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Determination of optical constants and polarizability studies on ferroic Tetramethylammonium Tetracholorozincate crystal

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ABSTRACT

Single crystal of Tetramethylammonium Tetrachlorozincate has been grown by slow evaporation method. The orthorhombic structure of the material is confirmed by single crystal XRD study. The formation of the material is further supported by Raman study predicting high orientation along '*a*' axis of the crystal. Ferroelectric hysteresis loop gives the evidence for the ferroelectric behaviour of the material. In optical studies, the insulating behaviour of the material is established by Tauc plot obtaining a large value of indirect optical band gap energy which is agreeable with the band gap energy value calculated along '*a*' axis. From the recorded reflectance values, the refractive index and dielectric constant values of the crystal have been calculated. The electronic polarizability also has been calculated using Clausius–Mossotti equation in the high frequency UV–vis–NIR optical region. In addition, the polarizability of the crystal in the lower frequency regions is determined via dielectric studies experimentally, and it is well matched with the theoretically obtained value from Penn analysis. Further, Penn analysis deduces the Plasmon and Fermi energy of the material.

1. Introduction

The discovery of ferroelectricity in Tetramethylammonium Tetrachlorozincate compound $[N(CH_3)_4]_2ZnC1_4$ [1] that crystallises in the high symmetry phase D_{4h} leading to wide numbers of experimental investigations. Among those, most of the studies concentrated on the structural phase transformations of the material due to the interesting behaviour of commensurate–incommensurate phase transition together with the many successive phase transitions. The incommensurate phase is generally characterized by the amplitudons and phasons [2]. The phasons could be detected only by the neutron inelastic scattering and the Brillouin scattering [3] whereas the soft mode behaviour of the amplitudons could be observed by Raman scattering studies [1–3]. In this context, Berger et al. [4] estimated the photoelastic coefficients of $[N(CH_3)_4]_2ZnC1_4$ by Brillouin scattering method. Harajamarki et al. [5] also used this method for their works on phase transitions. Some authors focused on the neutron inelastic scattering to get knowledge of the dynamic behaviour of this material [6,7]. Besides, neutron diffraction study on this material was undertaken by Durand et al. [8]. Most of the experimental researchers focused on the Raman scattering studies to analyse the successive transformations of the material in different dimensions. For instance, the incommensurate phase study with group theoretical method was thoroughly explained by Pal et al. [9]. The Raman spectra of the parent phase and low symmetry phases of this compound were well established by Torgasev et al. [10,11].

Few works were found to deal with the electron paramagnetic resonance (EPR) [12] and proton magnetic resonance [13,14] to examine the internal vibrations of this material. The heat capacities of $[N(CH_3)_4]_2ZnC1_4$ were determined by Melia et al. [15] and temperature–pressure diagram was established by Gerard et al. [16]. For the past three decades wide varieties of works had been established by various solid state researchers. However, the optical properties of this material hold little attention by several groups. Breczewski [17] reported the optical activity of the centrosymmetric incommensurate phase of $[N(CH_3)_4]_2ZnC1_4$. One of the recent article [18] reported the study of optical transmission and nonlinear optical property of this material. El-Korashy [19] calculated the optical band gap energy of the material in paraelectric phase. There are no extensive findings in this material on the determination of optical constants such as absorption coefficient, refractive index, dielectric constant together with the polarizabilty. Bearing this is in mind, the present work illustrate the above mentioned optical properties of $[N(CH_3)_4]_2ZnC1_4$ in detail. In addition, theoretical Penn analysis has also been made in support of the experimentally calculated polarizability values.

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2. Materials and methods

The single crystals of $[N(CH_3)_4]_2ZnC1_4$ were grown by the slow evaporation method at room temperature under normal pressure as prescribed elsewhere [20]. The selected good quality crystals were subjected to various studies. The crystals were subjected to single crystal X–ray diffraction using Bruker Kappa Apex II diffractometer with 0.71073 Å wavelength of radiation and the lattice parameters were determined. The Radiant Technology method (Tester Name: PMF0713-334) was used for hysteresis loop study. Raman spectra of powder samples were measured using a micro Raman spectrometer (Rienshaw, UK, model inVia) with 514 nm laser excitation from 1 cm^{-1} to 4000 cm^{-1}. The UV–Vis transmission and reflection spectra were recorded using Cary– 300 instrument in the range 200–1100 nm with a resolution of 1 nm in the solid state. The dielectric measurements were carried out using N4L Numetric Q PSM 1735 instrument in the frequency range 1 KHz–10 MHz. Polished grown crystal coated with silver paste was used for the measurements capacitance.

3. Results and discussion

The lattice parameters $a=8.981(8)$ Å, $b=12.256(6)$ Å and $c=15.513(7)$ Å and $V=1707.5(14)$ $Å^3$ obtained from single crystal XRD study agree well with the literature values [9] and confirm the orthorhombic structure of the material. The recorded Raman spectrum is given in Fig. 1. The vibrational modes present and their vibrational assignments are listed in Table 1 together with the reported values [10]. Lattice vibration is appeared at 57 cm^{-1} and the symmetric stretching vibrations of $ZnCl_4$ are emerged below 350 cm^{-1}. The C–N symmetric and asymmetric deformations modes are found at 370 and 461 cm^{-1} respectively whereas the symmetric and asymmetric stretching vibrations of C–N exhibited, peaks at 761 and 958 cm^{-1} respectively. The Raman absorption peaks at 1176, 1415 and 1457 cm^{-1} are assigned to the CH_3 rocking, symmetric and asymmetric deformations respectively. The CH_3 symmetric stretching vibrations appear at 2928, 2965 and 2980 cm^{-1} and the corresponding asymmetric stretching vibration is found at 3031 cm^{-1}. On seeing the polarised Raman spectrum reported in the ref. [10] our recorded powder Raman spectrum is in good agreement with the B_{2g} vibrational modes. In general, the D_{4h} space group symmetry consists of 8 vibrational modes which are described by A_g, B_{1g}, B_{2g}, B_{3g}, A_u, B_{1u}, B_{2u} and B_{3u}. Among those, A_g, B_{1g}, B_{2g} and B_{3g} vibrational modes are Raman active while others are Infra-red active. The Raman active modes are distributed as $65_{Ag}+52_{B1g}+65_{B2g}+52_{B3g}$ in the total 468 vibrational modes [10]. Among the 6 polarizability Raman tensor components the 3 *diagonal* tensor components belong to Ag modes and the remaining three B_{1g}, B_{2g} and B_{3g} vibrational modes correspond to the *off-diagonal* tensor components. Since the present vibrational modes belong to B_{2g} modes which has the polarizability tensor components as c(ac)a, it predict the occurrence of Raman scattering along '*a*' axis. It suggests that our grown crystal is highly oriented in the '*a*' direction which referred to the shortest unit cell axes.

Table 1
Raman vibrational assignments.

Raman wavenumber (cm^{-1})		
Observed	Literature (B_{2g}) c(ac)a	Assignments
57	52	
–	121	
130	133	Lattice vibrations
285	282	
370	374	C–N sym.def.
461	463	C–N asym.def.
761	761	C–N sym.stret.
958	956	C–N asym.stret.
961	962	C–N asym.stret.
1176	1179	CH_3–rock.
–	1297	CH_3–rock.
1415	1414	CH_3–sym.def.
1457	1458	CH_3–asym.def.
2928	2930	CH_3–sym.stret.
2965	2965	CH_3–sym.stret.
2980	2987	CH_3–sym.stret.
3031	3031	CH_3–asym.stret.

The ferroelectric hysteresis loop obtained (Fig. 2) using radiant technology is the evidence for the ferroelectric behaviour of the material. It is noticed that the remanant polarisation increases with the applied voltages. Further, ferroelectric ceramic behaviour is identified through the resistive leakage along the grain boundaries.

For the determination of optical constants we have undertaken the UV–vis transmission (T) and reflection (R) studies. The recorded transmittance spectrum displayed in Fig. 3 shows a better transmittance of the material in the visible region. The absorption coefficient (α) is calculated using the recorded transmittance values as follows

$$\alpha = \frac{\ln \frac{1}{T}}{t} \quad (1)$$

where, t is the thickness of the crystal. In the visible range of 575–

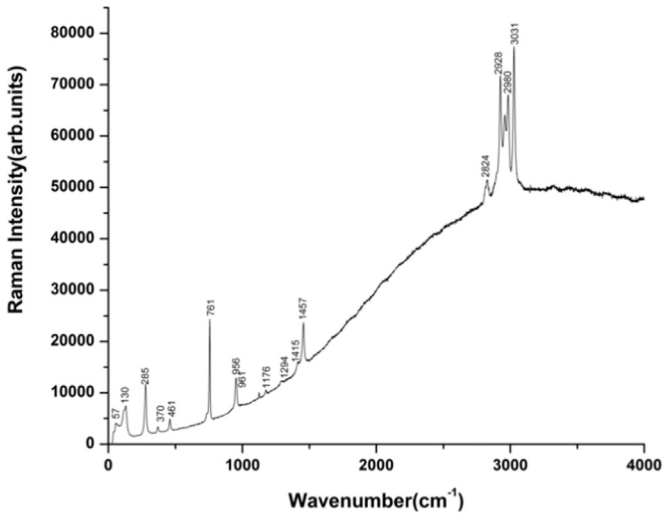

Fig. 1. Raman spectrum.

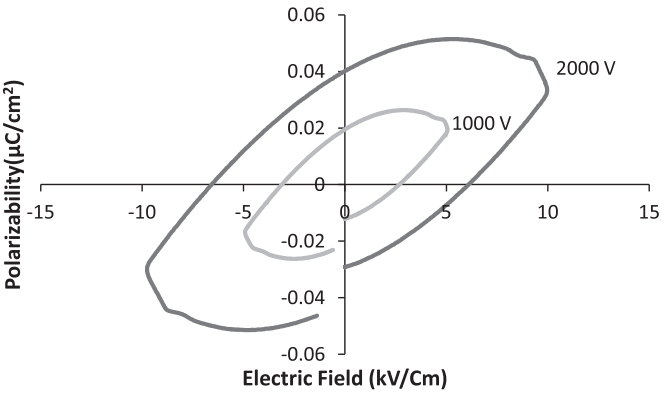

Fig. 2. Ferroelectric hysteresis loop study.