

## MATERIALS SCIENCE

# Comment on “Improper molecular ferroelectrics with simultaneous ultrahigh pyroelectricity and figures of merit” by Li *et al.*

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Li *et al.* (*Science Advances*, 29 January, p. eabe3068) claim the discovery of two improper ferroelectrics, dabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub> (dabco = 1,4-diazabicyclo[2.2.2]octane), and that these materials exhibit superior pyroelectric figures of merit. This information is misleading because of the fundamental methodological errors and false conclusions, not to mention that these ferroelectrics were reported more than 20 years ago. They are proper ferroelectrics, for which the spontaneous polarization is the macroscopic order parameter. We show that the useful pyroelectric coefficients of dabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub> are about 1000 times lower than the coefficients reported by Li *et al.*

In a recently published article, Li *et al.* (1) report the ferroelectricity of two hybrid organic-inorganic crystals, dabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub> (dabco, 1,4-diazabicyclo[2.2.2]octane; C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>), and claim that these materials exhibit superior pyroelectric properties related to the improper nature of ferroelectricity. This is a second rediscovery of ferroelectric properties in these NH···N bonded crystals, after the first rediscovery published by Xiong's group in 2016 (2). Both these papers (1, 2) carefully conceal the original report on ferroelectricity in dabco monosalts (3) published in 1999. Li *et al.* mention our report in page 5 of their paper, not in connection with the ferroelectricity of dabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub>, but incorrectly referring to “improper ferroelectricity in molecular materials (27–29)”, whereas there is no such information in our paper. Leaving aside the ethical issues, the paper by Li *et al.* contains many serious errors and discrepancies that need to be commented on and corrected.

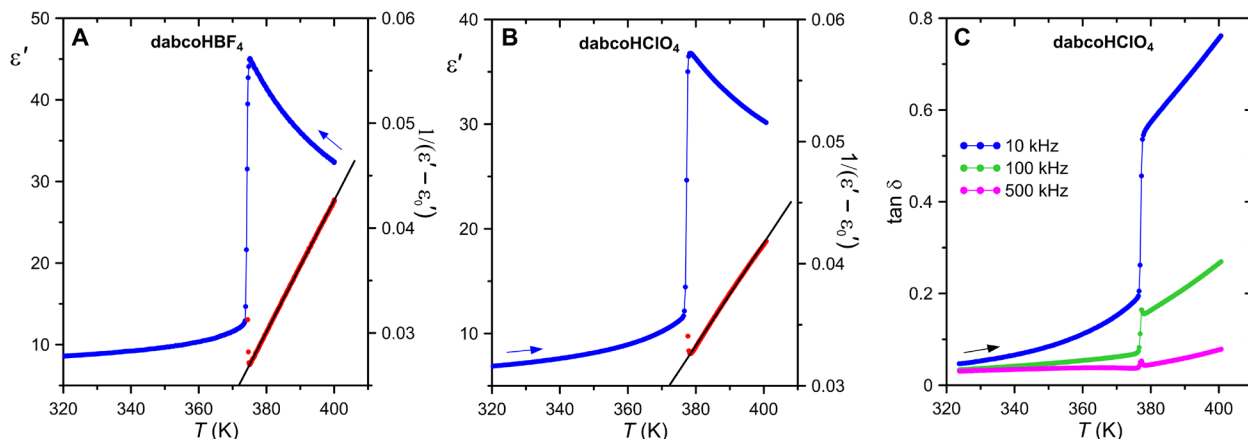
DabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub> can be described as ionic, molecular ionic, or hybrid organic-inorganic materials, but certainly not as molecular ones. The term “molecular crystals” is reserved solely for materials built from neutral atoms or molecules, and therefore, its use for other materials is misleading (4). The structural and symmetry information is essential for understanding the mechanism underlying the ferroelectric properties and phase transitions in dabco monosalts. Therefore, we have performed more than 50 single-crystal x-ray and neutron diffraction experiments (3, 5–7), as a function of temperature and pressure. The single-crystal measurements circumvent the overlapping of reflections inherent to powder x-ray diffraction (PXRD), hampering the precise structural determinations and location of the disordered atoms and protons. All our structural determinations were deposited in the Cambridge Structural Database (CSD) and can be received free of charge. Li *et al.* do not mention these CSD deposits and claim that they determined the structures of the ferroelectric and highly disordered paraelectric phases from in-house PXRD measurements. They incorrectly describe the symmetry of paraelectric phases of dabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub> as space group *P4/mmm* (No. 123) with the unit cell containing one

ionic pair ( $Z = 1$ ), while, as shown in our previous study (5), the true space group is *P4/nmm* (No. 129) and the unit cell is two times larger ( $Z = 2$ ). Despite the wrong space group and lattice parameters, the structural model presented by Li *et al.* in their figure 1 (D and F) is consistent with the correct larger unit cell and symmetry determined in our single-crystal experiments (5). The symmetry relation between the ferroelectric and paraelectric phases is of primary importance. For the symmetry change *Pm2<sub>1</sub>n* → *P4/mmm*, the translational symmetry of the crystals would be broken, suggesting a possible improper ferroelectricity (8), whereas the *Pm2<sub>1</sub>n* → *P4/nmm* transition is clearly equi-translational, and accordingly, dabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub> should be classified as proper ferroelectrics (9). Moreover, the improper ferroelectricity is associated with a minor change in the electric permittivity at  $T_C$ , and the Curie-Weiss law is not fulfilled in the paraelectric phase (8, 10). Figure 1 (A and B) shows the temperature dependence of electric permittivity  $\epsilon'(T)$ , measured by us at 500 kHz for the single crystals of dabcoHBF<sub>4</sub> and dabcoHClO<sub>4</sub> along the polar direction [010]. Clearly, there are no features characteristic of improper ferroelectrics. In contrast, the changes in  $\epsilon'$  at  $T_C$  are by an order of magnitude larger than in the classical improper ferroelectrics, such as gadolinium molybdate (11) or ammonium Rochelle salt (12). Also, the shape of the anomalies and the fulfillment of the Curie-Weiss law in the paraelectric phases fully reaffirm the proper ferroelectricity of both materials. Thus, dabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub> are neither molecular nor improper ferroelectrics, as claimed by Li *et al.* Their another doubtful information concerns the loss tangent ( $\tan \delta$ ) of dabcoHClO<sub>4</sub> they determined at 1 kHz as 0.001 below and 0.08 above  $T_C$  [figure 2A in (1)]. Such a low loss is exciting, but hardly possible for hybrid organic-inorganic H-bonded materials, exhibiting substantial dynamical disorder in the ferroelectric phase below  $T_C$ , and highly disordered above  $T_C$ . The dielectric loss measured for the single crystal of dabcoHClO<sub>4</sub> in dry atmosphere (Fig. 1C) is more than one order of magnitude higher compared to that reported by Li *et al.* for the polycrystalline sample. The strong frequency dispersion and large increase of the loss at low frequencies are of primary importance for pyroelectric and polarization hysteresis loop measurements. The effect of electric conductivity on the hysteresis loop is evident in Fig. 2A for the loop recorded at 346 K. We tested several single-crystal samples and each measurement proved impossible above ca. 360 K, whereas Li *et al.* observed the ferroelectric polarization loop even at

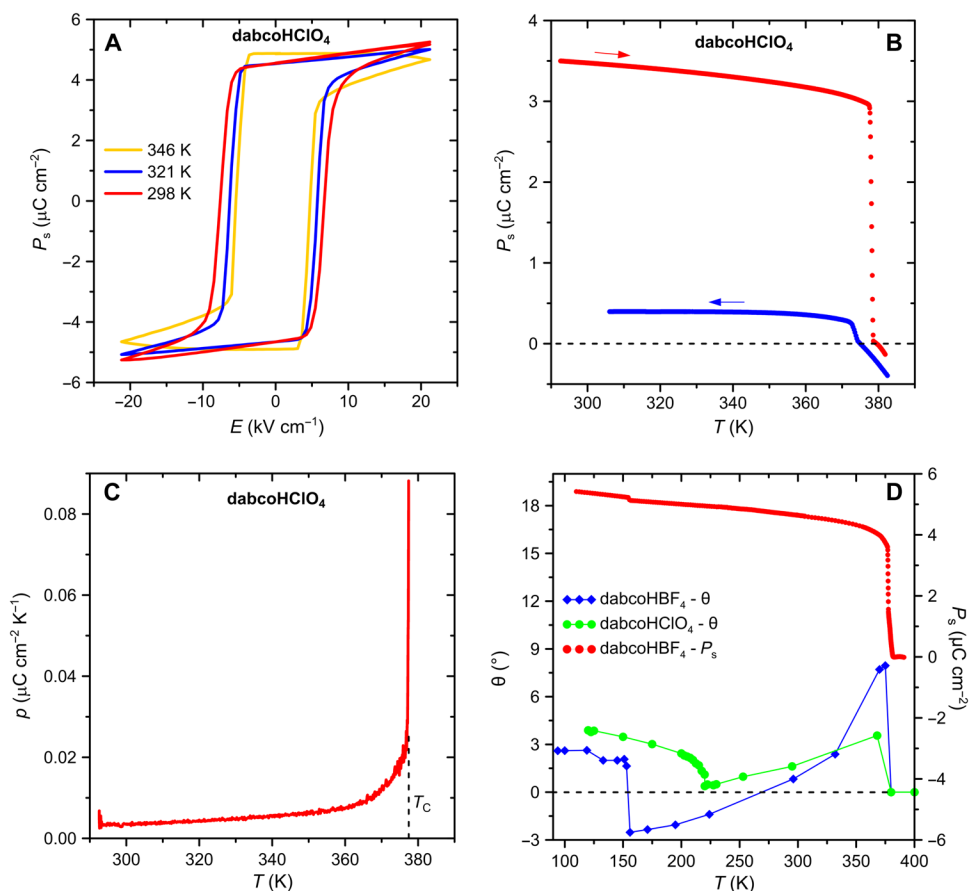
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**Fig. 1. Dielectric response of single crystals of dabcoHBF<sub>4</sub> and dabcoHClO<sub>4</sub>.** (A and B) The real part of electric permittivity,  $\epsilon'$ , measured at 500 kHz along [010] for temperature changing at a rate 0.1 K/min (blue plots, left axes) and the illustration of the Curie-Weiss law fulfillment (red, right axes). (C) The low-frequency loss tangent,  $\tan \delta$ , for dabcoHClO<sub>4</sub> in the vicinity of the ferroelectric-paraelectric phase transition. Arrows indicate the directions of temperature changes.



**Fig. 2. Spontaneous polarization and pyroelectric properties of dabcoHBF<sub>4</sub> and dabcoHClO<sub>4</sub>.** (A) The low-frequency (0.1 Hz) ferroelectric hysteresis loops measured at different temperatures on a single-crystal dabcoHClO<sub>4</sub> along [010]. (B) Spontaneous polarization measured on as-grown single crystal of dabcoHClO<sub>4</sub> along [010], during the heating (red) and subsequent cooling (blue) runs, at the rate of 2 K/min. (C) Pyroelectric coefficient  $p$  of dabcoHClO<sub>4</sub> determined from the heating run shown in (B). (D) Spontaneous polarization measured for single-crystal dabcoHBF<sub>4</sub> across the ferroelectric-paraelectric and ferroelectric-ferroelectric phase transitions according to Budzianowski *et al.* (7) (right axis) and the  $\theta$  angles (left axis) determined for dabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub> from our structural studies (3, 5–7).

383 K [figure 2B in (1)], i.e., in the paraelectric phase, 5 K above  $T_C$ . This is in clear contradiction with the nature of the paraelectric phase where  $P_s = 0$ , but it is also in disagreement with their own pyroelectric data presented in figure 2C (1). A high value of  $P_s = 6 \mu\text{C cm}^{-2}$  determined by Li *et al.* for the polycrystalline dabcoHClO<sub>4</sub> requires a comment, too. It is evident from the electric permittivity measurements presented in figure 2A in (1) that the crystalline grains were randomly oriented in the sample, as testified by 2.5 times lower permittivity in the paraelectric phase compared to our single-crystal results shown in Fig. 1B. Because  $P_s$  cannot rotate in a ferroelectric crystal, only its components parallel to the applied electric field can contribute to the ferroelectric loop. Therefore, a much lower value of polarization is expected for the polycrystalline sample than  $4.6 \mu\text{C cm}^{-2}$  determined by us from the single-crystal loop (see Fig. 2A). The spontaneous polarization and the related pyroelectricity are the key issues reported by Li *et al.* Unexpectedly, they determined the pyroelectric coefficient and the corresponding figures of merit [figure 2 (D to G) in (1)] at  $T_C$  of the first-order transition and compared them with the values determined off the phase transitions for other pyroelectric materials [figure 3 in (1)]. This is a serious methodological error leading to false conclusions. The sharpness of the transition in dabcoHClO<sub>4</sub> can be rated from our plots in Figs. 1B and 2B. Our experimental dielectric data measured on the pressed pellets (13) show that the ferroelectric-paraelectric transitions in the dabco ferroelectrics proceed in a jump-wise manner, also for polycrystalline samples. Therefore, a smearing of the transition, observed in figures 2 and 4 presented in (1), is hardly explainable. The  $P_s(T)$  in our Fig. 2B was measured on the virgin not poled crystal, which was spontaneously polarized, but most likely not completely, as for most of the as-grown crystals. It is apparent that the transition occurs in a very narrow temperature interval  $\Delta T < 1$  K, even for temperature changing at 2 K/min. By lowering this rate, the transition interval could be reduced to the limit  $\Delta T \rightarrow 0$ , and the pyroelectric coefficient  $p = dP_s/dT$  would ideally extend to infinity. It is clear that the so-determined  $p$  at  $T_C$  characterizes the transition process rather than the pyroelectric properties of the material. Moreover, it is not true that dabcoHClO<sub>4</sub> can be cycled across  $T_C$  without a poling field and without a worsening of pyroelectric properties. This is evident from a decay of the polarization in the cooling run plotted in our Fig. 2B. The  $P_s(T)$  dependences in Fig. 2B represent the raw data, not corrected for the electric conductivity, while its effect is clearly seen in the paraelectric phase, where the nonzero pyroelectric charge (current) originates from the increased dielectric loss (see Fig. 1C). The practically useful temperature region, where the pyroelectric coefficient values are reproducible, is below  $T_C$ . However, as shown in Fig. 2C, the coefficient  $p$  varies from  $35 \mu\text{C m}^{-2} \text{K}^{-1}$  at room temperature to  $250 \mu\text{C m}^{-2} \text{K}^{-1}$  in a close vicinity of  $T_C$ , and hence, dabcoHClO<sub>4</sub> in this respect is not superior compared to the best pyroelectric materials. Although the dielectric constants of dabco crystals in their ferroelectric phases are relatively low, which is favorable for pyroelectric figures of merit, the relatively low values of  $p$  and the dielectric loss increasing with temperature are disadvantageous for practical applications. On the other hand, the pyroelectric effect occurring at  $T_C$  is irreversible, and therefore hardly applicable, because a construction of one-time use sensors/detectors targeted at a single temperature is questionable.

The improper ferroelectric phase transitions are distinguished as a separate category not only because of their unique dielectric

characteristics but also from a theoretical point of view. As shown almost 50 years ago (8, 14), the order parameter of an improper ferroelectric transition has to exhibit specific properties: (i) It cannot be a one-component parameter, and (ii) its transformation properties must be different from those of polarization. Only with these restrictions regarding the order parameter can the approach of the Landau theory to the improper ferroelectrics be adequate. For example, a much less precise definition is used in the monograph by Lines and Glass (15), where the improper ferroelectric transitions are defined as driven by a primary instability that induces spontaneous polarization as a secondary order parameter. Without any further constraints, within this definition, a one-component primary order parameter is allowed, but, in this case, at most, the pseudoproper ferroelectrics can be described, which have nothing in common with improper ferroelectricity (14).

In the theoretical approach presented in (1), the authors try to apply the Landau-Devonshire theory to improper ferroelectrics. They use an inappropriate formula of free energy for improper ferroelectrics, incorrectly citing at this point their references 30 to 32 that are devoted mainly to proper ferroelectric and ferroelectric phase transitions. The improper ferroelectricity is mentioned only in their reference 32, but the formula for free energy there is completely different from that used in (1). Disregarding the proper nature of ferroelectricity in dabco monosalts, the approach by Li *et al.* is disqualified also by the incorrect choice of the order parameter, the dihedral angle  $\theta$  between three oxygen/fluorine atoms of the anion and crystal plane (010). Levanyuk and Sannikov (8) showed that, for improper ferroelectrics, the one-component order parameter is inapplicable because of the mixed terms  $\theta P_s$  in the thermodynamic potential. The presence of invariant  $\theta P_s$  in the free energy used by Li *et al.* in their equation 1 implies that  $\theta$  and  $P_s$  have the same transformation properties, and therefore, the transition cannot be improper, as they assume. In figure 4A of (1), they compare  $P_s(T)$  with their theoretical model, but it should be noted that the shape of the experimental  $P_s(T)$  is distorted by the nonequilibrium conditions of the pyroelectric method; hence, such a comparison is dubious. However, what is most astonishing is the modeling of  $P_s(T)$  in the phase transition region, above  $T_C$ , using a continuous function, whereas for the first-order phase transition,  $P_s$  should abruptly vanish at  $T_C$ . Also, it is puzzling why the schematic  $P_s(T)$  dependence for the first-order phase transition is presented as a continuous plot in their figure S10.

The inadequacy of angle  $\theta$  as the order parameter for dabco ferroelectrics is also evident from our plots in Fig. 2 (D and B). It is apparent that  $\theta(T)$  and  $P_s(T)$  are absolutely not related, while a tight coupling is predicted by the theoretical simulations illustrated in figure 4B in (1). For example, for dabcoHBF<sub>4</sub>, the  $\theta$  angle changes its sign at about 270 K and once again at the first-order transition at 155 K. No such changes are observed in the measured  $P_s(T)$  dependence. Actually, the discrepancy between  $P_s(T)$  and  $\theta(T)$  had to be expected, because  $P_s$  in dabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub> originates from the ionic displacements  $\delta$ , but not from the rotation of the tetrahedral anions. The structural origin of  $P_s$  was described in our paper (3) and successfully used for  $P_s(T)$  modeling (3, 7). Thus,  $\delta$  and  $P_s$  are the proper microscopic and macroscopic order parameters truly describing the ferroelectric-to-paraelectric phase transitions in dabcoHClO<sub>4</sub> and dabcoHBF<sub>4</sub>, as it was shown over 20 years ago.

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