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Impedance, AC conductivity and electric modulus analysis of L-leucine L-leucinium picrate

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ABSTRACT

In this paper, we report the measurements of impedance spectroscopy for the L-leucine L-leucinium picrate compound synthesized by slow evaporation technique at room temperature in the frequency and temperature ranges of 209 Hz − 1 MHz and 393–433 K, respectively. The Nyquist plots exhibited single semi-circular arcs which were well fitted to an equivalent circuit. The frequency dependence of the AC conductivity has been investigated using the Jonscher universal power law: $\sigma_{ac}(\omega) = \sigma_{dc} + A\,\omega^{s}$. The exponent s remains constant in the investigated temperature range and is almost equal to 0.62. Single relaxation peak is observed in the imaginary part of the electrical modulus, suggesting the response of grain. The close values of activation energies obtained from the analysis of hopping frequency, electric modulus and dc conductivity indicate that the transport in the title compound can be described through a simple hopping mechanism, dominated probably by the motion of L-leucinium cations.

1. Introduction

Recently, there is a surge in interest to develop new organic materials suitable for electronic applications due to low cost and low processing temperature [1,2]. Picric acid is an interesting organic acid because of the presence of three electron withdrawing nitro groups which makes it as a good π acceptor for neutral carrier donor molecule. Moreover, it also acts as an acidic ligand to form salts through specific electrostatic or hydrogen bond interactions. The picrate anions provide the potential for a large range of optical properties such as efficient luminescence [3–5] and second-order non-linear optical activity due to the proton transfer [6–8]. Moreover, picric acid complexes play a central role in bioelectrical and biological systems and exhibit good antibacterial and antifungal activities against various bacteria and fungi species [6]. Generally, picric acid derivatives are interesting candidates for the formation of salts with some amino acids which display special features such as molecular chirality, wide transparency in visible region and zwitterionic nature of the molecule such as L-alanine L-alaninium picrate monohydrate [9], DL-phenylalanine DL-phenylalaninium picrate [10], DL-methionine DL-methioninium picrate [11] and DL-valine DL-valinium picrate [12]. However, little work has been done on this kind of materials though other various interesting physical properties are expected. Our last published paper has been devoted to the X-ray powder diffraction and vibrational studies as well as DFT calculations of nonlinear optical properties of the organic compound L-Leucine L-Leucinium Picrate (LLLLP) [13]. Structural studies, characterization on second harmonic generation SHG and thermal analysis of LLLLP were carried out and reported earlier [14,15]. As an extension of our searches for exploring new properties concerning organic salts, we report in this paper, a detailed investigation of the electrical and electric modulus properties of the LLLLP compound using the impedance spectroscopy. This study may give valuable information on the electrical conductivity and can be also important for the improvement of practical applications.

2. Experimental procedure

Single crystals of LLLLP were grown by the slow evaporation technique. L-leucine and picric acid were dissolved respectively in water and acetone in the ratio 2:1 according to the following reaction:

$$2C_6H_{13}NO_2 + C_6H_3N_3O_7 \rightarrow C_6H_{13}NO_2[C_6H_{14}NO_2]^{+}[C_6H_2N_3O_7]^{-}$$

The resulting solution was then kept to evaporate at room temperature to finally lead to yellow needle crystals.

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The impedance spectroscopy was performed on a pellet of about 8 mm in diameter and 0.8 mm in thickness at frequency range from 209 Hz to 1 MHz with the TEGAM 3550 impedance analyzer. Measurements were carried out at temperatures from 393 to 433 K.

3. Results and discussion

3.1. Structural data

X-ray powder diffraction was used for the identification of the synthesized LLLLP crystal in our previous work [13]. Structural features at room temperature have been mentioned elsewhere [14]. In summary, the compound crystallizes in the triclinic system with the non centrosymmetric space group P1 (Z = 2) with a = 7.132(5)Å, b = 11.799(9)Å, c = 15.372(2)Å, α = 106.61 (6)°, β = 95.32 (6)° and γ = 90.97 (7)°. From the single crystal XRD data [14], the asymmetric unit of the title compound contains one unprotonated leucine residue, one protonated leucinium cation and one picrate anion. The structure is stabilized by an extensive network of O–H … O and N–H … O hydrogen bonds.

3.2. Impedance analysis

The complex impedance spectra of the explored compound for several temperatures are shown in Fig. 1 which present a single semicircular response corresponding to grain interior and no grain boundaries or electrode effects are involved in the patterns. Moreover, their centers are below the real axis, which indicates a non-Debye type of relaxation [16]. As temperature increases, the radius of semicircles decreases, indicating an activated thermal conduction mechanism in the studied temperature range. In order to study the electric properties of this compound, we have modeled the complex impedance spectra using Zview software and the best fit is obtained when employing an equivalent circuit formed by parallel combination of resistance R, capacitance C_1, and fractal capacity CPE_1 in series with capacitance C_2 as shown in the inset in Fig. 1. The variation of simulated values of Z′ and −Z″ are shown by solid lines in Fig. 1. The impedance of the capacitance and CPE are given, respectively by the relationships:

$$Z_C = \frac{1}{jC\omega} \tag{1}$$

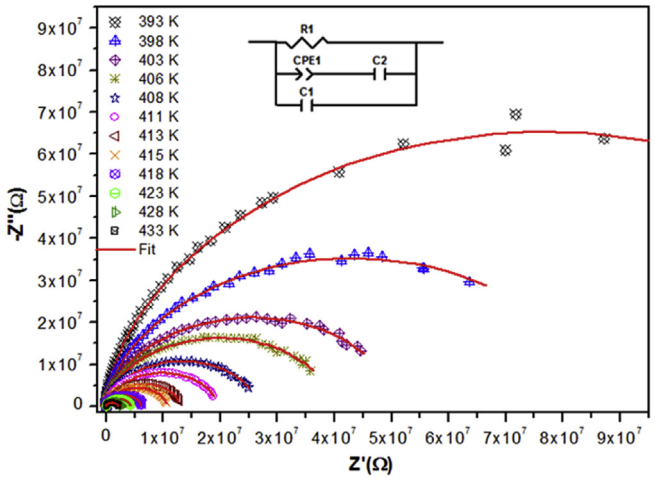

Fig. 1. The Nyquist plots for LLLLP at different temperatures.

$$Z_{CPE} = \frac{1}{Q(j\omega)^{\alpha}} \tag{2}$$

where Q is a proportional factor, ω is the angular frequency and α is an empirical exponent with values between 0 and 1 which indicates the capacitive nature of the element. The obtained parameters for the circuit elements are summarized in Table 1. The angular frequency dependence of the experimental values of Z′ and −Z″ for some temperatures with simulated ones using the extracted parameters of the equivalent circuit model are shown in Figs. 2 and 3, respectively. The excellent agreement between experimental data and simulated lines indicates that the equivalent circuit describes well the electrical properties of this compound. The amplitude of Z′ decreases with the rise in temperature at low frequency due to the increase in ac conductivity and all curves merge at high-frequency region for all temperatures. This behavior suggests a possible release of space charge and a consequent lowering of the barrier properties in the materials [17]. With the increase of frequency, the magnitude of −Z″ increases at the beginning, reaches a peak ($-Z''_{max}$) and then decreases with the rise in frequency at all measured temperatures. The broadening of peak and its shift towards higher frequency side with the increase of temperature demonstrate the presence of temperature dependent electrical relaxation phenomenon, and the relaxation time decreases with increasing temperature [18]. At higher frequency side all the curves are merged for all temperatures which might be caused by the reduction in space charge polarization at this frequency region.

3.3. Conductivity study

3.3.1. DC conductivity

DC conductivity σ_{dc} can be calculated using the values of the extracted circuit parameters as:

$$\sigma_{dc} = \frac{e}{S \times R} \tag{3}$$

where e, S and R represent, the thickness, the area of the pellet and the resistance, respectively. The temperature dependence of the conductivity Ln(σ_{dc}.T) versus (1000/T) in the studied temperature range is given in Fig. 4. The linearity of the obtained experimental points shows firstly that this compound does not have any phase transition in the studied temperature range which confirms the results of DSC measurements carried out by G. Bhagavannarayana et al. [15], and secondly the σ_{dc}.T exhibits an Arrhenius type behavior described by the following expression:

Table 1
The equivalent circuit parameters for the LLLLP.

T(K)	R (MΩ)	C_1(pF)	Q(nF)	α	C_2(pF)
393	151.00	2.51	0.20	0.40	1.97
398	85.00	2.51	0.27	0.40	2.80
403	50.40	2.52	0.44	0.39	2.51
406	39.60	2.52	0.43	0.40	3.02
408	26.40	2.53	0.56	0.40	3.26
411	19.50	2.54	0.72	0.40	3.22
413	13.00	2.57	1.07	0.38	3.22
415	10.70	2.57	1.19	0.39	3.34
418	6.23	2.61	1.87	0.37	3.39
423	4.32	2.60	2.56	0.37	3.46
428	2.73	2.68	4.21	0.34	3.57
433	2.14	2.68	4.51	0.34	3.65