Growth, spectral and thermal properties of Sulphanilic acid single crystals in the presence of L-proline and L-lysine monohydrochloride dihydrate as dopants

M. LYDIA CAROLINE*, G. MANI, S. KUMARESAN, M. KUMAR, S. TAMILSELVAN,
G. J. SHANMUGA SUNDAR
PG & Research Department of physics, Arignar Anna Govt. Arts College, Cheyyar - 604 407, Tamil Nadu, India

Single crystals of sulphanilic acid have been grown from aqueous solution by doping with L-proline and L-lysine monohydrochloride dihydrate by solvent evaporation technique, with the vision to improve the physiochemical properties of the sample. The characterization of the grown crystals were made by X-ray diffraction analysis and FTIR spectral analysis. Thermal analysis was performed to study the thermal stability and the maximum temperature for non linear optical applications of sulphanilic acid in the presence of dopants. Transmission range of the grown crystals were determined by UV-vis-NIR measurements. Frequency response of the dielectric constant and dielectric loss factor have been studied over the frequency range of 100Hz - 5MHz. Second harmonic generation (SHG) was confirmed in all the samples using the Kurtz and Perry powder technique. Thus the pure and doped single crystals of sulphanilic acid make them suitable for photonic device application.

1. Introduction

The organic molecular materials have emerged as a new class of promising nonlinear optical materials due to their potentially high nonlinearities and rapid response in electro-optic effect and tailor made flexibility compared to inorganic NLO materials. Sulphanilic acid ($NH_3^+C_6H_4SO_3^-$) is an important and interesting compound, which finds a number of applications including nonlinear optics [1]. Sulphanilic acid was reported to have dosimetric properties [2] owing to the presence of SO_3^- anion, which was proved to consist of dosimetric properties by several authors [3,4]. The SAA crystallizes in the orthorhombic structure with space group of $Pca2_1$ [5]. Search of new NLO materials with good thermal stability is very essential to fulfill the increasing demand in the field of telecommunication, optical computing and optical data storage. In the nucleation and growth of certain nonlinear optical crystals, amino acid is playing a vital role because of the fact that almost all amino acids contain asymmetric carbon atom and crystallizes in noncentrosymmetric space group. The amino acid contains a deprotonated carboxylic group (COO^-) and protonated amino group (NH_3^+). This dipolar nature exhibits peculiar physical and chemical properties in amino acids, thus proves them potential candidate for NLO applications [6-11]. Also, many complexes of amino acids with organic and inorganic acids exhibits nonlinear properties [12-15]. The thermal stability is also an essential criteria for the usuage of material in NLO applications. In the present investigation, systematic study has been carried out on the growth of pure SAA, amino acid L-proline doped SAA and semiorganic material L-lysine monohydrochloride dihydrate doped sulphanilic acid single crystals. The grown crystals were subjected to single crystal XRD, FTIR spectroscopy, thermal analysis, linear and nonlinear optical studies and dielectric studies.

2. Experimental

2.1 Material synthesis

Sulphanilic acid ($NH_3^+C_6H_4SO_3^-$) has good solubility of 18.0 g/100 ml in water at 45.0 ºC according to solubility data [16]. The required salt of Sulphanilic acid ($NH_3^+C_6H_4SO_3^-$) were thoroughly dissolved in deionized water of resistivity 18.2 MΩ and stirred well using a temperature controlled magnetic stirrer to yield homogeneous mixture of mother solution. The purity of the synthesized salt was further improved by successive recrystallization process. The prepared solution was allowed to dry at room temperature, which yielded light golden colour crystals of SAA as shown in Fig. 1a. The growth of L-proline doped SAA and L-lysine monohydrochloride dihydrate doped SAA was achieved by using the same procedure by individually adding 5 mol% of L-proline and 5 mol% L-lysine monohydrochloride to the SAA solution respectively. Fig. 1b & 1c shows the photographs of single crystals of L-lysine monohydrochloride dihydrate and L-proline doped SAA single crystals respectively.
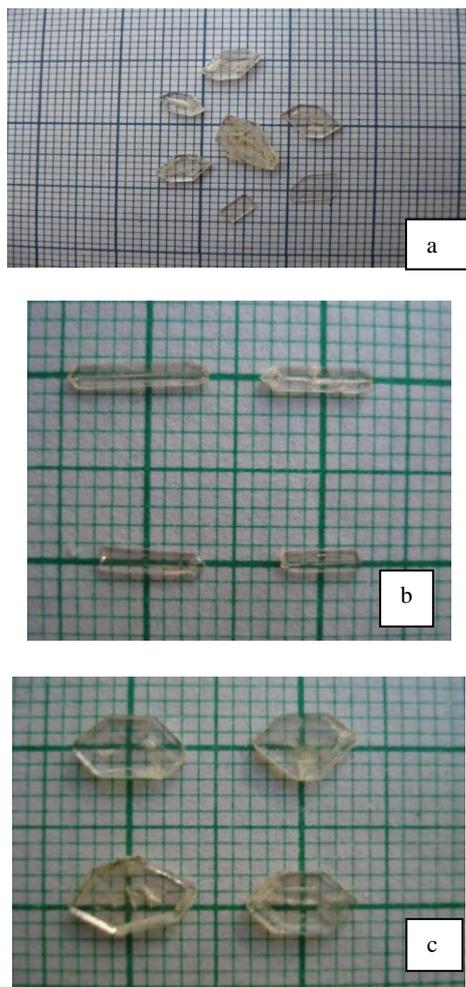
Fig. 1a. Single crystals of pure SAA 1b) L-lysine monohydrochloride doped SAA & 1c) L-proline doped SAA by slow – evaporation method

2.2 Characterization

In order to estimate the crystal data of pure and doped SAA crystals, single crystal X-ray diffraction studies have been carried out using Enraf Norius CAD4 diffractometer with MoKα (λ = 0.7170Å) to determine the cell parameters. The powder X-ray diffraction analysis (XRD) on the pure and doped SAA single crystals was also carried out using Xpert Pro diffractometer with CuKα (λ = 1.54060 Å) radiation over the range 10 to 60 degree at a scan rate of 0.02 degree/second. The optical transmission spectra of pure and doped SAA single crystals has been recorded in the region 200 -1100 nm using a Shimadzu UV-1061 UV–vis spectrometer. The coordination of dopants with sulphanilic acid was confirmed by FTIR studies using BRUKER 66V FT-IR spectrometer in the range 4000-400 cm^{-1} following KBr pellet technique. The thermal characterization was determined by thermogravimetric analysis and differential thermal analysis using a SDT Q600 V8.0 thermal analyzer in a nitrogen atmosphere. The NLO property of the grown samples were confirmed by Kurtz powder second

harmonic generation (SHG) test. HIOCKI 3532-50 LCR HITESTER instrument was employed to study the dielectric behaviour of the grown crystals.

3. Results and discussion

3.1 Single crystal X-ray diffraction

The single crystal X-ray diffraction studies of pure, L-proline and L-lysine monohydrochloride dihydrate doped SAA revealed that the both pure and doped SAA single crystals crystallize into orthorombic system and belongs to Pca2$_1$ space group. In the case of L-proline and L-lysine monohydrochloride dihydrate doped SAA crystals, slight variations in the lattice parameters and cell volume are observed when compared with pure SAA. These variations may be attributed to the incorporation of L-proline and L-lysine monohydrochloride dihydrate in the SAA crystal lattice are presented in Table 1. The crystallinity of doped SAA single crystals was confirmed by powder X-ray diffraction analysis and diffraction peaks are indexed (Fig. 2a & 2b) from crystal structure parameters obtained in the present study. Thus the variations in the intensity of peaks when compared with the powder X-ray diffraction of pure SAA [16] clearly indicates that the dopants (L-proline and L-lysine monohydrochloride dihydrate) could be incorporated into the pure SAA crystal lattice.

Table 1. Comparison of unit cell parameters of pure and doped SAA single crystals.

	SAA	L-lysine monohydrochloride	L-proline
a (Å)	7.279	7.296	7.322
b (Å)	7.511	7.524	7.545
c (Å)	13.898	13.981	13.913
V (Å)^3	759.86	767.48	768.61
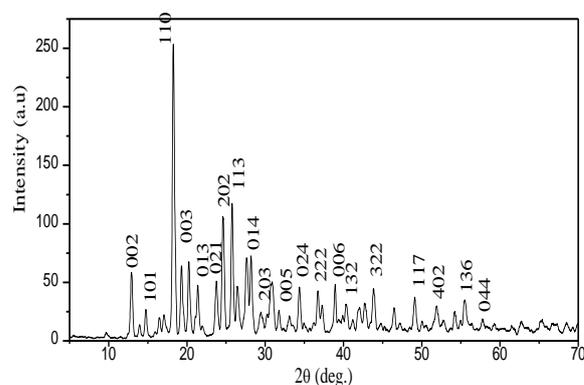
Fig. 2a. Powder X-ray diffraction pattern of l-lysine monohydrochloride doped SAA
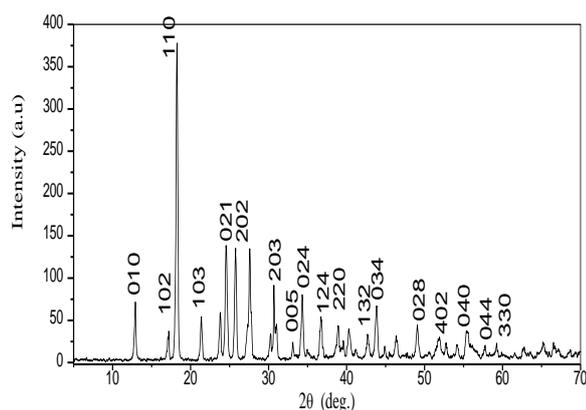
Fig. 2b. Powder X-ray diffraction pattern of L-proline doped SAA.

3.2 FTIR spectral analysis

The mid FTIR spectrum observed on the samples obtained due to influence of the dopents L-proline and L-lysine monohydrochloride dihydrate on pure sulphanilic acid single crystals along with the IR spectra of pure SAA is shown in Fig 3a, 3b & 3c respectively. This spectrum features characteristics of pure SAA different from the spectra of both L-proline and L-lysine monohydrochloride dihydrate doped SAA crystals. Hence the dopants namely L-proline and L-lysine monohydrochloride dihydrate might have incorporated in the SAA crystal lattice.
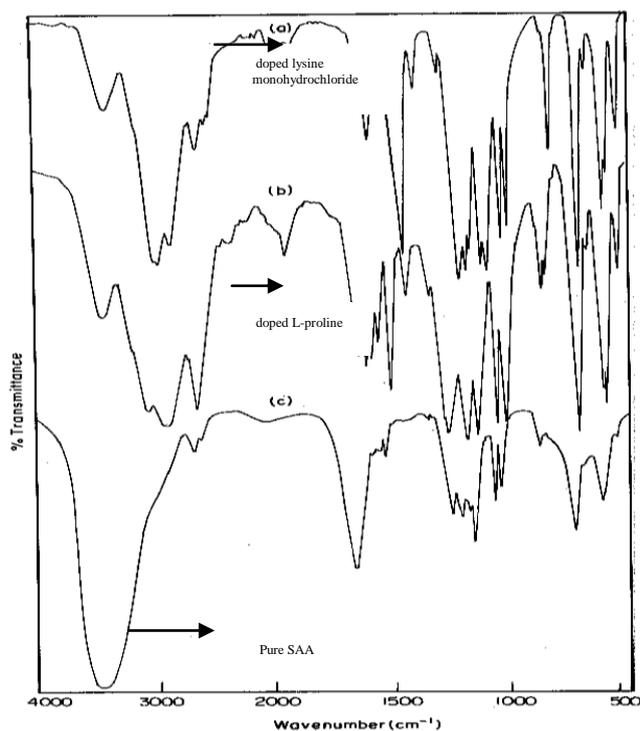
Fig. 3. FTIR spectrum of 3a) L-lysine monohydrochloride doped SAA, 3b) L-proline doped SAA and 3c) pure SAA

In the higher energy region, the peak at 3433 cm^{-1} is assigned to NH stretch of L-proline (Fig. 3a). Generally OH stretch of water also occurs close to this wave number. The nature of the NH stretch normally show sharper peak than OH stretch. More over the absence of water in the crystal is confirmed by TGA is discussed below. In addition the peak which appears just above 3000 cm^{-1} is also assigned to NH stretching. The blue shift is due to dopants interaction with sulphanilic acid. The aromatic CH vibration of sulphanilic acid should also produce its characteristic peak in this region. The peak at 2884 cm^{-1} is assigned to CH_2 vibrations of L-proline. Generally the CH_2 vibrations are to have peaks due to symmetric and asymmetric modes, but they appear to be overlapped in the spectrum. The peak at 2648 cm^{-1} is assigned to hydrogen bonded NH…O vibration of L-proline. The presence of hydrogen bonding is also supported by fine structure in the low energy portion of the broad band in the high energy region. The asymmetric bending vibration of sulphanilic acid NH_3 occurs at 1631 cm^{-1}. The aromatic ring skeletal vibrations produce peaks at 1601, 1499 and 1423 cm^{-1}. The peak at 1423 cm^{-1} is also applied to COO- symmetric vibrations and asymmetric vibration of COO- occurs at 1578 cm^{-1} of L-proline. The corresponding asymmetric vibration SO_3^- vibration gives peaks at 1320, 1245, 1158 and 1124 cm^{-1}. The peaks at 571 and 560 cm^{-1} are due to torsional oscillation of NH_3^+. Based on the appearance of the spectrum, that shows slight variations from the IR spectrum of sulphanilic acid [Fig.3c] it is to be confirmed that the crystal should contain L-proline as the dopant in the lattice of sulphanilic acid. The characteristics COO- vibrations at 1578 and 1423 cm^{-1} support this.

The FTIR spectrum of L-lysine monohydrochloride dihydrate doped sulphanilic acid is shown in Fig. 3b. It also carries NH vibrations at 3445 cm^{-1}. The peak at 3018 cm^{-1} is due to CH vibration of sulphanilic acid. Actually it appears as doublet due to overlapping of NH vibrations with CH vibration. The CH_2 vibrations of L-lysine monohydrochloride dihydrate gives its asymmetric stretching at 2913 cm^{-1}. The peak at 2672 cm^{-1} illustrates hydrogen bonding of NH…O vibration. The ring skeletal vibration of sulphanilic acid occur at 1599, 1491and 1421 cm^{-1}. The SO_3^- vibrations give peaks at 1312, 1220, 1188, 1125 and 1098 cm^{-1}. The tortional oscillations of NH_3^+, occurs at 573 cm^{-1}. Though the spectrum gives peak due to sulphanilic acid, based on the peaks at 2913 cm^{-1}, presence of L-lysine monohydrochloride is confirmed.

3.3 Optical transmittance and nonlinear optical studies

The optical absorption analysis revealed that doped SAA crystals have a UV cut-off wavelength below 300 nm (Fig. 4a & 4b), which is less compared to pure SAA [16] and also low percentage of absorption in the entire visible region, is an important criteria which makes them suitable for SHG laser radiation of 1064 nm or other application in the blue region. There is no appreciable absorption of light in the entire visible range, as in the case of all the aminoacids [15]. This shows the absence of any overtones

and absorbance due to electronic transitions above 500 nm. The optical transmittance study shows that pure and doped SAA crystals are potential candidates for SHG. The fundamental beam of 1064 nm from Q switched Nd:YAG laser of pulse energy 3.0 ± 2 mJ/s with pulse width of 8 ns and repetition rate of 10 Hz was used to test the second harmonic generation (SHG). The SHG efficiency of pure SAA is 0.7 times that of KDP, agree well with the literature [16]. The SHG efficiency L-proline doped sulphanilic acid is found to be comparable to that of KDP and enchanced SHG efficiency in the case of L-lysine monohydrochloride doped SAA. Both the doped SAA single crystals may be used for frequency doubling process upto its decomposition temperature which is higher than the pure SAA as discussed in thermal analysis below.
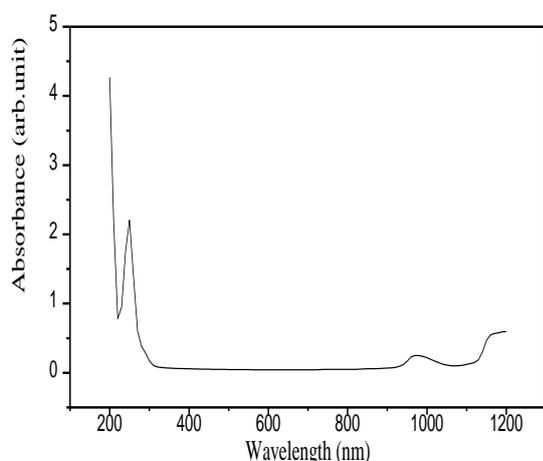
Fig. 4a. UV-visible spectrum of L-proline doped SAA single crystals
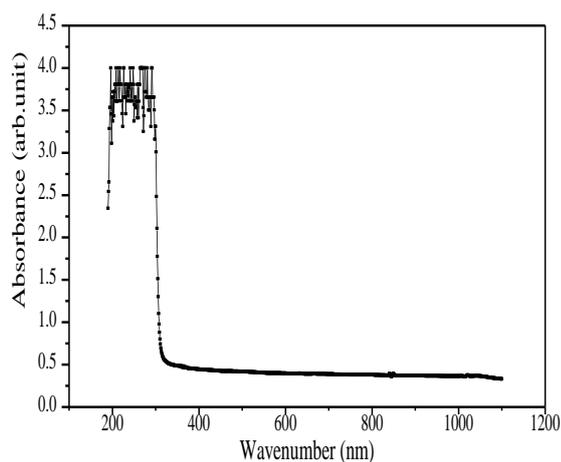
Fig. 4b. UV-visible spectrum of L-lysine monohydrochloride doped SAA single crystals

3.4 Thermal analysis

To analyze the thermal stability of pure and doped SAA crystals, the thermogravimetric analysis (TGA) and Differential Scanning caloriemetric (DSC) experiments

were carried out. The characteristic curves obtained from these analyses are shown in Fig. 5a & 5b. Major weight loss is observed starting close to 350 °C for pure SAA. It is assigned to decomposition of the crystal. As there is no weight loss below 350 °C the crystal is devoid of any entrapped water in the lattice. As the parent sulphanilic acid itself decomposes at lower temperature (around 350 °C) then the decomposition temperature of the doped SAA crystals (SAA doped L-lysine monohydrochloride dihydrate around 370 °C and SAA doped L-proline around 365°C), the doped crystals might have L-lysine monohydrochloride dihydrate and L-proline as the dopants in its lattice. As there is no other endotherm below this, the crystals might decompose without melting. The DSC trace shown in the Fig. 5b also shows sharp endotherms starting at 350 °C for pure and at around 370 °C for SAA doped L-lysine monohydrochloride dihydrate and at 365 °C for SAA doped L-proline matches well with the TG analysis. Thus compared to pure SAA, the dopants shows good thermal stability with increase in the decomposition temperature enabling their use in nonlinear optical applications.
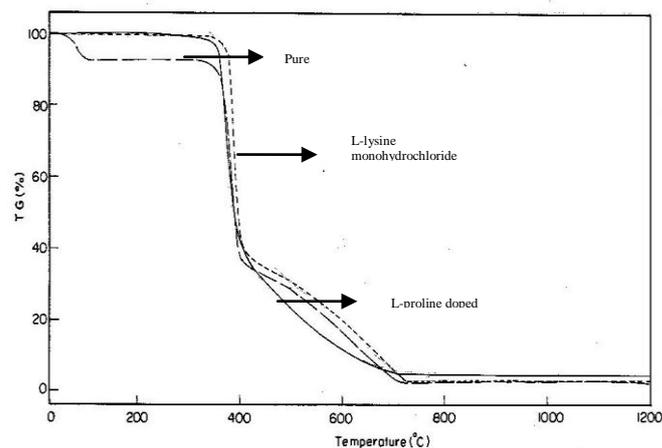
Fig. 5a. TG Curves of pure SAA, L-lysine monohydrochloride dihydrate doped SAA and L-proline doped SAA
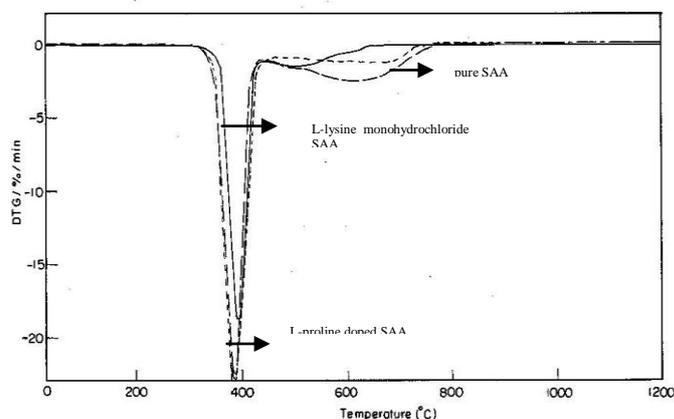
Fig. 5b. DSC Curves of pure SAA , L-lysine monohydrochloride dihydrate doped SAA and L-proline doped SAA

3.5 Dielectric studies

The dielectric study on pure SAA, L-proline and L-lysine monohydrochloride dihydrate doped SAA single crystals was carried using a HIOCKI 3532-50 LCR HITESTER instrument. The samples pure, L-lysine monohydrochloride dihydrate doped SAA and L-proline with dimensions $4.66 \times 4.75 \times 2.97$ mm^3, $5.48 \times 2.43 \times 2.22$ mm^3 and $5.72 \times 3.25 \times 1.29$ mm^3 were placed between the two copper electrodes and thus a parallel plate capacitor was formed. The capacitance on the sample was measured by varying the frequency from 100 Hz to 5 MHz. Fig. 6a & 7a & 8a shows the plot of dielectric constant (έ) versus applied frequency for pure SAA, L-proline and L-lysine monohydrochloride dihydrate doped SAA single crystals. The dielectric constant has a value of 1400 for pure SAA and 1700 for L-proline and 1900 for L-lysine monohydrochloride doped SAA single crystals in the lower-frequency region (100 Hz) and it then decreases (300 for pure SAA, 200 for L-proline doped SAA and 100 for L-lysine monohydrochloride dihydrate doped SAA) with the applied high frequency (5 MHz). The space charge polarization contributes to the dielectric constant at low frequency [17]. Fig. 6a, 7a & 8a implies the normal dielectric behaviour of pure SAA and doped SAA single crystals. It is normally accepted that in normal dielectric behaviour, the dielectric constant decreases with increasing frequency and reaches a constant value, depending on the fact that beyond a certain frequency of the electric field, the dipole are not responding and follow the alternating field. It is also concluded that doped SAA has high dielectric constant compared to pure SAA at lower frequency. The dielectric loss is also studied as a function of frequency at room temperature, as shown in Fig. 6b, 7b & 8b. for pure SAA and doped SAA crystals. These curves suggest that the dielectic loss strongly depends on the frequency of the applied field, similar to what commonly happens with the dielectric constant in the ionic system [18-19]. Dielectric loss is almost same for both pure SAA and L-proline and L-lysine monohydrochloride dihydrate doped SAA single at low frequency (100 Hz) and gradually decreases at high frequency (100 MHz) and practically becomes almost zero at 5 MHz.
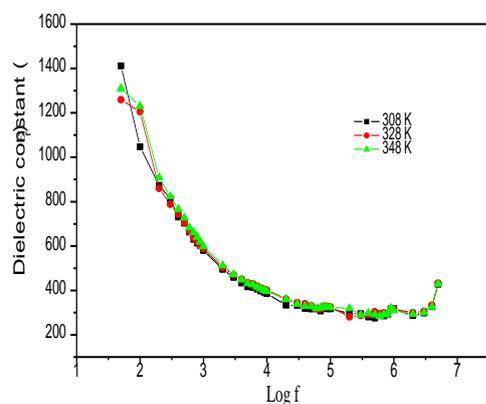
Fig. 6a. Variation of dielectric constant with frequency of the applied electric field of pure SAA
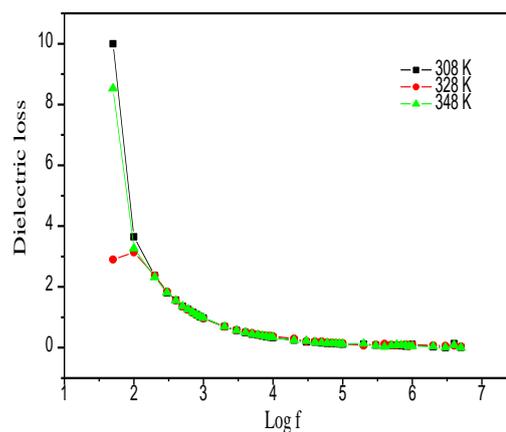
Fig. 6b. Variation of dielectric loss with frequency of the applied electric field of pure SAA
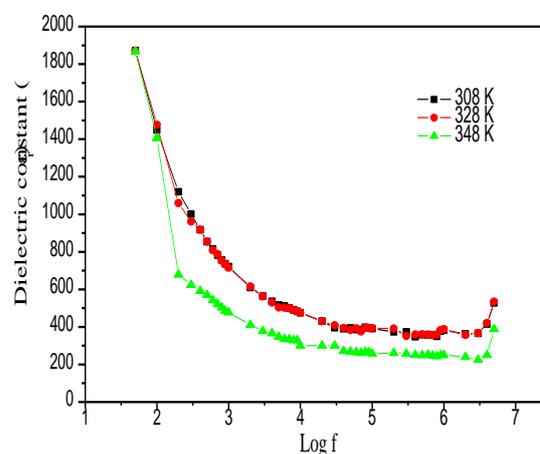
Fig. 7a. Variation of dielectric constant with frequency of the applied electric field of L-lysine monohydrochloride dihydrate doped sulphanilic acid
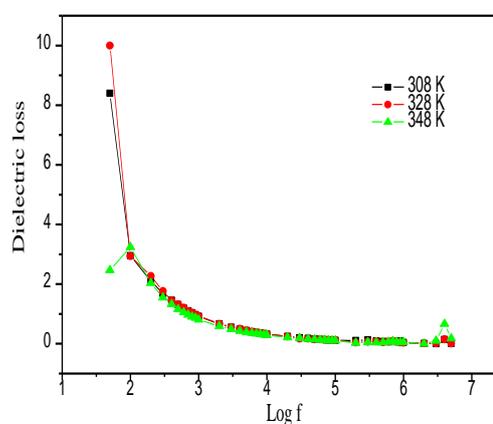
Fig. 7b. Variation of dielectric loss with frequency of the applied electric field of L-lysine monohydrochloride dihydrate doped sulphanilic acid
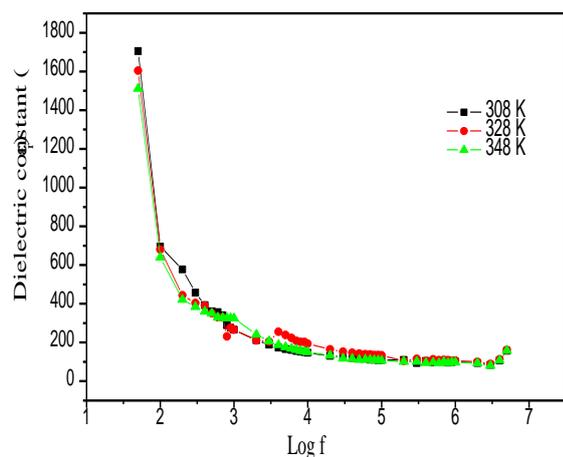
Fig. 8a. Variation of dielectric constant with frequency of the applied electric field of L-proline doped sulphanilic acid
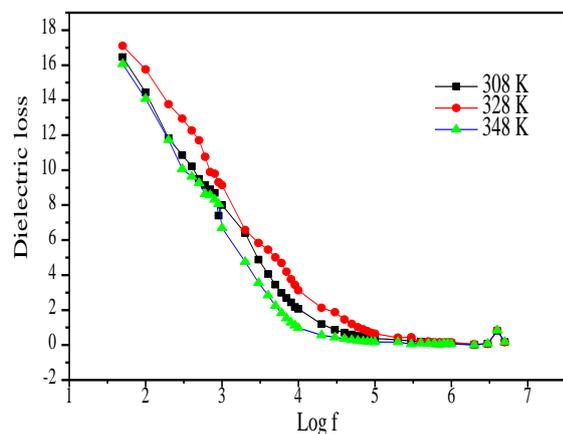
Fig. 8b. Variation of dielectric loss with frequency of the applied electric field of L-proline doped sulphanilic acid

4. Conclusions

Single crystals of pure SAA, L-proline and L-lysine monohydrochloride dihydrate doped SAA single crystals have been grown by slow evaporation from saturated aqueous solution at room temperature. The X–ray diffraction studies show that the small variation in lattice parameter values is due to the contribution of the dopants in the interstitial sites. The influence of the dopants L-proline and L-lysine monohydrochloride dihydrate on pure sulphanilic acid single crystals were confirmed by FTIR analysis. Transmission spectra reveals that doped SAA single crystals possess decrease absorption than pure SAA crystals enabling its use in optical applications. Thermal analysis reveals that there is an increase in the decomposition temperature due to the incorporation of dopants in pure SAA thus improving the thermal stability of doped SAA single crystals. The variations in dielectric constant and dielectric loss were studied with varying frequency at different temperatures. The SHG efficiency of L-lysine monohydrochloride dihydrate doped SAA is found better than the pure SAA crystal than L-proline doped SAA which is comparable with KDP enabling their use in nonlinear optical applications.

References

[1] R. Q. Brewster, W. E. Mcewen, "Organic chemistry; 3rd ed.", Prentice-Hall of India: New Delhi **862**, (2001).
[2] P. N. Kizer, J. R. Morton, K. F. Preston, J. Chem. Soc. Faraday Trans. **87**, 3147 (1991).
[3] J. Morton, F. Ahlers, C. Schneider, Appl. Radiat. Isotopes **40**, 851 (1993).
[4] A. Maghraby, E. Tarek, Radiat. Measurem. **41**, 170 (2006).
[5] John N. Low, Christopher Glidewell, Acta Cryst. C **58,** o209 (2002).
[6] T. Mallik, T. Kar, G. Bocelli, A. Musatti, Cryst. Res. Technol. **41**, 280 (2006).
[7] J. J. Rodrigues Jr., L. Misoguti, F. D. Nunes, C. R. Mendonca, S. C. Zilio, Opt. Mater. **22**, 235 (2003).
[8] E. Ramachandran, S. Natarajan, Cryst. Res. Technol. **39**, 308 (2004).
[9] R. Mahalakshmi, S. X. Jesuraja, S. Jerome Das, Cryst. Res. Technol. **4 1**, 780 (2006).
[10] M. Narayan Bhat, S. M. Dharmaprakash, J. Crystal Growth **236**, 376 (2002).
[11] T. Pal, T. Kar, Mater. Chem. Phys. **91**, 343 (2005).
[12] V. G. Dmitriev, G. G. Gurzadyan, D. N. Nikogosyan, second ed., Springer, New York, (1997).
[13] Ch. Bosshard, K. Sutter, Ph. Pretre, J. Hullinger, M. Florshemier, P. Kaatz, P. Gunter, "Organic Nonlinear Optical Materials", Gordon and Breach Publishers, Langhorne, PA, (1995).
[14] D. S. Chemla, J. Zyss, **1-2**, Academic Press, London, (1987).
[15] J. Zyss, Materials, Physics and Devices, Academic Press, New York, (1994).
[16] P. Mythili, T. Kanagasekaran, and R. Gopalakrishnan, Cryst. Res. Technol. **42**, 791 (2007).
[17] S. Boomadevi, R. Dhanasekaran, J. Cryst. Growth **261**, 70 (2004).
[18] K. V. Rao, A. Smakula, J. Appl. Phys. **36**, 2031 (1965).
[19] K. V. Rao, A. Smakula, J. Appl. Phys. **37**, 319 (1966).

_____
[*]Corresponding author: lydiacaroline2006@yahoo.co.in