Vibrational Analysis and Electrical Conduction Mechanism Investigations of Order Disorder Phase Transitions in $[\text{N(C}_3\text{H}_7\text{)}_4]_2\text{ZnBr}_4$ Compound

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Abstract

Bis-Tetrapropylammoniumtetrabromozincate has been synthesized and characterized by X-ray, vibrational spectroscopy and impedance spectroscopy. The Rietveld refinement of the XRD diffractogram confirms the crystallization of the compound through the monoclinic system (space group $C_{1}^{y}$). A temperature study of the Raman scattering revealed two phase transitions at about $T_c=340$ and $T_T=393K$. The evolution of the wavenumber and the line width versus the temperature showed some singularities associated with the transitions, suggesting that they are governed by the re-orientation of the $[\text{N(C}_3\text{H}_7\text{)}_4]_2^{+}$organic part. The complex impedance plotted as semicircle arcs in the temperature range and the centers of the semicircles lie below the real axis, which indicates that the material is non-Debye type. Double semicircles were related to bulk and grain boundary effects. Furthermore, the alternating current conductivity of the $[\text{N(C}_3\text{H}_7\text{)}_4]_2\text{ZnBr}_4$ obeyed the Jonscher's law: $\sigma_{dc}(\omega)=\sigma_{ac}+A\omega$ and the conduction could be attributed to the correlated barrier hopping (CBH) model in region (I) and (II) and the Non-overlapping Small Polaron Tunneling (NSPT) in region (III).

Keywords: Bis-Tetrapropylammoniumtetrabromozincate; Raman spectroscopy; Phase transition; Electrical conductivity; Conduction mechanism

Introduction

Organic-inorganic hybrid materials have attracted growing attention in recent research because they can combine specific properties of organic-inorganic frameworks including the formation of interactions [1]. In fact, regarding the nature (molecular, ionic, hydrogen bonding, etc...) of organic and inorganic components, many combinations may be achieved to elaborate the interesting materials with special physical properties in several fields of new scientific materials, such as nonlinear optical, electronic, magnetic [2]. These materials have recently attracted further interest due to their attractive potential for application [3]. More particularly, the hybrids compounds of the general formula $A\text{MX}_n$, where A is the alkylammonium group, M a divalent metal and X a halogen, has received much attention due to the presence of several phase transitions related to the re-orientation of the cationic parts [4-10]. Taking these aspects into account and as an extension of our previous studies on organic-inorganic hybrid materials, herein, we have successfully synthesized the bis-tetrapropylammoniumtetrabromozincate compound. Structurally, at room temperature, $[\text{N(C}_3\text{H}_7\text{)}_4]_2\text{ZnBr}_4$ crystals are monoclinic system (Space group $C_{1}^{y}$) with the following unit cell parameters: $a=33.145(5)\;\text{Å}$, $b=14.234(3)\;\text{Å}$, $c=15.081(2)\;\text{Å}$, $\beta=110.207(5)^\circ$. The atomic arrangement can be described by an alternation of organic and inorganic layers along the $[001]$ direction, which are made up of $[\text{N(C}_3\text{H}_7\text{)}_4]^+$ and $[\text{ZnBr}_4]^-$ atom (Figure 1). The inorganic groups are located in the (100) plane at $a=1/8$ and $3/8$ sandwiched between two different organic sheets [11]. In fact, the objective of this paper is to study the Raman scattering and electric propriety in order to investigate the phase transition for this compound.
Experimental Procedure

Synthesis

The organic–inorganic \([\text{N(C}_3\text{H}_7\text{)}_4]_2\text{ZnBr}_4\) crystals were grown using \(\text{ZnBr}_2\) (purity 98) and \([\text{N(C}_3\text{H}_7\text{)}_4]\)Br (purity 97%; FLUKA) are dissolved in an aqueous solution in a molar ratio of 1:1. After a few days, the white prismatic monocrystals are obtained through a slow evaporation at room temperature. Then, the single crystal is selected using a microscope.

X-ray powder diffraction

The phase purity and homogeneity were checked using X-ray powder diffraction analysis. Using a Phillips PW 1710 powder diffractometer operating with CuK\(\lambda\) (\(\lambda=1.5405\) Å), the XRD pattern was recorded in a wide range of Bragg angles (9<2θ<50). The Raman scattering spectra were recorded using a Horiba-Jobin-Yvon T64000 Raman spectrometer in the frequency range of 100-3200 cm\(^{-1}\) using the 514.5 nm radiation of an Ar/Kr laser as excitation. The studies of a function of temperature were performed in a Link Am heating stage up to 415 K. The wavenumbers and widths of the Raman lines were determined by fitting using the LabSpec5 software with a combined Lorentzian–Gaussian band shape. To study the electrical properties, the \([\text{N(C}_3\text{H}_7\text{)}_4]_2\text{ZnBr}_4\) compound are grinded and pressed into cylindrical pellet of 8 mm in diameter and 1.1 mm in thickness using 3t/cm uniaxial pressure. The performed measurements were executed in the frequency and temperature range of 200 Hz-5 MHz and 303 K-423 K, respectively, using a HP4284 impedance analyzer.

Results and Discussion

X-Ray powder diffraction

The X-ray diffraction pattern of the \([\text{N(C}_3\text{H}_7\text{)}_4]_2\text{ZnBr}_4\) compound at room temperature is shown in Figure 2. The Rietveld refinement was performed using the FULLPROOF software program. The circles symbolize the experimental data, and the line presents the simulated pattern. The purity of the studied compound was proved and the reflection peaks were indexed in the monoclinic system \((C\alpha_2/C\alpha_2\alpha_2)\) and the refined cell parameters are found to be as follows: \(a=33.132(5)\) Å, \(b=14.234(3)\) Å, \(c=15.081(2)\) Å and \(\beta=110.23(1)^\circ\). The quality of the refinement was evaluated through the goodness of fit \(R^2=6.67\). The values of the reliability factors obtained from the refinement are \(R_{wp}=8.99, R_p=8.15\) and \(R_{exp}=3.48\) and the fitted parameters were found to be in a good agreement the previously reported results in the literature [11].

Table 1: Assignments of most important observed bands in Raman spectra of \([\text{N(C}_3\text{H}_7\text{)}_4]_2\text{ZnBr}_4\) at room temperature.

| Intensity Raman (cm\(^{-1}\)) | Assignments     |
|-------------------------------|-----------------|
| 164                           | \(\nu_1(ZnBr)\) |
| 193                           | \(\nu_2(ZnBr)\) |
| 312                           | \(\nu_3(ZnBr)\) |
| 334                           | \(\rho(CH)\)   |
| 368                           | \(\delta(NC_4)+\delta(C-C-C)\) |
| 513                           | \(\delta(NC_4)+\delta(C-C-C)\) |
| 750                           | \(\nu_1(NC_4)\) |
| 780                           | \(\nu_2(NC_4)\) |
| 847                           | \(\delta(C-C-C)+\delta(C=N-C)\) |
| 872                           | \(\delta(C-C-C)+\delta(C-N-C)\) |
The strong Raman bands observed in the wavenumber, which range between 2988 and 2905 cm$^{-1}$ are assigned to the stretching vibrations of the CH$_3$ and CH$_2$ groups while the bands at 1460 and 1350 cm$^{-1}$ area scribed to the asymmetric and symmetric bending vibration of the CH$_n$ respectively. As for the bands observed in the range of 847-750 cm$^{-1}$, they emanate from the bending of the (C=C-C + C=N-C) groups and the N-C stretching vibrations. However, the internal modes of ZnBr$_2$ anion are below 312 cm$^{-1}$. In fact, the assignments of the observed bands are realized by comparing them to similar compounds, such as: [N(C$_4$H$_7$)$_4$]$_2$SbCl$_5$ compound [12]. [N(C$_4$H$_7$)$_4$]$_2$CoCl$_5$ compound [13]. [N(C$_4$H$_7$)$_4$]$_2$SnCl$_5$ compound [14]. [N(C$_4$H$_7$)$_4$]$_2$FeCl$_5$ [15] compound. [(C$_n$H$_m$)$_4$N][M(N(CN)$_4$)$_2$] compound [16] and [(C$_n$H$_m$)$_4$N][Cd(N(CN)$_2$)$_2$] compound [17]. These vibrational wavenumbers together with the proposed band assignments are listed in (Table 1).

The aim of this work is to find the modes sensitive to the phase transition at 340 and 393 K in the 2[N(C$_4$H$_7$)$_4$]ZnBr$_2$ compound. The Raman spectra at several temperatures are illustrated in (Figure 3a-3d). These spectra are devised into four areas of wavenumbers: the first from 100 to 320 cm$^{-1}$; the second from 320 to 1000 cm$^{-1}$, the third from 1000 to 1600 and the fourth from 2600 to 3200 cm$^{-1}$. It is obvious that several Raman mode wavenumbers change discontinuously at around the transitions evidenced at 340 and 393 K by DSC measurements [11]. A careful analysis of these spectra clearly shows that the results and discussion shapes of most bands obtained between 100 and 320 cm$^{-1}$, where the anionic part is found, do not change a lot below the phase transition temperatures (T=340 and 393 K), which means that these modes are not directly connected to the phase transition. However, several bands showed a significant shift in their frequency position and half-width assigned to the internal vibrations of the [((C$_4$H$_7$)$_4$N]$^+$ cation. The position and width at half maximum for the selected lines obtained between 320 and 1600 cm$^{-1}$ are depicted in (Figure 4a & 4b). The band related to the temperature dependence of the rocking vibration ($\rho(CH_2)$) located at 334 cm$^{-1}$ showed a variation in its position to the low wavenumber by 2 cm$^{-1}$ in the first transition and to the high wavenumber by 4 cm$^{-1}$ in the second transition ($T_2$). Besides, the half-width of this band shifts to low frequency by 7 cm$^{-1}$ before the first transition ($T_1$) and by 6 cm$^{-1}$ after the second transition ($T_2$). The peak observed at 780 cm$^{-1}$ is assigned to the symmetric stretching vibration of $\nu_4$(N$_2$) which is decreased by 3 cm$^{-1}$ and half-width is increased by 12 cm$^{-1}$ before the second transition. The wavenumber of bands located at 872 cm$^{-1}$ and 847 cm$^{-1}$ which is assigned to the ($\delta(CH_2)$ + $\delta(CH_4)$) and ($\delta(C-N)+\delta(C-C)$), respectively is decreased by 3 cm$^{-1}$ at around 393 K. It is clear that the bands located at 1350 cm$^{-1}$ assigned to the symmetric bending vibration of $\delta(CH_4)$ have vanished above the second transition ($T_2$). The anti-symmetric bending vibration of $\delta(CH_4)$ observed at 1460 cm$^{-1}$ presents a variation in the position by 9 cm$^{-1}$, while the half-widths increase by 10 cm$^{-1}$ at T K. The temperature dependence of the Raman spectra in the region of the stretching symmetric-and asymmetric vibrations between 2600 and 3200 cm$^{-1}$ is presented in (Figure 5a & 5b). The biggest change in the band position is observed for the mode at 2955 cm$^{-1}$ associated with the asymmetric stretching vibration of $\nu_4(CH_2)$. This band vanishes above the second transition ($T_2$). The

| Wavenumber (cm$^{-1}$) | Assignment |
|-----------------------|------------|
| 918                   | $\nu_4$(NC) |
| 937                   | $\delta$(C-N-C) |
| 972                   | $\delta$(C-N-C) |
| 1031                  | $\rho(CH_2)$+\rho(CH_4) |
| 1100                  | $\delta$(skeletal) |
| 1134                  | $\delta$(skeletal) |
| 1151                  | t(CH$_3$) |
| 1316                  | $\omega$(CH$_2$) |
| 1330                  | $\delta$(CH$_2$) |
| 1350                  | $\delta$(CH$_4$) |
| 1448                  | $\delta_\omega$(CH$_2$) |
| 1460                  | $\delta_\omega$(CH$_4$) |
| 2741                  | - |
| 2877                  | $\nu$(CH$_3$) |
| 2905                  | $\nu$(CH$_2$) |
| 2934                  | $\nu$(CH$_2$) |
| 2955                  | $\nu$(CH$_2$) |
| 2970                  | $\nu$(CH$_2$) |
| 2988                  | $\nu$(CH$_2$) |

$v_\omega$: symmetric stretching; $v_\omega^\prime$: asymmetric stretching; $\delta_\omega$: asymmetric bending; $\omega$: wagging; $t$: twisting; $\delta$: bending; $\rho$: rocking.
band at 2905 cm\(^{-1}\) related to the symmetric stretching \(\nu(CH_{2})\) mode shifts to higher wavenumber by 4 cm\(^{-1}\) at the second transition. A significant jump in the half-width of this band is observed at \(T_{x}\). Then, the anti-symmetric stretching vibration of \(\nu(CH_{2})\) observed at 2934 cm\(^{-1}\) presents a position variation by 3 cm\(^{-1}\), while the half-widths increase by 8 cm\(^{-1}\) around the second phase transition.

**Figure 3**: Evolution of the Raman spectrum as a function of temperature:

a. from 100-320 cm\(^{-1}\),

b. from 320-1000 cm\(^{-1}\),

c. from 1000-1600 cm\(^{-1}\), and

d. 2600-3200 cm\(^{-1}\)

**Figure 4**: Evolution of certain positions Raman (a) and (b) width at mid-height as a function of the temperature in the region 320-1600 cm\(^{-1}\).
The important changes in the Raman spectra are observed at 393K for some internal modes of cationic parts, which suggests that the dynamics of the [N(C₃H₇)₄]⁺ cationic parts evidence the contribution of the mechanism of phase transition [18]. In order to verify that the phase transitions are correlated with changes in the dynamical state of the cationic groups, a quantitative study about the band located at 2970cm⁻¹ (νas(CH₃)) was realized.

**Temperature dependence of the wavenumber**

The temperature dependence of the Raman wavenumber of a phonon connected to an order-disorder mechanism according to Andrade and Porto [19] can be described by:

\[
\nu^2 = \nu_0^2 \left[ 1 + \gamma(T - T_c) \right] \tag{1}
\]

Where \(\gamma\) is the thermal coefficient and \(\nu_0\) is the "hard-core wavenumber" at temperature transition \(T_c\). Generally, the values of \(\gamma\) are small so that we can approximate Eq (1) by [20]:

\[
\nu = \nu_0 \left[ 1 + \frac{\gamma}{2} (T - T_c) \right] \tag{2}
\]

The thermal coefficient depends on the variation of the wavenumber position and the volume of the crystal according to the following expression:

\[
\gamma_i = \frac{\Delta \nu_i}{\nu_i} \frac{V}{\Delta V} \tag{3}
\]

where \(\Delta \nu\) and \(\Delta V\) are the variations of the volume and of the wavenumber position, respectively, \(\nu\) symbolizes the original wavenumber and \(\nu_i\) the band position of the \(i\) mode at room temperature.

According to the approximation of Gruneisen, the relative change of any vibration is directly proportional to the relative change in the volume [21]. Figure 6 shows the dependency of the Raman wavenumber versus the temperature of the analyzed band at 2970cm⁻¹ fitted using Eq. (2). We obtain the expansion coefficient \(\gamma = 5.12 \times 10^{-3}K\) for \(T < T_s\), \(\gamma = 5.08 \times 10^{-3}K\) for \(T_s < T < T_2\) and \(\gamma = 5.10 \times 10^{-3}\) for \(T > T_2\). Hence, the decrease of the thermal coefficient related
to the changes of the wavenumber position indicates an increase of the cell volume due to a structural transformation. Indeed, an important weakening of the Vander Waals interaction and the CH$_3$ groups involved in the C-HCl Vander Waals interaction gain motional freedom [22].

**Temperature dependence of the full width of half maximum**

To verify that the phase transitions are correlated with changes of the [N(C$_3$H$_7$)$_4$]$^+$ groups, we followed the analysis of the full width at half maximum (FWHM), which is based on the theory used for the damping associated with an order-disorder mechanism. The analysis of the full width at half maximum (FWHM) described by Carabatos-Nedelec and Becker was followed [23]. The temperature dependence of the band-width is described by [24].

$$
\Gamma(\omega) = (a + bT) + c \exp\left(\frac{E_a}{k_B T}\right) \quad (4)
$$

where, $\omega$ is the phonon wavenumber and $\tau_r$ is the mean reorientation time of the atoms to jump from one potential to another; it is given by

$$
\tau_r = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (5)
$$

where, $E_a$ is the activation energy for the mode connected to the order/disorder transition, $k_B$ is the Boltzmann constant, $\tau_0$ is the relaxation time at infinite temperature. Eq. (4) can then be written by:

$$
\text{FWHM}(T) = (a + bT) + c \exp\left(\frac{E_a}{k_B T}\right) \quad (6)
$$

The linear part of Eq. (6) corresponds to the vibrational relaxation and the exponential term corresponds to the reorientational relaxation. The latter is connected to the thermal molecular reorientational motions of a diffusive nature. The thermal variation of FWHM of the band located at 2970 ($\nu_{as}$(CH$_3$)) is plotted in Figure 7. The activation energies obtained by fitting with Eq.(6) are: $E_a=112$ kJmol$^{-1}$ in region I, $E_a=110$ kJmol$^{-1}$ in region II and $E_a=88$ kJmol$^{-1}$ in region III. In fact, the decrease of activation energy is probably due to the decrease of the population involved in this vibration which can be due to the change of the conformation of the [N(C$_3$H$_7$)$_4$]$^+$ cation [25].

**Impedance studies**

Impedance spectroscopy is the most reliable technique to study the electrical properties and processes of the materials. It gives a direct correlation between the response of a real system and an idealized model circuit composed of discrete electrical components [26]. The complex impedance data (-Z''vsZ') of [N(C$_3$H$_7$)$_4$]$_2$ZnBr$_4$ compound for some representative temperatures are shown in Figure 8. All these plots are formed by two semi-circles. Thus, the lower frequency dispersion corresponds to the grain boundary and the higher one to the interior grain [27]. In other words, the centers of semicircles that compose the total electric response are centered below the real axis (Z), which confirms the presence of non-Debye type of relaxation in the materials. The impedance data have been fitted to an equivalent circuit model consisting of two parallel R-CPE circuits connected in series (Figure 8).

The impedance of the constant phase element (Z$_{CPE}$) is given by the following equation [28]:

$$
Z_{CPE} = \frac{1}{Q(\omega)^\alpha} \quad (7)
$$

Where, Q indicates the value of the capacitance of the CPE element and $\alpha$ is the degree of deviation with respect to the value of the pure capacitor.

The real and imaginary components of the whole impedance were calculated according to the following expressions:
The refinement results performed using the selected electrical model are summarized in Table 2. Let \((R_g, R_{gb})\) and \((Q_g, Q_{gb})\) be the resistance and capacitance of the CPE element of grains and grain boundaries, respectively, whereas \(0 < \alpha < 1\) is the fractal exponent. In order to check the choice of equivalent circuit, we present in Figures 9a & 9b the variations of the experimental values of \(Z'\) and \(Z''\) at some temperatures versus the simulate dones calculated using the parameters extracted from the equivalent circuit. From this figure, it is obvious that the slope obtained from a fit linear of these curves at each temperature is substantially equal to the unity. The good accordance between the experimental and theoretical data indicates that the used equivalent circuit describes reasonably well the electric properties of Bis-Tetrapropylammoniumtetrabromozincate sample. The continuous current (dc) conductivity from the grain contribution can be determined from the following expression

\[
\sigma_g = \frac{e}{S} \frac{1}{R_g}
\]

Where, \(e\) and \(S\) are respectively the thickness and the area of the pellet.

![Figure 9](image_url)

**Figure 9:** Measured and calculated values of the real part of the complex impedance

**Table 2:** The equivalent circuit parameters for the \([\text{N(C}_3\text{H}_7]_4\text{ZnBr}_4\) Compound.

| T(K) | \(R_g(\Omega)\) | \(Q_g(10^{-10} F)\) | \(\alpha_g\) | \(R_{gb}(\Omega)\) | \(Q_{gb}(10^{-8} F)\) | \(\alpha_{gb}\) |
|------|----------------|----------------------|-------------|----------------|----------------|-------------|
| 323  | 5.21 \(10^7\) | 3.073 | 0.98615 | 1.73 \(10^4\) | 0.13 | 0.91154 |
| 328  | 4.49 \(10^7\) | 2.74 | 0.98163 | 9.86 \(10^4\) | 0.18 | 0.90218 |
| 333  | 3.89 \(10^7\) | 2.93 | 0.97727 | 8.90 \(10^4\) | 0.18 | 0.90449 |
| 338  | 2.92 \(10^7\) | 2.5 | 0.98782 | 8.72 \(10^4\) | 0.17 | 0.90344 |
| 343  | 2.25 \(10^7\) | 2.3 | 0.99063 | 8.43 \(10^4\) | 0.13 | 0.91814 |
| 348  | 1.71 \(10^7\) | 2.54 | 0.98819 | 8.20 \(10^4\) | 0.15 | 0.91185 |
| 353  | 1.04 \(10^7\) | 2.78 | 0.9873 | 7.69 \(10^4\) | 0.09 | 0.94116 |
The thermal evolution of the bulk conductivity is shown in Figure 10. It was observed that the $\sigma_g$ increases with the increase of temperature and follows the Arrhenius behavior, which is given by

$$\sigma_g = \sigma_0 \exp\left(-\frac{E_a}{K_B T}\right)$$ (11)

Where, $E_a$ is the activation energy, $A$ is the pre-exponential factor and $k_B$ is the Boltzmann's constant.

All phase transitions appearing in the Raman spectroscopy are affirmed by the change of the curve slope at $T_1$ and $T_2$. The values of the activation energy determined from the linear adjustment to the data points are $E_{a(I)}=0.38\,\text{eV}$ in region I, $E_{a(II)}=0.61\,\text{eV}$ in region II and $E_{a(III)}=0.44\,\text{eV}$ in region III. It is worth noticing that the variation in the activation energies values can be explained by the movement in the cationic and anionic parts. As well as, it is probably, the mobility of the charge carriers is due to a hopping mechanism [29]. Then, a study of the ac conductivity for the sample was carried out to identify the origin of the conduction process. This makes it possible to study the transport mechanism of charge carriers as well as their interactions as a function of frequency [30].

$$\sigma_{ac}(\omega)=\sigma_0^{dc}+\frac{A\omega}{\omega^\alpha}$$ (12)

**Figure 10:** Temperature dependence of $\ln(\sigma_T)$ versus reciprocal temperature for $[\text{N(C}_3\text{H}_7\text{)}_4\text{]}_2\text{ZnBr}_4$ Compound.

**Figure 11:** Frequency dependence of the AC conductivity at various temperatures.
where, $\sigma_0$ is the direct current conductivity. $A$ is a constant depending on temperature and $s$ is an exponent representing the degree of interaction between mobile ions and surrounding lattices [33].

To determine the predominant conduction mechanism of the ac conductivity for the title compound, different theoretical models correlating the conduction mechanism of ac conductivity with the exponent $s$ ($T$) [33] are used. The variation of exponents($T$), which is obtained by the fitting of the experimental data of ac conductivity, is plotted as a function of temperature in Figure 12. It is clear from this figure that the exponent $s$ decreases with the rising temperature below and above the first phase transition ($T_1=340 K$) and increases with the rising temperature above the second phase transition ($T_2=393 K$). This result implies that the correlated barrier hopping model (regions I and II) and the non-overlapping small polaron tunneling (region III) model are the most probable models to describe the ac electrical conduction for the crystal in this range temperature.

![Figure 12: Temperature dependence of the frequency exponent $s$.](image)

**Conclusion**

In summary, it can be said that a novel organic-inorganic hybrid compound, \([N(C_{10}H_{21})_3][ZnBr_4]\), has been successfully synthesized at room temperature by slow evaporation. The Raman spectra at several temperatures were studied. It is clearly shown that the important changes in the Raman spectra are observed for some internal modes of cationic parts \([N(C_{10}H_{21})_3]^+\), which means that these modes are directly connected to the phase transition. Besides, the complex impedance analysis revealed the contribution of the grain and the grain boundary to electrical properties. In fact, a detailed analysis of the arcs revealed that the equivalent electrical circuit of this sample could be regarded as two elements ($R/\text{CPE}$) in series. Finally, the frequency-dependent (ac) conductivity has been interpreted in terms of Jonscher’s law. Then, the temperature dependence of $s$ is investigated to understand the conduction mechanism in the different regions, which is attributed to the CBH model in regions I and II and the NSPT model, in region III.

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