Growth, Nonlinear Optical, Electrical, Mechanical and Dielectric Properties of Zinc Sulphate Doped L-Alanine Single Crystal for Optoelectronic Applications

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Abstract. Zinc sulphate added L-alanine (LAZS) crystals were obtained from solvent evaporation of solution method. The obtained samples were taken for diverse characterizations tool such as, XRD, functional group identification, optical transparency, simultaneous thermal analysis, dielectric, hardness and second harmonic generation studies. Crystal diffraction study proves that LAZS crystal fit into orthorhombic system and having space group P2₁2₁2₁. FTIR confirms presences of various functional groups present in the sample. The thermal study infers that LAZS is steady up to 288 ºC. High transmittance and extended transparency of LAZS is noticed from linear optical study. The calculated hardness values were found to be considerable and the dielectric parameters are noticed characteristically followed by NLO study.

Keywords: alanine, zinc sulphate, evaporation, hardness, SHG

1. Introduction

Research on novel hybrid NLO materials is becoming fascinating since their nonlinear optical effects used in optical communication and other significant electro optical applications [1-7]. Organic molecules having conjugated bonds possess high inherent nonlinearity, synthetic flexibility, and noticeable laser damage threshold. On the other side, Inorganic materials are covalent and ionic and the NLO nature is a combined effect. In case of semi organic crystals, it so happens that, when organic materials are mixed with inorganic materials, the resulting hybrid materials share the characteristics of both the above with the improved properties. L-alanine (LA) having the zwitterionic structure (\(\text{NH}_3^+\) and \(\text{COO}^-\)) both in solid state and also in aqueous solution. LAL has orthorhombic nature with cell parameters values of \(a=6.302\text{Å}\) \(b=12.343\text{Å}\) \(c=5.78\text{Å}\) [8-10]. The various combinations of LAL single crystals have been accounted recently in the scientific literature [11-15]. In this context, LAZS crystal was grown by the solvent evaporation method and subjected to different characterizations to explore its potential properties and the results are discussed.
2. Experimental

2.1. Synthesis and crystal growth

The crystal under study was harvested using AR grade LA and zinc sulphate in a 1:0.1 molar ratio. The chemicals were methodically liquefied in the considered quantity of water and stirred well. The obtained solution is filtered and kept to crystallize. Because of homogeneous nucleation, seed crystals were created. Further, solvent evaporation led to crystals with the dimensions of 35x15x8 mm$^3$ were obtained in 38 days and is depicted in Figure 1.

![Figure 1. As grown LAZS crystals.](image)

3. Results and discussions

3.1. XRD studies

The diffraction study of LAZS crystals was carried out with a Bruker Smart Apex Duo diffractometer. The study validate that LAZS fit into orthorhombic crystal family having the space group $P2_12_12_1$ with unit cell parameter $a = 5.78$ Å, $b = 6.09$ Å, and $c = 12.35$ Å, $\alpha = \beta = \gamma = 90^\circ$ with volume $V = 430$ Å$^3$. These values of LAZS are in concurrent with the reported values of pure LA [9].

Well-grounded sample was examined by powder XRD (Bruker AXS D8). Typical 20 scan having rate of 2 degree/minute has been made from 10$^\circ$ to 70$^\circ$. In doped materials, both intensities and 2ø values were shifted due to the active role of dopant in the lattice of the grown crystal but there is no alteration in the crystal system. The obtained pattern is in Figure 2 and it reveals the well crystalline character.

![Figure 2. Powder X-ray diffraction patterns of LAZS](image)
3.2. **FTIR spectral analysis**

The presence of different functional groups in terms of molecular vibration and corresponding chemical bonding were noticed by Avatar 370 FT-IR spectrum spectrometer in the series 4000-400 cm\(^{-1}\) and Figure 3. is the resulting spectra.

![Figure 3. The FTIR spectra of the LAZS crystals.](image)

The wide-ranging peak at 3087 cm\(^{-1}\) could be of the NH\(_3^+\) asymmetric vibrations also the amine group of NH\(_3^+\) bending is with the intense peak at 1617.99 cm\(^{-1}\). Asymmetric bending vibrations of NH\(_3^+\) were at 2249 cm\(^{-1}\) and 2111 cm\(^{-1}\). The symmetrical stretching of CO\(_2\) is at 1412 cm\(^{-1}\). The peak at 1360 cm\(^{-1}\) indicates the C-H deformation in CH\(_3\). NH\(_3^+\) rocking and C-O stretching is attributed to the sharp peak at 1108 cm\(^{-1}\). The C = O bending is at 774 cm\(^{-1}\) and the deformation of COO\(^-\) is about 648.03 cm\(^{-1}\). FTIR analysis confirms the presence of the predictable groups of LAZS.

3.3. **UV-Visible absorption Studies**

It gives information about molecular information as it involves the electron movement in \(\sigma\) and \(\pi\) orbital from the lower to elevated states. The crystals with wide and high transmittance value possess improved SHG leads to better performing materials. In the range 200 to 1600 nm, the optical absorbance spectrum was recorded and is depicted in Figure 4. Further, there is no noticeable absorption peak region of study. The cutoff wavelength of the LAZS is found to be 282 nm which is sufficient for many applications. Hence, both fundamental and second harmonic wave transmission could be achieved which suggests for possible potential applications.
Figure 4. The UV spectra of LAZS crystals.

Generally, optical band gap ($E_g$) is the threshold for the photons to be absorbed. This calculation helps in understand the possible transitions in the crystal. Here, the absorption coefficient ($\alpha$) was calculated by

$$\alpha = \frac{1}{d} \log \frac{1}{T}$$

Here, $\alpha$ was calculated through the equation

$$ahv = Q(hv - E_g)^n$$

Where $Q$ a constant and $n$ is an index, which can have the values with respect to the type of the transitions. Accordingly the equation becomes

$$\alpha = \frac{A(hv - E_g)^{1/2}}{hv}$$

By considering the graph of $(ahv)^2$ versus $hv$ in eV as shown in the Figure 5, and the resulting band gap and is found to be 5.1 eV.

Figure 5. Graph of $(ahv)^2$ versus energy $hv$. 
Since refractive index ($n$) is a function of wavelength and it has influence on NLO nature. It is a photon energies reliant function showing the crystal internal ability which is required for the solid state devices. The calculated $n$ value of LAZS is 1.98 as obtained from below equation.

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \frac{E_g}{20}$$

Where, $E_g$ is the band gap

All these UV associated parameters used to compute the electrical susceptibility ($\chi_c$) based on the consideration that, generally the naturally obtainable ones are non-magnetic at optical frequencies and hence, their $n$ value is almost same as relative permittivity of the materials which is given by

$$\chi_c = \varepsilon_r - 1$$

Or

$$\chi_c = n^2 - 1$$

Thus, $\chi_c$ value of the crystal is found to be 2.94. If the resulting value of $n$ is greater than unity then, crystal can easily be polarized by exposing to intense light. These optical properties show the internal efficiency of LAZS for the solid state device applications.

3.4 SEM and EDAX studies

The surface character of LAZS was studied by JEOL JSM-6390LV model SEM instrument and the recorded image is depicted in Figure 6. Since organics are generally insulating, to make it conductive and to achieve good emission of secondary electrons the carbon coating was made before exposing the crystal to electron beam. LAZS crystal has almost smooth surface however, few micro cracks.

![Figure 6. SEM image & EDAX spectrum of LAZS crystals](image)

EDAX technique is essential in identifying the presence of elements in the sample wherein it measures the number of characteristic X-rays produced by the innermost shell of a specific element present in the sample. LAZS EDAX spectrum is depicted in Figure 6. and it confirms the presence of zinc sulphate in the L-alanine.

3.5. Thermal (TG-DTA) studies

These were used to determine the thermal activity of LAZS. The thermal behavior of LAZS was made in presence of nitrogen at the rate of 10°C/min. between ambient temperatures to 800°C. The
primary weight of LAZS was 8.4 mg. The TGA plot (Figure 7) signifies the single stage of sample decay.

![Figure 7. TG-DTA Thermogram of LAZS crystal](image)

In the beginning, there is no weight loss until the temperature exceeds 210°C, after which the sample starts to decay and reaches 289°C. The dissociation of LAZS causes mass loss between 210°C and 289°C. The dissociation of the LAZS structure is seen through strong endothermic peak in the DTA curve. The material's strong crystalline quality and purity are shown by the sharp curve. As a result of the TG-DTA analysis, LAZS is stable and can be used in devices up to 288°C.

3.6. SHG studies

To recognize the NLO property of LAZS, Kurtz powder method was used [16]. Nd:YAG laser (1064 nm) beam having input power of 1.9 mJ/pulse was used for the study. Well-grounded sample of same particle size (125-150 μm) were filled in a capillary and exposed to the laser with KDP and urea as reference. Emitted green light (532 nm) from the LAZS confirmed the SHG from the crystalline sample and it showed the corresponding efficiency of 0.9 and 0.6 times that of pure KDP and urea sample respectively.

3.7. Dielectric studies

The electric field distribution of the sample and its frequency dependence will decide the material applications. Dielectric measurements were carried out with HIOKI-LCR HiTester 3535 from 100Hz to 5MHz. The silver paste is added as parallel plates to the opposite faces of the crystal dielectric parameters and AC conductivity (σac) along with frequency dependence were observed at ambient temperature.

Dielectric constant (εr) was calculated through the relation εr=C/tεoA, and its variation with and applied frequency was noticed along with loss factor tanδ and are shown in Figures 8 and 9 respectively. It is seen that the value of εr weakens with frequency increment and finally attains constant at elevated frequencies which is a normal dielectric behavior. At low frequencies all the four polarizations are significant which depend on limpidness and perfection of the crystal. On increasing frequency, in sequence, the polarization mechanisms will be neutralized since they will become incapable to respond in accordance with change in electric field. At higher frequencies (10¹⁵Hz) electronic polarization will have major role. The low εr value materials possess the possible potential applications in microelectronics. Further, With increasing frequency, dielectric loss also decreases. The sample's low dielectric loss at high frequency indicates that it has good optical efficiency and minimum defects.
The AC conductivity was measured by using the relation \( \sigma_{\text{ac}} = \varepsilon_r \varepsilon_0 \omega \tan \delta \) where \( \varepsilon_0 \) is the free space permittivity and \( \omega \) is the applied field's angular frequency and is depicted in the Figure 10. The conductivity increases as the frequency increases, as seen in the graph. This feature is endorsed to the decrease in the electronic polarization at upper frequencies.

### Figure 8. Dependence of dielectric constant on frequency

### Figure 9. Variation of dielectric loss with frequency

### Figure 10. Variation of AC conductivity with frequency

#### 3.8. Microhardness studies

The hardness analysis assists in the comprehension of the crystal's strength and deformation. It's also important to note that the mechanical properties of NLO materials have a strong relationship with their resistance to structural destruction or deformation. Its value is determined by the elastic and plastic properties of the indenter under study, as well as the measurement conditions. The Micro Indentation Hardness Test is ideally suited for crystals, with forces usually below 2N.

The most commonly known pyramid indenter in which opposite sides converge at the apex at an angle (\( \alpha \)) of 136°. The ratio of the applied load to the region of the indentation is known as hardness. As a result, the Vicker's hardness number \( H_V \) is written as
\[ H_v = \frac{\text{Load}}{\text{Pyramidal area}} = \frac{2P \sin \left(\frac{\alpha}{2}\right)}{d^2} = \frac{1.8544P}{d^2} \text{ Kg/mm}^2 \]

The applied load \( P \) in gm, and the diagonal length \( d \) is measured in micrometers. Various weights from 5 to 250 gms may be used for indentation. The size of the indentation impression is determined using a calibrated microscope. The nature of calculated Hv values different loads is shown in the Figure 11.

![Figure 11. Variation of hardness number with applied load](image)

Here, Hv rises with increasing applied load and cracks were observed for loads greater than 100 gm. According to Mayer's law, the connection between applied load and indentation size is given by

\[ P = kd^n \text{ or} \]
\[ \log P = \log k + n \log d \]

Where, \( k \) is a particular material constant. The value of ‘n’indicates Mayer’s index. Plotting the graphs of log \( P \) and log \( d \) provides the value of \( n \) and which is normally linear in nature, and the resulting slope gives the \( n \) value. If \( n>2 \), Hv will increase as the load increases, and if \( n<2 \), Hv will decrease as the load increases. Moreover, for hard materials, the value ‘n’ should be between 1 and 1.6, while for soft materials, it should be greater than 1.6 [17]. Based on this, for the grown crystal the resulting graph is shown in Figure 12.

![Figure 12. Plot of log p versus log d](image)

The LAZS calculated ‘n’ value is 2.9 after the linear fitting suggest that it LAZS is soft material. Further, the elastic stiffness constant \( (C_{11}) \) gives an indication of the material’s peak energy absorption before a fracture occurs. It also expresses the concept of material resistance to deformation when a load is applied to a flat crystal surface. Further, In calculating the \( C_{11} \), the tightness of the bonding and
the rate of variance with the position of the atoms are the two most significant factors. The corresponding C11 value for the applied loads on the crystals was obtained from the following equation. According to Wooster’s formula given by

\[ C_{11} = (Hv)^{\frac{7}{4}} \]

Yield strength (\( \sigma_V \)) is the stress under which a material begins to warp plastically, before deforming elastically. The value of \( \sigma_V \) for the different loads was calculated by using the following equation and are tabulated in the table 2.

\[ \sigma_V = \frac{Hv}{2.9}[1 - (n - 2)] \left[ \frac{12.5(n - 2)}{1 - (n - 2)} \right]^{n-2} \]

### Table 1. Calculated mechanical parameters.

| Load P in gm | Hv (Kg/mm²) | \( \sigma_V \) (GPa) | C11x10¹⁴ Pa |
|--------------|-------------|----------------------|-------------|
| 25           | 43.55       | 12.79                | 7.38        |
| 50           | 57.1        | 16.78                | 11.86       |
| 100          | 79.5        | 23.36                | 21.16       |

4. Conclusions

L-alanine zinc sulphate (LAZS) crystal was grown by slow evaporation method. LAZS fit into orthorhombic system and is stable up to 288 °C as observed from diffraction and thermal studies respectively. UV study illustrates that LAZS has extensive transparency in complete visible and NIR regions with cutoff wavelength of 282 nm. According to dielectric studies LAZS has a normal dielectric nature with minimal defects. The SHG conversion efficiency of LAZS is 0.9 and 0.6 times that of KDP and urea respectively. The hardness of LAZS diminishes with load and also confirms the absence of liquid inclusions. With increased transparency, thermal stability and NLO efficiency of LAZS proposes that, it can be a useful candidate for device applications.

5. References

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