Discovery of amantadine formate: Toward achieving ultrahigh pyroelectric performances in organics

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GRAPHICAL ABSTRACT

PUBLIC SUMMARY
- Organic pyroelectrics have great potential in wearable devices for temperature sensing, IR detection, thermal imaging, and energy harvesting
- We report the first all-organic pyroelectric amantadine formate with properties better than that of TGS, a hybrid pyroelectric in use since the 1950s
- Amantadine formate has a large pyroelectric coefficient and a surprisingly small dielectric constant, which play a key role in its excellent pyroelectric performance
- The strategy of combining all-organic components and second-order phase transition will contribute to the exploration of new pyroelectrics
Pyroelectrics are a class of polar compounds that output electrical signals upon changes in temperature. With the rapid development of flexible electronics, organic pyroelectrics are highly desired. However, most organics suffer from low pyroelectric coefficients or low working temperatures. To date, the realization of superior pyroelectric performance in all-organics has remained a challenge. Here, we report the discovery of amantadine formate, an all-organic pyroelectric with ultrahigh voltage figures of merit ($F_v$), surpassing those of all other known organics and commercial triglycine sulfate, LiTaO$_3$ as well around room temperature. The key to the high $F_v$ is attributed to the large pyroelectric coefficients in a favorable temperature range resulting from a ferroelectric-paraelectric phase transition of second order at 327 K, small dielectric constant, and moderate heat capacity. In addition, amantadine formate is relatively lightweight, soft, transparent, low-cost, and nontoxic, adding value to its potential applications in flexible electronics. Our results demonstrate that a new type of pyroelectrics can exist in organic compounds.

**INTRODUCTION**

Pyroelectrics are polar materials whose electric polarizations can change with temperature. The ability to convert temperature changes into electrical signals allows them to be used in infrared detection, fire alarms, thermal imaging, and energy harvesting, etc.\textsuperscript{1,2} From a practical application point of view, the voltage figure of merit (FOM) $F_v = \rho/C_e$ is a particularly important parameter for gauging the electric output voltage efficiency, where $\rho$ is the pyroelectric coefficient, $C_e$ is the volume specific heat, and $\epsilon$ is the dielectric constant.\textsuperscript{3,4} Accordingly, high $F_v$ values require large pyroelectric coefficients, small dielectric constants and heat capacities. Pyroelectrics are highly related to ferroelectrics in dipole polarizations; in fact, ferroelectrics are a class of pyroelectrics. In general, ferroelectrics have larger pyroelectric coefficients than non-ferroelectrics. For example, lead magnesium niobate-lead titanate (PMN-0.25PT), a traditional perovskite oxide ferroelectric, exhibits a large pyroelectric coefficient of $\rho = -1,790 \text{ mC/m}^2\cdot\text{K}$, whereas non-ferroelectric aluminum nitride exhibits a small one, $\rho = 6-8 \text{ mC/m}^2\cdot\text{K}$.\textsuperscript{4} This correlation also holds in the polar interfaces, as recently revealed by Yang et al.\textsuperscript{5} However, the dielectric constant of the PMN-0.25PT single crystal is large ($\epsilon = 2,100$), leading to a low $F_v$ value of 0.039 m$^2$/C. Other inorganic ferroelectrics with large $\epsilon$ usually behave similarly: large $\epsilon$ and small $F_v$.

In comparison, triglycine sulfate (TGS), an organic-inorganic hybrid ferroelectric, has a smaller pyroelectric coefficient ($\rho = -280 \text{ mC/m}^2\cdot\text{K}$) and a considerably smaller dielectric constant ($\epsilon = 38$).\textsuperscript{6} Its $F_v$ value can reach 0.362 m$^2$/C, which is nine times higher than that of PMN-PT. Thus, TGS has been a commercial pyroelectric material since the discovery of its pyroelectricity in the 1950s.\textsuperscript{6,7} Another example is an organic perreniated hybrid [Al-H]ReO$_3$ that exhibits an $F_v$ value of about 0.45 m$^2$/C at 298 K.\textsuperscript{8} The key to this high $F_v$ can be attributed to the low $\epsilon$ and large $\rho$ in all-organic materials. In addition, these two hybrids, few pyroelectrics with such a high $F_v$ value have been found. Over the past decade, organic-inorganic hybrids have been found as new ferroelectrics with properties comparable to their inorganic counterparts.\textsuperscript{9-11} However, these reported organic-inorganic hybrid pyroelectrics suffer from either low Curie temperatures ($T_c$) or small pyroelectric coefficients.

The relatively small dielectric constant of TGS is largely due to the weak polarizing ability under electric fields of the organic component glycine and the moderate ability of sulfate ions in the structure, similar to the case of [Al-H]ReO$_3$. To further decrease the dielectric constant, all-organic ferroelectrics are good candidates for exploring pyroelectrics with better performance if their pyroelectric coefficients are sufficiently large. Moreover, organic materials are lightweight, flexible, and biocompatible, which are highly desired characteristics in the next generation of flexible devices.\textsuperscript{13-16} However, to date, all-organic pyroelectrics have either low working temperatures or smaller $F_v$ values than TGS, considerably limiting their applications.\textsuperscript{1,3,5,17-19}

It is known that molecules of various organic acids and amines are polar in structure. They can form simple organic salts; providing ample opportunities to find promising all-organic pyroelectrics. In TGS and other organic-inorganic hybrid pyroelectrics, the organic parts have negligible contributions to the total dipole polarizations in comparison with the organic parts. If both polar cations and polar anions are properly chosen in an organic salt, they are expected to simultaneously contribute to ferroelectricity and pyroelectricity. In addition, we expected the Curie temperature to be higher than room temperature within a range of several dozens of Kelvin and a continuous phase transition from ferroelectric to paraelectric with increasing temperature. This type of transition allows continuous change in the spontaneous polarization, instead of a sharp jump in the vicinity of the $T_c$, and enables to maintain a large pyroelectric coefficient over a certain temperature range.

In this study, we initially chose the appropriate polar ions that are conducive to the emergence of ferroelectricity. As the smallest organic carboxylate ion, the formate anion is more likely to undergo a order-disorder transition in a crystal. Meanwhile, spherical-like cations with low rotational energy barriers are promising candidates for inducing structural phase transitions.\textsuperscript{19-21} Based on these considerations, a novel all-organic ferroelectric amantadine formate (AF) is found. AF is composed of two polar organic ions (Figure S1A) with $F_v$ values of 0.362 m$^2$/C at 298 K, which is higher than that of TGS (322 K), but still close to room temperature. Structural analysis shows that both ions contributed to emergent ferroelectricity and pyroelectricity. Our measurements indicate that the ferroelectric-paraelectric phase transition in AF belongs to a continuous or second-order phase transition. As a result, the pyroelectric coefficient of AF is $-170 \text{ mC/m}^2\cdot\text{K}$ at 298 K. The room temperature dielectric constants of AF are only 13.5, 11.7, and 10.7 at 1, 10, and 100 kHz, respectively. The $F_v$ values are 0.705, 0.811, and 0.887 m$^2$/C at the corresponding frequencies, respectively, higher than those of all known organics, and even TGS. In addition, the strain-electric field measurements reveal that the piezoelectric coefficient of AF is $-16 \text{ pm/V}$, providing another example of the rare negative longitudinal piezoelectric effect.\textsuperscript{21-25} Our findings provide an all-organic material exhibiting high pyroelectric FOMs. AF has a low density of 1.21 g/cm$^3$ and a low hardness (0.46 GPA). Moreover, it is non-toxic and inexpensive, both in raw materials and in synthesis. These traits make it a potential material for applications in flexible pyroelectric devices.

**RESULTS AND DISCUSSION**

AF crystals up to 1 cm were grown by evaporating a mixed ethanol solution of amantadine and formic acid (Figures 1A and S1B). No other concomitant products were present, as confirmed by powder X-ray diffraction (Figure S2). Thermogravimetric analysis (TGA) indicates that AF is stable up to approximately 420 K (Figure S3). Although soluble in water, AF is very stable in air (Figure S4). The elastic module and hardness are measured to be 8.74 GPA and 0.46 GPA (Figure 1A), respectively, which are approximately one-third of the values for TGS (Figure S5) and one to two orders of magnitude smaller than the values for inorganic pyroelectrics.\textsuperscript{26} The crystal structures are determined from single-crystal X-ray diffraction (SCXRD) data (Tables S1-S3). AF crystallizes in a...
monoclinic system with space group P2$_1$ at 298 K with cell parameters $a = 8.2200(8)$ Å, $b = 6.5851(7)$ Å, $c = 10.4675(10)$ Å, $\beta = 106.952(3)^\circ$, and $V = 541.98(9)$ Å$^3$. The calculated density is 1.21 g/cm$^3$, slightly higher than that of water. The crystal structure is shown in Figure 1B. In the structure, a hydrogen atom of the formic acid molecule is ionized and acquired by the nitrogen atom of amantadine, forming two types of ions in the crystal: [C$_{10}$H$_{18}$N]$^+$ and [HCOO]$^-$. Each unit cell contains two AF molecules. There are several N–H···O hydrogen bonds with bond lengths from 2.771 Å to 2.795 Å connecting cations and anions. Both types of ions are polar, and the directions of the dipole moments are shown in Figure 1B. Thus, the net electric dipole moments of both [C$_{10}$H$_{18}$N]$^+$ and [HCOO]$^-$ arise along the $b$ axis. The spontaneous polarization of AF can be expressed as $\varepsilon_{33}V$ and is along the $b$ axis, where $\varepsilon$ is the electric dipole moment of the ions and $V$ is the volume.

We find that AF undergoes a structural phase transition with increasing temperature. At about 340 K, it recrystallizes in a centrosymmetric structure with space group P2$_1$/m, followed by the disappearance of the spontaneous polarization. The cell becomes slightly larger: $a = 8.2566(10)$ Å, $b = 6.6287(6)$ Å, $c = 10.4895(11)$ Å, $\beta = 107.054(13)^\circ$, and $V = 548.85(11)$ Å$^3$. All [C$_{10}$H$_{18}$N]$^+$ cations rotate a little and still remain ordered. Their net dipoles are lost as mirror planes that bisect the molecules now appear, as shown in Figure 1B. The [HCOO]$^-$ anions also rotate and become disordered since they locate at two equivalent orientations connected by a mirror plane perpendicular to the $b$ axis. Similarly, the net moment of the [HCOO]$^-$ anions is also lost. The hydrogen bonds form from the H atoms of the amino groups and random O atoms of the formate anions. Hence, the bond lengths span a slightly larger range, from 2.725 Å to 2.828 Å. This phase transition between point group 2/m and 2 is one of the 88 species of ferroelectrics summarized by Aizu.$^{27}$ A displacement of [C$_{10}$H$_{18}$N]$^+$ ions and an order-disorder type change of [HCOO]$^-$ ions occur when transiting from the ferroelectric to the paraelectric phase. Therefore, both contribute to polarization below the Curie temperature.

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**Figure 1.** Mechanical properties and crystal structure of AF (A) Optical photograph of a grown single crystal of AF, and the load-displacement curve of AF single crystal along the $b$ axis. The fitted elastic module and hardness are 8.74 GPa and 0.46 GPa, respectively. (B) Crystal structures of amantadine formate at 298 K (left) and 340 K (right), where the phase transition temperature is around 327 K. The arrows represent the directions of polarization of ions. The half red and half white balls represent the oxygen atoms with 50% occupation. Hydrogen atoms are omitted for clarity.

**Figure 2.** Ferroelectric-related properties (A) DSC data of AF during a heating and cooling cycle, revealing a phase transition around 327 K. (B) Temperature-dependent SHG intensity of polycrystalline sample of AF. (C) Polarization-electric field hysteresis loops along the $b$ axis at 298 K and 350 K. The external electric field is a triangle wave with a frequency of 0.01 Hz. (D) Temperature-dependent real part of dielectric constants along the $b$ axis at different frequencies. (E) Temperature-dependent imaginary part of dielectric constants along the $b$ axis at different frequencies. (F) Strain-electric field hysteresis loop along the $b$ axis at 298 K. The external electric field is a triangle wave with a frequency of 100 Hz.
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To confirm this ferroelectric-paraelectric phase transition, we first detected the thermal response of AF. Differential scanning calorimetry (DSC) revealed that a peak appears at 327 K during the heating process, and at 322 K during the cooling process at a temperature change rate of 5 K/min (Figure 2A). Strikingly, in contrast to the \( \lambda \)-shaped peaks (Figure S6) observed in the phase transition for most ferroelectrics,\(^{10,28,29} \) the peaks of AF are step-like in shape, similar to ferroelectrics Rochelle salt,\(^{13} \) but smaller than that measured by the Berlincourt method (Figure S11). The value is lower than that of most molecular ferroelectrics.\(^{13,36-38} \) As poling is a necessary procedure for ferroelectrics before being used in pyroelectric devices, such a low coercive field will reduce the cost in the poling process. Meanwhile, the strain-electric field curve exhibits a typical butterfly shape of ferroelectrics and reveals that AF is a negative piezoelectric (Figures 2F and S10), which has attracted much interest recently.\(^{21,25,29,41} \) The estimated \( d_{33} \) is around \(-16 \) pm/V, consistent with that measured by the Berlincourt method (Figure S11). The value is lower than the range (\(-37.7 \) pm/V for negative-piezoelectric PVDF\(^{22} \) and \(-95 \) pm/V for CuInP\(_2\)S\(_6\))\(^{23} \) but comparable to \(-6 \) to \(-16 \) pm/V for positive-piezoelectric LiNbO\(_3\).\(^{21} \) Furthermore, the structure and switching of domains are observed by piezoresistive force microscopy (PFM), strongly confirming the ferroelectricity of AF (Figure 3).

The temperature dependence of the pyroelectric coefficient was obtained by measuring the current response under temperature ramping from 250 to 360 K. The pyroelectric coefficient first increases and reaches the maximum at \( T_C \). Beyond \( T_C \), it drops rapidly to zero, indicating the occurrence of a polar-nonpolar phase transition (Figure 4A). The polarizations at different temperatures were obtained by integrating the pyroelectric current density over time. At 298 K, the value is \( 1.44 \mu\text{C/cm}^2\), which is in good agreement with that obtained from the P-E hysteresis loop measurement. At temperatures far below the phase transition, the polarization decreases slowly with increasing temperature. When approaching the temperature of the phase transition, the rate of decrease gradually accelerates. As a result, large pyroelectric coefficients can exist in this temperature range (\(-118 \mu\text{C/m}^2\cdot\text{K} \) at 290 K to about \(-440 \mu\text{C/m}^2\cdot\text{K} \) at 320 K). We also measured the current response under periodic temperature oscillations around 298 K.\(^{44,45} \) and obtained a pyroelectric coefficient of approximately \(-170 \mu\text{C/m}^2\cdot\text{K} \), which is close to the value obtained by temperature ramping. The corresponding pyroelectric current FOM is \( 0.83 \times 10^{-14} \) mV. Here, the volume specific heat measured by DSC is adopted in the calculation.
The room temperature pyroelectric coefficient of AF is comparable to that of perovskite oxides with polarization one order of magnitude larger than that of AF: LiTaO₃ (−176 μC/m²-K), PbTiO₃ (−180 μC/m²-K), and BaTiO₃ (−200 μC/m²-K). This is due to the second-order phase transition and the remnant polarization. In ferroelectrics, both first- and second-order ferroelectric-paraelectric phase transitions provide large pyroelectric coefficients near $T_c$. However, the polarization-temperature relationships of these two phase-transition types are different, resulting in different values of the pyroelectric coefficient. According to Landau theory, the order parameter $P$ can be described by the following relations for the two types of phase transitions:

$$P = \left[ -\beta + \sqrt{\beta^2 - 4a_0\gamma(T - T_c)} \right]^{1/2}$$

(Equation 1)

and

$$P = \frac{a_0(T_c - T)}{\beta}$$

(Equation 2)

where $a_0$, $\beta$, and $\gamma$ are constants. As shown in Figure S12, at temperatures $T < T_c$, the second-order phase transition ferroelectric has a larger pyroelectric coefficient than the first-order one if they have the same remnant polarization. The temperature dependence of the polarization of AF agrees well with the $\sim(T_c - T)^{1/2}$ law near $T_c$ (Figure S13), confirming the second-order phase transition again. As an illustration, electrical currents are easily induced when irradiating an AF crystal by an incandescent lamp and vary synchronously with alternating switching (Figure 4C), confirming the sensitivity to small changes in temperature.

Although those perovskite oxide ferroelectrics were found to have large pyroelectric coefficients, their $F_r$ values are low (usually <0.1 mC/m²) because of their large dielectric constants, whereas in AF, small dielectric constant and moderate volume specific heat (Figure S14) resulted in high values of $F_r$ (Figure 4D). At 298 K, $F_r$s are 0.705, 801, and 0.887 mC/m² at 1, 10, and 100 kHz, respectively. These $F_r$ values are considerably higher than those of most inorganic perovskites and even higher than that of TGS (Figure 5). In addition, other dielectric-constant-related pyroelectric FOMs of AF, such as detection capacity FOM ($2.17 \times 10^{-4}$ Pa⁻¹/₂) and energy harvesting FOM (5.94 $\times 10^{-11}$ m²/J) are comparable to those of commercial pyroelectric materials (Figure S15, Table S4). Thus, AF has a great potential to be used in highly sensitive thermal sensors. It should be noted that the secondary pyroelectric coefficients can be affected by piezoelectric behaviors through the expression $d_{22}P_2S_2K_3$, where $d$, $c$, and $a$ are piezoelectric, elastic, and thermal expansion coefficients, respectively. Here, a negative value of $d_{22}$ and a positive value of $a_{22}$ result in a negative component of secondary pyroelectric coefficient $-2.8 \mu$C/m²-K, where $c = 8.74$ GPa (Figure 1B) and $a = 2 \times 10^{-5}$ K⁻¹ (Figure S16) are used for the calculation. The total pyroelectric coefficient is slightly enhanced because the primary and secondary coefficients have the same signs. But on the other side, this may cause noise in some applications. In the present case, the noise amplitude is about 1.6%, which is negligibly small. Moreover, the polarization of the negative piezoelectric was found to be abnormally enhanced under stress ($\Delta P = d_{22}P_2S_2$, where $S_2$ is the stress). For AF, its polarization will nearly double under a stress of 1 GPa. The pyroelectric coefficient of AF is expected to be further enhanced under pressure.

![Figure 5. Comparison of pyroelectric coefficients, dielectric constants, and $F_r$s between AF in this work and some famous pyroelectrics. Where PVDF, P(VDF-TrFE), DTGS: SBN, and PMN-PT represent polyvinylidene fluoride, poly(50% vinylidene fluoride-50% trifluoroethylene), deuterated triglycine sulfate, Sr₀.₅Ba₀.₅Nb₂O₆, and 0.75Pb(Mg₀.₃Nb₂/₃O₆)₀.₃3BaTiO₃, respectively.](image)

**CONCLUSIONS**

In summary, we discovered an all-organic ferroelectric, AF, which shows a high pyroelectric FOM around room temperature, where the $F_r$ is higher than that of all known organic pyroelectrics, even TGS. A higher pyroelectric voltage output is expected in AF. The key to the high $F_r$ is attributed to the continuous phase transition from ferroelectric to paraelectric and low dielectric constant. Meanwhile, AF is a new example for negative piezoelectric effect. Like TGS, the pyroelectric performance of AF can be further improved through molecular doping or molecular modification. Owing to the low density, low hardness, and low cost of this all-organic material, AF is expected to find a great potential to be applied in flexible pyroelectric devices.

**MATERIALS AND METHODS**

The details of sample preparation and characterization are described in the supplemental information.

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