Phase Transitions

DOI: 10.1002/ange.201208952

Comment on Ferroelectricity in Bis(imidazolium) L-Tartrate

*Marek Szafrański**

crystal growth · dielectrics · ferroelectricity · materials science · phase transitions

In a recent Communication,[1] Sun et al. reported that co-crystallization of L-tartrate with imidazole, in the stoichiometric ratio of 1:2, results in a new ferroelectric of „an exceptional dielectric response and a good spontaneous polarization“. Indeed, the dielectric anomaly at 252 K, presented in their work in Figure 2 a,[1] appears to be exceptional, but in the respect that its shape is far from a typical ferroelectric-to-paraelectric phase transition and the frequency dependence of the dielectric response is also non-conventional. For ferroelectric–paraelectric phase transitions, it is commonly accepted that the low-frequency electric permittivity ε' obeys the Curie–Weiss law[2] $\varepsilon' = \varepsilon'_\infty + C/(T - T_0)$, where C is the Curie constant, T_0 is the Curie–Weiss temperature, and ε'_∞ is the high-frequency dielectric constant. Sun et al. show the fulfillment of this law by plotting $\varepsilon'^{-1}(T)$ in the inset in Figure 2 a,[1] but their analysis is not acceptable. First of all, there is no relationship, as it has to be, between the measured dependence $\varepsilon'(T)$ and the plotted $\varepsilon'^{-1}(T)$. This is especially striking in the temperature range between 260 and 290 K, where ε' is almost temperature-independent and therefore ε'^{-1} should also be nearly constant, but in the plot it increases from about 0.03 at 260 K to 0.2 at 290 K. Thus, the fulfillment of the Curie–Weiss law that is fundamental for ferroelectrics, the parameters derived from the fitting, and the related discussion, are doubtful. Moreover, the temperature dependence of the reciprocal electric permittivity led Sun and co-workers to a conclusion that the phase transition has a continuous character. This is in a distinct inconsistency with their results of calorimetric measurements (Supporting Information,[1] Figure S3), where the thermal anomalies observed in the heating and cooling runs occur with 20 K temperature hysteresis, which is a form of fingerprint for a first-order phase transition. Obviously, the transition cannot be continuous and discontinuous, simultaneously.

A necessary confirmation of ferroelectric properties is the spontaneous polarization (P_s) switching in an external electric field (E), which is most often demonstrated in a form of dielectric hysteresis loop.[2] The true ferroelectric loop $P_s(E)$ should be saturated and should have the concave regions, especially when the coercive field is low. The loops presented by Sun et al. (Ref. [1], Figure 4 a) do not satisfy these conditions, but resemble the false loops generated by lossy dielectrics or even such materials as a banana skin, as shown by Scott.[3] Moreover, the „coercive field“ derived from the presented loops increases with decreasing temperature, while for ferroelectrics an opposite dependence is observed as a rule. Therefore it is suspected that the parameters derived from the loops have in fact nothing to do with ferroelectricity.

To test this hypothesis, we have grown and re-examined crystals of bis(imidazolium) L-tartrate. Below 252 K, no any hysteresis loop was detected in the electric field up to 10 kV cm^{-1}, which is about ten times higher than the field intensity applied by Sun et al.[1] Furthermore, the crystal did not exhibit any dielectric anomaly around 252 K (Supporting Information, Figure S2), which is consistent with our calorimetric study. For differential scanning calorimetric (DSC) measurements, a good-quality small crystal was selected. The results shown in Figure 1 (curve a) indicate an occurrence of the thermal anomalies characteristic of a first-order phase transition. The onsets of the peaks at 232 and 252 K in the cooling and heating runs, respectively, are in perfect agreement with the data reported by Sun et al. However, for the powdered and dried sample (curve b) there is no trace of the

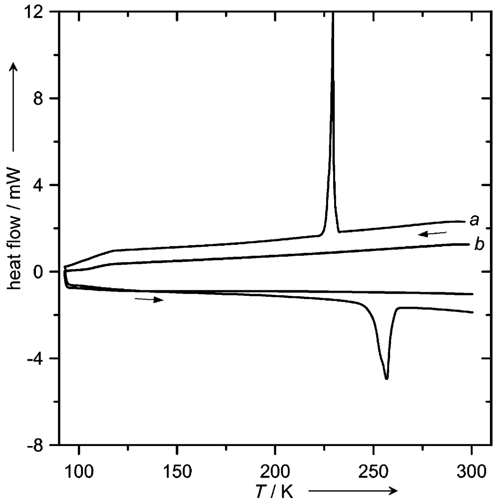

Figure 1. DSC heating and cooling runs measured on a single crystal (run a) and on a powdered sample (run b).

---

[*] Prof. M. Szafrański
Faculty of Physics, Adam Mickiewicz University
Umultowska 85, 61-606 Poznań (Poland)
E-Mail: masza@amu.edu.pl

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208952.

anomalies. Measurements repeated for different samples showed that most of the crystals generate peaks, practically at the same temperatures, but with a different magnitude of the thermal effect. After grinding and drying the samples, the anomalies disappeared. These experiments indicate that the peaks observed for the single crystals originate from the freezing/melting of the mother liquor confined into the crystals during the crystallization process. This supposition was confirmed by the DSC runs recorded directly for a droplet of the saturated solution (Supporting Information, Figure S4). In light of the above arguments, it is clear that bis(imidazolium) L-tartrate does not undergo a feroelectric-to-paraelectric or any other phase transition in the temperature range 100–300 K. In such a case the reported[1] symmetry change at 252 K from $P2_1$ to $P2_12_12_1$ does not take place and the crystal preserves its polar symmetry at room temperature. The crystal structure re-determinations at 150 and 295 K[4] fully confirmed this supposition. Therefore, the correct space group of the room-temperature structure is monoclinic $P2_1$. Of note, the crystal structures at 150 and 295 K both can be solved and refined in space group $P2_12_12_1$, although these models are much worse than those for the space group $P2_1$, as reflected in the higher values of the reliability R-factors and standard deviations of structural parameters. It is interesting that the monoclinic angle β decreases from 90.34° at 150 K to 90.25° at 295 K, and to 90.13° at 330 K, suggesting a possible monoclinic–orthorhombic transition at higher temperatures. Indeed, the calorimetric study revealed a second-order phase transition at 351 K, as shown in Figure 2. The total entropy gain $\Delta S = 1.4\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$ is close to $R\ln 1.18$ (R is a gas constant), indicating a displacive mechanism of the transition. This is consistent with the structure determination at 360 K,[4] which has shown that in the high-temperature phase the crystal structure remains ordered (Supporting Information, Figure S1). Above 351 K the crystal symmetry is orthorhombic, space group $P2_12_12_1$. Thus, the polar to non-polar symmetry change is realized in bis(imidazolium) L-tartrate, but at higher temperature by about 100 K than reported previously.[1] The transition has all features of a ferroelectric-paraelectric phase transition. The low-frequency electric permittivity exhibits a large peak in the temperature dependence of ε', with a characteristic, more steeply shaped ferroelectric than paraelectric slope, as illustrated in Figure 3 (see also Supporting Information, Figure S3). The $\varepsilon'(T)$ dependence perfectly obeys the Curie–Weiss law both in the paraeleectric and ferroelectric phase. The Curie constants determined from the fits $C_{\text{para}} = 1480.6$ K and $C_{\text{ferro}} = 570.7$ K give the ratio $C_{\text{para}}/C_{\text{ferro}} = 2.59$, which is close to the theoretical value of 2 that is valid for second-order phase transitions.

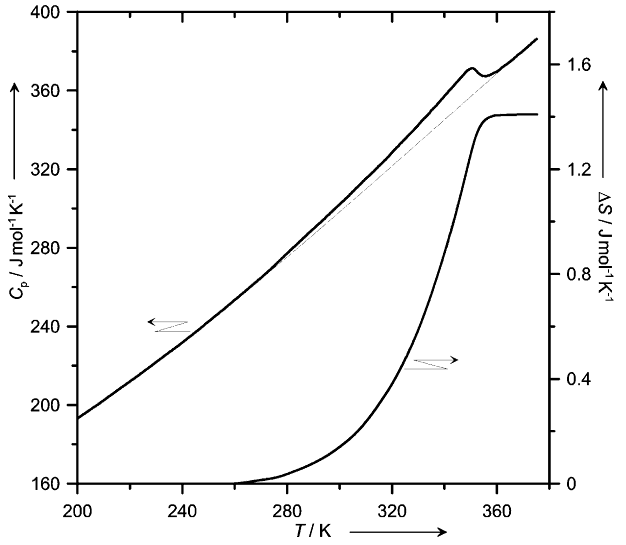

Figure 2. The heat capacity and entropy change in the vicinity of the second-order phase transition.

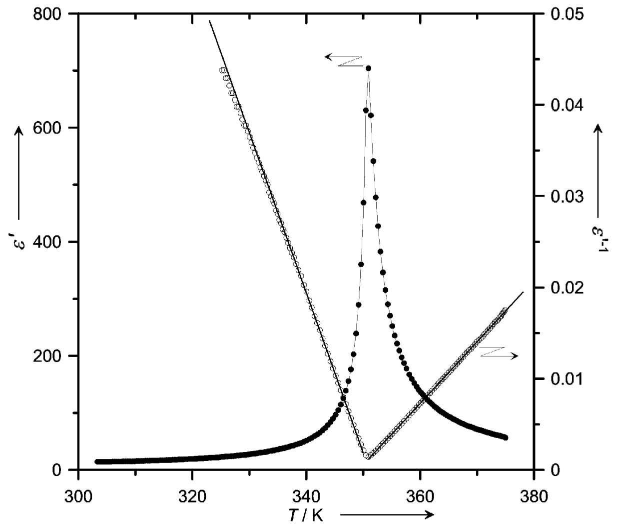

Figure 3. The temperature dependence of the real part of electric permittivity ε' (●) measured at the 500 kHz frequency of electric field, and of the reciprocal ε'^{-1} (○) fitted with the Curie–Weiss law (thin straight lines).

Convincing evidence for ferroelectricity is the polarization reversal in an external electric field. This feature of the crystal is seen in Figure 4. In a close vicinity of T_C, the loops were distorted owing to the contribution arising from the increase in electric conductivity with temperature, but below about 330 K the loops assumed a typical shape characteristic of classical ferroelectrics. Of note is a rapid increase of the coercive field E_c with decreasing temperature: at 328.5 K, the E_c value is $2.6\,\text{kV}\,\text{cm}^{-1}$, whereas at 301.7 K it rises to $10.2\,\text{kV}\,\text{cm}^{-1}$, and below room temperature the polarization reversal becomes unattainable because the required field is too high. Thus, it is clear that around 250 K, polarization switching could not be observed, especially in a field as small as $1\,\text{kV}\,\text{cm}^{-1}$.[1] The spontaneous polarization derived from the ferroelectric loops reaches $1.15\,\mu\text{C}\,\text{cm}^{-2}$ at 301.7 K and it decreases to about $0.95\,\mu\text{C}\,\text{cm}^{-2}$ when the temperature rises to 328.5 K (for $P_s(T)$, see the Supporting Information, Figure S6). These values are about four times higher than of the archetypical ferroelectric Rochelle salt.[2,5]

In summary, the results published by Sun and co-workers have been verified, and it has been shown that their conclusions are based on a misinterpretation of the exper-

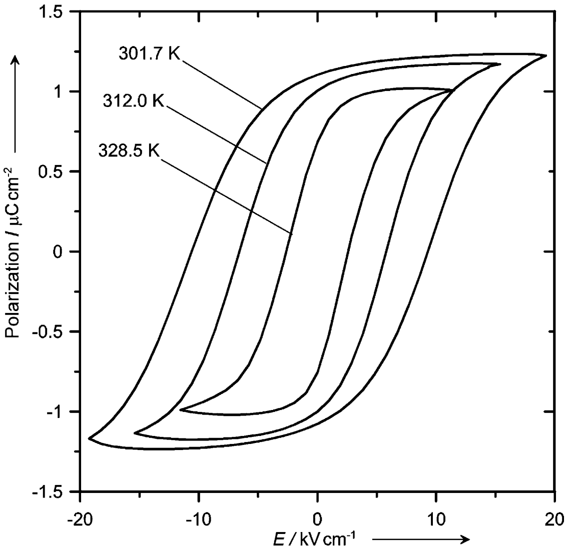

Figure 4. Ferroelectric hysteresis loops recorded in the low-temperature monoclinic phase at 328.5, 312.0, and 301.7 K.

imental data. We have also shown that bis(imidazolium) L-tartrate exhibits excellent ferroelectric properties at room temperature, which makes this material interesting for practical applications.

Eingegangen am 8. November 2012
Online veröffentlicht am 11. Juni 2013

---

[1] Z. Sun, T. Chen, J. Luo, M. Hong, *Angew. Chem.* **2012**, *124*, 3937–3942; *Angew. Chem. Int. Ed.* **2012**, *51*, 3871–3876.

[2] F. Jona, G. Shirane, *Ferroelectric Crystals*, Dover Publications, New York, **1993**.

[3] J. F. Scott, *J. Phys.: Condens. Matter* **2008**, *20*, 1–2.

[4] Crystal data, $C_{10}H_{14}N_4O_6$, at 150 K: monoclinic, $P2_1$, $a = 10.57500(11)$, $b = 8.39372(8)$, $c = 14.08650(13)$ Å, $\beta = 90.3392(16)°$, $V = 1250.35(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.521$ gcm^{-3}, $\mu = 0.127$ mm^{-1}, $R_1[I>2\sigma(I)] = 0.03\ 67$, wR_2(all data) = 0.0906; at 295 K: monoclinic, $P2_1$, $a = 10.6182(2)$, $b = 8.4455(2)$, $c = 14.1090(2)$ Å, $\beta = 90.2497(16)°$, $V = 1265.23(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.503$ g cm^{-3}, $\mu = 0.126$ mm^{-1}, $R_1[I>2\sigma(I)] = 0.0388$, wR_2 (all data) = 0.0943; at 360 K: orthorhombic, $P2_12_12_1$, $a = 8.47233(7)$, $b = 10.6376(1)$, $c = 14.12171(13)$ Å, $V = 1272.72(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.494$ g cm^{-3}, $\mu = 0.125$ mm^{-1}, $R_1[I>2\sigma(I)] = 0.0370$, wR_2 (all data) = 0.0970; CCDC 909622, 909623, and 909622 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[5] J. Valasek, *Phys. Rev.* **1921**, *17*, 475–481.