Growth and Characterization of Semiorganic Non-linear Optical Material: (((4-aminophenyl)sulphonyl)oxy)zinc(II)chloride Crystal

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ABSTRACT

Growth and characterization of nonlinear optical (NLO) crystal of (((4-aminophenyl)sulphonyl)oxy)zinc(II)chloride (4-ASZC), based on zinc chloride with sulphanilic acid by the slow evaporation method has been studied and reported in this paper. The single crystal X-ray diffraction study confirmed the monoclinic system with centrometric space group P21. The sharp Bragg’s peak in powder X-ray diffraction analysis identifies the crystalline nature. Optical properties, such as low cut-off wavelength (251 nm), optical band gap (Eg = 4.40 eV), reflectance (R), extinction coefficient (K) and refractive index (n), are calculated from the UV-vis-NIR spectrum. The presence of functional groups are confirmed by the FT-IR spectroscopy. The placement of protons and carbons was determined by the NMR technique. The photoluminescence study shows the green light emission. The grown crystal is thermally stable up to 184°C. The NLO efficiency is 0.5 times greater than that of standard KDP. The mechanical properties were analysed. The dielectric constant (ε'), dielectric loss (ε''), imaginary dielectric constant (ε'''), AC conductivity (σac) and Cole–Cole graphs were plotted. The surface morphology and the particle size of the crystal were determined by the FESEM technique.

1. Introduction

Nonlinear optical semi-organic materials play a wide role in fast-developing fields such as optoelectronics, optical modulation, optical switching frequency shifting, signal processing, sensor, and optical data storage for the development of technologies in telecommunication and information process [1–5]. This nonlinear optical materials are very important for the current researchers due to its commercial importance for producing the second and third harmonic generation and have been studied over the past three decades [6–8]. The special types of organometallic molecules and bulk size crystals have been examined for their optical properties [9,10].

In the review of literature of sulphanilic acid and its base crystals: methylammonium sulphanilate [11], tetrabutylammonium 4-aminobenzenesulphonate 2/3 hydrate [12], piperazine-1-4-dilium bis(4-aminobenzensulphonate) [13], sulphonic acid doped L-proline and L-lysine [14], sodium sulphanilate dehydrate (SSD) [15,16], lithium sulphanilate hydrates (LS) [17], potassium carbonate sulphanilic acid [18], lithium sulphate, zinc sulphate, cadmium sulphate [19] [Bi9O12(OH)] (NH2C6H4SO3)4 [20], sulphanilic acid monohydrate [21], N,N-thiocarbonyl bis(4-aminobenzenesulphonamide) with barium chloride [22], and shiff-based sulphanilic acid-based crystals, sulphanilic acid single crystal, bis(4-aminobenzenesulphonato-kappa N)bis(2,2′-biimidazole-kappa N-2,N′)copper(II)-dihydrate [23–30] have been studied and reported. Organic-based materials showed excellent mechanical and thermal responses compared with inorganic-based materials because of π-electron delocalization [31,32]. Similarly, pure sulphanilic acid has shown centrosymmetric properties, but when embedded with metals/metal ion it becomes a non-centro symmetric material, demonstrating nonlinear optical activity.

Intermolecular communications are responsible for crystal packing and gaining knowledge in this enables us to design new crystals with specific physical and chemical properties [33,34]. Intermolecular interactions, such as hydrogen bonding (π–π interaction), ion pairing, supramolecular interaction, acid base adducts, donor and acceptor interactions, are famous for making aggregates of molecules [35]. Hydrogen bonding interactions are very important to the organic and inorganic species because they aggregate and control self-assembly, in most of the cases sulphanilic acid-based compounds have hydrogen bonds. Sulphanilic acid (SAA) compound is widely used in the field of radiation therapy, biological, biomedical, supercapacitor and drug delivery application [14–16]. It is also used as a monomer for the preparation of various copolymers and shows a conductivity, bio-imaging, humidity...
sensor application [15,36,37]. The sulfanilate anion can act as a hydrogen bond donor and acceptor due to its aminogroup and protonated sulphonate moiety [21]. Similarly, sulfanilate anions can easily co-ordinate with transition metals through both the amine and the sulphonate groups [22].

In the present investigations of proton transfer, single crystals of (((4-aminophenyl)sulphonyl)oxy)zinc(II) chloride(4-ASZC) were grown by the slow evaporation solution technique. The grown crystal is characterized by single crystal X-ray diffraction, powder X-ray diffraction, Fourier transform infra red Spectroscopy (FT-IR), UV-Visible, Photoluminescence (PL), Nuclear magnetic resonance (NMR), thermal properties (TGA-DTA), dielectrical properties, nonlinear optical properties (NLO), Mechanical properties, Field effect scanning emission microscopy (FESEM) and Energy Dispersive Atomic X-ray Spectrometer (EDAX). All the obtained results are reported and discussed.

2. Experimental methods

2.1. Material synthesis and characterization

The compound sulphanilic acid (SAA) (98%) and zinc chloride (99%) were purchased from Sigma-Aldrich and Merck Chemicals Company, respectively. These chemicals were used without purification and the grown crystals were subjected to single crystal X-ray diffraction studies using an ENRAF NONIUS CAD4 diffractometer with MoKα radiation (λ = 0.71073 Å) to determine the unit cell dimensions and crystal system. The powder samples were analysed by using BRUCKER, Germany (model D8 Advance) X-ray diffractometer with cuk alpha (wavelength = 1.5405 Å) radiation. It was scanned over the range 10–80° at a scan rate of 1°/min. Infrared spectra were recorded using Alpha Bruker ATR-FT-IR with a resolution of 2 cm⁻¹ and the measurements were carried out at room temperature. ¹H & ¹³C NMR spectra of the crystals were run on a Bruker FT-NMR spectrophotometer operating at 400 MHz at room temperature using dimethylmethoxide (DMSO) as a solvent and tetramethylsilane (TMS) as an internal reference. The optical transmission spectrum was recorded using DOUBLE BEAM UV-Vis Spectrophotometer in the region 200–1200 nm. The excitation and emission spectra of crystal were recorded using the Cary Eclipse spectrophotometer. The thermal stability of the crystals was estimated using a thermogravimetric analysis (TGA), with the Dupont 951 thermogravimetric analyzer. The sample weight was 8–10 mg. The work was performed from 30 to 800°C at the heating rate of 20°C min⁻¹ in a nitrogen atmosphere with a gas flow rate of 100 ml min⁻¹. The Vicker’s hardness test was carried out on the grown crystal using SHIMADZU HMV microhardness tester fitted with a diamond pyramidal indenter. The dielectric constant and the dielectric loss of grown 4-ASZC crystal were estimated using HIOKI 3532-50 LCR HITESTER. The elemental analysis was done using the Oxford INCA EDAX.

2.2. Solubility

The solubility studies were carried out using water (polar solvent) and dimethyl formide (non-polar solvent) in the ranges from 35°C to 60°C. The solubility increases gradually with the increase of temperature, as indicated by the graph Figure 1. From the graph, it is understood that 4-ASZC possesses a positive temperature coefficient. It is concluded that the magnitude of water solubility is slightly higher compared with that of dimethyl formide due to N–O–H bond break in high temperature and the formation of ionic bond [36,37].

2.3. Growth of 4-ASZC crystal based on zinc metal with SAA

Zinc metal-based novel crystals were synthesized using the slow evaporation solution technique at a room temperature and the short procedure is presented in Table 1. The estimated amounts of sulphanilic acid, zinc chloride and de-ionized water were taken in a 400 ml round bottom flask and stirred by a constant magnetic stirrer to ensure homogenous mixing of solutions. The stirred reaction mixture is heated up to 40°C for 2 h, after which the temperature is slowly reduced to room temperature. Subsequently, the reaction mixture

![Figure 1. Solubility curve of 4-ASZC crystal.](image-url)

Table 1. Growth of 4-ASZC crystal.

| S.No | Techniques               | Slow evaporation                  |
|------|--------------------------|-----------------------------------|
| 1    | Solvent                  | De-ionized water                  |
| 2    | Zinc chloride and        | 1:1 molar ratio                   |
| 3    | Sulphanilic acid         | First 2 h 40°C and remaining      |
| 4    | Temperature              | 10 h room temperature             |
| 5    | Period of growth         | 65 days                           |
| 6    | Crystal size (dimension) | 8 x 6 x 2 mm³                     |
| 7    | Colour of crystal        | Colourless                        |
| 8    | Rate of growth           | 0.02–0.25 mm/day                  |
was stirred for 10 h at room temperature. The saturated solution was filtered four times with 4-micron pore size filter paper. The prepared clear solution was poured into a beaker and covered. The high degree of purification of synthesized crystal was achieved by the successive re-crystallization process with aluminium foil sheet and housed for slow evaporation of the solvent. After 65 days, the solvent was evaporated and good quality transparent crystals are obtained. The bulk crystal has formed with a dimension 8 × 6 × 1.5 mm.

Figure 2 shows the as-grown crystal of 4-ASZC scheme and Figure 3 is shown as a photograph of the grown crystal. The crystal parameters are listed in Table 1.

The grown 4-ASZC crystal consists of nitrogen (N), hydrogen (H) and oxygen (O) which make a new hydrogen bond like N–H–O \[34,36\]. Similarly, zinc metal ion (Zn\(^{2+}\)) formed a new coordinate bond with oxygen (O) like a bidentate ligand (Zn\(^{2+}\)–O–S) \[37\]. The formation of the chain and the bonding process was possible because of the embedded zinc metal ion to the zwitter ionic compound of SAA. The ORTEP structure of 4-ASZC crystals is shown in Figure 4.

3. Results and discussion

3.1. Single crystal analysis

The unit cell parameter of the grown 4-ASZC single crystal is given in Table 2 along with the previously reported data. It shows 4-ASZC is in a monoclinic form with non-centro symmetric space group P2\(_1\).

From the stereo dimensional frame work of the structural analysis, it is found that there are two strong interactions of hydrogen bonds N–H–O and H–O–H with an average length equal to 0.89 Å and 0.82 Å, respectively \[38,39\]. The proton transfer sulphonate anions interact with the opposite charged sulphanilic acid of anilinium cations to form the stacking structure along
Table 2. Unit cell parameters’ pure sulphanilic acid and embedded 4-ASZC grown crystal.

| Parameter              | SAA [14] | TBSA [22] | 4-ASZC |
|------------------------|----------|-----------|--------|
| Chemical formula       | C₆H₇NO₃S·H₂O | C₁₃H₁₂Cl₂N₄O₣S₃Ba₂⁺ | C₂₆H₂CINO₃SZN⁺²⁺ |
| Molecular weight       | 191.2    | 730       | 247.02 |
| a Å                    | 6.16     | 7.33      | 6.49   |
| b Å                    | 6.96     | 7.55      | 18.39  |
| c Å                    | 18.32    | 13.98     | 6.81   |
| α                      | 90°      | 90°       | 90°    |
| β                      | 90°      | 90°       | 90°    |
| γ                      | 90°      | 90°       | 90°    |
| V (Å³)                 | 786      | 773       | 810    |
| Crystal system, Space group | Orthorhombic P₂₁2₁2₁ | Orthorhombic P₂₁2₁2₁ | Monoclinic P₂₁ |
| Crystal size (mm³)     | 0.25 x 0.22 x 0.2 | 15 x 6 x 1.2 | 8 x 6 x 2 |
| Colour                 | Pale yellow | Light yellow | Colourless |

Figure 5. The stacking structure of 4-ASZC crystal.

Figure 6. Powder XRD pattern of grown 4-ASZC crystals.

Table 2. Unit cell parameters’ pure sulphanilic acid and embedded 4-ASZC grown crystal.

The crystallography forms shown in Figure 5(a,b) and structure 5(c). The crystal structure is established by the intramolecular hydrogen bond to form a three-dimensional network. The whole system of crystal is neutral due to the crystal system in zwitter ionic nature [36]. Hence it is concluded that the formation of N–H–O type of hydrogen bond interaction is the most possible one.

3.2. Powder X-ray diffraction analysis

In the present examination, powder XRD analysis of the sample was carried out by subjecting the fine powder of 4-ASZC crystals to intense X-rays of λ = 1.5418 Å at a scan speed of 5° per minutes in steps, over a 2θ range of 10°–80° and is shown in Figure 6. The sample is pure crystalline in nature which is established from the sharp peaks at the diffraction 2θ angles 13°(001), 18°(10-1), 21°(121), 24°(131), 26°(002) and 27°(051).

3.3. Optical transmission studies

The optical property material is widely used for studying the atomic structure, dielectric properties, electrical properties, energy band structure, impurity levels, localized defects, lattice vibrations, metal predictions and certain magnetic excitations [40]. The recorded optical spectrum is shown in Figure 7(a) for transmission spectra and Figure 7(b) for absorption spectra. From the spectrum, the cut-off wave length of the sample is at 251 nm.

The sharp, high-intensity peak confirms the formation of a new band between oxygen of sulphanilic acid and zinc chloride through zinc metal oxide O–Zn²⁺ [41–43]. Very low cut-off wavelength is a superior property for processing NLO activity and device application [43].

3.3.1. Determination of band gap and optical constant for 4-ASZC crystal

This data obtained from UV-Visible spectrometer are widely used to determine the band structure and the type of electron transition of grown crystal [40]. The optical absorption coefficient (α) was calculated from the measured transmittance (T) spectrum using the following equation.

\[ \alpha = \frac{(2.3026 \log(1/T))}{\tau} \] (1)
Here, $T$ is the transmittance and $t$ is the thickness of the crystal. As an optical band gap energy material, the crystal fulfils the following relation for high photon energies $(h_\nu)$:

$$\alpha h_\nu = A (h_\nu - E_g)^{1/2}$$  \hspace{1cm} (2)

where $E_g$ is the optical band gap energy $A$ is a constant. $h$ is the plank’s constant and $\nu$ is the frequency of the incident photon. The Tauc’s plot for the variation of $(\alpha h_\nu)^2$ versus photon energy $(h_\nu)$ is shown in Figure 8. Optical band gap energy was estimated by the extrapolation of the linear part and it is $E_g = 4.40$ eV. The wide band gap and large transmittance in the UV-Vis region clearly indicate the nature of the dielectric materials [23]. Previously reported UV cut-off wavelength and band gap energy of sulphanilic acid based crystals are compared in Table 3. In the table, the band gap energy and cut-off wavelength of grown crystal is slightly varied from the reported work.

From Equations (4) and (5), the refractive index $(n)$ can also be derived as

$$n = -\left(\frac{(R + 1) \pm \sqrt{3R^{2} + 10R - 3}}{2(R - 1)}\right)$$ \hspace{1cm} (6)

From the absorption spectra, the linear optical constants for example extinction coefficient, reflectance and refractive index of 4-ASZC crystal were calculated. The variation of reflectance, extinction coefficient and refractive index as a function of photon energy are plotted in Figures 9–11, respectively. The diagram of the extinction coefficient and reflectance show the dependency on the photon energies. The refractive index is 1.66.
3.4. FT-IR spectral studies

The FT-IR analysis of zinc chloride embedded with SAA crystal was carried out between 4000 and 400 cm\(^{-1}\). The spectrum of vibrational data is shown in Figure 12 and important functional groups are presented in Table 4.

![Figure 9](image_url1)  
**Figure 9.** The plot of reflectance (R) versus photon energy.

![Figure 10](image_url2)  
**Figure 10.** The plot of extinction coefficient (K) versus photon energy.

![Figure 11](image_url3)  
**Figure 11.** The plot of refractive index (n) versus photon energy.

### Table 4. The functional group and vibrational assignment peak of 4-ASZC.

| IR (cm\(^{-1}\)) | Assignment reference |
|------------------|-----------------------|
| 3697 and 3455    | N–H [23]              |
| 3002 and 2904    | C–H stretching        |
| 2652             | N–H stretching [22]   |
| 2904 and 2652    | N–H–O [36]            |
| 1669             | H–O–H [49]            |
| 1598             | NH\(_3\)+ [14]         |
| 1490 and 1420    | benzene ring           |
| 1367 and 1314    | SO\(_3\) stretching [14] |
| 1210             | C–N [16]               |
| 1170 and 1096    | S = O [16]             |
| 817              | C = S [40]             |
| 467 and 469      | Zn metal [43]          |

The peaks at 3697 and 3455 cm\(^{-1}\) are signature for N–H vibration that indicates all the NH\(_2\) converted into N–H in the lattices. The peaks observed at 2904 and 1096 cm\(^{-1}\) are assigned to C–H of phenyl ring and S = O stretching vibration, respectively. The presence of intramolecular hydrogen bond between sulphanilic acid and amine group is observed in the range of 2228 to 2652 cm\(^{-1}\). The asymmetric bending vibration of anilinium ion (–NH\(_3^+\)) occurs at 1598 cm\(^{-1}\). The asymmetric vibration of SO\(_3^−\) gives the peaks at the range of 1314 and 1367 cm\(^{-1}\). The C–N stretching vibration occurs at 1210 cm\(^{-1}\). The peak at 556 cm\(^{-1}\) is due to torsional oscillation of NH\(_3^+\). The symmetric structure of C = S stretching vibrations at 817 cm\(^{-1}\) is shifted to low-frequency region at 678 cm\(^{-1}\). This study confirmed the presence of Zn\(^{2+}\) metal in the grown crystal [42–46].

3.5. Proton and carbon NMR spectra

\(^1\)H NMR spectra of 4-ASZC crystal were taken to investigate the environment of different protons, as shown in Figure 13(a). The sharp singlet intense peaks obtained at 4.45 ppm are due to the presence of hydrogen atom of NH\(_3^+\) ion. The two separate doublet peak appeared at 7.0–7.8 ppm in the ortho, meta aromatic
protons. The $^{13}$C NMR spectrum of 4-ASZC crystal is given in Figure 13(b). The important peaks appeared at 123–143 ppm correspond to aromatic carbons. A signal appeared at $d = 143$ allocated to the carbon atom of $C_2$ and $C_6$ and the medium intensity peak shown at 132 ppm is attributed to $C_3$ and $C_5$ carbon atom of the sulphanilic moiety. The 4-ASZC crystal moiety appears as a resonance signal at the 143 ppm character of $C_1$ and $C_4$ carbon bearing (SO$_3$ and NH$_2$).

In this present study, photoluminescence (PL) measurement is an important tool for determining the crystalline quality of a system and its extension fine structure [42]. The PL spectral details of pure and doped crystal are shown in Table 5. Figure 14 exhibits PL emission spectrum recorded in the range of 150–900 nm with an emission wavelength of 593 nm. The emission peaks were seen at 517 and 593 nm, demonstrating the emission from green to red light. A higher intensity ratio specifies better purity and crystallinity of 4-ASZC. The broadening of emission band is due to lattice vibrations in the 4-ASZC crystal. The strong PL emission indicates its potential application in optoelectronic device and lighting technologies [40,47].

### 3.6. SHG efficiency spectra

The measurement of the second harmonic generation (SHG) efficiency was found out by the powder technique and developed by Kurtz and Perry [48–50]. For the SHG efficiency measurements, the output of a Q-switched Nd:YAG laser was used to generate about
2.8 mJ/pulse at 1064 nm fundamental radiation. A single shot mode of 8 ns laser pulse, rotation rate of 10 Hz with a spot radius of 1 mm was used. The input laser beam was allowed to pass through an IR reflector and then directed on the micro-crystalline powdered sample packed in a capillary tube of diameter 0.154 mm. The light emitted by the samples was measured by a photodiode detector and an oscilloscope. For the Nd:YAG laser, the fundamental beam of 1064 nm generates the second harmonic signal of 532 nm (green light).

The measurement of output pulse from 4-SAZC crystal is given in Table 6. Pure sulphanilic acid monohydrate crystal does not appear in the green signal due to the centrosymmetric crystal, but metal embedded SAA crystals show good SHG efficiency because of non-centrosymmetric materials. The enrichment of SHG efficiency for 4-SAZC crystal is due to the optically active \(\text{Zn}^{2+}\) metal which modified the structure into non-centro symmetry. The SHG efficiency of the 4-SAZC sample is 0.5 times that of standard KDP crystal. Thus the grown crystal has good NLO property.

### 3.7. Thermal analysis of 4-ASZC crystal

A comparative study of the thermal stability of sulphanilic acid-based crystal [14–23] reveals that the doping increases the melting point of the pure sulphanilic acid crystal. Hence the 4–ASZC crystal was subjected to TG/DTA analysis to examine the change in thermal stability. The obtained thermogram is shown in Figure 15.

The grown crystal 4-ASZC shows two-stage decomposition; initially, the negligible amount of weight is lost (0.4%) at 184°C and completely decomposed (99.6%) at 237°C. So this indicates the grown crystal is thermally strong up to 180°C, the fraction of decomposition of the crystal at 184°C is due to the breakage of intramolecular hydrogen bonding between sulphanilic acid and amine group and the remaining grown crystal part is fully decomposed at exothermic peak 237°C. The grown crystal is 100% water-free crystal because there is no peak in the TGA graph at the boiling point of water. It is concluded that the crystal has a high melting point and exhibits high thermal stability by the addition of \(\text{Zn}^{2+}\) metal.

### 3.8. Mechanical study of 4-ASZC crystal

It is important to find the hardness of the crystal. The network of the crystal, purity and nature of the bonded influences its hardness. The Vickers microhardness tests are the globally accepted techniques for the measurement of structural and mechanical properties of the crystal. This method is a non-destructive one and will quickly yield quantitative information about the strength of materials. The experiment was carried out using SHIMADZU HMV microhardness tester fitted with the diamond pyramidal indenter [51–56]. Figures 16 and 17 are the obtained Vickers microhardness graphs of the grown 4-ASZC crystal.

The indentation time was kept constant for 10s and the microhardness measurement was taken between...
the different applied load \((P)\) ranging from 25 to 100 g. The average diagonal length was determined. The Vicker’s hardness number was determined using the formula

\[
H_v = 1.8544P/d^2 \text{ (kg/mm}^2) \tag{7}
\]

A graph was plotted between \(H_v\) versus load \((P)\) as shown in Figure 16. It is concluded that \(H_v\) increases with the applied load, which is known as the reverse indentation size effect (RISE). For an indentation load of 100 g, a crack was noted on the crystal surface around the indent and it is due to the release of inside stress locally initiated by indentation. The work hardening coefficient \((n)\) was computed (6.0) from the slope of a straight line between log \(P\) and log \(d\) from Figure 17. It indicates that the grown crystal belongs to the soft nature of material. The yield strength of the material can be elucidated by the relation [56–58].

\[
\sigma_y = \frac{H_v}{3}(0.1)n - 2 \tag{8}
\]

where \(n' = n + 2\), \(\sigma_y\) is the yield strength of the material, \(H_v\) is the hardness number and \(n\) is the work hardening coefficient. The graph drawn for load \(P\) versus yield strength is shown in Figure 18.

It is shown that yield strength increases with the expansion of load, and it is concluded that the grown crystal has moderate high mechanical strength. As indicated by Wooster’s, the stiffness constant \((C_{11})\) for single crystal can be found by the relation

\[
C_{11} = \frac{H_v^{7/4}}{4}. \tag{9}
\]

A graph is plotted between load \(P\) and stiffness constant, as represented in Figure 19. Stiffness constant increases with load. The calculated stiffness constant \(C_{11}\), yield strength \(\sigma_y\) and Vickers’s hardness value for different loads are compiled in Table 7.
### Table 7. The mechanical properties of 4-ASZC crystal.

| Load P (g) | H, Kg/mm² | D µm | Yield strength (σₚ) Kg/mm² | Elastic stiffness constant (C₁₁) | Fracture toughness (Kc) x 10⁴ kg/m⁹/² | Brittleness index (B) m⁻¹/² |
|------------|-----------|------|--------------------------|-------------------------------|----------------------------------|-----------------------------|
| 25         | 30.3      | 39.055 | 0.436                    | 584.313                       | 5.291                            | 782.451                     |
| 50         | 47        | 44.378 | 0.676                    | 749.668                       | 7.241                            | 698.617                     |
| 100        | 78        | 49.0025 | 1.122                    | 2347.22                       | 13.854                           | 691.247                     |

3.9. Dielectric studies of 4-ASZC crystal

The dielectric constant with dielectric loss of the grown crystal 4-ASZC was calculated by the universally accepted equation [59–63].

\[ \varepsilon = \frac{cd}{A\varepsilon_0} \]  
\[ \varepsilon' = \varepsilon \tan\delta \]

here \( d \) is the thickness similarly \( A \) is the area of the sample.

Figures 20 and 21 display the variety of dielectric constant and dielectric loss, respectively, as a function of frequency at various temperatures. It is concluded from Figure 20 that the dielectric constant decreases with the increase in frequency from 50 Hz to 5 MHz and then becomes almost constant. The comparative pattern is estimated for different temperatures. It is furthermore seen that the estimation of dielectric constant increments with temperature. Such variation at higher temperatures may be credited to the accumulation of charge carriers at the electrodes. The decreases of dielectric constant at low-frequency region may be because of space charge polarization. Figure 21 exhibits that as the frequency increases, the dielectric loss decreases exponentially and then becomes constant. The low value of dielectric loss affirms that the sample possesses lesser imperfections.

The alternating current (AC) conductivity \( \sigma_{ac} \) is calculated using the equation [48–50],

\[ \sigma_{ac} = \frac{2\pi F\varepsilon_0\varepsilon'}{\tan\delta} \]
where \( \tan \delta \) is the dielectric loss estimated directly from the impedance analyzer and \( F \) is the frequency of the applied AC field (Hz). The graph is plotted with AC conductivity \( (\sigma_{ac}) \) verses \( \log f \) and it is shown in Figure 23. It was observed that the crystal has very low conductivity in the low-frequency region up to 40 kHz for all temperatures. Thereafter, the AC conductivity was found to be increasing feebly up to 4 MHz. This indicates the dielectric breakdown frequency of this material. The value of the total electrical resistance is evaluated from the Cole–Cole plots shown in Figure 24, plotted between \( Z' = Z \cos \Theta \) (real part of impedance) and \( Z'' = Z \sin \Theta \) (imaginary part of impedance). From these plots, the bulk resistance measured was found to be decreased with increasing temperatures, resulting in the enhancement of electrical conductivity at higher temperatures.

3.10. FESEM study of 4-ASZC

In order to analyse the nature and surface morphology, FESEM analysis was employed and the grown crystal was cut into few mm. The FESEM images of 4-ASZC crystal captured in four various magnifications are shown in Figure 25. The images show zinc metal ion incorporated in to 4-ASZC grown crystal, which suggests the existence of particle boundaries and the surface smoothness appears. This figure shows the presence of few cracks on the crystal surface.

3.11. EDAX analysis of 4-ASZC crystal

The basic investigation about the compounds present in a material is carried out by using the Oxford INCA Energy Dispersive Atomic X-ray Fluorescence Spectrometer (EDAX) [50]. This technique is widely used in the quantitative analytical method and the EDAX spectra of 4-ASZC crystal are shown in Figure 26. Although the presence of zinc chloride embedded 4-ASZC crystals was confirmed using the EDAX analysis, it is difficult to be quantified due to the small amount of crystal zinc metal atoms and limitation of the analysis to measure chloride composition. However, the presence of zinc metal and chlorine atom is shown and it is confirmed with the 4-ASZC crystal lattice. The atomic percentage and weight percentage of elements present in the crystal lattices are shown in the corresponding table.

![Figure 23. ac conductivity (δac) versus log f for 4-ASZC crystal.](image)

![Figure 24. Cole–Cole plots of 4-ASZC crystal.](image)
4. Conclusion

The successfully grown 4-ASZC crystal is based on SAA with zinc chloride, a semi-organic single crystal was accomplished by the slow evaporation technique from an aqueous solution. A slight change in the lattices parameters and volume of the crystal was discovered in 4-ASZC crystal and it is monoclinic with space group P2₁2. The UV cut-off wavelength 251 nm and this transparent nature in the entire visible region of UV-Vis-Nir spectrum reveal the grown crystal is the potential candidate for NLO applications. Optical band gap \( E_g = 4.40 \text{ eV} \) reflectance \( R \), extinction coefficient \( K \) and refractive index \( n \) are of 4-ASZC crystal as found using UV-Vis-Nir spectrum data. The FT-IR spectrum uncovers the formation of anilinium ion and formation of hydrogen bond N–H–O in the 4-ASZC crystal. From the photoluminescence studies shown in green light emission and the optical property materials are confirmed. The chemical structure and molecular arrangement position of the grown crystal were established by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectrum, respectively. The SHG of the powdered 4-ASZC has crystal that is around 0.5 times that of unadulterated KDP. The thermal behaviour of the grown crystal is shown with a melting point at 184°C and stable up to 237°C. From the mechanical studies, stiffness constant \( C_{11} \), yield strength \( \delta_y \), hardness \( H_v \) and hardening coefficient \( n \) are calculated and the corresponding graphs are plotted. From this study, the grown crystal shows high conduction at higher temperature with low frequency. The surface morphology and the particle size of the crystal were determined through the FESEM technique. The elemental analysis was carried out by energy-dispersive X-ray dispersion and it confirms the presence of Zn metal.
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