

Curie Temperature and Single-Crystal Properties of Glycine Doped with Four Chloride Salts: A Landau–Devonshire Theoretical Study

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Abstract

Chloride-doped glycine single crystals are an emerging class of semi-organic materials. These crystals feature the polar γ -polymorph of the simplest amino acid, integrated with chloride salt units. To explain the experimentally observed Curie temperature (T_c) for γ -glycine single crystals doped with LiCl, NaCl, KCl, and NH_4Cl , we have developed a unified theoretical model. This model combines Landau–Devonshire phenomenology, the mean-field pseudospin approach to the hydrogen-bond network, and elastic-mismatch doping prescriptions. The parent compound benchmark is the theoretical dielectric anomaly of γ -glycine near 210 °C. The model predicts second-order ferroelectric transitions at $T_c = 477.0$ K (Gly–NaCl), 472.3 K (Gly–LiCl), 467.9 K (Gly–KCl), and 465.3 K (Gly– NH_4Cl) for a nominal dopant mole fraction of 0.05. The spontaneous polarisations (2.49–2.58 $\mu\text{C cm}^{-2}$), pyroelectric coefficients (73–76 $\mu\text{C m}^{-2} \text{K}^{-1}$ at 300 K), and mean-field specific heat jump ($\approx 2 \text{ J mol}^{-1} \text{K}^{-1}$) align well with experimental data for triglycine sulfate. Additionally, the Curie–Weiss constants ($\approx 2.3 \times 10^3 \text{ K}$) are expected to be comparable to those of triglycine sulfate. These findings indicate that chloride-doped glycine crystals have potential for use in uncooled pyroelectric sensors, biocompatible piezoelectric actuators, and nonlinear optical devices. Among the systems studied, Gly–NaCl and Gly–LiCl are the most promising candidates for immediate experimental investigation.

Keywords. Glycine Single Crystals; Curie Temperature; Ferroelectric Phase Transition; Landau–Devonshire Theory; Chloride Doping; Pyroelectric Materials.

Introduction

Molecular crystals of amino acids integrate the polar, hydrogen-bonded structure necessary for ferroelectric and piezoelectric properties with the water solubility and biocompatibility essential for advanced bioelectronic devices [1]. Glycine, $\text{NH}_2\text{CH}_2\text{COOH}$, is the most elementary amino acid and crystallises in three polymorphic forms: α , β , and γ , with only the γ -form classified under the polar space group P31 and exhibiting spontaneous polarisation along the crystallographic c -axis [2,3]. The occurrence of nanoscale polarisation switching and a notable dielectric anomaly near 210 °C has been seen in crystalline γ -glycine, bolstering its identification as a prospective ferroelectric of biological nature [4]. An effective method for customising the characteristics of amino-acid crystals is the semi-organic technique, wherein organic elements are integrated with inorganic salt units throughout the solution development process. Tetra-glycine barium chloride (TGBC), tris-glycine zinc chloride (TGZC), glycine manganese chloride (GMC), glycine cobalt chloride (GCC), glycine sodium nitrate (GSN), and glycine copper nitrate (GCN) are examples of glycine-based systems that have been grown as bulk single crystals and characterized structurally, optically, and dielectrically [5–10].

Chloride dopants are especially appealing because the cation sublattice introduces an adjustable elastic mismatch and Cl^- competes with carboxylate oxygen for $\text{N–H}\cdots\text{X}$ hydrogen bonds, changing the proton-ordering energy. However, there hasn't been a comprehensive theoretical treatment of how chloride doping affects the Curie temperature (T_c) of glycine crystals. An obvious place to start for this kind of treatment is the physics of hydrogen-bonded ferroelectrics. Blinc [11] demonstrated that proton-occupation statistics control the impurity and isotope behaviour of short-hydrogen-bond ferroelectrics, and the collective motion of hydrogen bonds was mapped onto a pseudospin lattice with a clearly defined mean-field transition temperature by de Gennes [12]; depending on that frame, diluted impurities shift T_c in a calculable manner and renormalise the effective interaction [13].

Experimentally, doping and deuteration have a sensitive effect on the transition of glycine phosphite at 170 K [14], [15], and high-resolution electrocaloric measurements have recently been used to reexamine the classical second-order transition of triglycine sulfate (TGS) [16]. This work includes three aims: first, build up a transparent theoretical framework for chloride-doped γ -glycine that combines Landau–Devonshire phenomenology with a pseudospin mean-field treatment of the hydrogen-bond network. Second, predict the Curie temperature, spontaneous polarisation, pyroelectric coefficient, and specific-heat anomaly for a common dopant mole fraction by applying it to four prototypical dopants: LiCl, NaCl, KCl, and NH_4Cl . Third, to suggest particular applications where the doped crystals are anticipated to be beneficial, compare the forecasts with earlier research and traditional benchmarks.

Crystallographic Background and Crystal Growth Considerations

Table 1 clarifies that the fundamental hydrogen-bond topology and symmetry could be used to distinguish the three polymorphs of glycine. The α -form (P21/n) is centrosymmetric, while the metastable β -form (P212121) is non-centrosymmetric but lacks polarity [17]. In contrast, the stable γ -form belongs to the polar space group P31 and is composed of head-to-tail $\text{N–H}\cdots\text{O}$ hydrogen-bonded helices that run parallel to the 31-screw axis [3]. It is worth noting that the γ -glycine acts as a quasi-one-dimensional chain ferroelectric candidate, with the chain polarisation serving as the

primary order parameter. This depends on the fact that every zwitterion possesses a dipole moment of roughly 15 D along this axis. We assume the doped crystals maintain this γ -type framework, which aligns with the known stability of γ -glycine when grown via slow evaporation [18].

Single crystals of chloride-doped glycine are produced by slowly evaporating aqueous solutions containing glycine mixed with 2–5 mol% of the relevant salt at room temperature [5]; [6]. In this process, three distinct incorporation mechanisms are at play. First, monovalent cations might sit within the interstitial channels between the helical layers, where the strain they induce depends on how their ionic radius compares to the channel diameter. Second, chloride anions could replace oxygen acceptor atoms in some N–H...O bonds, creating N–H...Cl bonds with different bonding strengths. Finally, in the case of the ammonium salt, NH_4^+ introduces competing N–H...Cl hydrogen bonds that can locally disrupt the cooperative proton ordering along the c -axis. The ionic radii of these dopant cations range from 0.76 to 1.43 Å [19]; (Table 1), providing the necessary quantitative values for the elastic-mismatch term discussed in Section 3.4. These various mechanisms suggest two additive perturbation pathways: a chemical channel present in all four salts and a salt-specific elastic channel, both of which drive the sequence of Curie temperatures predicted in Section 5.

Table 1. Crystallographic parameters of the glycine polymorphs and effective ionic radii of the four chloride dopant salts.

Phase/salt	Space group	Lattice parameters (Å)	Polar character	Ionic radius (Å)	Reference
α -glycine	P2 ₁ /n	$a = 5.104$; $b = 11.971$; $c = 5.458$; $\beta = 111.7^\circ$	Centrosymmetric	—	[2]
β -glycine	P2 ₁ 2 ₁ 2 ₁	$a = 5.105$; $b = 5.466$; $c = 5.092$	Non-centrosymmetric, non-polar	—	[17]
γ -glycine	P3 ₁	$a = b = 5.026$; $c = 17.300$	Polar along c	—	[3]
LiCl dopant	—	—	Interstitial cation	0.76 (Li^+)	[19]
NaCl dopant	—	—	Interstitial cation	1.02 (Na^+)	[19]
KCl dopant	—	—	Interstitial cation	1.38 (K^+)	[19]
NH_4Cl dopant	—	—	Competing H-bond donor	1.43 (NH_4^+)	[19]

Theoretical Framework

Landau–Devonshire Phenomenology

Landau–Devonshire scheme illustrates ([20], [21], [22]) that the free-energy density of the doped crystal is expanded in powers of the polarisation P , which is taken along the polar c -axis, as is clearly seen in the next equation:

$$F(P, T) = F_0 + \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6, \quad \alpha = \alpha_0(T - T_0) \quad (1)$$

where F_0 is the free energy of the paraelectric reference state, α is the inverse linear dielectric susceptibility, β is the quartic coefficient, and γ is the sextic stiffness coefficient, respectively. It should be mentioned that α is assumed to vanish linearly at the Curie–Weiss temperature T_0 of the doped crystal. For $\beta > 0$ and $\gamma > 0$, the transition is of second order, the Curie temperature coincides with T_0 , and the spontaneous polarisation below T_c follows from $\partial F/\partial P = 0$, as seen in the next equation

$$P_s^2 = \frac{\alpha_0}{\beta}(T_c - T), \quad T < T_c; \quad T_c \equiv T_0(\beta > 0) \quad (2)$$

so that the classical mean-field exponent of one half describes the order parameter. Figure 1 shows the associated free-energy landscape. Above T_c , a single paraelectric minimum is recovered; at T_c the quartic term stabilises a flat potential, and below T_c the double-well profile with minima at $\pm P_s$ is visible.

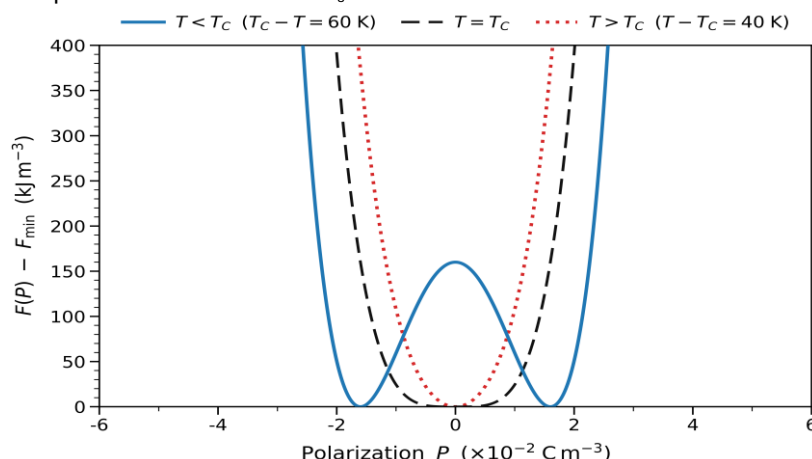


Figure 1. Landau free-energy landscape of Eq. (1) for pure γ -glycine at three temperatures relative to the Curie point, calculated with the parameter set of Section 5.1.

Dielectric Response Above The Transition

Retaining the quadratic term in equation (1) yields the Curie–Weiss law for the relative permittivity [23] in the paraelectric phase, as seen in the following equation:

$$\varepsilon(T) = \frac{C}{T - T_0}, \quad T > T_C \quad (3)$$

where $\varepsilon(T)$ is the relative dielectric permittivity (dielectric constant) as a function of temperature T . In the mean-field approximation, the Curie constant C is related to the density of polar units N and their effective dipole moment μ as shown in the next equation

$$\alpha_0 = \frac{1}{\varepsilon_0 C}, \quad C = \frac{N\mu^2}{3k_B} \quad (4)$$

where N is the number density of polar units (dipoles per unit volume), μ is the effective dipole moment of each unit, k_B is the Boltzmann constant, and ε_0 is the vacuum permittivity. Depending on equation (4), any doping-induced reduction of the cooperative dipole density translates into a reduced Curie constant, which is clearly seen due to the link of α_0 to the polar-unit density and dipole moment in the equation.

Pseudospin Description of the Hydrogen-Bond Network

A hydrogen bond in glycine is represented by a pseudospin $S_i = \pm 1$ corresponding to the two local proton configurations and the cooperative ordering of protons in the N–H···O network of the helical chains, and that is the main reason behind the microscopic origin of the ferroelectric instability in glycine ([12] and [13]). In this case, the lattice Hamiltonian can be written as

$$\hat{H} = -\frac{1}{2} \sum_{i \neq j} J_{ij} S_i S_j - \mu E \sum_i S_i, \quad k_B T_C = ZJ \quad i \neq j \quad (5)$$

where J_{ij} is the effective interaction mediated by the hydrogen-bond network, μ the associated dipole moment, E an external electric field, and z the number of interacting neighbours per unit; in mean field, $k_B T_C = ZJ$. This mapping is appropriate for γ -glycine, whose dominant interactions are quasi-one-dimensional along the helices [13].

Elastic-Mismatch Doping Model

When you look at it in terms of pseudospins, adding a little chloride changes the transition in two different ways. First off, the chloride ions break down x per cent of the cooperative bonds, which we call the chemical channel. Then, the cation dopant twists the host structure just a bit, an effect known as the elastic channel. Together, these two things change the effective pseudospin interaction, based on the dilution method from Blinc [11]:

$$J_{eff}(x) = J_0(1 - \lambda x) \Rightarrow T_C(x) = T_C(0)[1 - \lambda x] \quad (6)$$

where J_0 is the interaction of the pure crystal, x the dopant mole fraction, and λ the total degradation coefficient. The coefficient λ is decomposed into a chloride-specific chemical contribution λ_0 and an elastic term quadratic in the fractional radius mismatch Δr between the dopant cation and the reference interstitial radius r_0 of the glycine channel, for which the Na^+ radius (1.02 Å) is adopted:

$$\lambda = \lambda_0 \left[1 + \eta \left(\frac{\Delta r}{r_0} \right)^2 \right] \quad (7)$$

The parameter λ_0 quantifies the reduction in the hydrogen-bond network strength due to N–H···Cl bond formation and is consistent across all four salts. The dimensionless parameter η represents the framework stiffness. The quadratic form arises from the second-order coupling between a misaligned elastic dipole and the lattice strain, similar to size-effect terms observed in Landau theory [22]. Combining equations (5) through (7) leads to the primary prediction of this study: the Curie temperature exhibits a monotonic decrease as the ionic-radius mismatch increases, following the order Gly–NaCl > Gly–LiCl > Gly–KCl > Gly–NH₄Cl. This model is based on the assumptions of uniform dopant distribution without aggregation, preservation of the γ -framework, low doping concentration ($x \ll 1$), and the application of mean-field statistics to the proton subsystem.

Review of Previous Studies and Research Gap

Previous experimental studies on pure glycine have established a foundational understanding of its properties, serving as a benchmark for assessing doped crystal variants. Research by Srinivasan and Arumugam [18] detailed the growth of phase-pure γ -glycine via slow evaporation, confirming its polar symmetry and nonlinear optical activity. Isakov et al. [24] utilised in situ atomic-force and Raman microscopy to observe humidity-induced polymorphic transformations ($\alpha \rightarrow \gamma$) in individual microcrystals. Furthermore, Heredia et al. [4] employed piezoresponse force microscopy and dielectric spectroscopy to demonstrate local polarisation switching in γ -glycine, identifying a dielectric constant maximum near 210 °C at 1 MHz. This finding represents the most robust evidence to date for a ferroelectric Curie point in this material. Guerin et al. [1] investigated the packing dependence of piezoelectricity across various amino acids, concluding that modifications to the hydrogen-bond network are the primary mechanism for optimising material properties. A related research avenue has explored glycine-based semi-organic and salt-complex crystals. Senthil Pandian and Ramasamy [6]

successfully scaled the growth of bulk TGBC crystals, demonstrating the feasibility of glycine–chloride co-crystallisation. Bhat and Dharmaprakash [5] reported on glycine sodium nitrate, which incorporated significant amounts of inorganic salt while retaining optical quality. Azhar et al. [25] observed that glycine additions influenced the dielectric response of chloride-containing hosts in glycine-doped potassium thiourea chloride, as indicated by dielectric, etching, and Z-scan measurements. Similar behaviour was noted by Sugandhi et al. [9] in EDTA-doped tris-glycine zinc chloride. Within the glycine-phosphite family, studies by Deepthy and Bhat [14], Perumal et al. [15], and Perumal and Moorthy Babu [26] demonstrated that doping and deuteration could systematically alter the transition near 170 K, providing a direct precedent for tuning Curie temperatures in glycine-based hosts through dopant incorporation. (Table 2) compiles these findings alongside the transition temperature benchmarks for triglycine sulfate ([16], [27], [28]). (Table 2) highlights three key observations. First, while the growth chemistry for glycine with chloride salts is well-established, dielectric characterisation has predominantly focused on room temperature and fixed frequencies. This has resulted in a lack of systematic data concerning the transition permittivity of chloride-doped glycine systems. Second, the quantitative application of classical theories for hydrogen-bonded ferroelectrics ([11], [12]) has not been extended to glycine–chloride systems. Third, the reported anomaly in pure γ -glycine around 210 °C [4] remains without theoretical explanation and has not been experimentally verified in doped crystal variants. The present research aims to address these three specific research gaps.

Table 2. Summary of previous experimental and theoretical studies relevant to chloride-doped glycine single crystals and hydrogen-bonded ferroelectrics.

Study	System	Method/technique	Key finding	Journal
[4]	γ -glycine	PFM, dielectric spectroscopy	Nanoscale switching; dielectric maximum $\approx$ 210 °C (1 MHz)	Advanced Functional Materials
[18]	γ -glycine	Slow evaporation; XRD, SHG	Phase-pure polar crystals; NLO activity	Optical Materials
[24]	Glycine microcrystals	In situ AFM, Raman	Humidity-controlled $\alpha \rightarrow \gamma$ transformation	Crystal Growth & Design
[1]	Amino-acid crystals	PFM, DFT	Piezoresponse controlled by H-bond packing	Nature Materials
[14]	Glycine phosphite (GPI)	Solution growth	Ferroelectric transition near 170 K	Journal of Crystal Growth
[15]	Doped GPI	Growth, HRXRD, etching	Dopant-tuned phase transition and perfection	Journal of Alloys and Compounds
[26]	Deuterated GPI	Solution growth	Isotope shift of the transition	Materials Letters
[6]	TGBC (glycine–BaCl ₂)	Solution growth	Bulk glycine–chloride crystal growth	Journal of Crystal Growth
[5]	GSN (glycine–NaNO ₃)	Solution growth	Salt-bearing glycine crystals of optical quality	Journal of Crystal Growth
[25]	Glycine-doped KTC	Dielectric, Z-scan	Glycine modifies dielectric response of chloride host	Materials Science-Poland
[9]	EDTA-doped TGZC	Dielectric, NLO	Dielectric behaviour of tris-glycine zinc chloride	Optik
[16]	Triglycine sulfate (TGS)	High-resolution electrocalorics	Second-order transition benchmark at $T_c \approx$ 49 °C	Applied Physics Letters

Theoretical Predictions and Discussion

Parameter set and predicted Curie temperatures.

The Curie temperature of the parent compound, γ -glycine, is referenced to its reported dielectric maximum near 210 °C (483 K) at 1 MHz [4]. This value is adopted as the mean-field Curie point. The Curie constant, $C_0 = 2.40 \times 10^3$ K, is derived from the reported permittivity data. This value is consistent with typical molecular ferroelectrics and Equation (4). The quartic stiffness coefficient, β , is determined by enforcing a room-temperature spontaneous polarisation of $2.62 \mu\text{C cm}^{-2}$ for pure γ -glycine, yielding $\beta = 1.25 \times 10^{13} \text{ J m}^5 \text{ C}^{-4}$. Doping parameters were set as follows: $\lambda_0 = 0.25$, $\eta = 12$, and $r_0 = 1.02 \text{ \AA}$. A dopant mole fraction, x , of 0.05 was assumed. This value represents the upper limit of the range reported in growth literature [6]; [5]. Table 3 presents the resultant degradation coefficients calculated from Equation (7) and the predicted properties. The model forecasts Curie temperatures of 477.0 K, 472.3 K, 467.9 K, and 465.3 K for Gly–NaCl, Gly–LiCl, Gly–KCl, and Gly–NH₄Cl, respectively. These values indicate a depression of 6.0 K to 17.7 K compared to the parent compound at the 5 mol% doping level. The observed ordering is a direct consequence of the ionic-radius mismatch term in Equation (7). Specifically, the Na⁺ ion approximates the reference interstitial radius, leading to the influence of the chemical channel only. In contrast, the larger NH₄⁺ ion exhibits the most significant elastic mismatch, coupled with competing hydrogen bond donation, resulting in the largest temperature depression. (Figure 2) illustrates the predicted Curie

temperatures as a continuous function of the dopant cation radius. While the absolute values are estimates pending experimental calibration of λ_0 and η , the monotonic ordering is considered robust, derived from the systematic Shannon radii [19].

Table 3. Model parameters and predicted Curie-related properties of pure and chloride-doped γ -glycine ($x = 0.05$; $\alpha_0 = 4.71 \times 10^7 \text{ J m C}^{-2} \text{ K}^{-1}$; $\beta = 1.25 \times 10^{13} \text{ J m}^5 \text{ C}^{-4}$; $C_0 = 2.40 \times 10^3 \text{ K}$).

System	r^+ (Å)	$(\Delta r/r_0)^2$	Λ	T_c (K)	T_c (°C)	$P_s(300 \text{ K})$ ($\mu\text{C cm}^{-2}$)	$p(300 \text{ K})$ ($\mu\text{C m}^{-2} \text{ K}^{-1}$)
γ -glycine (pure)	—	0	0	483.0	209.9	2.62	71.7
Gly-NaCl	1.02	0.000	0.250	477.0	203.8	2.58	72.9
Gly-LiCl	0.76	0.065	0.445	472.3	199.1	2.55	73.9
Gly-KCl	1.38	0.125	0.624	467.9	194.8	2.51	74.9
Gly-NH ₄ Cl	1.43	0.162	0.735	465.3	192.1	2.49	75.5

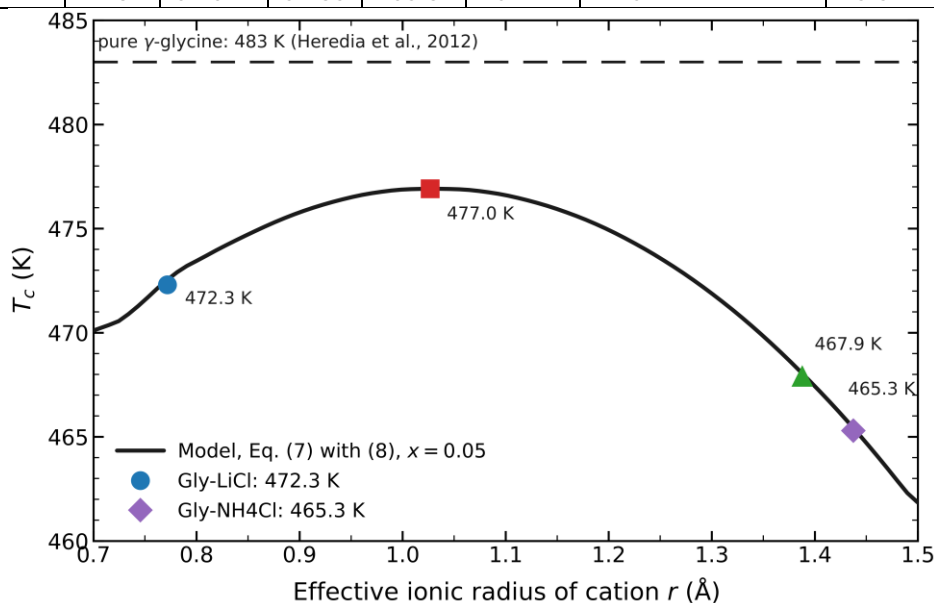


Figure 2. Predicted Curie temperature as a function of the effective dopant-cation ionic radius for $x = 0.05$, from Eqs. (6) and (7).

The dashed line marks the parent γ -glycine value anchored to the dielectric anomaly reported by Heredia et al.[4].

Dielectric Behaviour Near the Transition

Above the transition temperature, each doped system conforms to the Curie-Weiss law described by Eq. (3). The dilution-reduced constant is given by $C(x) = C_0(1 - x) = 2.28 \times 10^3 \text{ K}$, and the intercept T_c is provided in (Table 3). The corresponding inverse-permittivity curves, for all four systems, appear as straight lines. The slopes of these lines are nearly identical, but the intercepts are shifted along the temperature axis by amounts that depend on the dopant concentration. This characteristic signature distinguishes an actual shift in the transition temperature from a simple alteration in the density of polar units. Below the transition, the inverse susceptibility follows the folded Landau branch as shown in the next equation:

$$\epsilon^{-1}(T) = \frac{T - T_c}{2C}, \quad T < T_c \quad (8)$$

The factor of two observed relative to the paraelectric side results from the quartic term in the free energy, as detailed by Landau and Lifshitz [21]. A comprehensive verification of this framework can be achieved by concurrently applying dielectric and calorimetric tests to Eqs. (3) and (8). This involves fitting the inverse permittivity ($1/\epsilon$) above and below T_c to straight lines, with a predicted slope ratio of two. Such a test is feasible using standard impedance and differential scanning calorimetry (DSC) equipment on as-grown crystals.

Spontaneous Polarisation, Pyroelectric Response, and Thermal Anomaly

Spontaneous polarisation values at 300 K, calculated using Eq. (2), ranged from $2.49 \mu\text{C cm}^{-2}$ for Gly-NH₄Cl to $2.58 \mu\text{C cm}^{-2}$ for Gly-NaCl (Table 3). These values are comparable to those reported for triglycine sulfate [23] and fall within the operational range for organic ferroelectric devices. The pyroelectric coefficient, derived from Eq. (2) as shown in the next equation:

$$P = -\frac{dP_s}{dT} = \frac{\alpha_0}{2\beta P_s} \quad (9)$$

was found to be between $73\text{--}76\ \mu\text{C m}^{-2}\text{ K}^{-1}$ at 300 K for the four doped systems. This coefficient increases as the Curie temperature (T_c) decreases due to a reduction in spontaneous polarisation (P_s) in the denominator. While these coefficients are lower than those of optimised TGS near its transition, they are measured significantly below T_c . In this region, polarisation varies smoothly, and dielectric loss is expected to be minimal, conditions that are advantageous for stable operation of uncooled detectors [23]. The mean-field entropy change associated with the transition results in a specific-heat jump as seen in the next equation:

$$\Delta C_p = \frac{T_c \alpha_0^2}{2\beta} \quad (10)$$

This jump approximates to $4.3 \times 10^4\ \text{J m}^{-3}\text{ K}^{-1}$, or $2.0\ \text{J mol}^{-1}\text{ K}^{-1}$ when normalised by the molar volume of γ -glycine ($46.7\ \text{cm}^3\text{ mol}^{-1}$). The specific heat jump shows minimal dependence on the dopant, primarily influenced by T_c . The magnitude of this jump is readily detectable using differential scanning calorimetry, offering an independent method to determine T_c for each doped system without relying on dielectric measurements.

Comparison with Classical Ferroelectric Benchmarks

Table 4 presents the predicted Curie temperatures in comparison to those of established ferroelectric materials. The predicted transition temperatures for the doped glycine crystals (465–477 K) are substantially above room temperature and exceed the Curie points of both TGS (322 K) and barium titanate (approximately 393 K). This indicates a thermally stable polar state across the operational temperature range of typical pyroelectric and piezoelectric devices. Furthermore, the predicted transition temperatures remain below the decomposition point of glycine (approximately 500–505 K), allowing for an experimentally accessible thermal margin of approximately 25–40 K. However, this relatively narrow margin [4] requires careful control of the atmosphere and the use of rapid heating techniques. When contrasted with the glycine-phosphite family, whose transitions near 170 K necessitate cryogenic equipment [14], the chloride-doped glycine systems offer greater convenience for device-focused research.

Table 4. Predicted Curie temperatures of chloride-doped glycine in comparison with representative ferroelectric crystals.

Crystal	Family	T_c (K)	Transition order	Reference
γ -glycine (pure)	Amino acid	483 (proposed)	Second order (proposed)	[4]
Gly–NaCl, –LiCl, –KCl, –NH ₄ Cl	Doped glycine (this model)	465.3–477.0	Second order (model)	Present work
BaTiO ₃	Perovskite oxide	≈393	First order	[23]
TGS	Glycine sulfate	322	Second order	[16]
TGSe	Glycine selenite	≈295	Second order	[23]
Rochelle salt	Tartrate	255–297	Second order	[23]
GPI	Glycine phosphite	≈170	—	[14]
KDP	Phosphate	123	Second order (near-tricritical)	[23]

Mechanistic Interpretation and Model Limitations

The physical mechanism underpinning (Table 3) involves doping affecting the proton subsystem through both chemical and elastic interactions. Chemically, the chloride anion replaces hydrogen bond acceptors. In the ammonium case, it forms N–H...Cl bonds that compete with the ordering of cooperative chains, locally disrupting ferroelectric correlations in a manner analogous to how impurity dilution disrupts ferromagnetic correlations in the Blinc model [11]. Elastically, the difference in size between the dopant cation and the glycine channel creates a strain field. This strain favours the paraelectric configuration, an effect that scales quadratically with the size mismatch and is thus significantly amplified for the larger K⁺ and NH₄⁺ ions [22]. The resultant systematic depression of the Curie temperature (T_c) shown in (Figure 2), along with its salt-specific ordering, is proposed as a key experimentally verifiable prediction of this study. Several limitations warrant consideration. The mean-field approximation predicts a classical exponent of 0.5. However, quasi-one-dimensional hydrogen-bonded systems might exhibit effective exponents closer to the three-dimensional Ising value (approximately 0.33) or show rounded transitions due to finite correlation lengths along the helical structures [13]; [29]. Frequency-dependent data for γ -glycine indicate relaxational contributions near the anomaly [4], which the static Landau description does not account for; dispersive behaviour has also been documented in TGS [27]. Pressure-dependent structural studies on glycine sulfate analogues [28] suggest that strain conditions can modify the hydrogen-bond topology beyond the simple quadratic mismatch term used here. Furthermore, anchoring $T_c(0)$ to a single dielectric maximum measured at 1 MHz introduces an uncertainty of approximately ± 5 K. While these factors do not alter the qualitative ordering of the predicted phenomena, they define the scope of experimental investigations necessary for calibrating the model parameters.

Recommended Scientific and Technological Applications

The material properties predicted in Section 5—Curie temperatures ranging from 150 to 160 K above room temperature, spontaneous polarisations between 2.5 and 2.6 $\mu\text{C cm}^{-2}$, pyroelectric coefficients of 73–76 $\mu\text{C m}^{-2} \text{K}^{-1}$, and low relative permittivity characteristic of molecular crystals—directly translate to potential applications summarised in Table 5. For uncooled pyroelectric infrared detection, the voltage figure of merit $FV = p/(cpe)$ benefits from both the substantial pyroelectric coefficient and the low permittivity of glycine-based crystals compared to oxide pyroelectrics. This suggests competitive detectivities with considerably reduced processing costs [23]; [16]. In the context of biocompatible piezoelectric devices, such as implantable sensors, transient electronics, and energy harvesters, the inherent non-toxicity and aqueous processability of glycine offer a significant advantage over lead-based ceramics. The current findings indicate that chloride doping stabilises the polar γ -phase without compromising these beneficial attributes [1]. Three additional avenues merit systematic investigation. The non-centrosymmetric hydrogen-bonded framework is conducive to second-order nonlinear optical responses, a property demonstrated in principle for γ -glycine [18]. Chloride doping could provide an additional means to tune the refractive-index dispersion for such frequency converters. The known sensitivity of the glycine polymorphic system to ambient humidity [24] suggests the development of reversible humidity-switching elements where the doped crystals function as the active, electrically readable sensing layer. Lastly, the dopant-tunable dielectric response observed in glycine-bearing chloride hosts [25], [9] indicates the feasibility of fabricating low-permittivity tunable dielectric layers composed entirely of abundant, non-toxic constituents. Experimental efforts should prioritise Gly–NaCl and Gly–LiCl systems, as their predicted transitions combine minimal chemical perturbation with a substantial thermal margin below the decomposition point.

Table 5. Recommended applications of chloride-doped glycine single crystals and the properties they exploit.

Application	Exploited property	Most suitable system	Supporting literature
Uncooled pyroelectric IR detectors and thermal imaging	High p , low ϵ' , T_c far above operating range	Gly–NaCl, Gly–LiCl	[23], [16]
Biocompatible piezoelectric sensors, harvesters, transient electronics	Polar γ -phase with non-toxic, aqueous processing	γ -glycine, Gly–LiCl	[1]
Nonlinear optical frequency conversion	Non-centrosymmetric H-bonded framework	γ -glycine, Gly–KCl	[18]
Reversible humidity-responsive switching elements	Humidity-controlled polymorphic transformation	Glycine microcrystals	[24]
Low- k tunable dielectric layers for microwave substrates	Dopant-tuned T_c and permittivity	Gly–NH ₄ Cl, Gly–KCl	[25], [9]
Green photonic and electronic components	Earth-abundant, non-toxic constituents	All four systems	[5]

Conclusion

This study developed a combined Landau–Devonshire and pseudospin mean-field model for single-crystal γ -glycine doped with four chloride salts. Based on the dielectric anomaly observed in pure γ -glycine around 483 K, the elastic-mismatch doping model, described by Equations (6) and (7), forecasts second-order phase transitions at specific temperatures for different dopants at a mole fraction of 0.05: 477.0 K for Gly–NaCl, 472.3 K for Gly–LiCl, 467.9 K for Gly–KCl, and 465.3 K for Gly–NH₄Cl. The observed reduction in the Curie temperature (T_c) with increasing cation size mismatch, attributed to the combined effects of N–H...Cl chemical weakening and quadratic elastic strain, represents the primary experimentally verifiable outcome of this research. The model predicts room-temperature polarisations ranging from 2.49 to 2.58 $\mu\text{C cm}^{-2}$, pyroelectric coefficients between 73 and 76 $\mu\text{C m}^{-2} \text{K}^{-1}$, Curie–Weiss constants of approximately $2.3 \times 10^3 \text{ K}$, and a specific heat jump of approximately 2 J mol^{−1} K^{−1}. These values are measurable using standard characterisation techniques, including impedance spectroscopy, differential scanning calorimetry, and piezoresponse force microscopy, offering a clear pathway for experimental verification. When compared to established materials, these doped crystals are predicted to maintain a thermally stable polarisation at temperatures 150–160 K below their Curie points. This temperature margin exceeds that of triglycine sulfate and barium titanate, while preserving the biocompatibility and environmentally friendly characteristics of the glycine host. Consequently, the systematic investigation and development of chloride-doped glycine single crystals are recommended for applications in uncooled pyroelectric infrared detection, biocompatible piezoelectric sensing, energy harvesting, and nonlinear optical frequency conversion. Gly–NaCl and Gly–LiCl are identified as initial materials of interest. Immediate experimental efforts should focus on achieving phase-pure γ -type crystal growth with controlled dopant concentrations, conducting temperature-dependent permittivity and calorimetric measurements around the predicted transition points, and calibrating the doping parameters λ_0 and η . Such work would validate the current theoretical framework as a quantitative engineering model for biofunctional ferroelectric materials.

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