

CHAPTER - 5

INFLUENCE OF ALKYL GROUPS AND FERROELECTRIC PROPERTY OF TETRAMETHYLAMMONIUM TETRAETHYLAMMONIUM TETRACHLOROZINCATE CRYSTALS

5.1 Introduction

The crystals of alkylammonium tetrachloro metallates with the general formula $(NR_4)_2MCl_4$, with M corresponding to a divalent metal ion, have been widely investigated owing to their interesting ferroic and optical properties connected to the different phase transitions. Among those, crystals of metal ion replaced by Zn have been focused in earlier decades because of their commensurate ferroelectric incommensurate paraelectric phase transition. Crystal structure and properties of Tetramethylammonium Tetrachlorozincate ($TMAZnCl_4$) and Tetraethyl ammonium Tetrachlorozincate ($TEAZnCl_4$) crystals have been thoroughly analysed in the literatures [156-159]. Codoping of different ions (Cu and Co) into the position of Zn in $TMAZnCl_4$ and its phase transition mechanisms have been discussed [160, 161]. Other divalent metal ions such as Cu [158, 162], Co [163] and Mn [164] have been studied in the series of $(NR_4)_2MCl_4$ crystals. Similar to codoping of metal ions, crystal structure and dielectric properties of combination of tetramethyl ammonium and tetraethyl ammonium with zincates named tetramethylammonium tetraethylammonium tetrachlorozincate ($TMATEAZnCl_4$), can be commonly denoted as ABMX, have been studied in [165, 166]. It has two polymorphic forms named α - $TMATEAZnCl_4$ [165] and β - $TMATEAZnCl_4$ [167], in which title crystal cell parameters belong to β - $TMATEAZnCl_4$ form with chiral structure. The molecules

are arranged in a layered fashion, wherein organic TEA and TMA/ZnCl₄ layers are stacked with TEA layer at the bottom. Both TMATEAZnCl₄ and TMAZnCl₄ show five transitions whereas TEAZnCl₄ shows two transitions in the DSC thermogram [168]. The possibility of classical ferroelectricity presented in the TMATEAZnCl₄ has been predicted through degree of dielectric relaxation [169]. Until now, the ferroelectric study of ABMX compound comprising (TMA)⁺ and (TEA)⁺ has not been reported. Hence, in this report, a comparative analysis has been made on TMAZnCl₄, TEAZnCl₄ and TMATEAZnCl₄ crystals in optical as well as ferroelectric properties view. Finger print plot analysis has been undertaken to understand the influence of methyl and ethyl group interactions in ferroelectric properties of TMATEAZnCl₄ crystals.

5.2 Materials and methods

5.2.1 Crystal Growth

TMAZnCl₄, TEAZnCl₄, and TMATEAZnCl₄ crystals were grown by slow evaporation method using water as solvent at room temperature. The 2:1 molar ratio of tetramethylammonium tetrachloride (TMAC) and zinc chloride (ZnCl₂) were mixed in the aqueous solution using a magnetic stirrer. The solution was filtered using Whatman filter paper. The filtrate was covered with perforated foil and allowed to evaporate slowly at room temperature. The TMAZnCl₄ crystals were obtained after 13-15 days. In the same way, the crystals of TEAZnCl₄ crystals were grown using tetraethylammonium tetrachloride (TEAC) and ZnCl₂ as precursors. The equimolar ratio (1:1:1) of TMAC, TEAC and ZnCl₂ yielded the TMATEAZnCl₄ crystals in the solvent ethanol. Good optical quality single crystals were used for all the characterizations to probe the physical properties.

5.2.2 Characterization

The UV – Vis transmittance and reflection spectra were recorded using the instrument Cary – 300 in the range 200-1100 nm with a resolution 1 nm in the solid state. The dielectric measurements were carried out using N4L Numetric Q PSM 1735 instrument interfaced with impedance analyser in the frequency range 1KHz–10MHz. Polished grown crystal coated with silver paste was used to obtain good conducting surface for the measurements. The Radiant Technology method (Tester Name: PMF0713-334) was used to obtain the ferroelectric hysteresis loop. Intermolecular interactions of TMATEAZnCl₄ have been analyzed using Hirshfeld surfaces and fingerprint plots. The calculations were performed with Crystal Explorer [170] using the experimental crystal geometries as an input [167].

5.3 Results

5.3.1 Single crystal XRD study

The obtained lattice parameters from single crystal XRD analysis of all the grown crystals are well matched with the literatures values [165, 167, 168] (Table 5.1). The TMAZnCl₄ and TMATEAZnCl₄ are crystallized into orthorhombic structure whereas TEAZnCl₄ crystal is crystallized into tetragonal structure.

The lattice constants ‘a’ and ‘b’ values in the orthorhombic system of TMATEAZnCl₄ is about the same. Similarly, these values are same in tetragonal system of TEAZnCl₄. This similarity resembles the crystal systems of TMATEAZnCl₄ and TEAZnCl₄ even though it is different with different axis length of ‘a’ and ‘b’ (Table 5.1). However, in the case of orthorhombic TMAZnCl₄, a good variation is observed in the lattice constant values of ‘a’ and ‘b’. Hence, it is

expected that the TEAZnCl₄ and TMATEAZnCl₄ crystals may exhibit the same physical properties except for the phase transformation. It is to note that α -TMATEAZnCl₄ and TEAZnCl₄ crystallized in the tetragonal system [167].

Table 5.1 Obtained lattice parameter values along with the reported literature values

Crystals	Tetramethylammonium Tetrachlorozincate ((TMA) ₂ ZnCl ₄)		Tetraethylammonium Tetrachlorozincate ((TEA) ₂ ZnCl ₄)		Tetraethylammonium Tetramethylammonium Tetrachlorozincate(TMATEAZnCl ₄)	
Structure	Orthorhombic		Tetragonal		Orthorhombic	
Lattice parameters	Observed	Literature	Observed	Literature	Observed	Literature
a(Å)	8.981	8.988	9.018	9.04	13.132	13.099
b(Å)	12.256	12.276	9.018	9.04	13.149	13.119
c(Å)	15.513	15.546	15.005	14.99	11.822	11.812
α°	90	90	90	90	90	90
β°	90	90	90	90	90	90
γ°	90	90	90	90	90	90

5.3.2 Optical properties

The recorded transmittance spectrum and calculated absorption coefficient plot of TEAZnCl₄ (**Fig. 5.1**) and TMATEAZnCl₄ (**Fig. 5.2**) crystals are given in the wavelength range 200-1100 nm. Both crystals show high transmittance in the visible region which indicates that the crystals are suitable for optical applications. From the recorded transmittance spectrum, the absorption coefficient is calculated using the equation

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

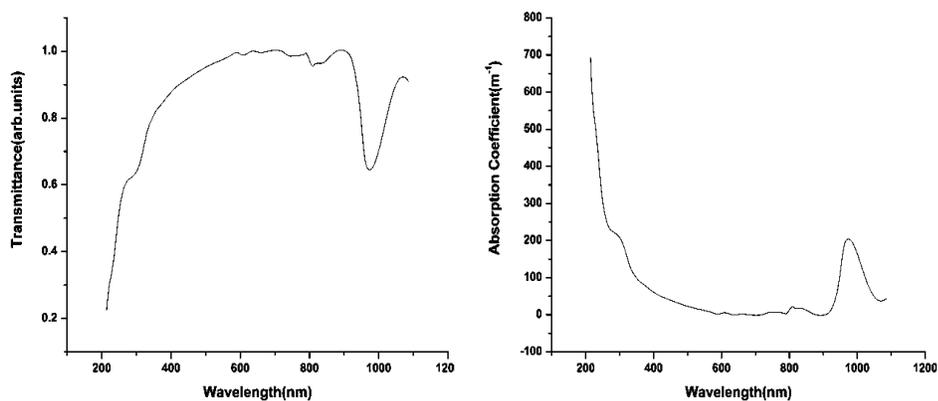


Fig. 5.1 Transmittance and calculated absorption coefficient spectrum of Tetraethylammonium Tetrachlorozincate

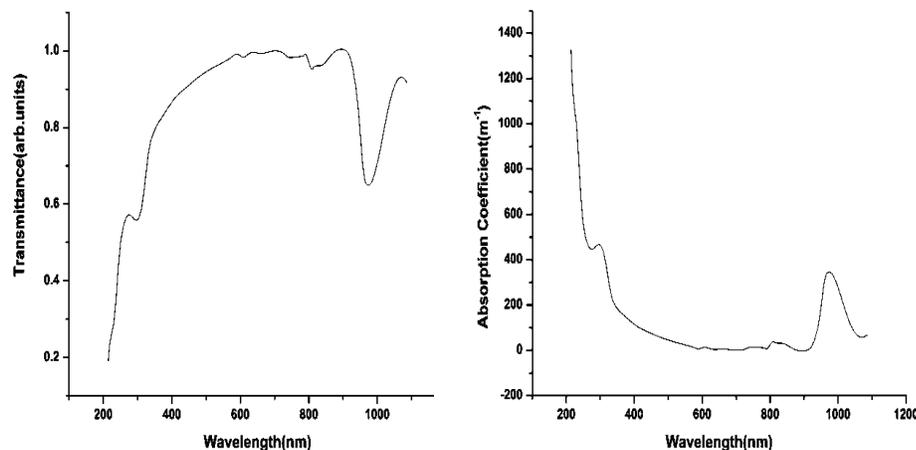


Fig. 5.2 Transmittance and calculated absorption coefficient spectrum of Tetramethylammonium Tetraethylammonium Tetrachlorozincate

The absorption coefficient value is in the order of 10^2 to 10^3 m^{-1} indicating the indirect band gap nature. The bandgap energy has been calculated by using Tauc plot [171]

$$\alpha h\nu = A(h\nu - E_g)^n \dots \dots \dots (2)$$

where $h\nu$ is the photon energy, E_g is the optical bandgap, A is a constant, n is an index which assumes the values $1/2$, $3/2$, 2 and 3 depending on the nature of electronic transitions responsible for absorption. Since the material exhibits indirect band gap nature, we have used $n = 2$ for the calculation. The Tauc plots of the TEAZnCl_4 and TMATEAZnCl_4 are shown in **Fig. 5.3**. The obtained band gap energy values are 3.72 eV for TEAZnCl_4 and 3.93 eV for TEATMAZnCl_4 . In the case of TMAZnCl_4 , the optical band gap energy was found to be 4.45 eV [172] in our earlier

study. On comparison, a slight deviation is observed in the band gap energy value of TEAZnCl₄ and TEATMAZnCl₄.

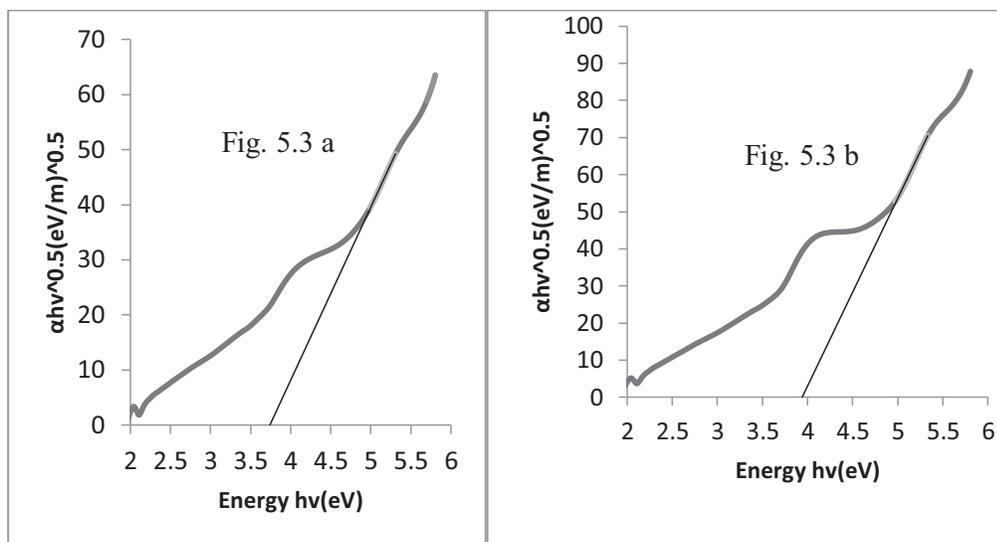


Fig. 5.3 a. Tauc Plot of Tetraethylammonium Tetrachlorozincate

5.3 b. Tauc Plot of Tetramethylammonium Tetraethylammonium
Tetrachloro zincate

This result indicates that the presence of ethyl group reduces the bandgap energy value whereas methyl group increases the band gap energy. The reduction in band gap generally favours the presence of charged domain walls and serves as a channel for the movement of charge carriers [173]. This in turn summing up dipoles in different domains gives rise to higher dipole moment for ethyl substitution.

5.3.3 Dielectric study-Determination of polarization

The insulating nature recommends materials to obtain high dielectric response to the applied electric field. The polarizability (α) at lower frequencies has been calculated through dielectric studies using the Clausius-Mosotti equation [174]

$$\alpha \cong \frac{\left[\frac{\epsilon_r - 1}{\epsilon_r + 2} \right] \left[\frac{M}{\rho} \right]}{2.53} \times 10^{24} \text{ cm}^3 \dots \dots \dots (3)$$

where M is the molecular weight and ρ is the density of the crystals. The dielectric constant of the crystal was calculated using the relation

$$\epsilon_r = \frac{C_{cry}}{C_{air}} \dots \dots \dots (4)$$

As the area of the electrode is greater than the area of the sample, then the Eq. (4) becomes

$$\epsilon_r = \frac{\left[(C_{cry} - C_{air}) \left(\frac{1 - A_{cry}}{A_{air}} \right) \right] A_{air}}{C_{air} A_{cry}} \dots \dots \dots (5)$$

where C_{cry} is the capacitance of the crystal and C_{air} is the capacitance of the air of the same dimension as the crystal. A_{cry} and A_{air} are the area of the crystal and area of the electrode respectively [175]. From the calculated dielectric constant values, the polarizability can be obtained and the average polarizability is found to be $1.44 \times 10^{-22} \text{ cm}^3$ for TEAZnCl₄. The polarizability value is $1.20 \times 10^{-22} \text{ cm}^3$, a little low for TMATEAZnCl₄.

5.3.4 Ferroelectric study

The high polarizability values derived from the dielectric study evident the ferroelectric properties of the crystals and could be verified through ferroelectric hysteresis loop study. The ferroelectric hysteresis loop is obtained at the electric field of 1000 V for TMAZnCl₄ [172]. On the other hand, it is observed at a very low voltage (10 V) for TEAZnCl₄ (Fig. 5.4 a). Due to the presence of methyl group, the

polarizability has been reduced to some extent and the ferroelectric hysteresis loop is obtained at 100 V for TMATEAZnCl₄ crystal (**Fig. 5.4 b**).

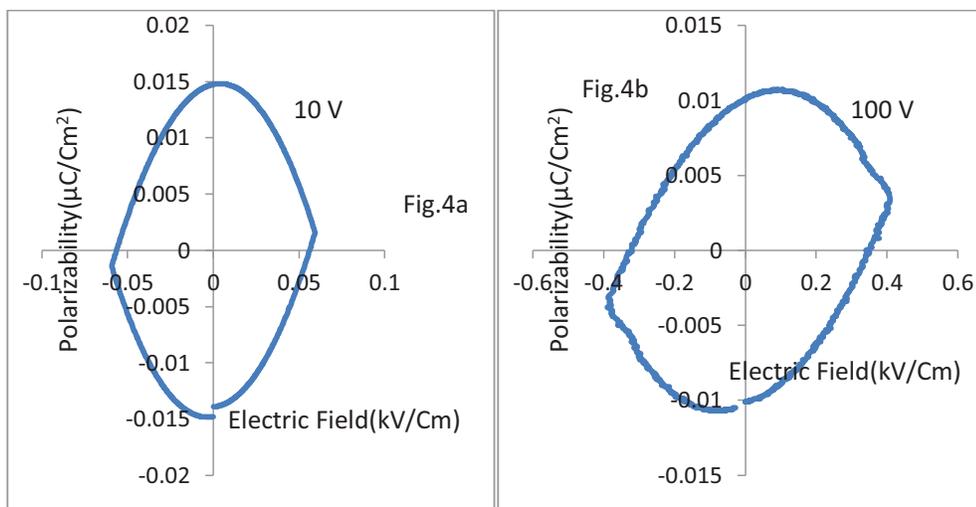


Fig. 5.4 a. P-E hysteresis loop of Tetraethylammonium Tetrachlorozincate

5.4 b. P-E hysteresis loop of Tetramethylammonium Tetraethyl-
ammonium Tetrachloro zincate

However, TEAZnCl₄ and TMATEAZnCl₄ do not contain any resistive leakage on its hysteresis loop path whereas it is presented in the hysteresis loop of TMAZnCl₄ [172]. The remnant polarization (P_r) and coercive field (E_c) of TEAZnCl₄ and TMATEAZnCl₄ are $.015 \mu\text{C cm}^{-2}$ (at 10V) & $.010 \mu\text{C cm}^{-2}$ (at 100V), and $.055\text{kV cm}^{-1}$ & $.34 \text{ kV cm}^{-1}$ respectively.

5.4 Discussion

It has been proven that the precursor TEAC has more hydrophilic nature and TMAC is hydrophobic [176]. During the synthesis of TMATEAZnCl₄, these two materials have been added as precursors with ZnCl₂ in the solvent ethanol as described in the experimental section. Compared to TMAC, TEAC is easily dissolved in the polar solvent, which might lead to the active incorporation of TEAC

rather than TMA with another precursor ZnCl_2 . Hence, the crystal TMATEAZnCl_4 behaves like TEAZnCl_4 crystal both in structural and properties point of view with slight modifications. A possible reason for the higher value of polarizability in TEAZnCl_4 compared to TEATMAZnCl_4 is due to the presence of more number of charged domain walls in the material with the presence of ethyl group leading to summing up of dipoles in domains. In other words presence of methyl group in TMATEAZnCl_4 significantly reduces the polarizability. Another reason for the higher ferroelectric behaviour in TEAZnCl_4 might be due to higher degree of freedom which leads to high spin lattice relaxation values of the ethyl ammonium cation in TEAZnCl_4 compared with TMAZnCl_4 [177]. It is to note that alkyl chain length enhances the polarizability value in non-centrosymmetric optical crystals [178]. The effect of alkyl chain on the ferroelectric properties of liquid crystal is investigated in [179]. The layered structure of organic (TEA) and TMA/ ZnCl_4 has been observed in the $(\text{NR}_4)_2\text{MCl}_4$ type crystals. For instance, methyl group in TMAZnCl_4 is more ordered but ethyl groups were slightly distorted with variation of bond length in the TEAZnCl_4 structure [167]. This disorderliness also plays a role in TEATMAZnCl_4 crystal but which is controlled under the influence of ordered methyl group. Intermolecular interactions of TMATEAZnCl_4 have been analysed using fingerprint plots (Fig. 5.5). Each point in the Hirshfeld surface corresponds to a (d_i, d_e) pair, where d_i and d_e denote the distances from the Hirshfeld surface to the nearest interior and exterior atom, respectively. The fingerprint plots of the interactions were obtained in the form of plots of d_i versus d_e .

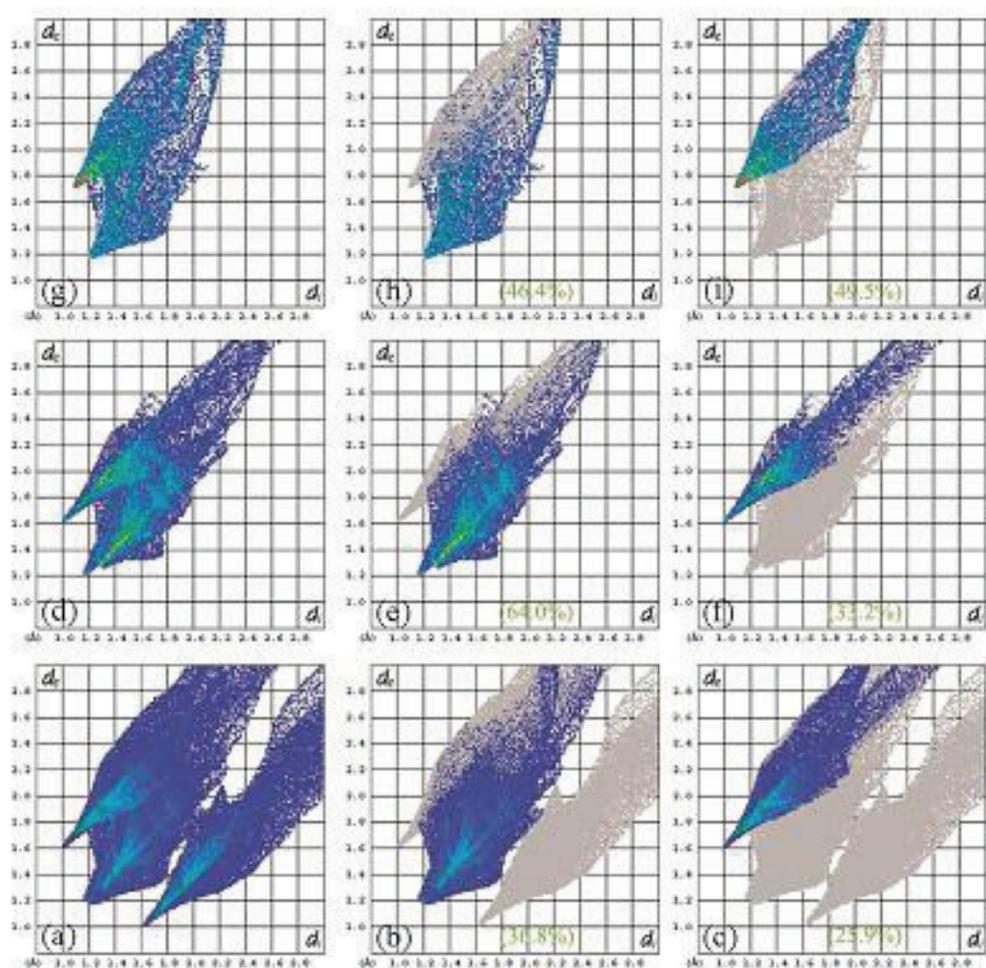


Fig. 5.5 Fingerprint plots (d_e vs d_i) of TMATEAZnCl₄ (a-c) tetraethyl ammonium (d-f) and tetramethyl ammonium (g-i) in TMATEAZnCl₄. Distances between the hydrogen atoms and hydrogen atoms (H \cdots H) on the surrounding molecules (second column). Distances between the hydrogen atoms and chlorine atoms (H \cdots Cl) on the surrounding molecules (third column). The value within the bracket indicates % of interaction. Sky blue and light green to red indicates strong interaction.

Three spikes in **Fig. 5.5 (a)** indicate interaction between alkyl groups and ZnCl_4 . The $d_i, d_e=1.2$ represents the $\text{H}\cdots\text{H}$ interaction between alkyl groups. The $d_i, d_e=1.0, 1.6$ and $d_i, d_e=1.6, 1.0$ represents interaction of ZnCl_4 on alkyl groups and vice versa respectively. The $\text{H}\cdots\text{Cl}$ interaction of ZnCl_4 on tetramethyl ammonium is dominant compared with tetraethyl ammonium. This interaction is clearly identified in **Figs. 5.5 (f), 5.5 (i)**. The interaction between tetraethyl ammonium and ZnCl_4 is 33.2 % whereas 49.5 % for interaction between tetramethyl ammonium and ZnCl_4 . However, it can be identified from the **Fig. 5.5 (c)** that the $\text{H}\cdots\text{Cl}$ interaction has been reduced in TMATEAZnCl_4 compared to tetramethyl ammonium and ZnCl_4 . The introduction of ethyl group in the TMATEAZnCl_4 creates disorder in the layered structure, which may be identified by less interaction of $\text{H}\cdots\text{Cl}$ and leads to high polarization for the applied electric field. The $\text{H}\cdots\text{H}$ interaction is high in tetraethyl ammonium (**Fig. 5.5 e**) compared with tetramethyl ammonium (**Fig. 5.5 h**) and TMATEAZnCl_4 (**Fig. 5.5 b**).

5.5 Summary and Conclusion

The single crystals of TMAZnCl_4 , TEAZnCl_4 and TMATEAZnCl_4 have been grown by slow evaporation method. The resemblance in the crystal of structure of TMATEAZnCl_4 and TEAZnCl_4 has been observed. The bandgap energy calculated from the transmittance spectrum of crystals are in the sequence of TMAZnCl_4 (4.45 eV) > TMATEAZnCl_4 (3.93 eV) > TEAZnCl_4 (3.72 eV). The interaction between alkyl group and ZnCl_2 contributes more on the properties of TMATEAZnCl_4 crystals. The introduction of ethyl group in the TMATEAZnCl_4 crystal creates disorder in the layered structure, which reduces the interaction between alkyl group and ZnCl_4 . This has been clearly identified through fingerprint plots. The

disorderliness and alkyl chain length substantially influence on the degree of polarizability of TEAZnCl₄ crystals, shows high polarizability value (1.44×10^{-22} cm³) compared with TMATEAZnCl₄ (1.20×10^{-22} cm³). This has been confirmed through ferroelectric hysteresis loop. Even at lesser voltages (10 volts), ferroelectric hysteresis has been observed in TEAZnCl₄ crystals (100 volts for TMATEAZnCl₄) because of high orientation of dipoles having greater polarizability value and summing up of dipoles of charged domain walls.