

## ARTICLE OPEN



## Data-driven methods for discovery of next-generation electrostrictive materials

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All dielectrics exhibit electrostriction, i.e., display a quadratic strain response to an electric field compared to the linear strain dependence of piezoelectrics. As such, there is significant interest in discovering new electrostrictors with enhanced electrostrictive coefficients, especially as electrostrictors can exhibit effective piezoelectricity when a bias electric field is applied. We present the results of a study combining data mining and first-principles computations that indicate that there exists a group of iodides, bromides, and chlorides that have electrostrictive coefficients exceeding  $10 \text{ m}^4 \text{ C}^{-2}$  which are substantially higher than typical oxide electrostrictive ceramics and polymers. The corresponding effective piezoelectric voltage coefficients are three orders of magnitude larger than lead zirconate titanate.

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## INTRODUCTION

The development of novel materials exhibiting exceptional strain response in the presence of an external electric field is imperative to the development of tunable electromechanical devices<sup>1–8</sup>. Promising applications involve next-generation transducers<sup>9</sup>, ultra-efficient actuators<sup>1,2,10</sup>, sonars<sup>11</sup>, and low-power logic devices<sup>12</sup> with application spaces in medicine, astronomy, and consumer electronics. Recent discoveries of ‘giant’ electrostrictors, for example, Gd-doped ceria<sup>8</sup>, and (Nb, Y) doping in bismuth oxide<sup>13</sup> and lanthanum molybdenum oxide<sup>7</sup>, soft nano-composite based on carbon nanotubes (CNT)<sup>14</sup> and liquid crystalline graphene<sup>6</sup> have opened promising applications for superior electromechanical properties, and also as a replacement of lead-based  $\text{Pb}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  (PZT) solid solutions that are widely used in current applications. Of particular interest is the possibility to induce an effective piezoelectric behavior under a bias electric field, generating extraordinarily large piezoelectric coefficients ( $d_{33} \sim 2 \times 10^5 \text{ pC N}^{-1}$ )<sup>15</sup>. These ‘giant’ electrostrictors have been reviewed recently<sup>16</sup>. There is a clear advantage in utilizing electrostrictive materials that exhibit a quadratic strain in response to an electric field. This may allow for a more significant strain response for a given applied external field, as well as take advantage of the anhyseretic nature of electrostriction for high-precision displacements.

This effect is mediated via an applied electric field ( $E_i$ ) and the dielectric polarization ( $P_i$ ) vectors as described by

$$x_{ij} = d_{ijk}E_k + M_{ijkl}E_kE_l \quad (1)$$

$$x_{ij} = g_{ijk}P_k + Q_{ijkl}P_kP_l \quad (2)$$

where  $x_{ij}$  are the strain components,  $d_{ijk}$  and  $g_{ijk}$  are piezoelectric tensors, and  $M_{ijkl}$  and  $Q_{ijkl}$  are fourth-rank tensors describing the electrostrictive response. In Eq. (1), the total strain (at constant stress) is expressed in terms of an applied electric field, whereas in Eq. (2) it is given as a function of the polarization. The  $M$  tensor is of particular interest for actuator applications whereas  $Q$  is used as a design criterion in sensing applications.

The search for novel electrostrictors has historically appeared bounded by the universal empirical relation connecting the electrostrictive coefficient to the ratio of the elastic compressibility over the permittivity<sup>5</sup> until the discovery of ‘giant’ electrostrictors that are several orders of magnitude greater than the empirically expected values<sup>16</sup>. These include materials such as  $\text{La}_2\text{Mo}_2\text{O}_9$  ( $M_h \sim 10^{-18} \text{ m}^2 \text{ V}^{-2}$  and  $Q_h \sim 20 \text{ m}^4 \text{ C}^{-2}$ ), (Nb,Y)-stabilized  $\text{Bi}_2\text{O}_3$  ( $M_h \sim 4.7\text{--}12.5 \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$  and  $Q_h \sim 83\text{--}273 \text{ m}^4 \text{ C}^{-2}$ )<sup>13</sup>,  $\text{CeO}_{2-x}$  ( $M_h \sim 300 \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$ )<sup>15</sup>, lead halide perovskites ( $M_h \sim 730\text{--}900 \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$  and  $Q_h \sim 1266\text{--}1417 \text{ m}^4 \text{ C}^{-2}$ )<sup>17</sup>, and  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  ( $M_h \sim 6.5 \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$ )<sup>6–8</sup>. The electrostriction coefficients of these materials are three orders larger than typical perovskites, including  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{SrTiO}_3$ , and  $\text{Pb}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  for which  $Q_h$  is in the range  $0.02\text{--}0.07 \text{ m}^4 \text{ C}^{-2}$ <sup>5</sup>.

Using large open materials databases composed of accurately determined materials properties, the programmatic search for materials exhibiting specific properties becomes possible. In line with data-driven methods, advanced modeling approaches across length scales, and the successful insertion of the concept of materials genomics that allows for rapid development and deployment of novel materials<sup>18,19</sup>, we employ here a combination of data mining and first-principles modeling in the discovery of materials exhibiting exceptional electrostrictive coefficients. Our results show several non-oxide inorganic compounds with electrostrictive properties one or two orders of magnitude higher than existing oxide ceramics and with comparable or higher electrostriction coefficients than polymers.

## RESULTS

## Assessment of electrostrictive properties

The tensorial notation that has been employed in Eqs. (1) and (2) can be reduced to the following criteria to assess the magnitude of the electrostrictive properties of a wide variety of materials (see Supplementary Information), which is also defined as the Newnham’s proxy  $Q_h^{\text{proxy}}$ , based on the approach presented in

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refs. 5,10.  $M_h^{\text{proxy}}$  can be derived from  $Q_h^{\text{proxy}}$  as below:

$$Q_h^{\text{proxy}} = \left( \frac{s_R}{\epsilon_0 \epsilon_r} \right) \approx (K_R \epsilon^*)^{-1} \quad (3)$$

$$M_h^{\text{proxy}} = \frac{\epsilon^*}{K_R}. \quad (4)$$

Here  $\epsilon^*$  is the average eigenvalue of the dielectric tensor  $\epsilon$  with  $\epsilon = \epsilon_0 \epsilon_r$ ,  $\epsilon_r$  the relative permittivity of the material, and  $\epsilon_0$  the permittivity of vacuum.  $s_R$  in Eq. (3) is the Reuss elastic compressibility given as<sup>20,21</sup>

$$\frac{1}{K_R} = s_R = (s_{11} + s_{22} + s_{33}) + 2(s_{12} + s_{23} + s_{31}) \quad (5)$$

The Supplementary Information provides a more detailed treatment to define constitutive relations for the electrostrictive coefficients  $M_{ijkl}$  and  $Q_{ijkl}$ . Equations (3) and (4) follow from specific electrical and mechanical boundary conditions corresponding to hydrostatic pressure/expansion and a single electric field component (uniaxial applied electric field in a short-circuit configuration) as discussed in the Supplementary Information. We note that Eq. (3) describes the  $Q_h$  criterion used by Newnham et al. in their landmark paper that classified electrostriction for a range of materials over an extensive response space<sup>5</sup>. We add here an additional criterion for  $M_h$ <sup>16,22</sup>. Although closely related, the quantities  $M_h$  and  $Q_h$  are not interchangeable as converse effects (Supplementary Information). Subtle differences in how these are defined give rise to slightly different criteria for the proxy derivation used to approximate  $M_h$  and  $Q_h$ .  $M_h$  is the readily accessible physical parameter in experiments.

In addition to the static empirical relations in Eqs. (3) and (4), it is advantageous to use the differential forms of  $Q_h$  and  $M_h$  as described in the Supplementary Information, which is essentially the dielectric response with a change in external hydrostatic pressure ( $p$ ). In the following,  $Q_h$  and  $M_h$  derived from our density functional theory (DFT) calculations are defined as  $Q_h^{\text{DFT}}$  and  $M_h^{\text{DFT}}$ , respectively. Thus,

$$Q_h^{\text{DFT}} = -0.5 \left( \frac{\partial(1/\epsilon^*)}{\partial p} \right) \quad (6)$$

$$M_h^{\text{DFT}} = 0.5 \left( \frac{\partial \epsilon^*}{\partial p} \right) \quad (7)$$

It must be noted that Eqs. (6) and (7) capture the mechanical response as differential in pressure ( $p$ ) and the equations are independent of Eq. (3) and Eq. (4).

DFT has been used to study the electrostriction properties of compounds having high structural symmetry<sup>23,24</sup>. Of particular interest in this regard is the study by Tanner et al. wherein the electrostrictive coefficients of cubic dielectric materials were computed using the differentials of the lattice parameters, which is similar to differentials of hydrostatic pressure for cubic crystal system<sup>25</sup>. We have adopted the latter method using Eqs. (6) and Eq. (7). In our computations, the trace of the external stress tensor, defined as  $pstress$ , is treated as the hydrostatic pressure with the conventional notation that positive and negative  $pstress$  values mean hydrostatic expansion and compression, respectively. This approach allows for uniform evaluation of electrostrictive coefficients over all seven crystal systems independent of their crystal structure.

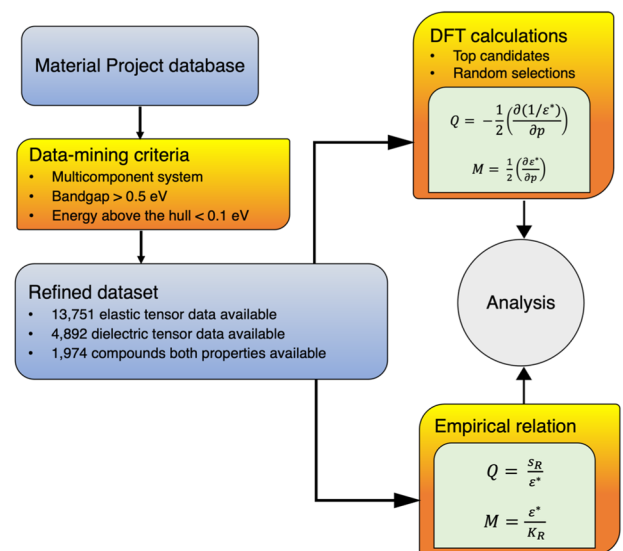
### Data mining

To assign proxies for selecting materials exhibiting high electrostriction, we utilize a set of relationships between the dielectric response, the elastic coefficients, the electric field-induced strain, and the electrostrictive properties of materials as described in the previous section. A similar methodology developed by Newnham

et al. has shown a semi-empirical connection between the elastic compliance, the dielectric response, and the hydrostatic electrostrictive coefficient  $Q_h$ <sup>4,5</sup>.

Existing databases of calculated functional properties provide easy access to data that can be used to shortlist materials with exceptional properties via a simple database query of related proxies<sup>26,27</sup>. The Materials Project (MP) serves as an ideal platform for novel materials discovery, given the large number of calculated material properties and optimized crystal structures contained in the database<sup>28</sup>. The database contains 124,515 inorganic compounds with properties calculated via medium/high accuracy DFT methods. The MP team has calculated the elastic tensors for 13,751 and the dielectric tensors for 4892 inorganic materials so far<sup>28</sup> and made these publicly available<sup>20</sup>. In addition, there are currently 1974 materials for which MP has calculated both the dielectric and elastic properties. This set of materials is ideal for data mining and training machine learning models to predict electrostrictive response. Starting from this set, we down-select using a set of simple property filters to find new promising candidates for electrostriction applications. We limit the materials by considering non-elemental (>1 element) dielectrics with a bandgap >0.5 eV and seek compounds that should exhibit relative stability as determined via the energy above the hull (<0.1 eV). The schematic representation of the workflow is shown in Fig. 1.

These materials are then separated into centrosymmetric and non-centrosymmetric datasets based on their point group symmetries. This discretization serves the purpose of allowing us to consider materials lacking an inversion symmetry (non-centrosymmetric), which exhibit a spontaneous polarization via a piezoelectric response resulting from the dielectric and electrostrictive contributions separately from those that solely display an electrostrictive response (see Fig. 1). Taking these latter materials, it is then possible to consider the ratio of ( $s_R/\epsilon^*$ ) for each material and rank these according to the proxies described in Eqs. (3) and (4). To reduce the dielectric and elastic tensors to a scalar value for each data point, the inverse of the Reuss average bulk modulus was used in place of the elastic compressibility ( $s_R \approx 1/K_R$ ) and the averaged dielectric tensor eigenvalue in place of  $\epsilon^*$ , thus  $Q_h = (K_R \epsilon^*)^{-1}$  is considered a replacement for  $s/\epsilon$  and a proxy for predicting  $Q_h$ . Alternatively,  $M_h = (\epsilon^*/K_R)$  is the expression used for querying for high  $M_h$ . These proxies are utilized throughout the rest of the study in combination with DFT-calculated values for



**Fig. 1** Flow chart showing data curating and first-principles computation on data-mined compounds. Data-mining Materials Project database and DFT computation workflow for search of high electrostriction materials.

shortlisting materials which should exhibit exceptional electrostrictive strain response to an applied external electric field.

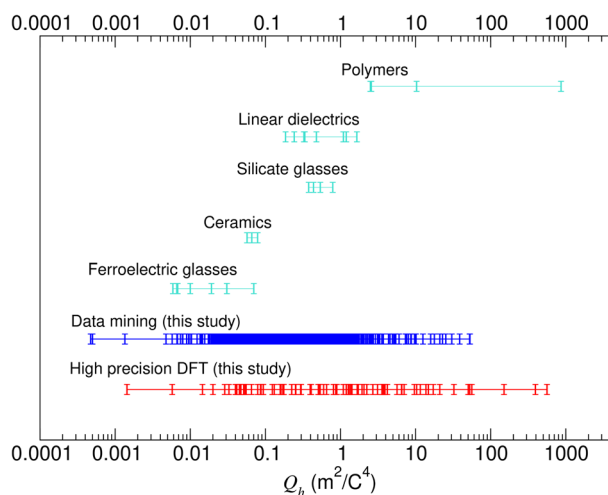
### First Principles (DFT) validation

The accuracy of DFT for materials properties that are determined at the electronic and atomic levels has been well tested; it provides a platform to bridge the gap between fundamental theory, high-throughput computational data science, and experiments<sup>29–37</sup>. Here, we perform first-principles calculations with DFT using the plane-wave pseudopotential method<sup>38</sup>. The structural units of the compounds are taken from the MP database. We have used the PBEsol exchange–correlation functional<sup>39</sup> in place of the standard general gradient approximation (GGA) in the MP. PBEsol is a revised Perdew–Burke–Ernzerhof GGA chosen due to the enhanced prediction of equilibrium properties of densely packed solids, such as the dielectric and elastic tensors for insulating materials compared to GGA<sup>25</sup>. Geometric optimization was carried out to obtain the equilibrium lattice parameters and corresponding atomic positions. The  $k$ -points grid size was set to  $9 \times 9 \times 9$ , but models with atoms larger than 20 were treated with  $7 \times 7 \times 7$  grid size. The kinetic energy cutoff for the plane waves is 800 eV. The symmetry tag was switched on for the calculations so that the system did not deviate from the initialized structures. Non-spin-polarized calculations were performed as most compounds were not expected to have a magnetic ground state. Geometrical optimization for the models was carried out with the tolerance for total energy convergence set to  $10^{-5}$  eV and was performed in five cycles. The relaxed model from one cycle was then fed as the initial model for the next cycle to ensure a thorough relaxation. The calculations were performed with the Vienna ab initio simulation package (VASP)<sup>40–42</sup>.

The elastic compliance tensor was calculated by performing six finite distortions of the supercells and constructing the Hessian matrix from total energies obtained from density functional perturbation theory (DFPT)<sup>43</sup>. The static ion-clamped dielectric matrix was computed using DFPT via the linear Sternheimer equations<sup>44,45</sup>. This method bypasses the complexity of computing the dielectric function through relaxation under finite electric fields. Equations (6) and (7) rely on the change in dielectric response as a function of hydrostatic pressure<sup>46</sup>. The DFT computation of the dielectric function was done at 25 kbar  $p$ stress above and 25 kbar  $p$ stress below the equilibrium volume for which the  $p$ stress is zero. The mechanical perturbation of the order  $\pm 25$  kbar is well within the harmonic approximation and provides minimal deviation of the unit cell symmetry. We found slight variations in the equilibrium lattice parameters when compared to the MP. This is due to differences in the pseudopotentials that were utilized in this study in the relaxation procedures.

### DISCUSSION

Applying the selection criteria developed in Section III has allowed us to shortlist a set of materials that may potentially exhibit a significant electrostrictive strain response.  $Q_h^{\text{proxy}}$  values estimated from the MP data using Eqs. (3) and (4) are compared with the experimental data taken from Refs. 3–5,47 in Fig. 2. It is observed that specialized polymers have generally larger  $Q_h$  than ceramics or glasses. Comparing  $Q_h$  of materials from the MP dataset, one finds larger  $Q_h$  in several ceramics and covalent salts that surpass polymers by almost 400% if the data from ref. 3 corresponding to polyurethane elastomer is considered an outlier. The top electrostrictive materials from MP are explored in more detail using more accurate DFT computations. The  $Q_h^{\text{DFT}}$  values based on Eq. (6) display even more promising results with electrostrictive coefficients over 500% larger than typical electrostrictive polymers.



**Fig. 2 Comparison of  $Q_h$  electrostrictive coefficient between different materials classes.** Magnitude of  $Q_h$  values obtained from experiments (data taken from ref. 3) and compared to  $Q_h^{\text{proxy}}$  and  $Q_h^{\text{DFT}}$  from our study.

**Table 1.** Comparison of  $Q_h$  from Newnham's proxy and DFT computation.

Materials	$Q_h^{\text{proxy}}$	Materials	$Q_h^{\text{DFT}}$
TeBr <sub>2</sub>	7387.95	GaBr <sub>3</sub>	560.53
MgCl <sub>2</sub>	5666.93	WCl <sub>6</sub>	393.32
SiCl <sub>4</sub>	3512.25	PBr <sub>3</sub>	150.39
BCl <sub>3</sub>	2564.01	PBr <sub>3</sub> O	89.60
PCl <sub>3</sub>	1824.01	IBr	56.01
GaBr <sub>3</sub>	872.82	BCl <sub>3</sub>	52.49
WCl <sub>6</sub>	862.60	PCl <sub>3</sub>	50.18
MgI <sub>2</sub>	831.07	SiCl <sub>4</sub>	48.97
SF <sub>6</sub>	751.43	SbCl <sub>3</sub>	32.34
AlI <sub>3</sub>	718.53	GaCl <sub>3</sub>	20.97

The list of top ten  $Q_h$  materials predicted from Newnham's proxy relation ( $Q_h^{\text{proxy}}$ ) and our DFT calculations ( $Q_h^{\text{DFT}}$ ). The unit of  $Q_h$  is  $\text{m}^4 \text{C}^{-2}$ . All calculations were carried out at 0 K and therefore on materials in their solid states.

The top ten  $Q_h$  ( $Q_h^{\text{proxy}}$  and  $Q_h^{\text{DFT}}$ ) and  $M_h$  ( $M_h^{\text{proxy}}$  and  $M_h^{\text{DFT}}$ ) candidates from MP and DFT calculations are listed in Tables 1 and 2, respectively. It is encouraging to find that five out of our top ten high  $Q_h$  materials appear in both proxy and DFT data sets. These are: SiCl<sub>4</sub>, BCl<sub>3</sub>, PCl<sub>3</sub>, GaBr<sub>3</sub>, and WCl<sub>6</sub>. On the other hand, three out of the top ten  $M_h$  materials appear in both the proxy and DFT data sets. These are SbSI, SbCl<sub>2</sub>, and WCl<sub>6</sub>. Materials in the top ten list of  $Q_h^{\text{proxy}}$  and  $M_h^{\text{proxy}}$  include MgCl<sub>2</sub>, MgI<sub>2</sub>, SiCl<sub>4</sub>, WCl<sub>6</sub>, and PCl<sub>3</sub>. Likewise, materials common to the top ten list of  $Q_h^{\text{DFT}}$  and  $M_h^{\text{DFT}}$  are WCl<sub>6</sub>, GaBr<sub>3</sub>, and SbCl<sub>3</sub>. Overall, the data supports that the halide groups, especially the chlorides, the bromides, and the iodides are promising materials for electrostriction functionality.

There are important differences in the output value of  $Q_h$  that should be noted. For example, our  $Q_h^{\text{proxy}}$  values for WCl<sub>6</sub> and PBr<sub>3</sub> are  $22.83 \text{ m}^4 \text{C}^{-2}$  and  $20.99 \text{ m}^4 \text{C}^{-2}$ , respectively, while  $Q_h^{\text{DFT}}$  for these compounds is significantly larger:  $560.53 \text{ m}^4 \text{C}^{-2}$  for WCl<sub>6</sub> and  $393.32 \text{ m}^4 \text{C}^{-2}$  for PBr<sub>3</sub>. Other materials such as GaCl<sub>3</sub> have similar values from the empirical and DFT relations ( $20.97 \text{ m}^4 \text{C}^{-2}$  and  $17.78 \text{ m}^4 \text{C}^{-2}$ , respectively). We also plot a comparison of  $Q_h^{\text{proxy}}$  with  $Q_h^{\text{DFT}}$  and  $M_h^{\text{proxy}}$  with  $M_h^{\text{DFT}}$  in Fig. 3a, b, respectively.

**Table 2.** Comparison of  $M_h$  from Newnham's proxy and DFT computation.

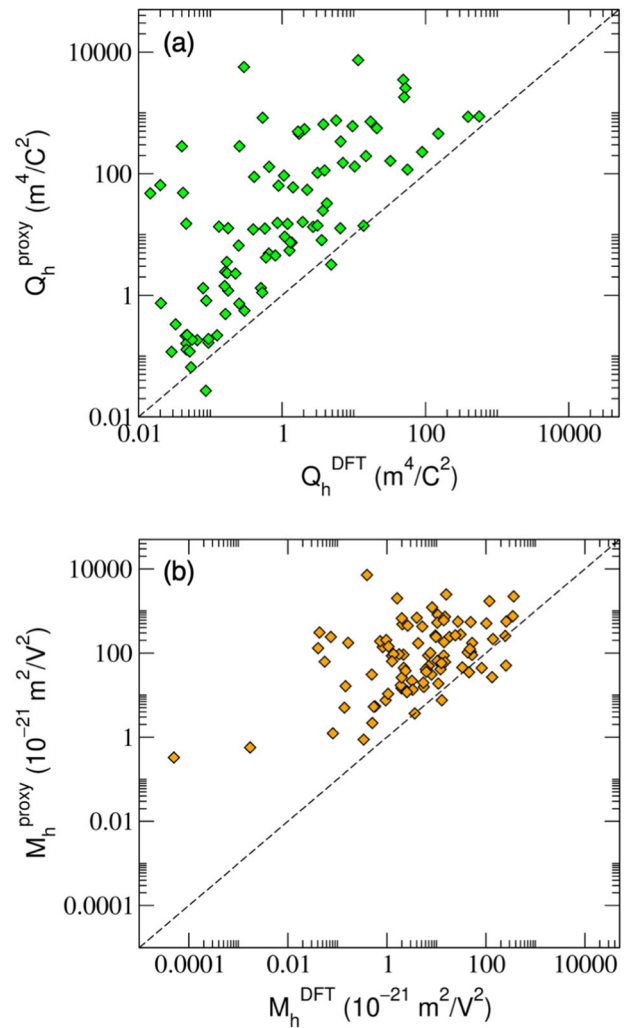
Materials	$M_h^{\text{proxy}}$	Materials	$M_h^{\text{DFT}}$
MgCl <sub>2</sub>	720.364	SbSI	36.375
GaCl <sub>2</sub>	244.796	WCl <sub>6</sub>	35.0125
SbSI	220.457	GaBr <sub>3</sub>	25.797
MgI <sub>2</sub>	198.097	SnBrF	25.429
SbCl <sub>3</sub>	169.936	NaTaN <sub>2</sub>	24.595
Ta(II)Cl <sub>2</sub>	120.947	LiBiS <sub>2</sub>	13.865
SiCl <sub>4</sub>	80.925	SnClF	13.275
WCl <sub>6</sub>	74.850	SbCl <sub>3</sub>	11.743
PCl <sub>3</sub>	72.277	Sr <sub>2</sub> HfO <sub>4</sub>	10.210
CaI <sub>3</sub>	68.584	TePb	8.194

The list of top ten  $M_h$  materials predicted from  $Q_h^{\text{proxy}}$  and our DFT calculations ( $Q_h^{\text{DFT}}$ ). The unit of  $M_h$  is  $10^{-21} \text{ m}^2 \text{ V}^{-2}$ . All calculations were carried out at 0 K and therefore on materials in their solid states.

There are significant deviations from the linear correlation that follows from the Newnham semi-empirical correlation between  $s_R/\epsilon^*$  and  $Q_h$ . The result ascertains that Newnham's semi-empirical relation,  $Q_h^{\text{proxy}}$  is not a universal measure that is applicable across all materials.

The most striking aspect of the top compounds is that they are halides, chlorides, bromides, and iodides. We anticipated this due to recent observations of high electrostrictive properties in fluorides such as CaF<sub>2</sub>, BaF<sub>2</sub>, SrF<sub>2</sub>, LiF, and NaF with electrostrictive responses around  $0.36\text{--}0.46 \text{ m}^4 \text{ C}^{-2}$ <sup>3-5,47</sup>. It is interesting to note that none of these compounds made our top ten obtained either via data mining of MP or from the further refinement of MP results through high-precision DFT. The materials that are discovered through our approach are mainly binary non-cubic semi-metal halides. We note that three materials appear common to the top ten  $Q_h^{\text{DFT}}$  and top ten  $M_h^{\text{DFT}}$  datasets: GaBr<sub>3</sub>, WCl<sub>6</sub>, and SbCl<sub>3</sub>. These compounds have not yet been explored with respect to their electrostrictive properties. We certainly hope that our results will generate more experimental work to verify our predictions. We note that not all the compounds in Table 1 are viable materials, some are liquid at room temperature (e.g., SiCl<sub>4</sub>, PCl<sub>3</sub>, PBr<sub>3</sub>O), some are gases or volatile at room pressure (e.g., BCl<sub>3</sub>, SF<sub>6</sub>, or WCl<sub>6</sub>). But others such as GaBr<sub>3</sub> with  $Q_h^{\text{DFT}}$  of  $560.53 \text{ m}^4 \text{ C}^{-2}$  show significant promise.

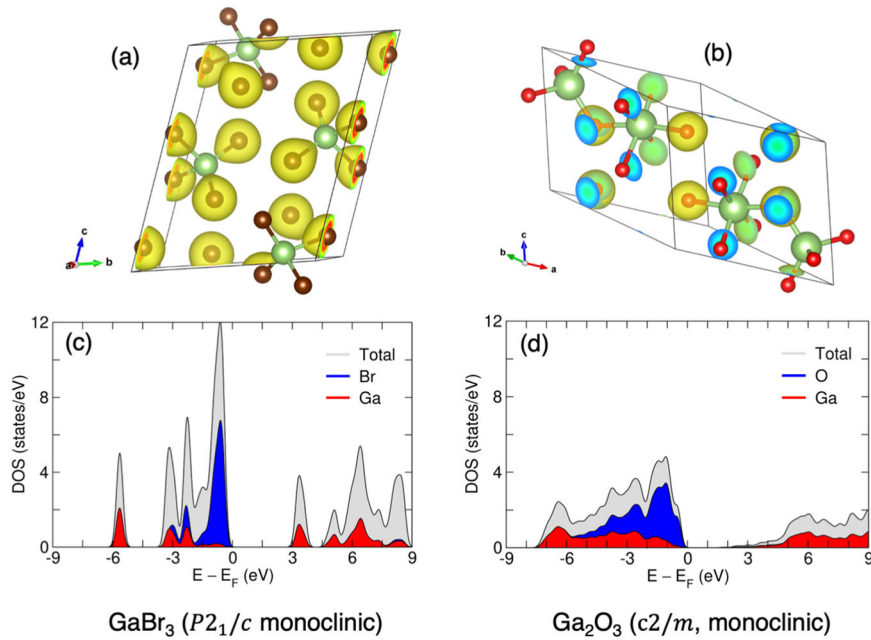
To explain these results and to identify the origin of the giant electrostrictive properties of materials displayed in Tables 1 and 2, we carried out a detailed analysis of bonding, charge distribution, and hybridization for selected compounds. For example, we have examined GaBr<sub>3</sub>, one of the top candidates with  $Q_h^{\text{DFT}} = 560.53 \text{ m}^4 \text{ C}^{-2}$  and  $M_h^{\text{DFT}} = 2.58 \times 10^{-19} \text{ m}^2 \text{ V}^{-2}$ . Its oxide counterpart Ga<sub>2</sub>O<sub>3</sub> has a significantly lower electrostriction response factor,  $Q_h^{\text{DFT}} = 0.02 \text{ m}^4 \text{ C}^{-2}$  and  $M_h^{\text{DFT}} = 1.38 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$ . As such, Ga<sub>2</sub>O<sub>3</sub> did not make it to our lists even within the top 50 materials. The crystal structure and the atomic charge densities of GaBr<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> are shown in Fig. 4a, b, respectively. The atom-resolved density of states (DOS) of the respective materials is plotted in Fig. 4c, d. Despite each having 24 electrons per formula unit in their valence band, the DOS is quite different. The bandgap observed from the DOS of the two compounds is 3.36 eV for GaBr<sub>3</sub> and 2.04 eV for Ga<sub>2</sub>O<sub>3</sub>, which is >0.5 eV, a criterion used for our data mining. This corroborates with the charge separation observed between the cation and anion sites shown in Fig. 4a, b for GaBr<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub>, respectively. Owing to the large band gaps, the two materials have a similar order of magnitude permittivities ( $\epsilon_r = 2.86$  for GaBr<sub>3</sub> and  $\epsilon_r = 9.28$



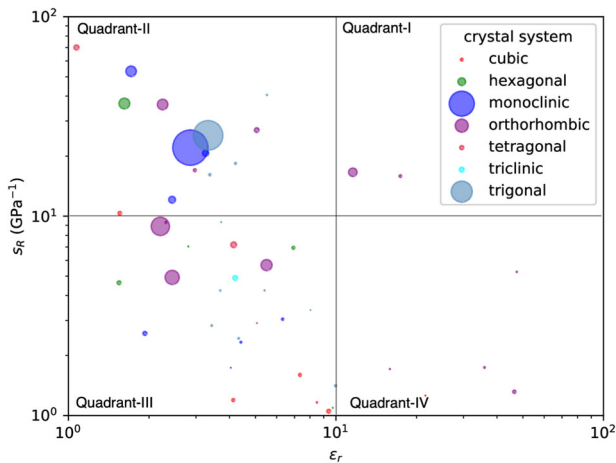
**Fig. 3 Comparison of electrostrictive coefficients of  $Q_h$  and of  $M_h$  obtained from proxy and DFT computation.** Comparison of **a**  $Q_h^{\text{DFT}}$  versus  $Q_h^{\text{proxy}}$  and **b**  $M_h^{\text{DFT}}$  versus  $Q_h^{\text{proxy}}$  obtained from direct application of the empirical formula to the Materials Project data and our DFT computations.

for Ga<sub>2</sub>O<sub>3</sub>). The overall energy spread of both the valence and conduction bands of GaBr<sub>3</sub> is smaller than for Ga<sub>2</sub>O<sub>3</sub>. In addition, within these bands, the DOS is composed of narrow peaks for GaBr<sub>3</sub> whereas Ga<sub>2</sub>O<sub>3</sub> exhibits a more continuous dispersion of its DOS.

The consequence of DOS differences is fundamentally connected with differences in elastic properties and thus on the compressibility  $s_R$ , which for GaBr<sub>3</sub> is  $22.67 \text{ GPa}^{-1}$ . This value is three orders of magnitude larger than  $s_R$  of Ga<sub>2</sub>O<sub>3</sub> ( $0.06 \text{ GPa}^{-1}$ ). The plot of  $\epsilon_r$  versus  $s_R$  is shown to gain an insight into which physical factors play a more important role in the derived properties. Figure 5 is a four-dimensional plot with  $\epsilon_r$  and  $s_R$  as the abscissa and ordinate. The color coding differentiates the crystal system of the compounds, and the circle diameter scales according to the value of  $Q_h$ . Note that the values of  $s_R$  and  $\epsilon_r$  are independently computed using DFT. The figure is divided into four quadrants. Quadrant-II covers the region of large  $s_R$  but small  $\epsilon_r$ , and has large  $Q_h$ . Conversely, the quadrant-IV covers the region of small  $s_R$  but large  $\epsilon_r$ , and has smaller  $Q_h$ . These seem consistent with the semi-empirical relation of Eq. (1). However, we observe that quadrant-III is filled with data points showing that there are several materials with low  $s_R$  and low  $\epsilon_r$  that make up the chemical



**Fig. 4** Electronic structure of selected compounds. The crystal structure and the charge densities of GaBr<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> are shown in (a) and (b). The atom-projected electronic density of states for GaBr<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> are shown in (c) and (d).



**Fig. 5** Plot of permittivity versus compressibility obtained from DFT calculations. Electrostrictive coefficient  $Q_h^{\text{DFT}}$  as in Eq. (3) falls along the quadrants I and III with larger  $Q_h^{\text{DFT}}$  values appearing in quadrant-III and small  $Q_h^{\text{DFT}}$  values in quadrant-I.

space. On the other hand, quadrant-I is almost empty. The result does not reflect the same trend as shown in refs. <sup>5,10</sup>, indicating that electrostrictive properties cannot be generalized using Newnham's proxy defined through Eqs. (3) and (4). The  $\epsilon_r$  and  $s_R$  derived from the Materials Project data are shown in Fig. S1 for all the datamined compounds and are provided in the Supplementary Information.

As a cross-check of the quality of data obtained from our study, we calculated the effective piezoelectric coefficients  $d$  and  $g$  from the derived  $Q_h$  and  $M_h$ . The electrostriction coefficients are related to piezoelectric charge ( $d$ ) and voltage ( $g$ ) coefficients as

$$d = 2M_h^{\text{DFT}} F_b \quad (8)$$

$$g = 2\epsilon^* Q_h^{\text{DFT}} F_b, \quad (9)$$

where  $F_b$  is the breakdown voltage. This quantity essentially determines the maximum amount of strain that can be obtained

**Table 3.** Dielectric breakdown and piezoelectric constant of DFT predicted materials.

Materials	$F_b$	Materials	$d$	Materials	$g$
BF <sub>3</sub>	5928.45	GaBr <sub>3</sub>	58.00	Sr <sub>2</sub> HfO <sub>4</sub>	75.35
PF <sub>5</sub>	1623.23	Sr <sub>2</sub> HfO <sub>4</sub>	42.19	BiCl <sub>3</sub>	18.83
BN	860.15	WCl <sub>6</sub>	36.09	SbCl <sub>3</sub>	9.49
SF <sub>6</sub>	838.29	PBr <sub>3</sub> O	34.13	GaBr <sub>3</sub>	9.10
RbAlF <sub>4</sub>	755.88	SbSI	34.06	WCl <sub>6</sub>	3.97
AlClO	678.54	SnBrF	29.85	PBr <sub>3</sub> O	3.27
BeCl <sub>2</sub>	673.20	SbCl <sub>3</sub>	29.13	BF <sub>3</sub>	2.75
BCl <sub>3</sub>	508.29	BF <sub>3</sub>	25.89	NaTaN <sub>2</sub>	2.40
Rb <sub>2</sub> GeF <sub>6</sub>	457.35	NaTaN <sub>2</sub>	25.91	SnCl <sub>2</sub>	2.34
Cs <sub>2</sub> NaYF <sub>6</sub>	433.43	SnClF	19.72	GaCl <sub>2</sub>	2.26

Values of dielectric breakdown,  $F_b$ , piezoelectric coefficients  $d$ , and  $g$  computed from calculated from Eqs. (8), Equation (9), and Eq. (10), respectively. The unit of  $F_b$ ,  $d$ , and  $g$  are MV m<sup>-1</sup>, 10<sup>-12</sup> m V<sup>-1</sup> and, V m N<sup>-1</sup>, respectively. The data for top-ten materials are tabulated. All calculations were carried out at 0 K and therefore on materials in their solid states.

through an applied electric field which is also true for electrostrictors. For stress sensing, the piezoelectric charge coefficient ( $d$ ) relates the applied stress ( $X_{jk}$ ) to the dielectric displacement generated ( $D_i = d_{ijk} \cdot X_{jk}$ ) in short-circuit conditions whereas the piezoelectric voltage coefficient ( $g$ ) relates the applied stress to the generated electric field ( $E_i = -g_{ijk} \cdot X_{jk}$ ).

There is no direct way of computing  $F_b$ . We used the breakdown voltage expression from refs. <sup>48,49</sup>:

$$F_b = 24.442 \exp(0.315 \sqrt{E_g \omega_{\max}}) \quad (10)$$

where  $\omega_{\max}$  is the maximum phonon frequency at the  $\Gamma$ -point that was calculated from the linear response approach and  $E_g$  is the DFT obtained band gap. Although the band gap is underestimated in DFT, we do not expect it to affect the results of  $F_b$  because Eq. (10) is a machine-learned relationship that already accounts for the underestimated band gaps.

Table 3 lists the top ten materials for  $F_b$ ,  $d$ , and  $g$ . The magnitudes of  $d$  for these materials are smaller than what generally is accepted as promising in the field of linear dielectrics, i.e., few hundreds of  $10^{-12} \text{ m V}^{-1}$ . The values of  $g$ , on the other hand, are three orders of magnitude larger than those commonly appear in linear dielectrics applications. This complements the extremely large effective piezoelectric coefficients obtained on ceria ( $d_{33} \sim 2 \times 10^5 \text{ pC N}^{-1}$ ), a known ‘giant’ electrostrictor, and underlines the potential of electrostrictors as an alternative to piezoelectrics. As for the top candidates, we find 70% of the materials common in the top ten list of  $d$  and  $g$ . The data signifies further that fluorides, chlorides, bromides, and iodides are promising material systems for both linear and quadratic dielectric response.

We have used a data mining backed by first-principles calculations approach to down-select materials for the discovery of novel electrostrictive materials. Our analysis shows that the halides—fluorides, chlorides, bromides, and iodides, are promising materials systems for high electrostriction response. However, unlike linear dielectrics and ferroelectric glasses, they do not follow Newnham’s relation. We note that some of these materials may have significantly larger electrostrictive coefficients ( $Q_1$ ), than even electroactive polymers. The discovery of electrostrictors with electrostrictive coefficients comparable to the ‘giant’ electrostrictors, where the physics is governed by active defects, presents the prospect of applications that are not limited to low-frequency response as is the case for ‘giant’ electrostrictors. The corresponding effective piezoelectric voltage coefficients obtained under a bias electric field surpass classical piezoelectrics by three orders of magnitude and constitute an appealing alternative to piezoelectrics. We believe that this combination of computational and informatics-based approaches will provide the necessary guidance for future experimental work, resulting in a new generation of electrostrictors with exceptionally high property coefficients.

## METHODS

The Materials Project database was used for sourcing, compiling, and curating the crystal structure data and the existing elastic compliance and permittivity. The electrostriction coefficient was computed based on Newnham’s proxy. It provided early-stage learning for shortlisting a list of compounds for carrying out more detailed first-principles calculations. A set of top candidates was selected for first-principles calculations. A set of randomly selected compounds was also included in the list. Detailed density functional theory (DFT) calculations using the Vienna Ab initio Simulation Package (VASP) were carried out with generalized gradient approximation (GGA) as the exchange-correlation functional and a high-density  $k$ -points mesh. The electrostatic coefficient was calculated as a differential of pressure, where DFT calculations were applied with pressure constraint with the  $p$ stress tag.

## DATA AVAILABILITY

The data supporting the results are available upon reasonable request to the authors.

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## AUTHOR CONTRIBUTIONS

The concepts presented herein were conceived by P.E.J. and S.P.A. D.T. performed the data mining process and provided the initial analysis. A.G. carried out DFT calculations under the supervision of S.K.N. All authors analyzed the data and prepared the manuscript for publication.

## COMPETING INTERESTS

The authors declare no competing interests.

## ADDITIONAL INFORMATION

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