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Research Article

SPECTRAL, MECHANICAL AND LINEAR OPTICAL STUDIES OF SODIUM HYDROGEN CARBONATE DOPED SULPHAMIC ACID SINGLE CRYSTALS

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ABSTRACT

Sodium hydrogen carbonate doped sulphamic acid crystals were grown by solution method. The grown crystals are colorless and transparent and they were subjected to various studies for characterization. From the characterization studies, it is confirmed that the grown crystal are with the enhancement of properties compared to the properties of the pure sample crystal. The unit cell parameters of the grown crystal were confirmed by single crystal X-ray diffraction. Good crystalline nature of the grown material is confirmed by the appearance of sharp peaks. The functional groups of the grown crystal were found by FTIR study. UV- Visible transmittance is recorded for the sample to analyze the transparency of the grown crystal. The value of band gap energy was found to be 4.8 eV. The Hardness studies reveal that the grown crystal belongs to soft category.

Keywords: Growth from Solution, X-ray diffraction, FTIR, Hardness, Optical studies.

1. INTRODUCTION

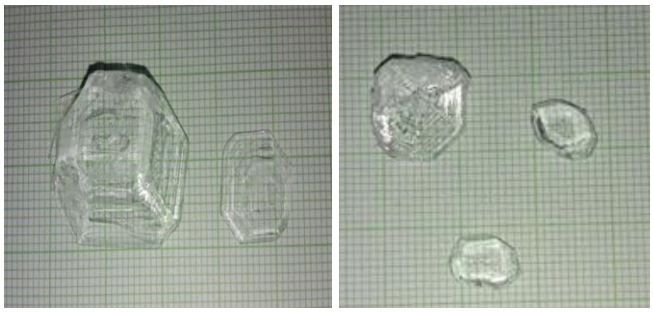
Nonlinear optical (NLO) materials exhibiting second harmonic generation have been in great demand over the last few decades due to technological importance in the fields of optical communication, signal processing, and instrumentation. In view of the applications of the nonlinear optical crystals, a new impetus is being given in the present investigations on studying the effect of sodium hydrogen carbonate (SHC) on sulphamic acid single crystal. Nonlinear optical materials will be the key elements for future photonic technologies based on the fact that photons are capable of processing information with speed of light. The search for new and efficient materials in which to carry out nonlinear optical processes has been very active since SHG was first observed in single crystal quartz. Inorganic compounds have property such as they are ionic bonded molecules and soluble in water. This colorless, water -soluble compound finds many applications and it is mainly precursor to sweet - tasting compounds. The molecular weight of this compound is 97.1g/mol [1] and its melting point is 205°C. An added advantage in sulphamic acid (SA) is that large single crystals can be grown from low temperature solutions [2]. They are extremely good in their mechanical strength. Sulphamic acid (H_2NSO_3H) is the monoamide of sulphuric acid and is formed as orthorhombic crystal. It is highly stable and it can be kept for years without any change in properties. It is a strong inorganic acid; while mixing it with water it exhibits zwitterionic form

Hence the objectives of this paper are aimed at growing sodium hydrogen carbonate (SHC) doped sulphamic acid (SHC: SA) single crystal by slow evaporation technique and to study its characteristics. The grown crystals were characterized by XRD, FT-IR, UV-Visible spectrum and Micro hardness.

2. EXPERIMENTAL PROCEDURE

Growth of Sodium Hydrogen Carbonate doped Sulphamic acid crystals were achieved by solution method with slow evaporation technique. The mother solution of SA was dissolved by de-ionized water using magnetic stirrer for about 2 hours. The analytical reagent chemicals in series of Sulphamic acid doped with SHC, mixed in molar ratios such as 1:0.015 in 20 ml, 1:0.02 in 19 ml of double distilled water was used to grow bulk crystals. The solutions were constantly stirred for about 2 hours using a hot magnetic plate stirrer for completely dissolving the solvents and were filtered using micro filter paper. The filtrate was then taken in Borosil

beakers (growth vessel). The growth temperature was maintained at room temperature through a constant temperature bath. The system was then allowed to stand for a period of about 12 days. After a week duration, the crystals started to grow. Small-sized crystals were obtained by taking small amount of saturated solution in a beaker by slow evaporation. Good quality small sized crystals were placed in a large quantity of saturated solution in a beaker to harvest large-sized crystals. The large sized crystals were harvested and polished to study the micro hardness studies. Also, the crystals were fine grained by mortar and pestle to study the characterization like UV and FTIR. The photograph of SHC doped SA crystals (1.5mol% of SHC doped SA and 2mol% of SHC doped SA) is displayed in the figure 1(a) and in figure 1(b).



3. RESULTS AND DISCUSSION

3.1. X- diffraction study

Single crystal X-ray diffraction analyses that the grown both pure and 1.5mol % of SHC doped sulphamic acid crystals belong to orthorhombic crystal system. The obtained lattice parameters of grown crystals are shown in table 1.

Table 1 Lattice parameters of the grown crystals

Lattice parameters	Undoped SA	1.5mol% of SHC added SA
a (Å)	8.063	8.071
b (Å)	8.099	8.094
c (Å)	9.208	9.237
α (deg)	90	90
β(deg)	90	90
γ (deg)	90	90
Volume (A3)	601.3	603.42
System	Orthorhombic	Orthorhombic

3.2. Fourier Transform Infrared Spectroscopy (FTIR) Studies

FTIR spectrum arises due to transitions induced between the vibrational energy level of a molecule and the absorption of radiation belonging to the infrared radiation. IR spectrum is showed by a molecule when vibrational motion is accompanied by a change in the dipole moment of the molecule. The given below figure illustrated the recorded spectrum on the crystal. The IR spectral assignments for the crystal are provided in the table 2.

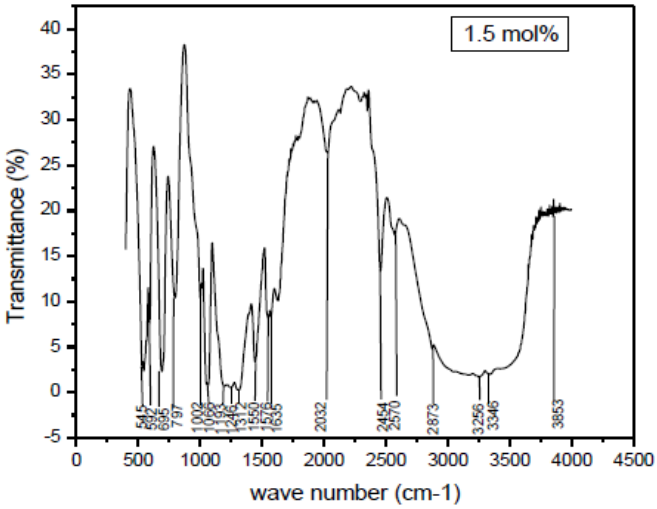


Fig. 2(a): FTIR spectrum of 1.5mol% of SHC doped SA

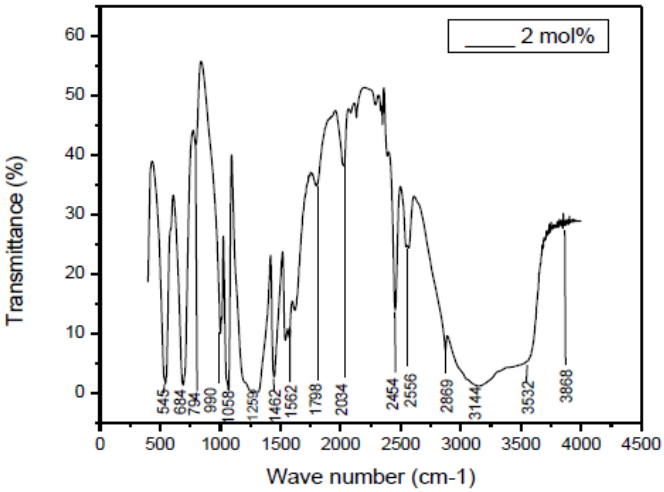


Fig. 2(b): FTIR spectrum of 2 mol% of SHC doped SA

The FTIR spectral assignments are given in accordance with the data reported in the literature. The deformation was viewed at 545 cm^{-1}, *i.e.* SO_3^- deformation, arises due to the degeneracy. Then NH_2 and N-H wagging was assigned at 684 cm^{-1}. The peak observed at 1002 cm^{-1} is due to NH_3^+ rocking. It also arises due to the degeneracy factor. Once again the SO_3^- deformation was viewed at 1066 cm^{-1}. This deformation occurs due to the degeneracy factor. The symmetric NH_3^+ is deformed and

is viewed at 1462 cm^{-1}. The NH_3^+ is started completely deforming and is viewed at 1550 cm^{-1}. The S-H stretching is appeared at 2556 cm^{-1}. The broad absorption peak observed at 2869 cm^{-1} is assigned symmetric stretching of $NH_3^+cm^{-1}$. The degenerate stretching of NH_3^+ is viewed at 3144 cm^{-1}.

Table 2: Vibrational band assignments for SHC doped SA single crystal for 1.5mol% and 2mol%

Wave number (cm^{-1})		Assignments
Pure SA	SA+SHC	
536	545	Degen. SO_3^- deformation
690	684	NH_2 and N-H wagging
1001	1002	Degen. NH_3^+ Rocking
1063	1066	Degen. SO_3^- deformation
1455	1462	Sym. NH_3^+ deformation
1538	1550	Degen.NH_3^+ deformation
2555	2556	S-H stretching
2871	2869	Sym. NH_3^+ Stretching
3211	3144	Degen. NH_3^+ Stretching

3.3. Mechanical studies

In order to study the mechanical stability of the crystal material, the micro hardness analysis of SHC doped SA has been performed along < 0 0 1> plane of crystals at 10, 20, 50 and 100g using the shimadzu HMV-2T micro hardness analyzer. Hardness is defined as the ratio of the load applied to the surface area of the indentation. To calculate the Vicker's hardness number (H_v), several indentations were made on the crystal surface for each load and the corresponding diagonal length of indentation was recorded. The hardness number was calculated using the relation,

$$H_v = 1.8544 * P/d^2 \ (kg/mm^2)$$

Where, P is the applied load in kg and d is the diagonal length in mm. the variation of hardness with applied load is shown in figure 3.

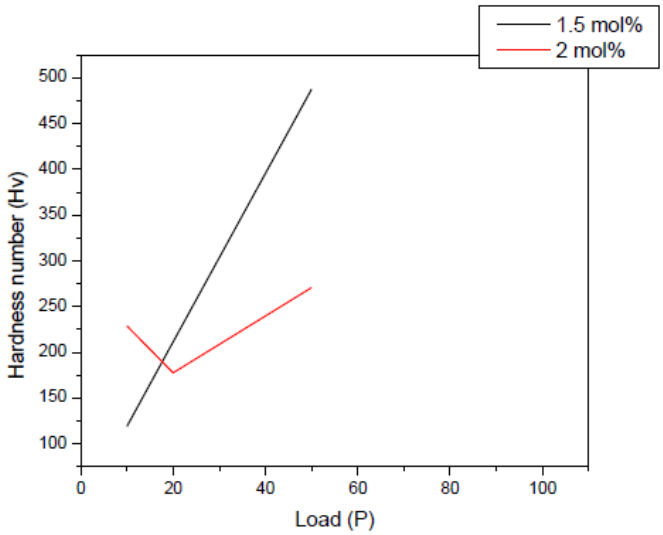


Fig. 3: Load dependent hardness

The Meyer's relation, $P=ad^n$ explains the effect of applied load on work hardening index (n) of the crystal. So that $d^2 = (1.8544*P*1000) / (H_v)$. It is calculated from the plot of log P versus log d, as displayed in figure 4. The value for n is found to be 3 for SHC doped SA crystals. In accordance to Onitsch and Hannemen study, as the value of n exceeds 1.6, the material belongs to the category of soft nature.

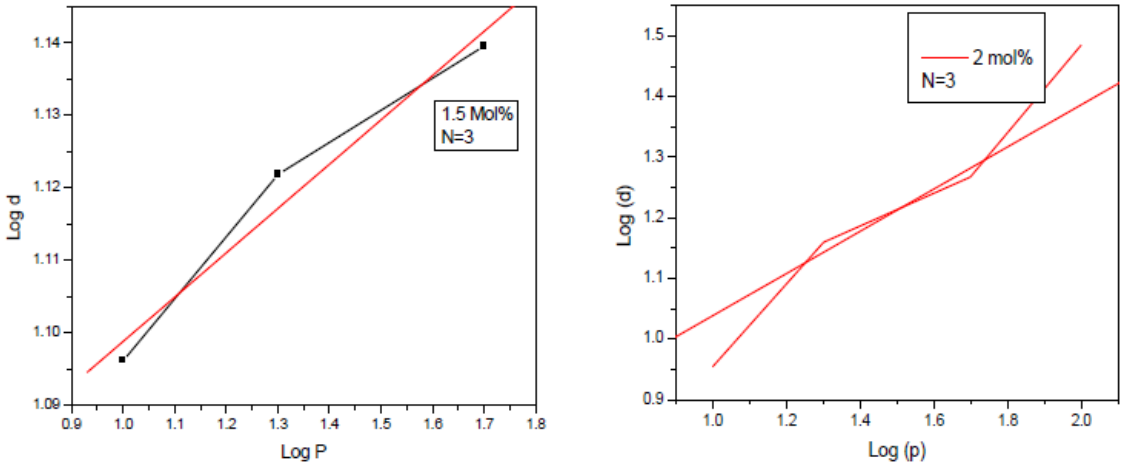


Fig. 4: log P vs log d

The improved mechanical properties are necessary to avoid loss of material while polishing and processing for device fabrication, for which the hardness reliant properties, such as yield strength $(H_v*9.8*(0.1)^{n-2})/3$(MPa) and elastic stiffness constant (given by wooster's empirical relation, $C_{11} = (H_v*9.8*10^6)^{7/4}$(Pa) have been

calculated. The higher magnitude of σ_y and C_{11} confirms the constructive impact of dopants in enhancing the intermolecular bond strength. The analysis of graph (shown in figure 5 and figure 6) confirms excellent mechanical behaviour of SA crystal in presence of SHC.

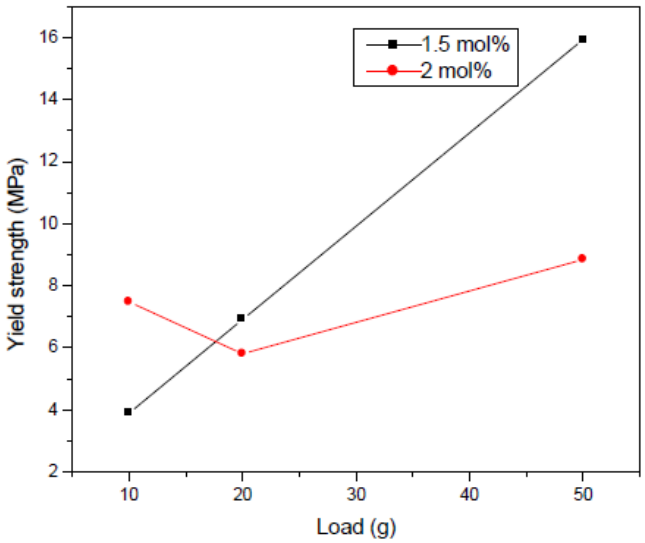


Fig. 5: Load vs yield strength

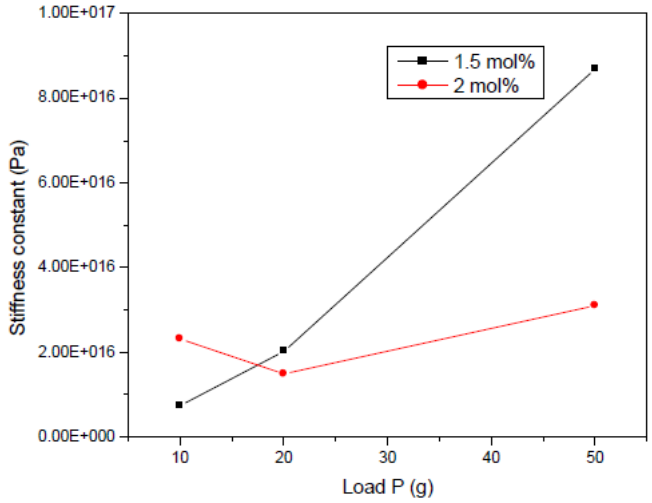


Fig. 6: Load vs stiffness constant

3.4. Optical studies

3.4.1. UV-visible Transmission studies

Transmission and absorption spectra are very important for any single crystal which can be useful for any practical application, only if it has a wide transparency window [3, 4]. UV-visible spectral analysis gives useful information about electronic transitions in the compound. In the optical transmission studies, the transmittance of doped crystal has been examined in the wavelength range 200-800 nm using Philips PV8700 UV-visible scanning spectrometer. For this study, an optically polished single crystal of thickness 1.0 mm was used and the recorded transmittance spectrum is shown in figure 7. The UV cut off wavelength of (SHC doped SA for 1.5mol%, SHC doped SA for 2mol %) crystals are found to be at 257 nm and 250 nm. It has been observed that both SHC doped SA crystal samples has increased transparency window compared to the pure SA crystal whose cut off wavelength is 270 nm. The crystals show good transmittance percentage in the range of 200-1100 nm. This spectral study would be assisted in the understanding of electronic structure and the optical band gap of the crystal. From the spectrum, it is observed that SHC doped SA crystal has high transmittance in the entire visible, near infrared region and this property enables the material holds good for optoelectronic applications. The samples are optically transparent in the entire visible region.

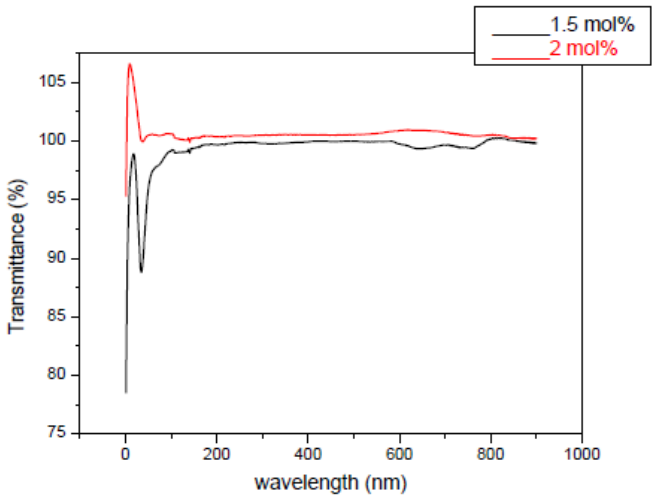


Fig. 7: UV-visible transmittance spectrum of SHC doped SA

3.4.2. Optical Band gap energy (E_g) calculation.

For optical device fabrication, the crystal should have high transparency in a considerable range of wavelength [5]. It is useful to make them potential material for optical device fabrication. The optical absorption coefficient (α) was calculated using the relation,

$$\alpha = 2.303 \log (1/T)/d \quad \ldots\ldots (1)$$

Where d is the thickness of the crystal and T is the transmittance.

The grown SHC doped SA crystal was estimated by plotting absorption coefficient (α) versus wavelength (nm) and it is shown in figure 8.

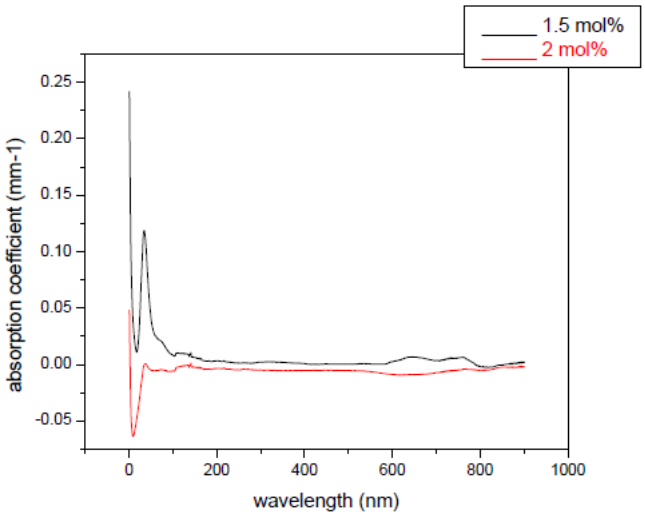


Fig. 8: UV-visible absorption coefficient of SHC doped SA single crystal

Owing to the direct band gap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (hν),

$$h\nu\alpha = (h\nu - E_g)^{1/2} \quad \ldots\ldots (2)$$

Where A is a constant, E_g is the optical band gap, h is the planck's constant, and ν is the frequency of the incident photons [6]. The band gap of energy of SHC doped SA crystal was estimated by plotting $(h\nu\alpha)^2$ versus (hν) and it is shown in figure 9. The band gap energy of (SHC doped SA for 1.5mol%, SHC doped SA for 2mol %) crystals are found to be at 4.83eV and 4.89 eV. This indicates the consequences of wide band gap and large transmittance of the grown crystal.

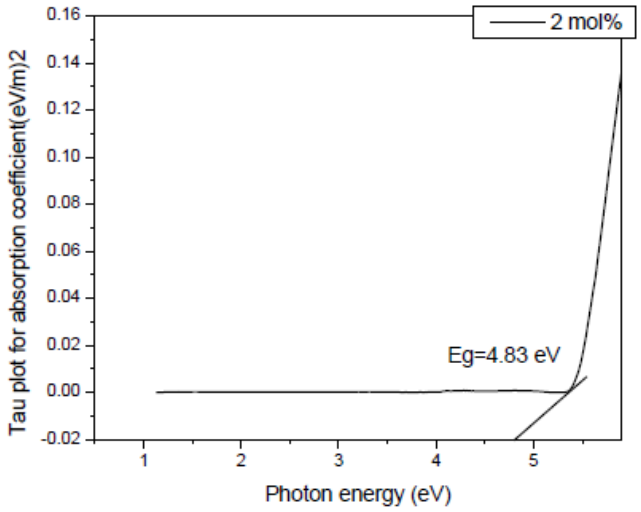


Fig. 9: plot of photon energy versus $(h\nu\alpha)^2$ of SHC doped SA crystal for 2mol%.

3.4.3. Determination of optical constants

The optical behaviour of materials is important to determine their usage in optoelectronic devices [7]. The study of optical constants of a material such as refractive index and extinction coefficient is quite essential to examine the material's potential optoelectronic applications [8]. Further the optical properties may also be closely related to the material's atomic structure, electronic band structure and electrical properties. k value was determined by

$$k = \alpha\lambda/4\pi \quad \ldots. (3)$$

Figure 10 shows the plot of wavelength (nm) versus extinction coefficient (k). It is observed that as the wavelength increases, extinction coefficient decreases up to 298 nm and remains constant thereafter .This means the absorbance is low in the visible and near IR region. This prediction is also confirmed from UV-VIS-NIR spectrum. Hence the grown crystal SHC doped SA can easily transmit the wavelength range from 200 to 1200 nm.

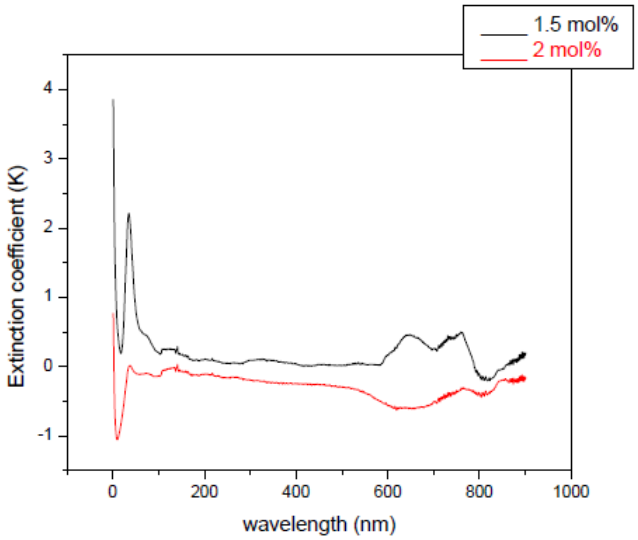


Fig. 10: plot of wavelength versus Extinction coefficient of SHC doped SA crystal

The Reflectance (R) can be determined by,

$$1 = A + T + R \quad \ldots. (4)$$

Where, A is a Log (1/T), Tis a transmittance in percentage.

The Refractive index (n) can be determined from the Reflectance (R),

$$n = (\sqrt{R}+1)/(1-\sqrt{R}) \quad \ldots. (5)$$

The calculated refractive index value using the above equations for the grown SHC doped SA crystal and it is shown in figure 12.

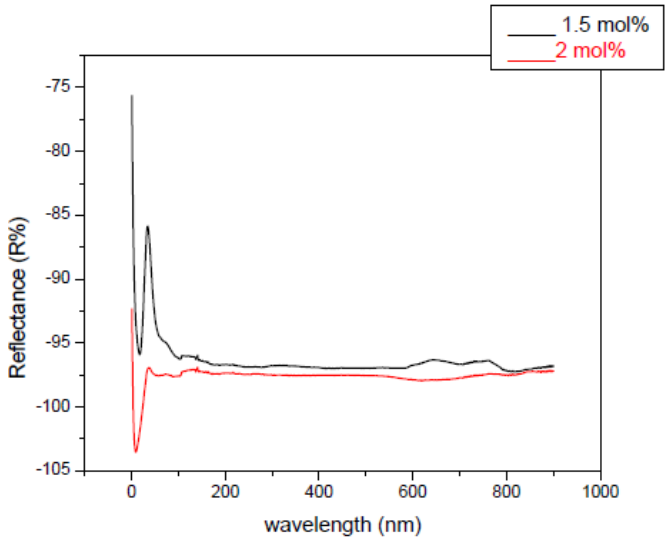


Fig.11: UV-visible Reflectance (R %) of SHC doped SA single crystal.

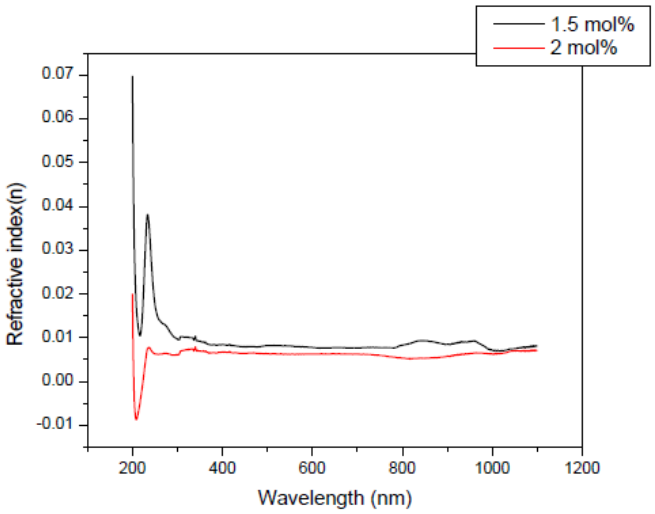


Fig. 12: UV-Visible Refractive index (n) of SHC doped SA single crystal

4. CONCLUSION

In the present work, the growths of optically high transparent single crystals of SHC doped SA have been carried out by solution method with slow evaporation technique. The lattice parameters were determined by using single crystal X-ray diffraction analyses. The presence functional groups in the grown crystal have been analyzed by FTIR spectroscopy. Vicker's micro hardness test confirms that the grown crystals are soft materials. The optical transparency of the grown sample has been revealed by UV-Visible Transmission Studies and its UV cut off wavelength of (SHC doped SA for 1.5mol%, SHC doped SA for 2mol %) crystals are found to be at 257 nm and 250 nm. The value of band gap energy was found to be 4.8 eV. The presence of dopants has improved the optical property of the grown crystals. Optical studies also confirm the high transparency of SHC doped SA crystal in the visible region. Hence these crystals can be used for optoelectronic applications.

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