Phase transition in triglycine family of hydrogen bonded ferroelectrics: An interpretation based on structural studies

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Abstract. Using the crystal structure, a comprehensive interpretation of the origin of ferroelectricity in the hydrogen bonded triglycine family of crystals is given. Our detailed analysis showed that the instability of nitrogen double well potential plays a driving role in the mechanism of the ferroelectric transitions in these crystals.

Keywords. Triglycine sulphate; order–disorder; phase transitions; displacive.

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1. Introduction

Hydrogen bonded ferroelectric crystals form a subclass of ferroelectrics in which hydrogen bonds play an important role in determining the properties. Triglycine family is one such class which includes triglycine sulphate (TGS), triglycine selenate (TGSe), triglycine fluoroberyllate (TGFBe), mixed crystals like $TGS_{0.75}TGSe_{0.25}$, doped ones like L-alanine doped TGS (LATGS) as the members. Of these, TGS is important for understanding the physics of the ferroelectric phenomenon as well as for its applications. Despite its complicated chemical and crystallographic form, it is being studied for several years mainly for two reasons: firstly, its excellent pyroelectric properties and high figures of merits make it suitable for use in the low-power detector applications where high detectivities are required, e.g. in the set up of spectrometers. Secondly, it is one of the very few ferroelectrics known to exhibit a typical second-order order–disorder type of phase transition, offering a spectrum of possibilities for understanding the basic mechanism of group–subgroup type of phase transitions in crystalline solids. The crystal structure of TGS was characterized in detail by neutron diffraction in the year 1973 [1,2].

Recently, we have carried out structural studies of TGS and its doped crystals by neutron and X-ray diffraction. Using these results and a detailed theoretical analysis, the structural origin of ferroelectricity and the characteristics of the phase transition in TGS family have been investigated. Results will be discussed.
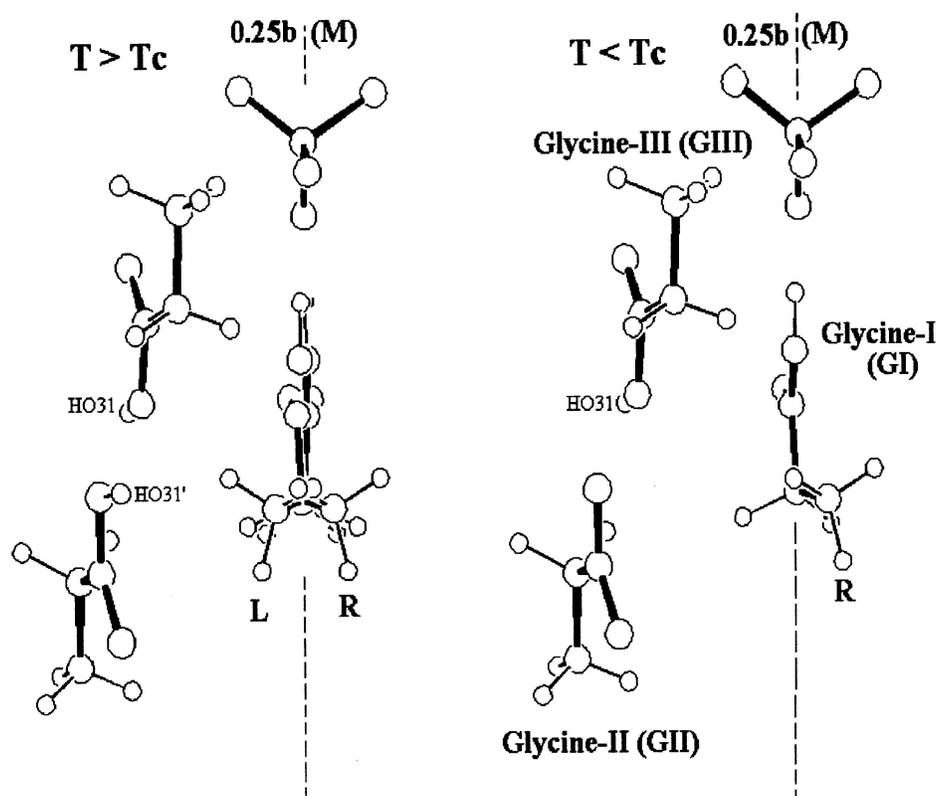
Figure 1. TGS structure in paraelectric and ferroelectric phases.

2. Structures of crystals belonging to triglycine family

The unit cell of TGS consists of three glycine groups, namely glycine-I (GI), glycine-II (GII), glycine-III (GIII) and a sulphate ion in an asymmetric unit. The structures of its ferroelectric and paraelectric phases were determined using neutron as well as X-ray diffraction [1,2] with the space groups being $P2_1$ and $P2_1/m$ respectively. As shown in figure 1, the two glycine groups GII and GIII are quasi-planar. They are arranged nearly perpendicular to the polar b-axis and are connected together by a strong hydrogen bond GIII-HO31–GII. The hydrogen atom in this H-bond has two equivalent positions, HO31, HO31′, which are closer to GIII and GII respectively. The GI lies close to the ac plane at $0.25b$ with its two carbon atoms and two oxygen atoms lying almost in the ac plane at $0.25b$ whereas the nitrogen is displaced significantly from the plane. The NH_3^+ group of GI has two equivalent positions, one on the left (L) and the other on the right (R) of the above-mentioned ac plane. For temperatures higher than transition temperature (T_c), the hydrogen in the H-bond GIII-H–GII and the NH_3^+ group of GI are disordered between their equivalent sites making the ac plane (at $0.25b$ (M)) a statistical mirror plane [3]. A comparison of the average amplitudes of motion of the heavy atoms near T_c shows

that the nitrogen atom of GI has a maximum amplitude in the b direction, which points to a possible driving role for the nitrogen double-well instability in the mechanism of the ferroelectric transition. Also, the insignificant effect of deuteration on the dielectric properties of TGS (e.g. T_c is increased by only about 3% in TGS as compared to 80% increase in KDP) suggests that the role of hydrogen tunneling in the H-bond GIII-H–GII may be less dominant as compared to the dynamics of NH_3^+ group of GI. The structure of the two ferroelectric domains of TGS are a mirror mage of each other [3]. When the polarization of a TGS unit cell reverses, the NH_3^+ group of GI moves from one of its equivalent positions, say L to the other R and the hydrogen in the H-bond GIII-H–GII moves along the bond from one of its equivalent positions HO31′ to the other HO31.

The major disadvantage of using ferroelectric crystals as pyroelectrics is the possibility of a single domain crystal becoming multi-domain (i.e. depoling of the crystals) during the application. One of the effective ways of preventing depoling in TGS is by doping it with alanine (NH_2CHCH_3COOH), which is a molecule similar to glycine (NH_2CH_2COOH) with the only difference being the presence of –CH_3 group in alanine in place of one of the two α-hydrogens of glycine. It is found that the addition of alanine to TGS results in a net internal bias field and the crystals containing alanine retain their self-bias even after prolonged heating above the Curie temperature as well as after the application of large reverse bias electric fields.

In order to understand the origin of this self-bias field, we carried out single crystal neutron diffraction study on L-alanine doped TGS (LATGS) crystals at Dhruva reactor, Trombay [4]. The results of the refinement of the structure ($R(F_0^2) = 0.0439$) were inconclusive as far as the indication in difference Fourier map was concerned. However, assuming a partial substitution at some of the glycine sites, the modeling of alanine in TGS unit cell lead to the conclusion that the zwitterionic site (GII) in TGS is the most preferred site of occupation of L-alanine [5]. This was contrary to the earlier view (which is based mainly on dielectric studies on LATGS) that the substitution may take place at GI site [6]. The problem with this interpretation, which stated that the prevention of depoling in LATGS is a result of the destruction of mirror symmetry of the unit cell by keeping the alanine at GI site, was that the substitution at not only the GI site but also at the GII or GIII site can break the mirror symmetry. Hence, according to the above argument, GII and GIII can also be possible sites of occupancy of alanine. A close look at the structural changes taking place in TGS during the polarization reversal shows that NH_3^+ group of GI undergoes maximum displacement during polarization reversal suggesting that the most effective way of preventing polarization reversal in TGS is by preventing the movement of NH_3^+ group of GI. Based on this, the prevention of depoling of TGS by L-alanine substitution at zwitterionic site (GII) could be explained as follows: when an L-alanine molecule occupies a zwitterionic GII, its CH_3 group has close steric contact with the NH_3^+ group of GI when it occupies one of its equivalent positions L (figure 2). This is because the two groups, i.e., CH_3 group of L-alanine and NH_3^+ group of GI at L site, occupy the same region in the asymmetric unit. As a result, in the unit cells in which L-alanine occupies the zwitterionc site (GII), the NH_3^+ group of GI is forced to occupy the R site alone leading to the prevention of polarization reversal of the unit cell. Such unit cells
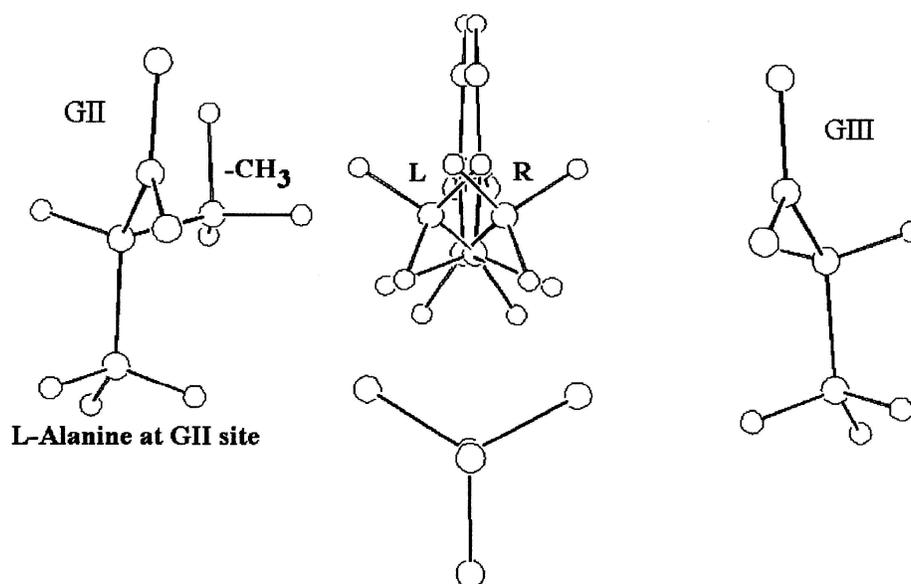
Figure 2. An asymmetric unit of LATGS unit cell with L-alanine molecule occupying GII site. The figure shows close steric contact between –CH$_3$ group of L-alanine and the NH$_3^+$ group of glycine-I occupying L position.

with irreversible polarization directions act as permanent dipoles embedded in the TGS lattice resulting in a net internal bias field within the crystal.

We also took up structural study of triglycine selenate (TGSe) which is isomorphous to TGS with the only difference being the presence of a selenate group (SeO$_4^{2-}$) in TGSe in place of the sulphate group (SO$_4^{2-}$) of TGS. Starting with the structural parameters of TGS, we have refined the structural parameters of TGSe with a final R-factor of 9.11% by Rietveld refinement using X-ray powder diffraction data and the Rietveld refinement software MPROF [7]. From these results, the cell parameters of TGSe were obtained as $a = 9.520(1)$ Å, $b = 12.8477(2)$ Å, $c = 5.8658(6)$ Å, $\beta = 110.554(5)$ with the unit cell volume 671.77 Å^3 which is about 5% larger than that of TGS. This is consistent as the selenate group is bigger in size than sulphate group.

3. Potential energy contour of NH$_3^+$ group of glycine-I in triglycine crystals

As explained above, the NH$_3^+$ group of GI plays an important role in the mechanism discussed. To get more insight into its importance, we have modeled the potential energy contour of the NH$_3^+$ group of GI as it flips between its two equivalent sites L and R in TGS. The coordinates (N1i) of the nitrogen atom of GI at its intermediate positions were generated by assuming that the atom moves along the arc N1–N1′ of a circle with its center at CA1 and radius equal to CA1–N1 bond length (figure 3a). N1 and N1′ are the positions of the nitrogen atom of GI when the NH$_3^+$ group

occupies R and L positions respectively. Assuming ideal staggered conformation of NH_3^+ at each of its positions (N1i), the coordinates of the three hydrogen atoms (Hs1i, Hs2i, Hs3i) of the group were generated. This was a reasonable assumption since the maximum deviation from the ideal staggered conformation as the group moves from R to L is within $\pm 10°$. The energies of the three hydrogen bonds made by the NH_3^+ group of GI (N1i$^+$–Hs1i–Os1, N1i$^+$–Hs2i–O21, N1i$^+$–Hs3i–O12) were calculated at each of its positions using the potential function (V_{HB}) for bent N$^+$–H–O bonds proposed in [8,9].

$$
\begin{aligned}
V_{HB} = &\, D_1\{1 - \exp(-n_1(r - r_{01})^2/2r)\} \\
&- CD_2\{\exp(-n_2(d - r_{02})^2/2Cd)\} \\
&+ A\exp(-b(R - R_{min})) - B/R^6,
\end{aligned}
\tag{1}
$$

where $D_1 = 104.0$ kcal/mol, $D_2 = 110.8$ kcal/mol, $r_{01} = 1.014$ Å, $r_{02} = 0.957$ Å, $n_1 = 9.30$ Å^{-1}, $n_2 = 9.06$ Å^{-1}, $C = 0.715$, $A = 5.050$ kcal/mol, $b = 7.854$ Å^{-1}, $B = 1.812 \times 10^3$ Å^6 kcal/mol, $R_{min} = 2.83$ Å. The variation of net hydrogen-bond energy V ($V = V_{HB1} + V_{HB2} + V_{HB3}$) of the group with the distance x from the ac plane at $0.25b$ [10] (figure 3b) was found to be of the form $V_{TGS}(x) = B_0 + Bx^2 + Ax^4$, where $B_0 = 11.83 \pm 0.51$ kcal/mol, $B = -99.55 \pm 3.6$ Å^{-2} kcal/mol, $A = 152.12 \pm 4.5$ Å^{-4} kcal/mol. When a L-alanine molecule occupies GII in LATGS unit cell, the two minima of $V_{TGS}(x)$ no longer remain equivalent due to the increase in the energy of NH_3^+ group when it occupies the L site because of the presence of CH_3 group in close vicinity to it.

In a similar way as described above, starting with the structural parameters of TGSe as obtained by the Rietveld structure refinement, the potential energy contour for the NH_3^+ group of GI in TGSe (figure 3b) was obtained as $V_{TGSe}(x) = B_0' + B'x^2 + A'x^4$, where $B_0' = 2.5 \pm 0.31$ kcal/mol, $B' = -37.04 \pm 2.9$ Å^{-2} kcal/mol, $A' = 68.00 \pm 4.7$ Å^{-4} kcal/mol. It was found that $V_{TGSe}(x)$ is three times shallower than $V_{TGS}(x)$ (figure 3b). This is mainly because the unit cell of TGSe is larger than that of TGS and hence the steric hindrance, which is the main cause of increase in potential energy as the group moves toward the plane M, is lesser in TGSe than in TGS.

4. Dipolar interaction energy between the –NH$_3^+$ groups of glycine-I in triglycine crystals

The bond between a nitrogen and a hydrogen is a polar bond having an average permanent dipole moment of 1.3 Debye. The NH_3^+ group in TGS has three such polar bonds arranged in tetrahedral geometry; hence it has a net permanent dipole moment ($\mathbf{p}$) of magnitude 1.4 Debye and direction along N–C bond. These permanent dipoles associated with the NH_3^+ group of GI interact with each other and the net dipolar interaction energy of a dipole at the ith lattice site was calculated [10] using the expression $E_i = 1/4\pi\varepsilon_0 \sum_j [\mathbf{p}_i \cdot \mathbf{p}_j - 3(\mathbf{p}_i \cdot \mathbf{r}_{ij})(\mathbf{p}_j \cdot \mathbf{r}_{ij})/\mathbf{r}_{ij}^2]/\mathbf{r}_{ij}^3$. Here $\mathbf{r}_{ij}$'s are the displacement vectors between the dipoles $\mathbf{p}_i$ and $\mathbf{p}_j$ which are generated using the space group symmetry and cell parameters of the crystals. Considering the symmetry of the unit cell, the net dipole moment of a unit cell (μ_{cell}) due to these permanent dipoles ($\mathbf{p}$) associated with the NH_3^+ group of GI was obtained as
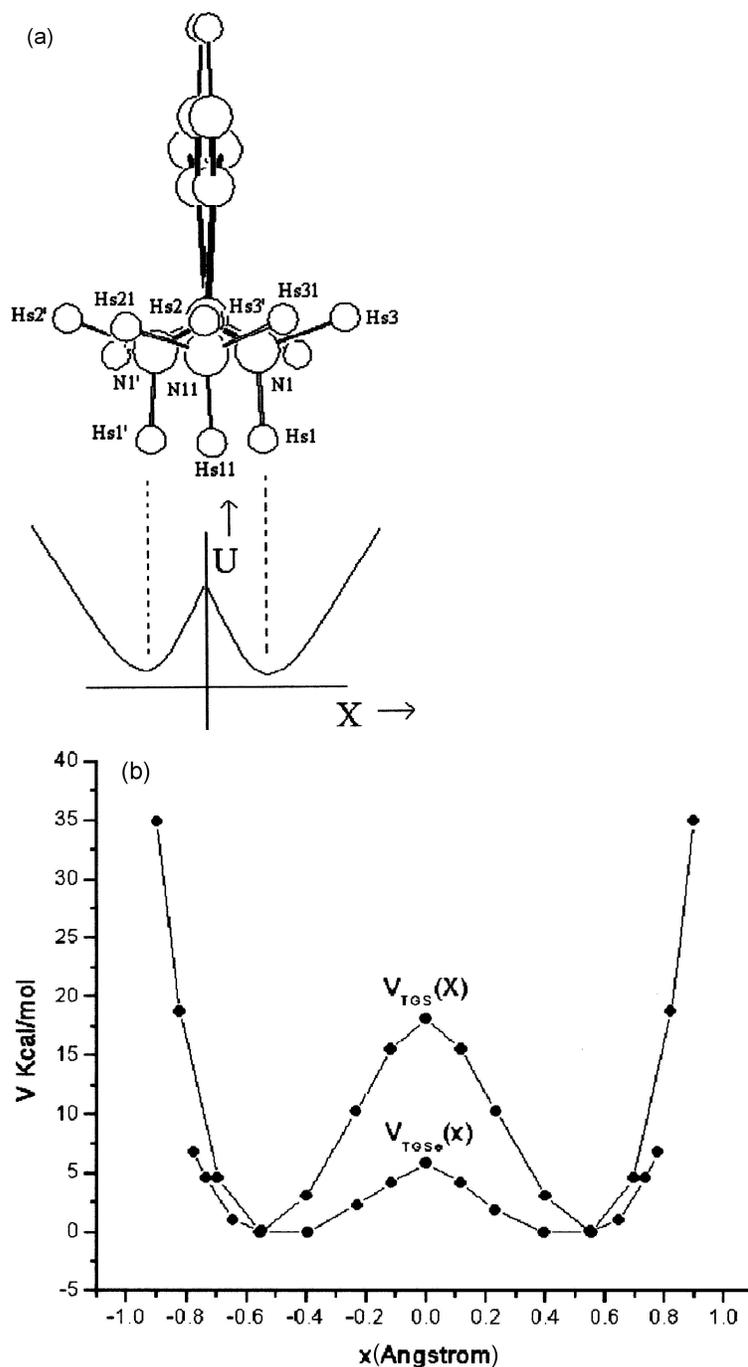
Figure 3. (a) Flipping of the NH_3^+ group of glycine-I. (b) Potential experienced by the NH_3^+ group of glycine-I in TGS and TGSe.

$\mu_{\text{cell}} = 2(p_b)\mathbf{b}$, where p_b is the component of $\mathbf{p}$ along b-axis and $\bar{b}$ is the unit vector $\mathbf{b}$. Thus, the dipolar interaction energy (E_i) between the polar NH_3^+ groups of GI in TGS, as calculated using the structural parameters is -0.71 kcal/mol with the unit cell dipole moment (μ_{cell}) as 1.21 Debye. For TGSe, these values are -0.66 kcal/mol and 1.21 Debye respectively. A decrease in the dipolar interaction energy (E_i) in TGSe as compared to that in TGS could be attributed to the increase in the distances $(\mathbf{r}_{ij})$ between the dipoles due to increase in the unit cell dimensions.

It is seen that the magnitude of dipolar interaction energy (E_i) of both TGS and TGSe are comparable with their respective thermal energies kT_c (0.64 kcal/mol and 0.58 kcal/mol, respectively) at the transition points indicating that the transition at T_c occurs due to a competition between ordering effect of these dipolar interactions and the disordering effect of the thermal energy. For $T > T_c$ thermal energy dominates whereas for $T < T_c$ dipolar ordering is more important.

5. Coupled anharmonic oscillator model for ferroelectrics

A unified oscillator model for order–disorder and displacive ferroelectrics has been proposed in [11–15]. This model consisted of an assembly of oscillators moving in the anharmonic potential $V(x) = Ax^4 + Bx^2$ where x stands for the displacement of an oscillator, A is taken to be definitely positive, while B may be either positive or negative. The local potential $V(x)$ seen by an oscillator had one or two minima depending on whether B was positive or negative. Also, a bilinear interaction between the oscillators of the system, which was treated in the Weiss molecular field approximation, was introduced which caused instability of the system. Lastly, the interaction of the oscillators with an external field $\mathbf{E}$ was considered. This model was described by a Hamiltonian $H = (M/2)(\mathrm{d}x/\mathrm{d}t)^2 + Ax^4 + Bx^2 - \gamma\langle x\rangle x + Ex$, where M is the mass of the oscillator and γ is the coupling constant. This system underwent a second-order phase transition in both $B < 0$ and $B > 0$ cases at a Curie temperature (T_c) which is determined by γ. Some important results of this model are as follows:

for $B > 0$ or $k_B T_c \geq B^2/4A$: Displacive
for $B < 0$ and $k_B T_c \ll B^2/4A$: Order–Disorder
$T_c/(B^2/4Ak_B) = 2\gamma/|B|$
$x_0 = (|B|/2A)^{1/2}$
$\langle x\rangle/x_0 = [(\gamma - 2B)/2|B|]$
$\Delta S = k_B/2 \ln(3\gamma/2|B| - 2)$ when $B > 0$
$\Delta S = k_B/2 \ln(3\gamma/|B| + 4)$ when $B < 0$.

We applied this coupled anharmonic oscillator model for describing the ferroelectric phase transition in triglycine family. In this case, the oscillator is the NH_3^+ group of GI, which is known to play a vital role in the phase transition, the long-range dipolar interaction between the dipoles associated with these NH_3^+ groups causes the phase transition at T_c. The local potential $V(x)$ experienced by this group was obtained as described above with the parameter x being the distance of the group from the mirror plane. In the calculations, the experimental value of T_c and the local potential parameters $B = -99.55 \pm 3.6$ Å^{-2} kcal/mol and $A = 152.12 \pm 4.5$ Å^{-4} kcal/mol of TGS were used to get the value of coupling constant $\gamma_{\text{TGS}} = 1.95$ kcal/mol Å^{-2} [10]. Using this value the mean interaction

energy $-\gamma_{\text{TGS}}\langle x\rangle^2_{\text{TGS}}$ of an oscillator in TGS was calculated to be -0.62 kcal/mol. This value agrees well with the dipolar interaction energy $E_i = -0.71$ kcal/mol calculated above, indicating that the model is well-suited to describe the phase transition.

Since TGS and TGSe are structurally very similar, it was assumed that the value of the coupling constant γ also to be the same, i.e., $\gamma_{\text{TGSe}} \approx \gamma_{\text{TGS}} = 2$ Å^{-2} kcal/mol. Using this value of coupling constant along with the local potential parameters $B' = -37.04 \pm 2.9$ Å^{-2} kcal/mol, and $A' = 68.00 \pm 4.7$ Å^{-4} kcal/mol, the transition temperature for TGSe was estimated to be 273 K. This value agrees with the experimental value 295 K, indicating that the model describes the transition in TGSe as well. From these calculations, the average interaction energy $-\gamma_{\text{TGSe}}\langle x\rangle^2_{\text{TGSe}}$ of an oscillator in TGSe is estimated to be -0.51 kcal/mol, which is closer to the dipolar interaction energy $E_i = -0.66$ kcal/mol as calculated above.

According to the coupled anharmonic oscillator model for ferroelectrics, the displacive character of the phase transition with $B < 0$ increases as the height of the barrier $(B^2/4A)$ between the two minima of local potential $V(x)$ decreases. This becomes purely displacive for $B^2/4A < kT_c$. It was noticed that the local potential $V(x)$ in TGSe is almost three times lower than that in TGS mainly because of the larger volume for the unit cell of TGSe. Hence, the phase transition in TGSe was expected to have more displacive character than that in TGS. This has been confirmed experimentally by a recent dielectric study [16].

6. Generalized effective field approach to the phase transition in triglycine crystals

Within the framework of a generalized effective field approach, characteristics of ferroelectric phase transition in TGS family was analysed [16] in which the effective field was given as

$$E_{\text{eff}} = E + \beta P_{\text{d}}[1 + g(P_{\text{d}}/N\mu)^2 + h(P_{\text{d}}/N\mu)^4 + \cdots], \qquad (2)$$

where E is the external applied field, P_{d} is the dipolar polarization, N is the number of dipoles per unit volume, g and h are dimensionless coefficients and μ is an elementary dipole moment. The equation of state and Curie temperature were given as $P_{\text{d}}/N\mu = \tanh(\mu E_{\text{eff}}/k_{\text{B}}T)$ and $T_{\text{c}} = \beta N\mu^2/k_{\text{B}}$. If the elementary dipole μ is considered to be the unit cell dipole (μ_{cell}) which results from the dipoles associated with the polar NH_3^+ group of GI, the values of the transition temperatures for TGS and TGSe becomes $(T_{\text{c}})_{\text{TGS}} \approx N\mu^2_{\text{cell}}/k_{\text{B}} = 382$ K and $(T_{\text{c}})_{\text{TGSe}} \approx N\mu^2_{\text{cell}}/k_{\text{B}} = 365$ K (since $\beta \approx 4\pi T_{\text{c}}/C$ for both TGS as well as TGSe is close to unity). These values are of the order of the experimentally obtained values 322 K, 295 K for TGS and TGSe respectively indicating that the assumption $\mu \approx \mu_{\text{cell}}$ is reasonable.

It has been stated earlier that the polarization direction of unit cell in which one of the glycine sites is occupied by an alanine molecule is frozen as a result of the substitution of alanine in TGS. If the number of such unit cells per unit volume is N_a then the bias field (E_a) due to these irreversible dipoles can be obtained within the framework of generalized effective field approach as: $E_a = \beta N_a \mu_{\text{cell}}$. For 2% alanine in a LATGS crystal [17], the internal bias field will be around 11.4 kV/cm

and this value compares well with the experimentally obtained value [17] of bias fields in LATGS crystals.

7. Conclusions

Starting with the structural information, a complete understanding of the origin of ferroelectric phase transition in triglycine family of crystals has been obtained. Results showed that the dynamics of polar NH_3^+ group of glycine-I plays a dominant role and the structural phase transition in these crystals is a result of the dipolar interaction between these polar groups. The influence of dopants like alanine in TGS on these results was also examined. Further structural studies on the mixed crystals $(TGS)_x(TGSe)_{1-x}$ are under progress.

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