Prediction of properties of organic ferroelectrics and piezoelectrics by first-principles calculation

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In response to the application of an electric field, the refractive index varies linearly for certain class of materials. This effect is known as the Pockels effect and is one of the second-order nonlinear optical effects. In the present study, we simulated the Pockels effect in organic ferroelectric crystals of croconic acid (CRCA) and 5,6-dichloro-2-methylbenzimidazole (DC-MBI) [1].

Simulations were carried out in the following three modes: (1) with a clamped cell and clamped atomic positions (an optimized structure at $E = 0$), (2) with a clamped cell and relaxed atomic positions at E, and (3) with a relaxed cell and relaxed atomic positions at E. In the first mode, the response to electric field application is purely electronic. In the second mode, the ionic response was included. For the third mode, the piezoelectric effect was also added to the electronic and ionic responses. A dielectric constant ε at an electric field of E was evaluated using the formula $\varepsilon = 1 + (1/\varepsilon_0)(\mathrm{d}P/\mathrm{d}E)$, where ε_0 is the vacuum permittivity. Electric polarization values P were calculated at $E, E \pm 0.1, E \pm 0.2$ (MV cm^{-1}). By applying linear regression to the relationship between E and P, $\varepsilon(E)$ values were obtained. Pockels coefficients r_{ijk} were evaluated by applying linear regression to $1/\varepsilon(E)$. For CRCA, E values were sampled as $0, \pm 1, \pm 2$ (MV cm^{-1}) while for DC-MBI, simulations were also carried out at ± 3 (MV cm^{-1}) because its electro-optic response was small. For these organic crystals, the van der Waals interaction is critical, and two types of van der Waals density functionals vdW-DF-cx and rVV10 were used. These functionals reproduce the lattice parameters of CRCA and DC-MBI successfully [2]. All the calculations were performed using the QMAS code.

Table 1: Percentages from piezoelectric, ionic and electronic contributions.

	piezoelectric	ionic	electronic
CRCA*	32.2	57.7	10.1
CRCA†	24.4	61.8	13.8
DC-MBI*	54.1	24.5	21.4
DC-MBI†	58.5	21.0	20.5

* vdW-DF-cx, † rVV10

For CRCA and DC-MBI, the r_{333} values are obtained as 17.0 and 2.7 (pm/V) with the vdW-DF-cx functional while as 12.4 and 2.0 (pm/V) with the rVV10 functional, respectively. Percentages from piezoelectric, ionic and electronic contributions are shown in Table 1. It is shown that the ionic contribution is important particularly for CRCA. These calculated results are reasonable compared with the experimental ones [1].

References

[1] K. Sunami, S. Horiuchi, S. Ishibashi, and J. Tsutsumi: Adv. Electron. Mater. **11**, 2400346 (2025).

[2] S. Ishibashi, S. Horiuchi, and R. Kumai: Phys. Rev. Mater. **5**, 094409 (2021).