

CHAPTER - 6

OPTICAL BAND GAP ENERGY AND POLARIZABILITY

CALCULATIONS OF FERROELECTRIC 1-(2,3-DIMETHYLPHENYL) PIPERAZINIUM TETRACHLOROZINCATE(II) MONOHYDRATE AND BIS (2-AMINO-6-METHYLPYRIDINIUM) TETRACHLOROZINCATE(II) SINGLE CRYSTALS

6.1 Introduction

Ferroelectric and nonlinear optical materials (NLO) play a vital role in advanced laser technology and optoelectronics applications. Due to the poor chemical, thermal and mechanical stability, the organic crystals are currently limited in their industrial applications [180]. Hence, the preparation of inorganic anion and organic cation salts continues to be a focus area in chemistry and material science because of their abilities to combine the properties of organic and inorganic compounds within one single molecular scale, so as to exhibit some interesting crystal structure and some special properties, such as second-order nonlinear optical (NLO) response, magnetism, luminescence, and even multifunctional properties [181, 182]. It is therefore vital to design and synthesize novel salts with inorganic anions and organic cations so as to explore their various properties. The present work is devoted to determine the detailed study of the 1-(2,3-dimethylphenyl)piperazinium Tetrachlorozincate(II) Monohydrate $[1-(2,3-(\text{CH}_3)_2\text{C}_6\text{H}_3)\text{C}_4\text{H}_{10}\text{N}_2]\text{ZnCl}_4 \cdot \text{H}_2\text{O}$ and Bis(2-amino-6-methylpyridinium) Tetrachlorozincate(II) $(\text{C}_6\text{H}_9\text{N}_2)_2[\text{ZnCl}_4]$.

Generally organic cations with inorganic anions of type $ZnCl_4$ form layered structure compounds [183-185] and the single crystals grown in our previous studies are all belong to this type of structures. Basically the inorganic anion of the type $ZnCl_4$ has tetrahedral coordination where the neighbouring anions chains have coordination with different layers resulting hindrance to the motion of the chains. Here the isolated $ZnCl_4$ tetrahedra are connected by weak N-H...Cl hydrogen bonds results in less space restriction due to which there is intercalation of chains among neighbouring layers [186,187]. The above said facts give rise to conformational transformation of the chains leading to less disorder state even at higher temperature. This is the reason for us to keep the $ZnCl_4$ tetrahedral geometry common along with different organic cations.

The physical mechanism based on the phase transition on these type of crystals are the sandwiching of alkyl chains by inorganic layers, the characteristics of metal atom, the tilting of MCl_4 anion in different coordination, the alkyl chain length, the various inter-chain reactions and hydrogen bonding schemes [188,189]. Gyrotropy present in $C2Zn$ and $C5Zn$ [190], ferroelasticity present in $C1Zn$ [191] and $C3Zn$ [192] and conformational disordered phases present in $n>3$ [193] prompted us to study the underlying ferroelectric property. Hence the two system of choice here are aimed to understand the ability of coordination of the cation and anion through various types of hydrogen bonding and the possible reason for their comparison to elucidate the ferroelectric property.

6.2 Materials and methods

The studied single crystals were grown from aqueous solution by slow evaporation technique by dissolving a stoichiometric amount of 1-(2,3-

dimethylphenyl) piperazine, HCl, and ZnCl₂ (1:2:1) and ZnCl₂, aqueous HCl and 2-amino-6-methylpyridine in a 1:1:2 molar ratio. The Reactions yield the required crystals 1-(2,3- dimethylphenyl) piperazinium Tetrachlorozincate (II) Monohydrate [1-(2,3-(CH₃)₂C₆H₃) C₄H₁₀N₂] ZnCl₄·H₂O (system1) and Bis (2-amino-6-methylpyridinium) Tetrachlorozincate (II) (C₆H₉N₂)₂[ZnCl₄] (system 2) respectively.

6.3 Results and Discussion

6.3.1 Single crystal XRD study

The grown crystals are subjected to single crystal XRD study to obtain the lattice parameters and volume of the unit cell. The obtained parameters are $a = 10.211(9)\text{\AA}$, $b = 6.326(3)\text{\AA}$, $c = 13.561(1)\text{\AA}$ and $\alpha = 90.00(0)^\circ$, $\beta = 107.51(1)^\circ$, $\gamma = 90.00(0)^\circ$, Volume = $835.3(2)\text{\AA}^3$ which confirm the monoclinic structure of the material 1-(2,3- dimethylphenyl)piperazinium Tetrachlorozincate(II) Monohydrate . The triclinic structure of the material Bis(2-amino-6-methylpyridinium) Tetrachlorozincate(II) is identified by the obtained lattice parameters $a = 7.680(2)\text{\AA}$, $b = 7.917(2)\text{\AA}$, $c = 15.664(8)\text{\AA}$ and $\alpha = 98.88(3)^\circ$, $\beta = 100.90(4)^\circ$, $\gamma = 90.00(0)^\circ$, Volume = $923.7(6)\text{\AA}^3$. Both the results are well confirmed with the reported literature values [194, 195].

6.3.2 Ferroelectric Study

The electric field response of polarization is displayed in **Fig.6.1a & 1b** for fixed voltage of 1000 V. The hysteresis loop [196] obtained shows the ferroelectric nature of the material with their highly nonlinear dielectric behaviour generally hysteric as a consequence of domain wall motion. The parameters such as Coercive field E_c , Remnant Polarization P_r , Saturation Polarization P_s and the area of the loop are very important in understanding of the material behaviour. In the case of ceramic

material the poling condition to be adopted can be also found. On looking at the ferroelectric loops of these systems, one can readily tell about the comparison among the parameters mentioned. The magnitude of the coercive field is 2 kV/cm, for system 1 and 7.5 kV/cm, for system 2, indicating system 2 is sufficiently harder consequently more difficult to pole or de-pole [197]. Also to remove the remnant polarization a field in the negative direction should be applied and consequently removed when the field reaches a critical value called coercive field E_c . This field as mentioned is higher for system 2. That means the dipoles of system 2 are much more strongly oriented than system 1, indicating higher polarizability for sample 2. Moreover the remnant polarization P_r (poled states) for both system 1 and system 2 are $0.015 \mu\text{C}/\text{cm}^2$ and $0.05 \mu\text{C}/\text{cm}^2$, indicating the retaining capacity of polarization in zero field is more for system 2. This also confirms the better ferroelectric behaviour of system 2. The saturation polarizability is also more for system 2 signify the dipoles response to the electric field is much better than system 1. The determination of the loss factors [198] can be found with the help of the area of the hysteresis loop. More the area of the loop the more is the loss factors. System 2 has more loop area and the dielectric losses are more or otherwise system 2 is lossier dielectric compared to system 1.

In lossy dielectric, the area of the hysteresis loop is proportional to loss tangent of the device and the slope is proportional to capacitance [199]. As the slope of the loop in system 2 is obviously greater, this system has higher capacitance value.

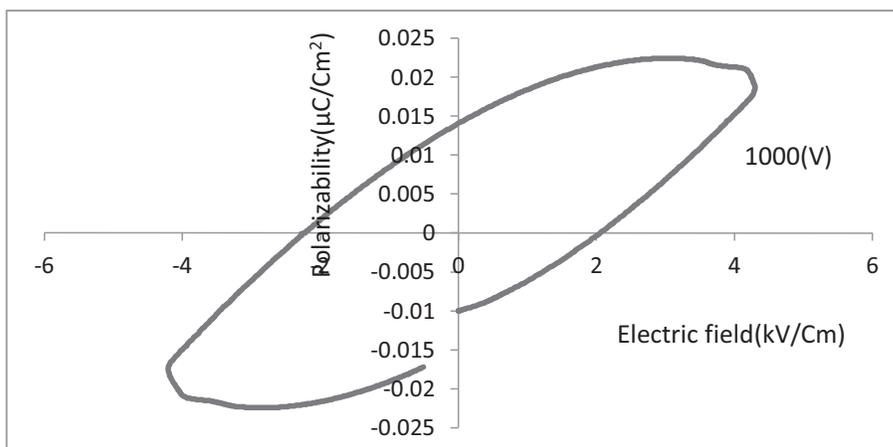


Fig. 6.1.a Hysteresis loop of 1-(2,3-dimethylphenyl) piperazinium
Tetrachlorozincate(II) Monohydrate

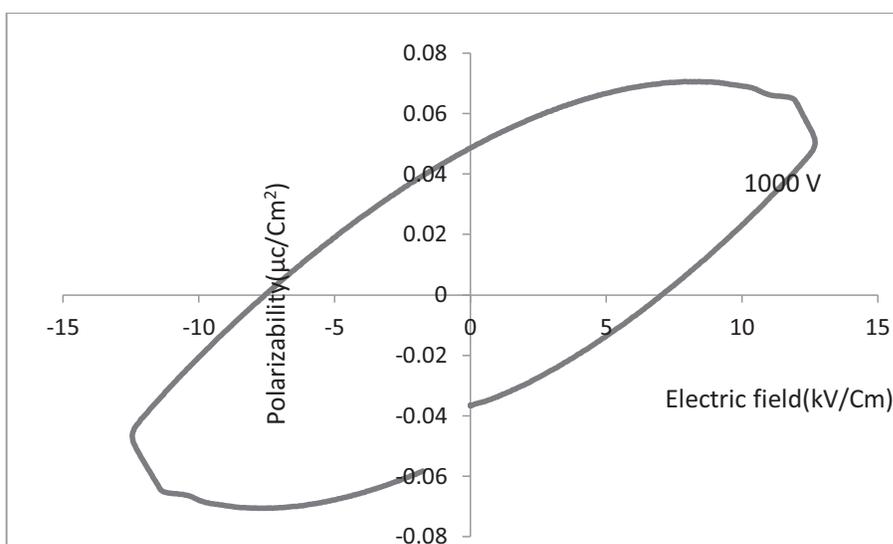


Fig. 6.1.b Hysteresis loop of Bis (2-amino-6-methylpyridinium)
Tetrachlorozincate (II)

On comparison, it is quite obvious that Bis(2-amino-6-methylpyridinium) Tetrachlorozincate(II) has higher ferroelectric behaviour/ polarizability value than 1-(2,3- dimethylphenyl)piperazinium Tetrachlorozincate(II) Monohydrate

6.3.3 Optical studies

From the recorded transmittance values the absorption coefficient (α) is calculated using the following relation

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

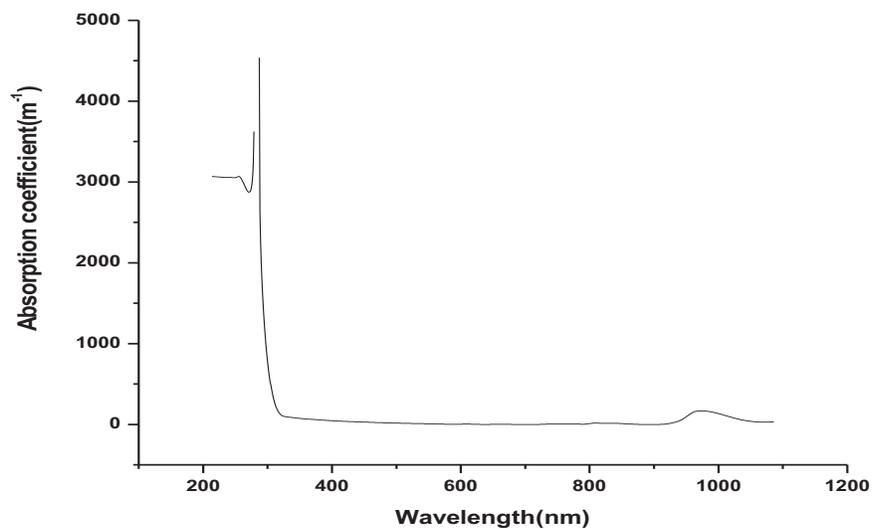


Fig. 6.2.a Absorption coefficient plot of 1-(2,3-dimethylphenyl) piperazinium
Tetrachlorozincate (II) Monohydrate

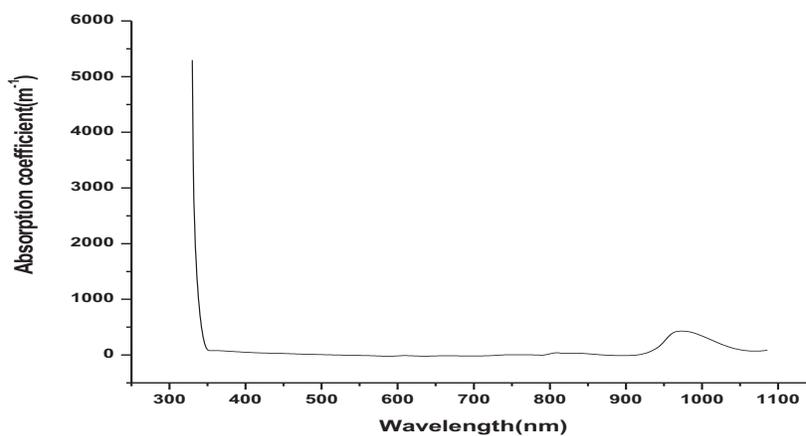


Fig. 6.2.b Absorption coefficient plot of Bis (2-amino-6-methylpyridinium)
Tetrachlorozincate (II)

The variation of absorption coefficient as a function of incident wavelength is portrayed in **Fig. 6.2 a & b**. It is inferred from the graph that the absorption coefficient values monotonically decrease with the increase of wavelength. The absence of absorption in the visible region indicates the insulating behaviour of the material. The absorption peak found at the IR region (974 nm) is the phonon absorption peak which arises due to lattice vibration. The absorption coefficient values are in the order 10^3 m^{-1} and it indicates the indirect allowed transition of the materials. The optical bandgap energy is determined from the absorption coefficient values using Tauc relation. For insulating material

$$\alpha h\nu = A(h\nu - E_g \pm E_p)^n$$

where $n = 2$ for indirect allowed transition. The $(h\nu \text{ vs } (\alpha h\nu)^{1/2})$ plot gives the x -intercept value corresponds to the zero absorption coefficient which is the optical bandgap energy. The calculated bandgap energy value of 1-(2,3-dimethylphenyl)piperazinium Tetrachlorozincate(II) Monohydrate is 3.88 eV and it is 3.52 eV for the material Bis(2-amino-6-methylpyridinium) Tetrachlorozincate(II) (**Fig. 6.3**) and it suggests the insulating behaviour of the materials. Hence, these materials favour for dielectric response. In addition, there is only one straight line observed in the Tauc plot which indicates the lattice phonon energy $E_p \approx 0$ for our material.

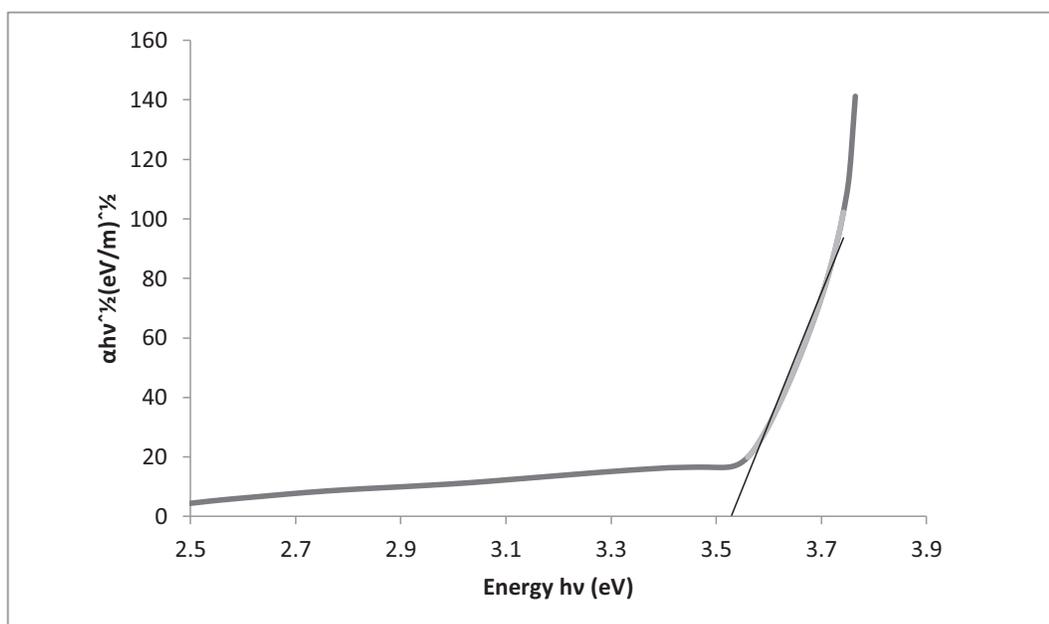
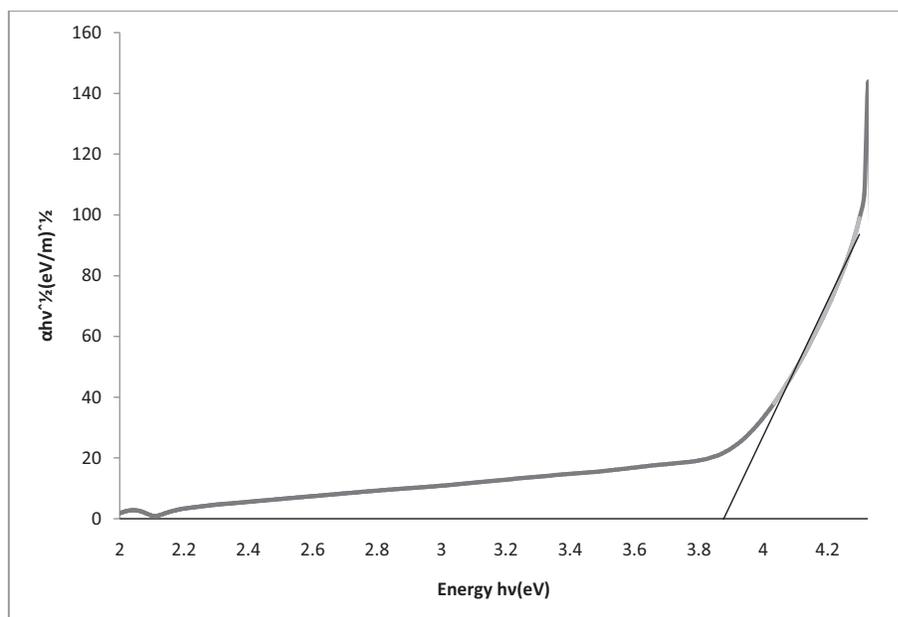


Fig. 6.3. Tauc Plot of 1-(2,3-Dimethylphenyl) piperazinium Tetrachlorozincate(II) Monohydrate and Bis(2-amino-6-methylpyridinium) Tetrachlorozincate(II) respectively.

6.3.4 Dielectric studies

Dielectric properties of the materials are based on the interaction of an external field with the electric dipole moment of the sample. If the crystal area is less than the electrode area, the dielectric constant values of the crystals are calculated from the measured capacitance values by using the following equation

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

where C_{crys} is the capacitance of the crystal. C_{air} is the capacitance of the air of the same dimension as that of the crystal, A_{crys} and A_{air} are the area of the crystal and area of the electrode respectively. For the material 1-(2,3-dimethylphenyl) piperazinium Tetrachlorozincate (II) Monohydrate the calculated dielectric constant at the frequency 1000 Hz is 167 whereas it is 548 for the material Bis (2-amino-6-methylpyridinium) Tetrachlorozincate(II) at the same frequency. Therefore, high polarizability is expected in the material Bis(2-amino-6-methylpyridinium) Tetrachlorozincate(II) than 1-(2,3- dimethylphenyl) piperazinium Tetrachlorozincate (II) Monohydrate .

From the calculated dielectric constant values, the polarizability of the material due to the contribution of all polarizability components is calculated by Clausius-Mossotti equation. The average polarizability is found to be $1.02052 \times 10^{-22} \text{ cm}^3$ for the material 1-(2,3-dimethylphenyl) piperazinium Tetrachlorozincate(II) Monohydrate and it is $1.0925 \times 10^{-22} \text{ cm}^3$ for material Bis(2-amino-6-methylpyridinium) Tetrachlorozincate(II) . This result is also well confirmed by Penn analysis. The polarizability α is obtained as

$$\alpha = \left[\frac{(\hbar\omega)^2 S_0}{(\hbar\omega)^2 S_0 + 3E_p^2} \right] \frac{M}{\rho} 0.396 \times 10^{-24} \text{ cm}^3$$

where E_p is the Penn gap and S_0 is a constant for the material which are defined by

$$E_p = \frac{\hbar\omega}{(\epsilon_r - 1)^{1/2}} \text{ (eV)}$$

$$S_0 = 1 - \frac{E_p}{4E_F} + \frac{1}{3} \left(\frac{E_p}{4E_F} \right)^2$$

where E_F is the Fermi energy and it is calculated as follows

$$E_F = 0.2947(\hbar\omega)^{\frac{4}{3}} \text{ (eV)}$$

The calculated polarizability values of 1-(2,3- dimethylphenyl) piperazinium Tetrachlorozincate (II) Monohydrate and Bis (2-amino-6-methylpyridinium) Tetrachlorozincate (II) are $1.0219 \times 10^{-22} \text{ cm}^3$ and $1.0944 \times 10^{-22} \text{ cm}^3$ respectively and the larger polarizability value of Bis(2-amino-6-methylpyridinium) Tetrachlorozincate (II) which is obtained earlier from ferroelectric study is also verified here.

6.3.5 Fingerprint analysis

The single crystal XRD studies give the hypothetical information about hydrogen bonds between the two electronegative atoms. Hence, the identification and quantitative analysis of the intermolecular interactions using Hirshfeld surfaces and the corresponding finger print plot analysis are recent approaches in molecular crystals [200]. Hirshfeld surface analysis was performed to visualize, explore and quantify intermolecular interactions in the crystal lattice. Hirshfeld analysis of 1-(2,3-Dimethylphenyl) piperazinium Tetrachlorozincate (II) Monohydrate (compound 1) and Bis(2-amino-6-methylpyridinium) Tetrachlorozincate(II) (compound 2) were carried out using Crystal explorer. Initially, the coordinates obtained from Cambridge Structural Database (CSD) of single crystal XRD result has been taken as input for the analysis. The classical hydrogen bonding interactions are well reflected

in the shape of d_{norm} surface [201]. The obtained plots (**Fig. 6.4**) are used to describe various intermolecular interactions including $\text{O}\cdots\text{H}$, $\text{H}\cdots\text{H}$, $\text{C}\cdots\text{H}$, $\text{H}\cdots\text{Cl}$ and other contacts present in crystal structures.

The fingerprint plot shows that the present compounds have the highest percentage of $\text{H}\cdots\text{Cl}$ interactions which is due to the effect of interaction between the piperazinium/ 6-methylpyridinium and ZnCl_4 . These interactions give the appearance of ‘spikes’ in the fingerprint plot. The interaction between piperazinium and ZnCl_4 is 50.9 % whereas the interaction of 6-methylpyridinium and ZnCl_4 is 40.2 %. This results shows that the $\text{H}\cdots\text{Cl}$ interaction of ZnCl_4 piperazinium is dominant compared with 6-methylpyridinium. So the $\text{H}\cdots\text{Cl}$ interaction has been reduced in 6-methylpyridinium compared to piperazinium and ZnCl_4 . The less $\text{H}\cdots\text{Cl}$ interaction is leading to high polarization for the applied electric field.

Both compounds have same $\text{H}\cdots\text{H}$ interactions (36 %) give the appearance of ‘wings’ in the fingerprint plot. The larger $\text{H}\cdots\text{H}$ interactions bring about the loose packing of the crystal. In Fig. 6.4 (c and f), the $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ interaction appear as wings with the contribution of 5.2 % for compound 1 and 9.4 % for compound 2.

This categorically proves the superiority of system 2 in terms of its ferroelectric behaviour.

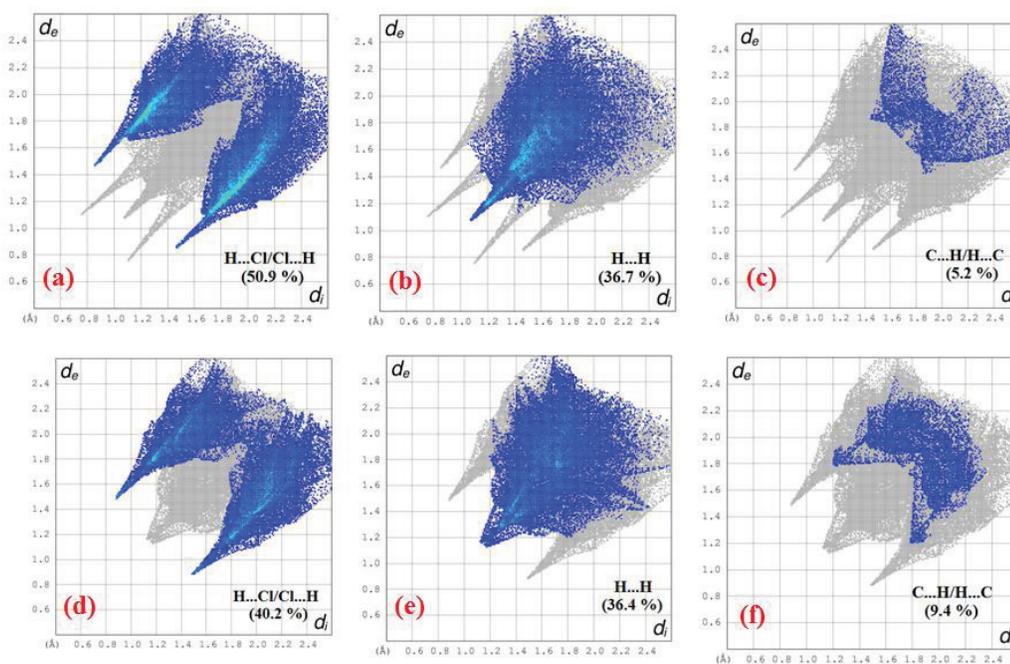


Fig. 6.4 Fingerprint plots (d_e vs d_i) of compound1 (a-c) and compound 2 (d-f).

6.4 Conclusions:

Grown single crystals 1-(2,3-dimethylphenyl) piperazinium Tetrachlorozincate(II) Monohydrate (system1) and Bis (2-amino-6-methylpyridinium) Tetrachlorozincate (II) (system 2) were characterized by XRD and the obtained lattice parameters confirmed the monoclinic and triclinic structures respectively. The higher value of coercive field and Remnant Polarization from ferroelectric hysteresis loop confirmed the system 2 has better ferroelectric behaviour than system1. The value of absorption coefficient from optical studies suggests the indirect bandgap nature and the optical bandgap found for system 1 and 2 are 3.88 eV and 3.52 eV validated the insulating behaviour of the material. The value of dielectric constant obtained from dielectric studies are 167 and 548 for system 1

and 2. The polarizability calculated using Clausius – Mossotti equation making use of the dielectric constant for the two systems suggest that system 2 has higher value of polarizability. This has been verified well by the theoretical Penn analysis. Using hydrogen bonding profile fingerprint analysis confirmed the higher value of polarization in system 2 with respect to applied electric field, well supported the findings in our work. This leads to the conclusion that system 2 has better ferroelectric behaviour.