First-principles analysis of a molecular piezoelectric meta-nitroaniline

Fu Wang, a Zelin Dai, a Yu Gu, a Xiaomeng Cheng, a Yadong Jiang, a Fangping Ouyang, b Jimmy Xu a c and Xiangdong Xu a ✉

The piezoelectric and elastic properties of a molecular piezoelectric meta-nitroaniline (mNA) in its single-crystal form were investigated in the framework of first-principles density functional perturbation theory (DFPT). Results support the recent experimental findings those despite being soft and flexible, mNA’s piezoelectric coefficients are an order of magnitude greater than that of ZnO and LiNbO3. A molecular-level insight into the piezoelectric properties of mNA is provided. These results are helpful not only for better understanding mNA, but also for developing new piezoelectric materials.

1. Introduction

Piezoelectric materials are ideally suited for electromechanical transductions. By producing dielectric polarization with a mechanical strain and, conversely, a mechanical response with an applied electric field, they have found applications in sensors, energy harvesting, actuators, oscillators and many other fields. Most recent studies have focused on inorganic piezoelectric materials, such as AlN, ZnO, LiNbO3, and lead zirconate titanate (PZT). These inorganic piezoelectric ceramics have large piezoelectric coefficients, but are generally stiff and brittle, and some even contain environmentally unfriendly elements, including the champion piezoelectric PZT. For many applications, flexible, thin, lightweight, scalable, low processing temperature, and biophilic piezoelectrics are more desirable. These are difficult challenges for conventional piezoelectric ceramics, but can be met with molecular piezoelectrics, in the form of either an organic composite film or crystal. On the other hand, the piezoelectricity of commonly known organic piezoelectrics such as poly(vinylidene fluoride) (PVDF) is rather low. The electromechanical conversion efficiency of the PVDF has only reached 17.8%, limiting its applications. However, given the numerous possibilities of synthesizing (engineering) highly polarizable molecules with non-centrosymmetry, it is rational to speculate that there exist molecular structures of greater piezoelectricity or ones that could be specially made by informed designs. Experimentally, findings are still few, but at least two have emerged as especially promising, one of which is meta-nitroaniline (mNA).

Structurally, mNA is a relatively simple molecular species, but still complex by the standard of piezoelectrics. It has long been known for its large second or third optical nonlinearities, in accompany with its non-centrosymmetry. The non-centrosymmetry is also suggestive of piezoelectricity. Indeed, piezoelectricity of mNA crystal has been experimentally measured by Avanci, Bain, and Isakov et al. In fact, these experimental reports presented rather impressive piezoelectric coefficients, comparable to or even larger than some of the well-known inorganic piezoelectric ceramics. Among them, some of the measured results reported by Bain and Isakov are similar. Therefore, the measured results of Avanci and Bain will be mainly discussed in this work. But the numerical values measured by Avanci are about one order of magnitude larger than those by Bain, which could result from various experimental constraints and measurement errors as pointed out in ref. 17 and is reasonable at the early stage of discovery. One source of uncertainty in accuracy could be in the shear force applied to the mNA crystal in measurements and therefore in determining the pertinent tangential components of the piezoelectric tensor. While discrepancies in experimental findings are natural in the early phase and will narrow down as the methods refine along with the material itself, a first-principles based computational model could add value by serving as a reference framework and shedding light on the origins of factors contributing to the piezoelectric responses and on the complex relationships between the macroscopic properties and the underlying molecular structure.

In this paper, the piezoelectric and elastic properties of organic mNA crystal were modeled in the framework of the density functional perturbation theory (DFPT). Results support the experimental findings that the piezoelectric coefficients of mNA $d_{33}$ is about one order of magnitude larger than that of...
some well-known conventional inorganic piezoelectric ceramics such as ZnO and LiNbO3, and comparable to the poled BaTiO3. As it is conventionally defined, $d_{33}$ is a measure of the material’s response in terms of surface charge density to a normal strain, its value depends on both the molecular orbital charge density redistribution, dipolar reorientation, and the elastic deformation of the material. In the case of a molecular piezoelectric both are much more complex than in an inorganic piezoelectric and more difficult to compute.

2. Computational model

The piezoelectric and elastic constants of mNA crystals were calculated based on the DFPT together with the generalized gradient approximation revised Perdew–Burke–Ernzerhof (GGA-rPBE) functional implemented in the Vienna Ab-initio Simulation Package (VASP).25 The PBE pseudopotential file was used in this work, PREC is set to accurate mode, and the accuracy of the calculation are set as EDIFF = 2 × 10−6 and EDIFFG = −1 × 10−3. The Brillouin zone integration is obtained by a 1 × 3 × 3 Monkhorst–Pack k-points mesh and the energy cutoff was set to 800 eV. In our calculations, the DFT-D3 method proposed by Grimme and co-workers26 was employed to introduce the dispersion correction term into the calculations, in which the van der Waals interactions were described via a pair-wise force field. The DFPT method is known as an efficient way for calculating various physical response properties of insulating crystals, including elastic, dielectric, Born charge, and piezoelectric tensors. It has been successfully applied to calculations of piezoelectricity of many materials, such as BaTiO3 (ref. 27) and poly(lactic acid) (PLA) polymorphs.28 Compared with the alternative popular Berry phase method, the DFPT method can avoid the so-called “improper piezoelectricity”,29 and automatically produce the proper piezoelectric constants. The initial mNA crystal structure for geometry optimization was determined by Kanoun et al.30 at room temperature.

3. Results and discussion

The mNA crystal belongs to the orthorhombic space group Pbc21, point group mm2 with a unit cell containing four mNA molecules. The molecule of the mNA unit cell is drawn with atom label in Fig. 1a and the crystal configuration is displayed in Fig. 1b. Considering that the piezoelectric properties are ground-state properties, a full relaxation or optimization of the molecular structure is needed. The optimized lattice parameters by our set-up are summarized in Table 1, and are compared with those experimentally measured.37,30,31 They are in good agreement with each other. The maximum deviation of the optimized structural parameters is 6.29% in comparison with those previously reported.37,30,31

The piezoelectric coefficients of materials can be described in two forms: one is the piezoelectric stress coefficient $e_{ij}$, another is the piezoelectric strain coefficient $d_{ai}$. The piezoelectric stress coefficient $e_{ij}$ is defined as:32,33

$$e_{ij} = \frac{\partial P_s}{\partial \epsilon_j}$$

(1)

where $P_s$ is the polarization in the direction $\alpha$, $\epsilon_j$ is the applied stress along the direction $j$. Similarly, the piezoelectric strain coefficient $d_{ai}$ is defined as:32

$$d_{ai} = \frac{\partial P_s}{\partial \sigma_i}$$

(2)

where $P_s$ again is the polarization in the direction $\alpha$, but $\sigma_j$ is the strain along the direction $i$. The stress constants $e_{ij}$ and strain constants $d_{ai}$ are related by:

$$e_{ij} = d_{ai}C_{ij}$$

(3)

where $C_{ij}$ is the elastic coefficients that are defined as the second derivative of the total energy ($U$) to the strain ($\epsilon_i$ and $\epsilon_j$):34

$$C_{ij} = \frac{1}{V} \frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j}$$

(4)

which represents the mechanical hardness of a material relative to its deformation.

The elastic constant $C_{ij}$ tensor can be expressed in a $6 \times 6$ square matrix, with 36 components. Given the symmetry of the mNA crystal, there are only 9 independent elastic tensor components, which are $C_{11}$, $C_{12}$, $C_{13}$, $C_{22}$, $C_{23}$, $C_{33}$, $C_{44}$, $C_{55}$,

![Fig. 1](image)

The optimized structure of mNA: (a) single isolated mNA molecule, (b) the unit cell of mNA crystal.

Table 1. Comparison of the calculated lattice constants of mNA crystal and the data previously reported. Numbers in parentheses are the relative errors (in percent) with respect to the calculated lattice constants

| Authors          | $a$(Å)  | $b$(Å)  | $c$(Å)  |
|------------------|---------|---------|---------|
| Avanci et al.    | 6.501(−2.98) | 19.330(+3.20) | 5.082(+6.25) |
| Kanoun et al.    | 6.499(−3.01) | 19.369(+3.41) | 5.084(+6.29) |
| Goeta et al.     | 6.484(−3.24) | 18.905(+0.93) | 5.016(+4.87) |
| This work        | 6.701     | 18.731   | 4.783    |

Ref. 17. Ref. 30. Ref. 31.
and $C_{66}$. Similarly, of the piezoelectric stress constants and the piezoelectric strain constants only 5 ($e_{15}$, $e_{24}$, $e_{31}$, $e_{12}$, $e_{33}$) are independent. Hence, for mNA, eqn (3) can be written as:

$$
\begin{align*}
\varepsilon_{15} &= d_{15} C_{55}, \\
\varepsilon_{24} &= d_{24} C_{44}, \\
\varepsilon_{31} &= d_{31} C_{11} + d_{32} C_{21} + d_{33} C_{31}, \\
\varepsilon_{32} &= d_{31} C_{12} + d_{32} C_{22} + d_{33} C_{32}, \\
\varepsilon_{33} &= d_{31} C_{13} + d_{32} C_{23} + d_{33} C_{33}.
\end{align*}
$$

(5)

To the best of our knowledge, no prior analysis of the piezoelectric properties of mNA crystal has been reported in literatures, aside from the experimental findings of the longitudinal components ($d_{31}$, $d_{32}$, $d_{33}$) of the piezoelectric tensor of the mNA crystal in the past twenty years.

The calculated elastic stiffness constants of the mNA crystal and the experimentally measured ones are summarized in Table 3. The relaxed-ion elastic constants are of the same order of magnitude as those experimentally measured. Especially, the computed $C_{12}$, $C_{33}$, $C_{44}$, $C_{55}$, $C_{66}$ are in good agreement with the experimental values.

The computed results also naturally satisfy the Born mechanical stability criteria:

$$
\begin{align*}
C_{ii} > 0, \quad (i = 1, 2, 3, 4, 5, 6) \\
C_{11} C_{33} > C_{13}^2, \quad C_{11} C_{22} > C_{12}^2, \quad C_{11} C_{33} > C_{13}^2, \\
(C_{12} C_{33} + 2 C_{23} C_{31}) (C_{11} C_{22} C_{33} C_{12}) > (C_{11} C_{23}^2 + C_{22} C_{13}^2 + C_{33} C_{12}^2).
\end{align*}
$$

(8)

This indirectly reconfirms that the optimized lattice structure of the mNA crystal generated from the computational optimization process described earlier is stable.

| Elastic constant (GPa) | Our results | Previous calc. | Previous expl. |
|------------------------|-------------|----------------|----------------|
| $C_{11}$               | 205         | 226\(+10.24\) | 209\(+1.95\)  |
| $C_{12}$               | 138         | 139\(+0.72\) | 120\(-13.04\) |
| $C_{13}$               | 122         | 123\(+0.82\) | 104\(-14.75\) |
| $C_{33}$               | 202         | 242\(+19.80\) | 211\(+4.46\)  |
| $C_{44}$               | 33          | 40\(+21.21\) | 44\(+33.33\)  |
| $C_{66}$               | 33          | 44\(+33.33\) | —              |

$\varepsilon_{15}$ $\varepsilon_{24}$ $\varepsilon_{31}$ $\varepsilon_{12}$ $\varepsilon_{33}$

$-0.50$ $-0.74$ $1.41$

Table 2 Comparison of the elastic constants and relaxed-ion piezoelectric stress coefficients of hexagonal ZnO calculated by DFPT and those previously reported. Numbers in parentheses are the relative errors (in percent) with respect to our calculated results.

To obtain the strain tensor $d_{ij}$, we need to calculate the stress tensor $e_{ij}$ and elastic tensor $C_{ij}$ which can be directly obtained in the DFPT approach without multiple ground-state calculations as required in the Berry Phase framework.

For checking the feasibility and correctness of the DFPT approach in calculating the piezoelectric properties of materials, we further applied the DFPT approach to calculate the properties of the well-studied and matured piezoelectric ZnO. As shown in Table 2, the calculated results at zero temperature are in good agreement with those previously measured and calculated. While the DFPT calculations are subject to several approximates, such as the GGA-pRPE itself which is associated with the errors of lattice parameters (Table 1), and the frozen-core approximation originated from the use of pseudopotentials, the calculated results are consistent with the experiment data at room temperature.

| Elastic components | Clamped-ion (GPa) | Relaxed-ion (GPa) | This work | Experiment$^a$ |
|--------------------|-------------------|-------------------|-----------|---------------|
| $C_{11}$           | 295.955           | 16.320            | 10.47\(-35.8\) |
| $C_{12}$           | 97.694            | 7.225             | 6.27\(-13.2\)  |
| $C_{13}$           | 105.091           | 8.874             | 14.07\(+58.6\) |
| $C_{22}$           | 348.615           | 35.071            | 13.91\(-60.3\) |
| $C_{23}$           | 84.171            | 19.870            | 9.73\(-51.0\)  |
| $C_{33}$           | 155.558           | 16.425            | 22.07\(+33.4\) |
| $C_{44}$           | 122.356           | 16.264            | 12.17\(-25.2\) |
| $C_{55}$           | 137.926           | 6.956             | 4.64\(-33.3\)  |
| $C_{66}$           | 157.735           | 3.212             | 4.26\(+32.6\)  |

$^a$ Ref. 17.
It is also worth noting that the elastic constants of mNA are approximately one order of magnitude smaller than that of inorganic piezoelectric materials such as GaN,[36] and AlN,[37,38] providing a relative measure of the flexibility of mNA crystal.

The piezoelectric stress coefficients of the mNA crystal, as defined in eqn (1), were calculated and are shown in Table 4.

| Stress constant | Clamped-ion (C m$^{-2}$) | Relaxed-ion (C m$^{-2}$) |
|-----------------|--------------------------|-------------------------|
| $e_{15}$        | 0.001                    | -0.059                  |
| $e_{24}$        | -0.048                   | -0.022                  |
| $e_{31}$        | 0.046                    | -0.339                  |
| $e_{32}$        | 0.164                    | -0.257                  |
| $e_{33}$        | 0.083                    | 0.168                   |

Table 5 Calculated clamped-ion and relaxed-ion piezoelectric stress coefficients of mNA, compared with those experimentally measured. Numbers in parentheses are the relative errors (in percent) with respect to the calculated results in this work.

| Strain constant | Clamped-ion (pC/N) | Relaxed-ion (pC/N) |
|-----------------|-------------------|--------------------|
|                 | This work         | Expt.$^a$         | Expt.$^b$         | Expt.$^c$         |
| $d_{13}$        | 0.010             | -8.488            | -         | -         | -         |
| $d_{24}$        | -0.395            | -1.359            | -         | -         | -         |
| $d_{31}$        | -0.061            | -64.950           | 73.1(+12.5)| 30.79(+52.6)| 20(-69.2)  |
| $d_{32}$        | 0.493             | -49.949           | 165.7/149.3(+231.7/+199.3)| 2.55(+94.9)| -         |
| $d_{33}$        | 0.232             | 115.757           | 103.8(-10.3) | 6.81(+94.1)| 4.0(-95.5)|

$^a$ Ref. 17. $^b$ Ref. 22. $^c$ Ref. 23.
piezoelectric materials. While the theoretical analysis is in general agreement with the experimental findings, however still few and varied, it also can provide a more complete assessment in details and guidance for possible molecular modifications. In the case of a simpler and well-established piezoelectric material such as ZnO, the calculated results are in excellent agreement with the experimental data.

Conlicts of interest
There are no conicts to declare.

Acknowledgements

Financial supports of this work by the National Natural Science Foundation of China (NSFC 61377063, 61071032, 61235006, and 61421002) and by the Chang-Jiang Chair Professor program are acknowledged.

References

1 S. Zhang and F. Yu, J. Am. Ceram. Soc., 2011, 94, 3153–3170.
2 H. D. Akaydin, N. Elvin and Y. Andreopoulos, J. Intell. Mater. Syst. Struct., 2010, 21, 1263–1278.
3 H. D. Akaydin, N. Elvin and Y. Andreopoulos, Exp. Fluids, 2010, 49, 291–304.
4 M. Rakotondrabe and I. A. Ivan, IEEE Trans. Autom. Sci. Eng., 2011, 8, 824–834.
5 X. Chu, J. Wang, S. Yuan, L. Li and H. Cui, Rev. Sci. Instrum., 2014, 85, 065002.
6 S. H. Zhang, J. P. Zhou, Z. Shi, P. Liu and C. Y. Deng, J. Alloys Compd., 2014, 590, 46–49.
7 Y. Oshima, M. Nakamura, Y. Masa, G. Villora, K. Shimamura and N. Ichinose, J. Electrochem. Soc., 2012, 127, 2455.
8 T. J. Bukowski, K. McCarthey, F. McCarthey, G. Teowee, T. P. Alexander, D. R. Uhmann, J. T. Dawley and B. J. J. Zelinski, Integr. Ferroelectr., 1999, 17, 339–347.
9 M. M. Fejer, G. A. Magel and E. J. Lim, SPIE-Int. Soc. Opt. Eng., Proc., 1999, 1148, 213–225.
10 Y. Li, W. Chen, Q. Xu, J. Zhou, Y. Wang and H. Sun, Ceram. Int., 2007, 33, 95–99.
11 M. D. Maeder, D. Damjanovic and N. Setter, J. Electroceram., 2004, 13, 385–392.
12 B. Mohammad, A. A. Yousefi and S. M. Bellah, Polym. Test., 2007, 26, 42–50.
13 Y. Jiang, H. Hamada, S. Shiono, K. Kanda, T. Fujita, K. Higuchi and K. Maenaka, Procedia Eng., 2010, 5, 1466–1469.
14 G. D. Jones, R. A. Assink, T. R. Dargaville, P. M. Chaplya, R. L. Clough, J. M. Elliott, J. W. Martin, D. M. Mowery and M. C. Celina, J. Electron. Packag., 2005, 131, 51–55.
15 F. Pan, Z. Xu, L. Jin, P. Pan and X. Gao, IEEE Trans. Ind. Appl., 2017, 53, 3890–3897.
16 S. Gilmour, R. A. Pethrick, D. Pugh and J. N. Sherwood, Philos. Mag. B, 1993, 67, 855–868.

4. Conclusions

In summary, the elasticity and piezoelectric properties of the mNA crystal were analyzed through numerical modeling based on the first-principles density functional perturbation theory (DFPT). The calculated results confirm the experimental findings that the relatively simple molecular material of mNA is capable of superior piezoelectric responses. While experimental findings are still few and varied, which is natural in an early phase of discovery, the theoretical modeling analysis provides an independent framework of reference and assessment. It also offers molecular structural insights to the highly anisotropic piezoelectric and elastic properties of the mNA crystal. The DFPT method as an efficient method for predicting the piezoelectricity and elastic properties of molecular
17. L. H. Avanci, L. P. Cardoso, S. E. Girdwood, D. Pugh, J. N. Sherwood and K. J. Roberts, *Phys. Rev. Lett.*, 1998, **81**, 5426–5429.

18. J. L. Oudar, D. S. Chemla and E. Batifol, *J. Chem. Phys.*, 1977, **67**, 1626–1635.

19. A. C. Fantoni, C. G. Pozzi and G. Punte, *J. Phys. Chem. A*, 2009, **113**, 9527–9532.

20. T. Kanagasekaran, M. Gunasekaran, P. Srinivasan, D. Jayaraman, R. Gopalakrishnan and P. Ramasamy, *Cryst. Res. Technol.*, 2010, **40**, 1128–1133.

21. P. V. Adhyapak, M. Islam, R. C. Aiyerb, U. P. Mulik, Y. S. Negi and D. P. Amalnerkar, *J. Cryst. Growth*, 2009, **310**, 2923–2927.

22. A. M. Bain, N. Ei-Korashy, S. Gilmour, R. A. Pethrick and J. N. Sherwood, *Philos. Mag. B*, 1992, **66**, 293–305.

23. D. Isakov, S. Vasilev, E. D. M. Gomes, B. Almeida, V. Y. Shur and A. L. Khoklin, *Appl. Phys. Lett.*, 2016, **109**, 162903.

24. X. Gonze, *Phys. Rev. A*, 1995, **52**, 1096–1114.

25. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.

26. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.

27. H. Takahashi, Y. Numamoto, J. Tani and S. Tsurekawa, *Jpn. J. Appl. Phys.*, 2006, **45**, 7405–7408.

28. T. Lin, X. Y. Liu and C. He, *J. Phys. Chem. B*, 2012, **116**, 1524–1535.

29. D. Vanderbilt, *J. Phys. Chem. Solids*, 2000, **61**, 147–151.

30. M. B. Kanoun, E. Botek and B. Champagne, *Chem. Phys. Lett.*, 2010, **487**, 256–262.

31. P. V. Adhyapak, M. Islam, R. C. Aiyerb, U. P. Mulik, Y. S. Negi and D. P. Amalnerkar, *J. Cryst. Growth*, 2008, **310**, 2923–2927.

32. X. Wu, D. Vanderbilt and D. R. Hamann, *Phys. Rev. B*, 2005, **72**, 035105.

33. J. D. Gale and A. L. Rohl, *Mol. Simul.*, 2003, **29**, 291–341.

34. W. F. Perger, J. Criswell, B. Civalleri and R. Dovesi, *Comput. Phys. Commun.*, 2009, **180**, 1753–1759.

35. A. S. Bhalla, W. R. Cook jr. and S. T. Liu, *Low Frequency Properties of Dielectric Crystals: Piezoelectric, Pyroelectric and Related Constants*, Springer, Berlin, 1993.

36. G. Irmer, C. Röder, C. Himcinschi and J. Kortus, *Phys. Rev. B*, 2016, **94**, 195201.

37. K. Kim, W. R. L. Lambrecht and B. Segall, *Phys. Rev. B*, 1996, **53**, 16310–16326.

38. F. Peng, D. Chen, H. Fu and X. Cheng, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **403**, 4259–4263.

39. G. Ryu and C. S. Yoon, *J. Cryst. Growth*, 1998, **191**, 190–198.

40. J. L. Oudar, D. S. Chemla and E. Batifol, *J. Chem. Phys.*, 1977, **67**, 1626–1635.

41. A. E. Goeta, C. C. Wilson, J. Ellena and G. Punte, *Chem. Mater.*, 2000, **12**, 3342–3346.

42. X. Wu, D. Vanderbilt and D. R. Hamann, *Phys. Rev. B*, 2005, **72**, 035105.