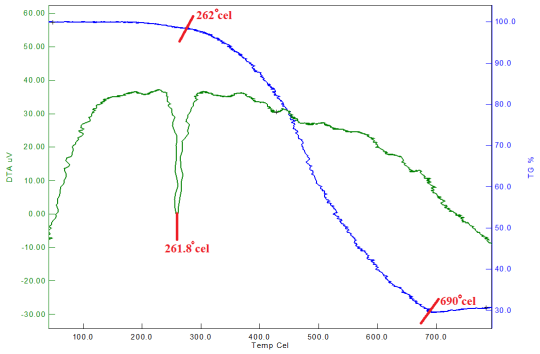

FIGURE 7. TG/DTA Analysis of LSFA single crystal

stable up to 262°C and single stage weight loss is observed. The CH doublet and triplet peaks of L-Leucine is confirmed by Proton NMR Spectra which confirms the crystal structure of LSFA.

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