

Supplementary Information

Large Piezoelectric Response of van der Waals Layered Solids

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A. Comparison of Experimental and Calculated Piezoelectric Modulus

Using density functional theory, we have calculated longitudinal piezoelectric modulus (d_{33}) of well-known piezoelectric compounds. The predicted modulus are found to be in good agreement with experimentally measured values. Since, they are all exist in bulk 3D crystal, standard GGA-PBE exchange correlation functionals have been used for these calculations. Plane wave cutoff energy of 540 eV is used for structural relaxation, calculation of elastic tensors and piezoelectric coefficient tensor. k-point grid, defined by $n_{\text{atoms}} \times n_{\text{kpoints}} \approx 1000$, where n_{atoms} is number of atoms in the primitive cell and n_{kpoints} is the number of k -points, is used throughout the calculations. A very high tolerance of 10^{-8} eV for energy convergence is used for all three calculations.

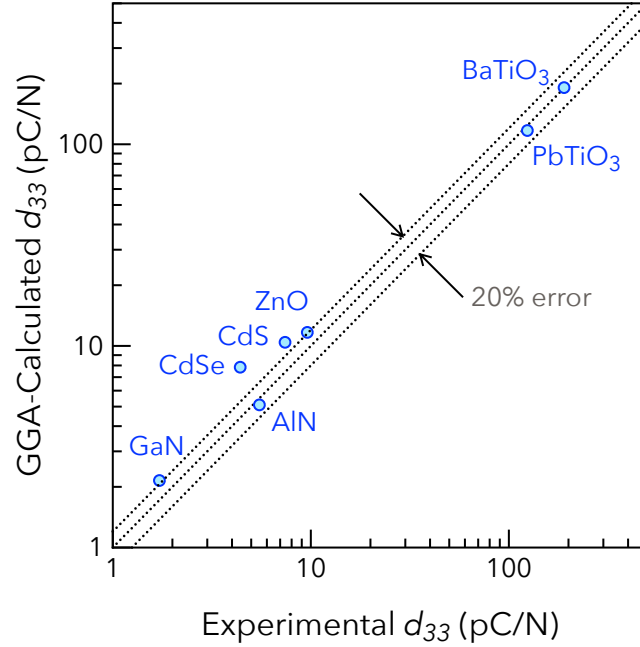


FIG. S1: Calculated d_{33} with GGA functional vs experimentally measured d_{33}

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B. Axial Anisotropies: \mathbf{C} vs \mathbf{e}

We have investigated all the possible correlations among the axial anisotropies of \mathbf{d} , \mathbf{e} , and \mathbf{C} . In the main text, we have described the axial anisotropy dependence of \mathbf{d} on the axial anisotropies of \mathbf{C} and \mathbf{e} . The remaining plot between axial anisotropy of \mathbf{C} and \mathbf{e} is shown in Figure S2.

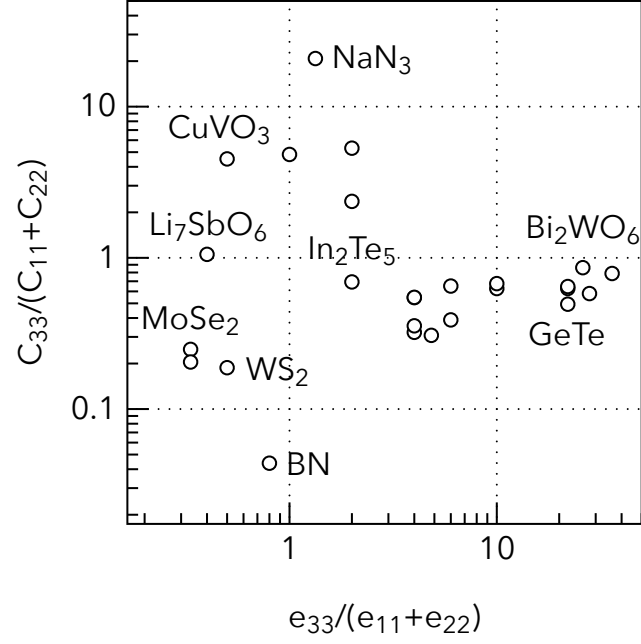


FIG. S2: Axial anisotropy in \mathbf{C} vs axial anisotropy in \mathbf{e}

C. Experimentally Measured Elastic Constants of Quasi-2D Materials

TABLE S1: Reference table for Figure 6. The measured values of C_{ij} are reported in GPa unit

Material	SG	C_{11}	C_{12}	C_{33}	C_{44}	Technique	Temperature
TiSe ₂ [1]	164	120	42	39	14.3	Neutron Inelastic Scattering	300K
Bi ₂ Te ₃ [2]	166	74	-	52	31.35	Wave Resonance Technique	4.2K
GaSe[3]	187	103	28.9	34.1	9	Brillouin Scattering	300K
InSe[3]	194	73	27	36	11.7	Brillouin Scattering	300K
GaS[3]	194	123.3	34.7	38.2	9.96	Brillouin Scattering	300K
PbI ₂ [4]	166	27.7	9.6	20.2	6.2	Neutron Inelastic Scattering	293K
BiI ₃ [5]	162	29	5	26	7	Brillouin Scattering	83K
NiTe ₂ [6]	164	109.5	41.9	52.6	20.4	Neutron Spectrometry	300K
TaSe ₂ [7]	194	229	36.6	54	18.5	Neutron Spectrometry	300K
NbSe ₂ [7]	194	194	91	42	17.6	Neutron Spectrometry	300K
HgI ₂ [8]	137	33	5.6	16.3	7.23	Ultrasound Propagation Technique	293K
CdI ₂ [9]	164	41.21	16	21.8	18.6	Brillouin Scattering	-
SnS ₂ [9]	164	124	33	28.9	10.2	Brillouin Scattering	-
MoS ₂ [10]	194	238	-54	51	21.7	Neutron Inelastic Scattering	308K

D. Schematics of Different Modes of d

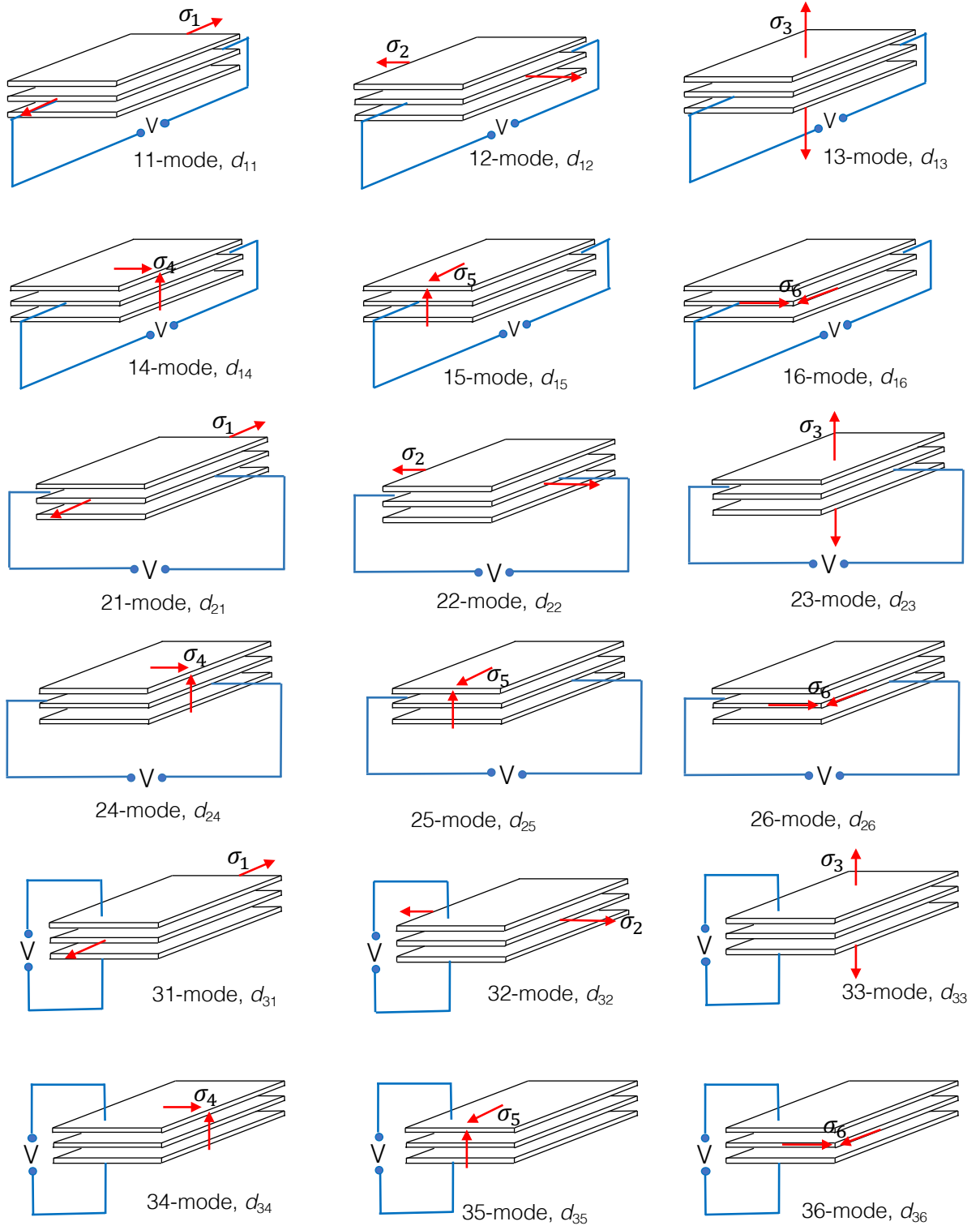


FIG. S3: Schematics of the modes of d with their measuring polarization directions and deformation stresses. Each mode represents each component of d -matrix

E. Rotation of d , e , & C -matrices

In our reported 63 quasi-2D piezoelectric materials, we found that in 19 candidates the layer stacking direction is not along [001]-direction. To maintain consistency and capture the effect of van der Waals bond on piezoelectric response, we rotate their d , e , and C -matrix into the co-ordinate frame such that the layering direction is always along [001]-direction. The matrix transformation in going from the old to the new coordinate system[11, 12] is,

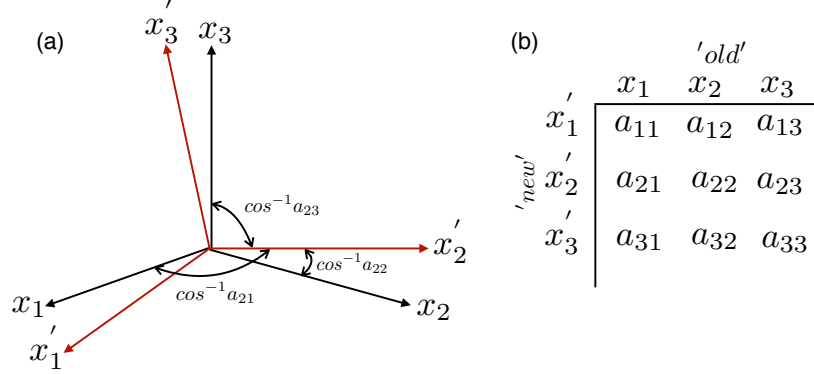


FIG. S4: (a) 'old' and 'new' co-ordinate frames (b) The angular relations between the axes is specified by drawing up a table of direction cosines which is denoted by \mathbf{a} -matrix

$$\mathbf{e}' = (\mathbf{a})(\mathbf{e})(\alpha^{-1}) \quad (1)$$

$$\mathbf{d}' = (\mathbf{a})(\mathbf{d})(\alpha^{-1}) \quad (2)$$

$$\mathbf{C}' = (\alpha)(\mathbf{C})(\alpha_t) \quad (3)$$

Where, \mathbf{a} is the direction cosine matrix, given by,

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

Elements of α is given by,

$$\begin{bmatrix} (a_{11}^2) & (a_{12}^2) & (a_{13}^2) & (2a_{12}a_{13}) & (2a_{13}a_{11}) & (2a_{11}a_{12}) \\ (a_{21}^2) & (a_{22}^2) & (a_{23}^2) & (2a_{22}a_{23}) & (2a_{23}a_{21}) & (2a_{21}a_{22}) \\ (a_{31}^2) & (a_{32}^2) & (a_{33}^2) & (2a_{32}a_{33}) & (2a_{33}a_{31}) & (2a_{31}a_{32}) \\ (a_{21}a_{31}) & (a_{22}a_{32}) & (a_{23}a_{33}) & (a_{22}a_{33}) + (a_{23}a_{32}) & (a_{21}a_{33}) + (a_{23}a_{31}) & (a_{22}a_{31}) + (a_{21}a_{32}) \\ (a_{31}a_{11}) & (a_{32}a_{12}) & (a_{33}a_{13}) & (a_{12}a_{33}) + (a_{13}a_{32}) & (a_{13}a_{31}) + (a_{11}a_{33}) & (a_{11}a_{32}) + (a_{12}a_{31}) \\ (a_{11}a_{21}) & (a_{12}a_{22}) & (a_{13}a_{23}) & (a_{12}a_{23}) + (a_{13}a_{22}) & (a_{13}a_{21}) + (a_{11}a_{23}) & (a_{11}a_{22}) + (a_{12}a_{21}) \end{bmatrix}$$

For detail derivation of these transformations please see reference [11, 12].

F. Comparison of d_{max} with different vdW corrected functionals.

We also calculate d_{max} using Grimme D3 and Tkatchenko & Scheffler corrected functional. The results are shown in Table S2.

TABLE S2: Comparison of d_{max} (in pC/N) calculated with optB86, Grimme D3 and self-consistent Tkatchenko & Scheffler functionals (SCTS) vdW-corrected functionals. The component in the parenthesis describes d_{ij} appearing as d_{max}

	$d_{max}(\text{optB86})$	$d_{max}(\text{D3})$	$d_{max}(\text{SCTS})$
GeTe	148.4 (d_{15})	147.7 (d_{15})	199.4 (d_{15})
BiInO ₃	56.1 (d_{33})	56 (d_{33})	38.4 (d_{33})
NaI ₃ O ₈	48.4 (d_{14})	48 (d_{14})	52.1 (d_{14})
NaN ₃	40.7 (d_{36})	23.5 (d_{35})	40 (d_{32})
Cs ₂ Te ₃	31.3 (d_{36})	12 (d_{36})	12 (d_{36})
Bi ₂ MoO ₆	28.7 (d_{26})	24.6(d_{33})	24.6(d_{33})
AgI	27.8 (d_{33})	166.7 (d_{33})	135.1 (d_{33})
SbF ₂ Cl ₃	24.4 (d_{15})	62.5 (d_{15})	71.4 (d_{15})
PbRb ₂ O ₃	22.2 (d_{34})	40.5 (d_{15})	16.6 (d_{15})
BiGeO ₅	21.1 (d_{33})	31.6 (d_{33})	33.4 (d_{33})

G. Quasi-2D materials with isotropic axial elastic anisotropy and anisotropic axial piezoelectric coefficient

We have inspected the crystal structures of materials that have isotropic axial elastic modulus. Although these materials have layered structures, the spatial gap between the layers is very small. They rather fall in the borderline category between bulk 3D and quasi-2D structures. The crystal structures of these materials are shown in Figure S5. The crystal structures of these materials are shown in Figure S5. The reason for isotropic axial elastic anisotropy is the small vdW gap implying residual chemical interactions between the layers. The axial anisotropic behavior between elastic modulus and piezoelectric responses differ from each other since the elastic tensor implies straining chemical bonds whereas the piezoelectric coefficient tensor describes the charge redistribution upon straining the bonds. One example that illustrates this is AlN, which has an isotropic elastic modulus but highly-anisotropic piezoelectric coefficients [13].

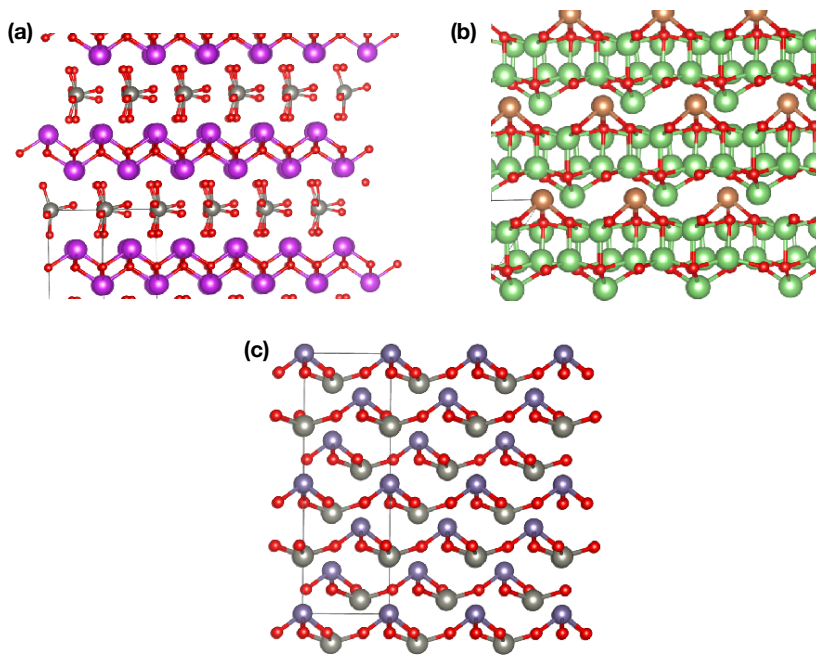


FIG. S5: Crystal structures of (a)Bi₂WO₆, (b) Li₇SbO₆, and (c) GeZnO₃. All these materials have layered structures with small vdW gap.

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