Crystal growth and enhancement of Optical, and Electrochemical properties in L-asparagine monohydrate admixtured with oxalic acid dihydrate (1:1 ratio) for optoelectronic and photonic applications

Abstract

Single crystals of L-Asparagine monohydrate admixtured with oxalic acid dihydrate in a (1:1 molar ratio) were successfully synthesized through the slow solvent evaporation method. The optical properties of the grown crystals were investigated using UV-DRS analysis. The absorbance and transmittance spectra reveal high optical transmittance within the visible spectral range, characterized by a well-defined lower cut-off wavelength, indicating minimal optical loss. fundamental optical parameters, such as the extinction coefficient, refractive index, reflectance, and optical conductivity, were analyzed as a functions of incident photon energy, providing insights into the light – matter interaction and electronic structure of the crystal. The electrochemical characteristics of the grown crystal were thoroughly examined using cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS). The cyclic voltammogram exhibits stable and reproducible electrochemical behaviour with no significant redox peaks, indicating good electrochemical stability and the absence of electroactive impurities within the measured potential window. The electrochemical impedence (EIS) measurements display a depressed semicircular arc, corresponding to the bulk response of the crystal and revealing non-Debye type relaxation behaviour. The large impedance values and high bulk resistance confirm the insulating nature of the crystal with minimal charge carrier mobility and reduced defect density. Electrochemical impedance bode plots characterize the system's frequency-dependent impedance, revealing a transition from resistive to capacitive behavior These electrochemical characteristics, combined with the inherent stability of the material, suggest that the prepared sample is well suited for photonic and optoelectronic applications.

Keywords: optical properties, cyclic voltammetry, Electrochemical impedance spectroscopy: optoelectronics and photonics.

Introduction

Over the years, the development of novel organic single crystals has garnered significant interest owing to their combined advantages of organic flexibility, low dielectric constant, and favorable optical properties making them promising materials for optoelectronic and photonic device applications **[1]**. Among amino acid-based crystals, L-asparagine monohydrate has emerged as an important material owing to its zwitterionic nature, wide optical transparency, and favorable optical characteristics **[2].** The incorporation of suitable organic acids as admixtures represents a potent approach to modulate the optical, impedance and electrochemical properties of such crystals.

Oxalic acid dihydrate is a well-known dicarboxylic acid that can form strong hydrogen-bonding networks with amino acids, leading to improved crystal quality and modified charge transport behaviour **[3, 4]**. L-asparagine monohydrate admixture with oxalic acid dihydrate in a (1:1 ratio) is expected to enhance the optical transparency, Impedence and electrochemical stability of the resulting single crystal through intermolecular interactions and reduced defect density **[5]**. However, systematic investigations on the electrochemical properties of this single-crystal system remain limited.

Optical transparency and electrical insulation are crucial requirements for materials intended for optoelectronic and photonic devices **[6]**. UV-DRS analysis provides valuable information on optical absorbance, transmittance and bandgap characteristics, while cyclic voltammetry offers insight into the electrochemical integrity and redox response of the sample **[7]**. Furthermore, electrochemical impedance spectroscopy serves as a powerful tool to evaluate bulk resistance, charge transport mechanisms, and dielectric relaxation behaviour, which are directly related to crystal quality and defect concentration

In this work, high-quality single crystals of L-asparagine monohydrate admixtured with oxalic acid dihydrate (1:1 ratio) were prepared by the slow solvent evaporation method **[8]**. The grown crystals were systematically characterized using UV-DRS spectroscopy, cyclic voltammetry, and electrochemical impedance spectroscopy to assess their optical transparency, electrochemical stability, and insulating nature **[9, 10]**. The obtained results demonstrate the potential of the developed crystal for optoelectronic and photonic device applications **[11]**.

Synthesis and crystal growth method

L-Asparagine monohydrate admixtured with oxalic acid dihydrate single crystals were synthesized by the slow solvent evaporation method. L-Asparagine monohydrate and oxalic acid dihydrate were combined in a 1:1 eqimolar ratio and dissolved separately in deionized water at ambient conditions. The resultant solutions were continuously stirred by a magnetic stirrer for approximately 5 hours to achieve a clear and homogeneous solution, ensuring complete dissolution and uniform molecular interaction between the constituents. The prepared solution was carefully filtered using whatman filter paper to eliminate insoluble impurities and suspended particles. The clear filtered solution was transferred into a clean crystallization vessel, covered with perforated sheets to facilitate controlled evaporation, and maintained undisturbed in a dust free environment without any disturbance. Gradual solvent evaporation led to gradual supersturation, resulting in the formation of transparent, well-defined single crystals with high optical quality after a growth duration of approximately 15 days.

Fig. 1 Photographic picture of APOD single crystals

Results and Discussion

1). UV-DRS

The optical characteristics of the prepared material were investigated by UV-Diffuse Reflectance spectroscopy (UV-DRS) over the spectral range of 200-800 nm **[12]**. The absorbance profile exhibits a sharp lower cut-off wavelength at 323 nm, which is attributed to the electronic transitions, predominantly ($n - \pi^*$) and (π -π^*) excitations associated with the functional groups incorporated within the crystal lattice. In particular, the presence of alcohol (-OH) groups contributes to these electronic transitions due to lone pair electrons on the oxygen atom **[13]**. The transmittance spectrum reveals a lower cut-off wavelength at 258 nm, indicating good optical transparency in the visible spectral region. The absence of significant absorption beyond the cut-off region confirms the potential of the crystal for optical applications **[14]**.

The wavelength dependent-refractive index was evaluated, and the dispersion curve was plotted over the spectral range of 200-800 nm, where the refractive index varies from 0.02 to 0.12, showing normal dispersion behavior. The reflectance spectrum, recorded over the same wavelength range, shows values ranging from -55 to -20, further supporting the optical response of the material **[15]**. These results collectively demonstrate the favorable optical characteristics of the synthesized crystal for potential optoelectronic and nonlinear optical applications **[16]**.

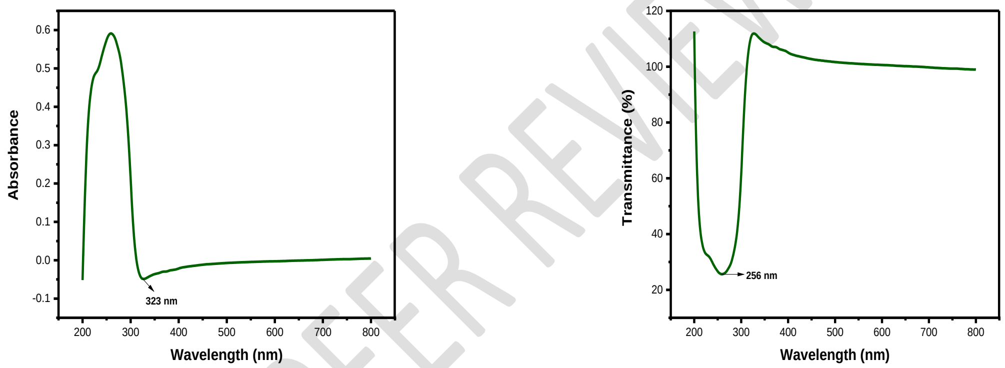
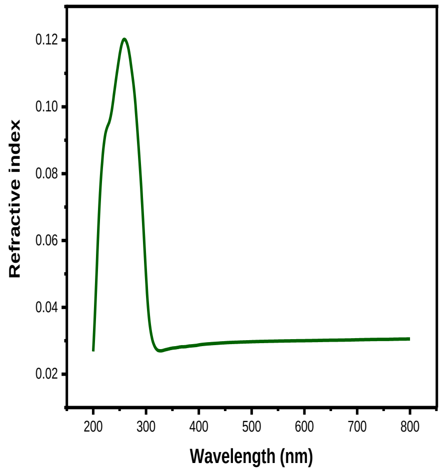


Fig. 2 (a) UV DRS - Absorbance **Fig. 2 (b)** UV DRS - Transmittance



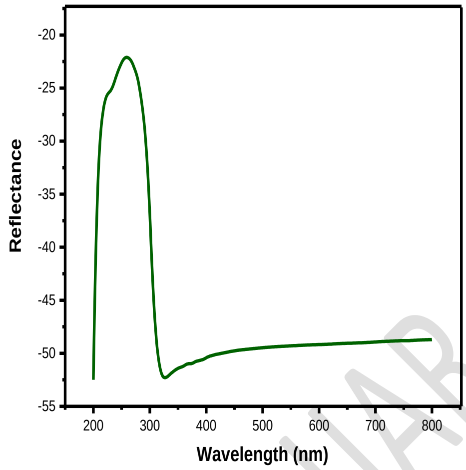


Fig. 2 (c) UV DRS – Refractive index

Fig. 2 (a) UV DRS- Reflectance

2). Cyclic voltammetry analysis

Cyclic voltammetry measurements were performed to evaluate the electrochemical behaviour, redox characteristics, and charge transport properties of the grown L-Asparagine monohydrate admixtured with oxalic acid dihydrate single crystal **[17]**. The cyclic voltammograms were recorded within a defined potential window at various scan rates. The obtained Cyclic voltagramm show smooth and well-defined current responses during both forward and reverse potential sweeps, without the presence of prominent anodic and cathodic redox peaks, indicating the absence of irreversible electrochemical reactions within the investigated potential range **[18]**. This behaviour confirms the good electrochemical stability and chemical inertness of the crystal

The near-symmetrical nature of the anodic and cathodic curves suggests a reversible electrochemical process and stable electrode- electrolyte interfacial behaviour **[19]**. A gradual increase in current response with increasing scan rate is observed, which implies diffusion-controlled charge transport within the crystal lattice. The recorded current values are in the microampere range, indicating low charge carrier density and minimal polarization effects. Such characteristics are desirable for nonlinear optical materials, as they reduce electrical losses and enhance long-term stability under applied electric fields **[20]**. The absence of significant hysteresis further confirms the stability of the material under repeated potential cycling. Overall, the cyclic voltammetry results indicate that the prepared single crystal displays favorable electrochemical stability and charge transport behaviour, supporting its potential applicability in optoelectronic, and photonic device applications **[21]**.

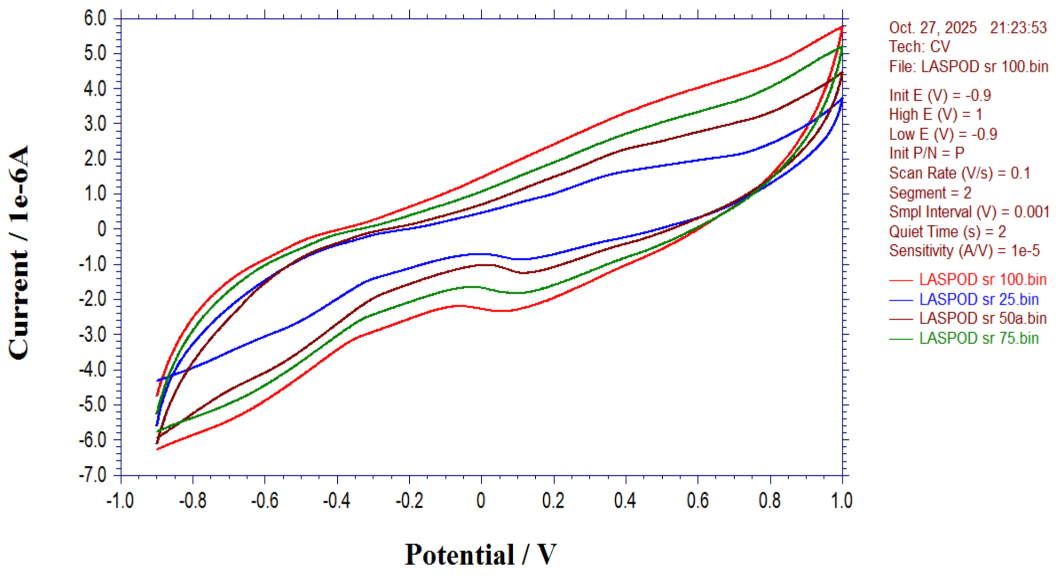


Fig. 3 (a) Cyclic voltammetry plot for LASPOD single crystals at different scan rates

3). Electrochemical impedance analysis

Electrochemical impedance spectroscopy (EIS) was utilized to examine the electrical response as well as the charge transport behaviour of the grown single crystal over a wide frequency range **[22]**. The Electrochemical graph reveals a depressed semicircle followed by an inclined linear segment in the low-frequency domain, indicating the combined contribution of bulk resistance and electrode-electrolyte interfacial effects. The absence of a well-defined complete semicircle suggests non-Debye type relaxation behaviour, which is commonly observed in crystalline materials with structural inhomogeneity. The maximum frequency domain corresponds to the bulk properties of the crystal, whereas the low-frequency dispersion is associated with space-charge polarization and ion migration effects. The relatively large impedance values indicate high electrical resistivity of the crystal, which is a desirable characteristic for photonic applications. Overall, the EIS results confirm that the grown crystal exhibits good insulating behaviour with stable charge transport properties **[23]**.

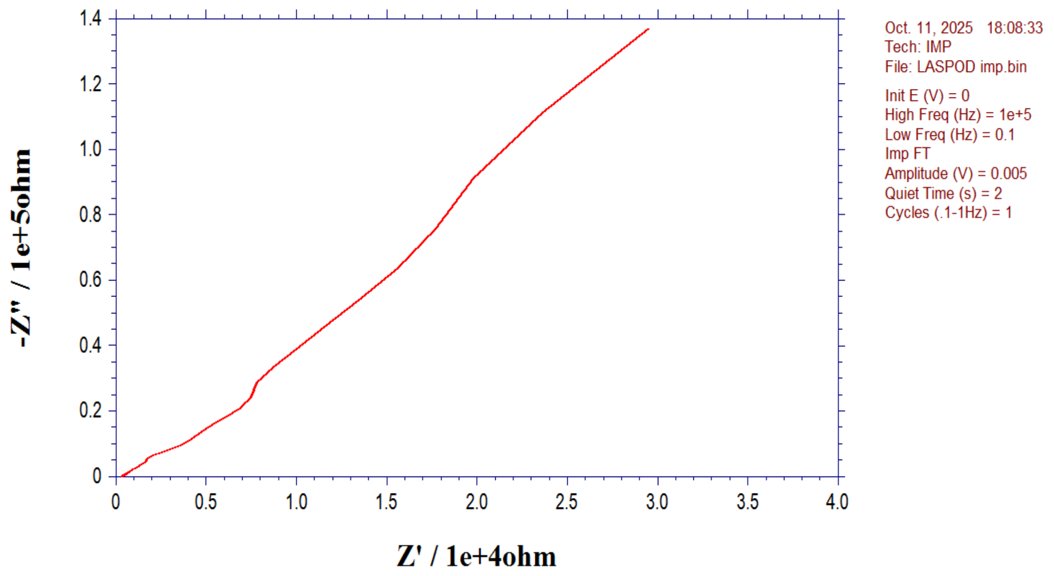


Fig. 4 (a) Electrochemical impedance spectrum of the LASPOD single crystals

Electrochemical impedance spectroscopy (EIS) was carried out to further examine the electrical transport and dielectric relaxation behavior of the grown single crystal. The Electrochemical impedance plot exhibits a well-defined depressed semicircular arc in the high- and intermediate-frequency regions, indicating that the electrical response is predominantly governed by the bulk resistance and bulk capacitance of the crystal **[24]**. The deviation from an ideal semicircle suggests non Debye type relaxation, which may arise from lattice imperfections or localized charge carrier trapping within the crystal matrix. The absence of a pronounced low-frequency spike confirms minimal electrode-sample contact. The relatively large diameter of the semicircle corresponds to high bulk resistance, implying low charge carrier mobility and enhanced insulating nature of the crystal. Such high resistivity and stable impedance response are favorable for nonlinear optical applications, as they reduce leakage currents and improve the performance of optoelectronic and photonic devices.

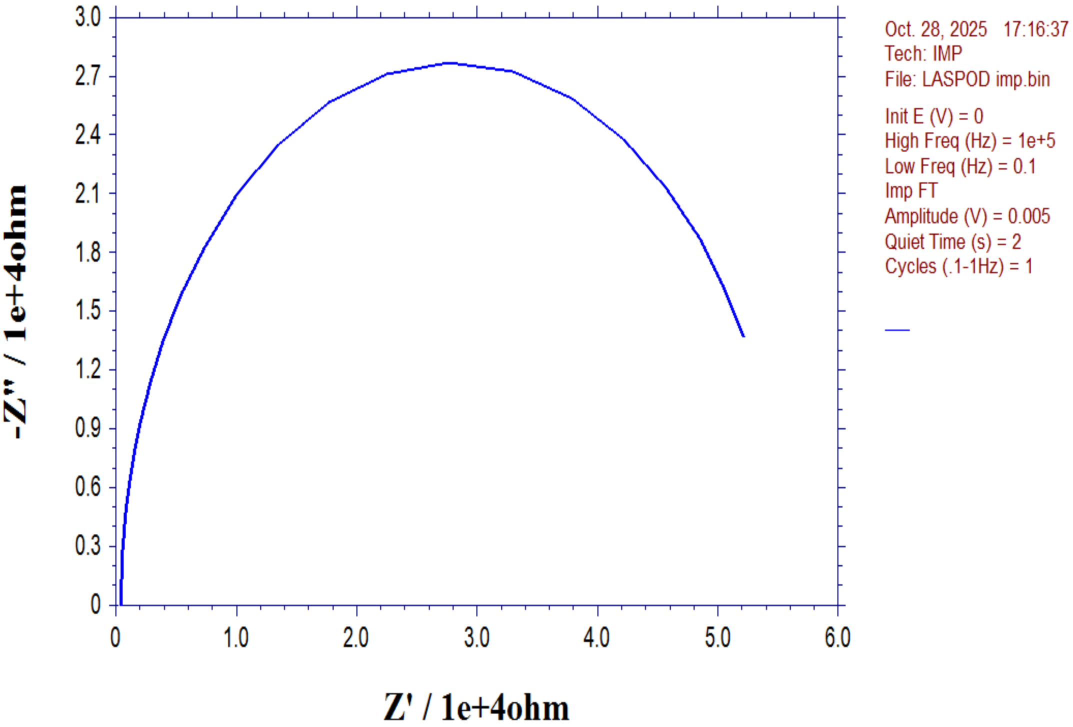


Fig. 4 (a) Electrochemical impedance spectrum of the LASPOD single crystals

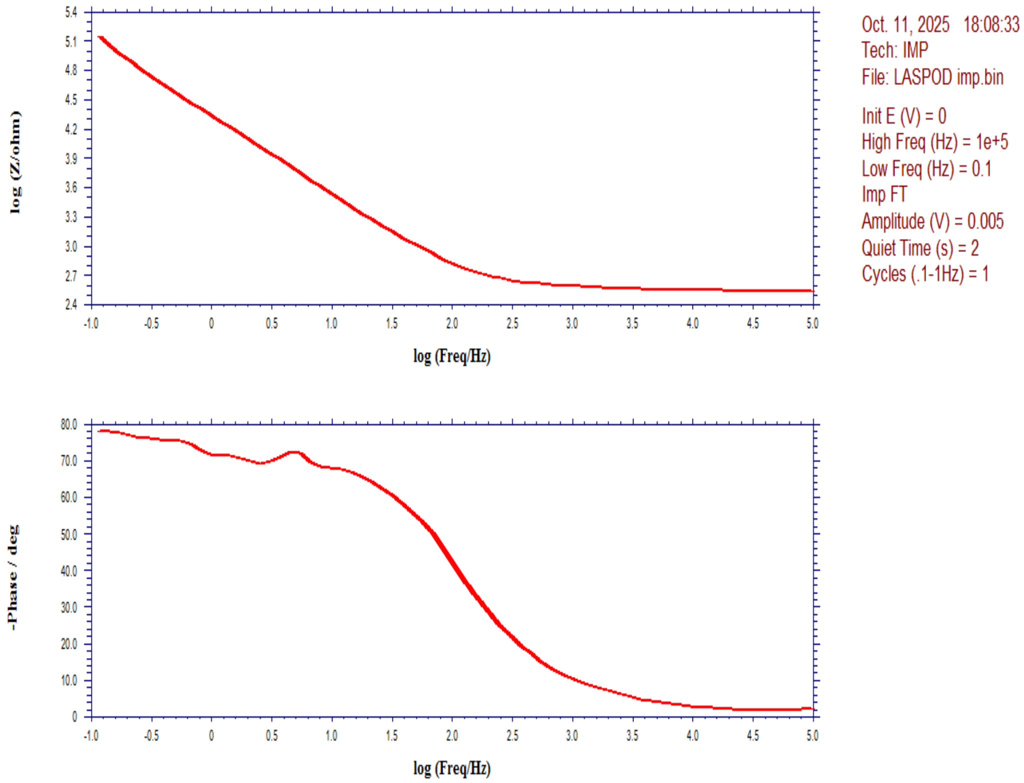


Fig. 4 (b) Bode plot of LASPOD single crystals

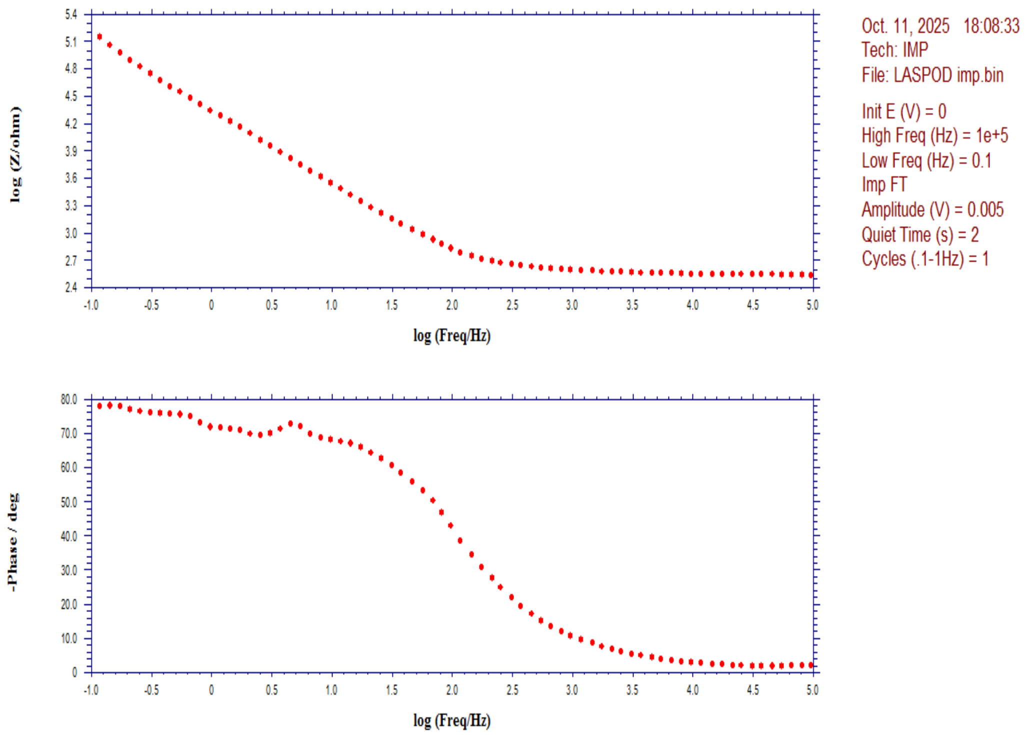


Fig. 4 (c) Bode plot of LASPOD single crystals

The electrochemical impedance characteristics of the synthesized crystal were assessed using Electrochemical impedance spectroscopy, and the corresponding bode graphs of impedance magnitude and phase shift are presented in Fig. 4 (b) and 4 (c). The impedance modulus decreases progressively with increasing frequency, indicating enhanced charge carrier mobility at higher frequencies. The relatively higher impedance observed in the low-frequency domain is due to interfacial polarization and charge transfer resistance at the electrode-electrolyte interface.

The phase angle variation with frequency reflects the combined resistive and capacitive response observed on the intermediate frequency region confirms the contribution of double layer capacitance and dielectric relaxation mechanisms. Overall, the impedance analysis demonstrates that the grown crystal exhibits stable electrochemical behaviour with efficient charge transport properties **[25].**

Conclusion

A high-quality single crystal of L-Asparagine monohydrate admixed with oxalic acid dihydrate (1:1 ratio) was successfully prepared by the slow solvent evaporation method. The UV-DRS analysis revealed a broad transparency range in the visible spectrum with an absorbance lower cut-off wavelength at 328 nm, indicating excellent optical quality of the grown crystal. The transmittance graph, with a lower cut-off at 258 nm, confirms the wide bandgap nature of the sample, making it suitable for optoelectronic applications. Cyclic voltammetrey analysis revealed stable and reproducible redox behaviour, confirming the excellent electrochemical stability of the prepared sample. Electrochemical impedance spectroscopy analysis indicated a high bulk resistance with minimal electrode polarization effects, demonstrating the insulating nature and reduced defect of the crystal. The observed electrical stability and high resistivity are advantageous for minimizing leakage currents in device applications. The bode plots confirm a stable electrochemical interface with near-ideal capacitive response at low frequencies. Overall, the combined optical and electrochemical characteristics establish the grown L-Asparagine monohydrate admixtured with oxalic acid dihydrate single crystal is a promising sample for optoelectronic and photonics.

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