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Design rules for strong electro-optic materials

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The explosive rise of silicon photonics has led to renewed interest in the electro-optic (EO) or Pockels effect due to its potential uses in many next generation device applications. To find materials with a strong EO response in thin film form, which are essential for low power and small footprint devices, one needs to find a general design rule for strong Pockels materials. To elucidate what makes the Pockels effect strong, we study the effect in LiB_3O_5 (LBO) and CsB_3O_5 (CBO) and use these materials as prototypical examples of where conventional wisdom breaks down. We find the Pockels tensor components to be extremely small in both materials, despite the large degree of anharmonicity in the crystals, which has been used as a proxy for the presence of nonlinear electronic effects. We relate the lack of EO response to the large optical phonon frequencies (despite the relatively large Raman susceptibility) in LBO and to the small Raman susceptibility (despite the low phonon frequencies) in CBO, respectively. We shed light on the underlying physical phenomena behind the Raman susceptibility, which we find to be intimately linked to the electron-phonon coupling strength of the near-edge electronic states, and identify a route to discovering new strong EO materials.

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INTRODUCTION

The remarkable ability of a noncentrosymmetric crystal to change its index of refraction in response to an applied electric field, known as the Pockels effect¹, has been the subject of increasing study in recent years due to its potential to facilitate high-speed, low-power electro-optical modulation in integrated photonics applications^{2–6}, including intrachip data transmission, neuromorphic logic optical chips⁷, and photonic integrated circuits for quantum computing^{8,9}. Being linear in the field, the Pockels, or linear electro-optic (EO), effect coexists with the much smaller Kerr effect¹⁰ (which is the second order in the field) and with second harmonic generation (SHG). The Pockels effect is most commonly used for optical modulation in the telecommunications industry, where LiNbO_3 (LNO), with an unclamped Pockels coefficient of $r_{51} = 33 \text{ pm/V}$ ¹¹, is the current “gold standard” material^{1,12,13}. Due to the complexity of integrating LNO^{14–17} on Si, however, perovskite titanates have recently become the primary subjects of both theoretical^{18–22} and experimental^{7,17,23–32} studies on the use of the Pockels effect in Si photonics. The main focus of these efforts has been BaTiO_3 (BTO), due to its integrability with Si (001)^{27,28,33} and its very large unclamped Pockels effect ($r_{42} = 1300 \text{ pm/V}$ ³⁴), which can retain bulk-like values even in thin films⁷.

It is of paramount importance to find materials with large Pockels responses in order to decrease the power consumption and/or size of integrated EO devices. However, because it is not currently clear what mechanism drives the extremely high response of BTO as compared to other materials, the search for potentially better alternatives has so far proceeded rather empirically.

Recent theoretical studies of the Pockels effect in perovskite titanates^{18–20} offer a systematic way forward. Fredrickson et al.¹⁹ explored strain engineering in BTO. They found critical biaxial strains at which the Pockels response diverged and specific phonon modes went soft. Hamze and Demkov¹⁸ studied the same phenomenon in strained SrTiO_3 (STO), and through the analyses of mode Grüneisen parameters related anharmonicity (soft modes) to an emergent EO response^{35,36}. Paillard et al.²⁰ reported similar

behavior in the EO response of strained PbTiO_3 (PTO). These crystals all have in common soft phonons and large crystal anharmonicity. A 1-D anharmonic oscillator model of the Pockels effect³⁷ shows the Pockels parameter is directly proportional to the coefficient of the anharmonic force term, reinforcing the assumed relationship between anharmonicity and the EO response. Noticing that, in these materials, the Pockels effect is dominated by the lattice, the appropriate figure of merit is the ratio of the Raman susceptibility and square of the phonon frequency. One may therefore infer the following design rule: highly anharmonic, noncentrosymmetric crystals should exhibit a large Pockels effect.

Crystal anharmonicity is often associated with large thermal expansion coefficients. In Table 1, we list a selection of noncentrosymmetric crystals and their material properties. BTO, STO, and PTO all have large thermal expansion coefficients, as do many other strong Pockels materials. Therefore, an ideal candidate to test the proposed design rule is LiB_3O_5 (LBO). Though there are no reported Pockels measurements of LBO (Fig. 1), it is a commonly used nonlinear optical crystal³⁸ with many favorable optical properties^{39,40} and it boasts a thermal expansion coefficient an order of magnitude larger^{41,42} than that of BTO, STO, or PTO.

In this article, using first principles calculations, we set out to identify the microscopic origin of a material's large Pockels response. Our calculations have uncovered a deeper, more complex physics than previously demonstrated. Contrary to our initial expectations, LBO has a very weak Pockels response due to the low atomic mass of Li leading to high phonon frequencies. We attempt to induce a stronger response by softening the modes through replacement of the light Li atoms with much heavier Cs atoms by considering the related CsB_3O_5 (CBO) crystal. This successfully softens the phonon modes but does not improve the Pockels response, thereby highlighting the importance of a different property, the Raman susceptibility, a connection originally pointed out by Johnston and Kaminow^{43,44}. We contrast our results for the LBO and CBO to previous work on strained STO

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Table 1. Physical properties of known EO materials.

Crystal	Space group	a ($10^{-6} \text{ }^{\circ}\text{C}^{-1}$)	T ($^{\circ}\text{C}$)	r (pm/V)	n	λ (nm)	n^3r (pm/V)	E_g (eV)	Sources	Notes
$\text{Bi}_{12}\text{SiO}_{20}$	$I23$	11.42 [^]	22–502 [^]	$r_{41} = 5$	2.54	633	82	3.2	70–72	[^] Nd: $\text{Bi}_{12}\text{SiO}_{20}$ (1102067)
$\text{Bi}_{12}\text{GeO}_{20}$	$I23$	15	20	$r_{41}^{\sigma} = 3.22$	2.54	666	53	3.2	70–73	(1938283)
$\text{Bi}_{12}\text{TiO}_{20}$	$I23$	–	–	$r_{41}^{\sigma} = 5.5$	2.578	633	94	2.53	74,75	(1635168)
LiNbO_3	$R3c$	15.9	0–500	$r_{51}^{\sigma} = 33$	2.286	633	389	4.9	11,72,76–78	(543592)
LiTaO_3	$R3c$	16.2	0–500	$r_{33}^{\sigma} = 30.5$	2.18	632.8	316	3.41–4.56	10,78–80	(553579)
BaTiO_3	$P4mm$	16.9	25	$r_{42}^{\sigma} = 1300$	2.45	546	24,118	3.2	34,72,81–83	(1925967)
$\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$	$P4bm$	13.42 [^]	20–50 [^]	$r_{\text{eff}}^{\sigma} = 350$	2.36	510	4600	3.67	1,84–88	[^] SBN:59
$\text{Ba}_{0.25}\text{Sr}_{0.75}\text{TiO}_3$	$P4bm$	12.7	0–90	$r_{\text{eff}}^{\sigma} = 844$	2.37	510	11,235	3.88	1,85–87,89–91	–
KNbO_3	$Amm2$	14	20–180	$r_{42}^{\sigma} = 450$	2.329	633	4801	3.43–3.6	1,92–94	(1923882)
MgO:LiNbO_3	$R3c$	–	–	–	2.39	355	–	3.92	95,96	(1414411)
$\beta\text{-BaB}_2\text{O}_3$	$R3c$	45	20–700	$r_{22}^{\sigma} = 2.5$	1.67	514	12	6.43	97–99	(556972)
LiB_3O_5	$Pna2_1$	108.2	17–790	–	1.68	253.7	–	7.78	39,42,97,98	(311713)
KTiOPO_4	$Pna2_1$	8.2	–	–	1.94	430	–	3.52	100–102	(1321840)
RbTiOAsO_4	$Pna2_1$	14.5	–	–	1.92	532	–	–	103,104	(1410606)
$\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$	$P4mm$	11	700	$r_{\text{eff}} = 230$	2.34	600	2496	3.45	1,105–108	α : $x = 0.24$, (551305); n , r_{eff} : $x = 0.7$, E_g : $x = 0.5$
$\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$	$P4mm$, $R3c$	8	527	$r_{\text{eff}}^{\sigma} = 109$	2.45	633	1603	3.4–3.6	1,109–113	Tetragonal: (380620); Trigonal: (1228661); n , r_{eff}^{σ} , E_g : $x = 0.4$; α : $x = 0.19$
BeO	$P6_3mc$	10.57	727	–	1.74	440	–	10.6	114–117	(1500435)
$\kappa\text{-Al}_2\text{O}_3$	$Pna2_1$	8.1	840	–	2.5	124	–	5.4	118,119	–
$\text{P}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{2-y})_{1-x/4}\text{O}_3$	$P4mm$, $R3c$	5.7*	25	$r_{\text{eff}}^{\sigma} = 153$	2.64 [^]	633	2815	3.5	1,120–124	[^] x , y , $z = 0.08, 0.1, 0.9$: trigonal (1222146); * x , y , $z = 0.07, 0.65, 0.35$: tetragonal (1141504); E_g : x , y , $z = 0.05, 0.54, 0.46$

Physical properties of many crystals known to have a linear EO response and the conditions under which they were measured, as well as some nonlinear crystals with unknown Pockels coefficients. All of them have noncentrosymmetric space groups (a necessary condition for a nonzero EO response), and all of them are highly nonlinear (as compared to silicon, which is highly linear and has $a = 2.93 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ¹²⁵), especially those with very high EO response. LiB_3O_5 stands out with $a = 108.2 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, a full order of magnitude larger than any other crystal on the table. Space groups of the crystals are from Pearson's Crystal Database, and the seven-digit numbers in parentheses in the Notes column are the reference numbers of specific entries in the database¹²⁶. Thermal expansion coefficients listed are the largest ones found for the given materials. Refractive indices and wavelengths are either values that closely coincide with r_{eff} if r_{eff} is specified, or are the largest values found. Effective Pockels coefficients, labeled r_{eff} , were measured in thin film materials. Where reported, we labeled whether the measured Pockels coefficient is clamped or unclamped.

The symbols point towards the Notes column, where additional pieces of information for the measurement marked is presented.

and, using a simple tight-binding model, associate large Raman susceptibilities with the deformation potential of the material. Now, our refined design rule states that in addition to the absence of inversion symmetry, a large Raman susceptibility (strong electron–phonon coupling) and soft phonons are essential ingredients to produce a large EO response.

RESULTS

Theoretical framework

All calculations are performed within density functional theory (DFT) using ABINIT^{45–51} and follow the theoretical framework developed by Veithen et al.⁴⁹ (see the “Methods” section for details). Macroscopically, the Pockels coefficient r relates the change in the index of refraction to an applied electric field as $n(E) = n_0 - \frac{1}{2}m_0^2 E$, where n_0 is the index of refraction under no field¹. In a crystal, a modulating electric field can couple directly to the electrons, to the lattice, or can cause a lattice modulation via the inverse piezoelectric effect. Therefore, in general, one can write the change of the dielectric tensor in response to the external field as⁵²

$$\frac{d\epsilon_{ij}}{dE_k} = \sum_{mn} \frac{\partial \epsilon_{ij}}{\partial \pi_{mn}} \frac{\partial \pi_{mn}}{\partial E_k} + \sum_l \frac{\partial \epsilon_{ij}}{\partial P_l} \frac{\partial P_l}{\partial E_k} + \frac{\partial \epsilon_{ij}}{\partial E_k}. \quad (1)$$

Here, π is strain and P is the ionic polarization. The last term is the direct effect of the applied field on the polarizability, and only electrons can respond at the optical probing frequency; this is SHG ($\chi^{(2)}$). The first term describes the effect of strain caused by the applied field and is present at low modulating frequencies—this is the unclamped response, meaning the lattice has time to deform in response to the applied field, and it can be neglected at high modulating frequencies. The second term is the so-called ionic or lattice contribution to the EO response and is at the center of our study.

Microscopically, the Pockels coefficient is a tensor r_{ijk} that relates the change in the ij component of the inverse dielectric tensor of a noncentrosymmetric crystal to a static, external electric field applied in the k -direction^{10,49,53}

$$\Delta(\epsilon^{-1})_{ij} = \sum_k r_{ijk} E_k. \quad (2)$$

There are three contributions to the Pockels tensor: an electronic component, an ionic component, and a piezoelectric component due to the converse piezoelectric effect⁴⁹. These three

Fig. 1 **LiB₃O₅ crystal structure.** The crystal structure of LBO. Its space group is *Pna2₁* and its structure^{41,127,128} consists of a helical network of B₃O₇ rings that share one of their oxygen atoms with neighboring B₃O₇ groups. Two of the B atoms threefold coordinated and one is fourfold coordinated. The Li atoms reside in the voids of the B₃O₇ helices, which are along the *c*-axis. **a** Unit cell of LiB₃O₅ (at room temperature⁴¹), and **b** the B₃O₇ rings that make up the helical chains.

components are given by (in the principal axes of the crystal)⁴⁹

$$r_{ijk}^{\text{piezo}} = \sum_{\mu, \nu=1}^3 p_{ij\mu\nu} d_{k\mu\nu}, \quad (3)$$

$$r_{ijk}^{\text{ion}} = -\frac{4\pi}{\sqrt{\Omega_0 n_i^2 n_j^2}} \sum_m \frac{\alpha_{ij}^m p_{m,k}}{\omega_m^2}, \quad (4)$$

$$r_{ijk}^{\text{el}} = -\frac{8\pi}{n_i^2 n_j^2} \chi_{ijl}^{(2)} \Big|_{l=k}, \quad (5)$$

where n is the index of refraction, $\chi_{ijl}^{(2)}$ is the nonlinear optical susceptibility, Ω_0 is the volume of the unit cell, and α_{ij}^m , $p_{m,k}$, and ω_m are the Raman susceptibility, the mode polarity, and the frequency of the mode m at the Γ point, respectively, $p_{ij\mu\nu}$ is the elasto-optic (photoelastic) tensor, and $d_{k\mu\nu}$ is the piezoelectric tensor. Equations (3–5) are the microscopic forms of the first, second, and third terms in Eq. (1), respectively. The Raman susceptibility and mode polarity are given by

$$\alpha_{ij}^m = \sqrt{\Omega_0} \sum_{\gamma, \beta} \frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\gamma\beta}} u_m(\gamma\beta), \quad (6)$$

$$p_{m,k} = \sum_{\gamma, \beta} Z_{\gamma, k\beta}^* u_m(\gamma\beta), \quad (7)$$

where γ labels an atom, β labels a direction, $\tau_{\gamma\beta}$ is a displacement of atom γ in direction β , $\chi_{ij}^{(1)}$ is the electronic dielectric susceptibility tensor, $Z_{\gamma, k\beta}^*$ is the Born effective charge, and $u_m(\gamma\beta)$ is the eigendisplacement of atom γ in direction β in mode m (which relates to the eigenvector by a factor of $1/\sqrt{M_\gamma}$, where M_γ is the mass of atom γ). The total Pockels tensor is grouped into two parts, a strain-free (clamped) part and a stress-free (unclamped) part. The clamped Pockels tensor r_{ijk}^η is the sum of the electronic and ionic contributions, and the unclamped tensor

r_{ijk}^σ adds the piezoelectric contribution

$$r_{ijk}^\eta = r_{ijk}^{\text{el}} + r_{ijk}^{\text{ion}}, \quad (8)$$

$$r_{ijk}^\sigma = r_{ijk}^\eta + r_{ijk}^{\text{piezo}}. \quad (9)$$

Note that we use Voigt notation¹⁰ to collapse the first two indices when reporting our predictions of the Pockels tensor.

In our analysis of the crystal anharmonicity, we make use of isotropic mode Grüneisen parameters³⁵ (Eq. (S1))—a brief overview of how to compute them is provided in the Supplementary information. Finally, we also calculate deformation potentials^{54–56}, which give a measure of the electron–phonon coupling, for select phonon modes. The deformation potential d_m for optical phonon m is defined by the change in the energy of the conduction band minimum (CBM) E_C under displacements of the ionic positions according to the phonon mode m with amplitude δ_m

$$d_m^C = \frac{\partial E_C}{\partial \delta_m}. \quad (10)$$

Therefore, once the deformation potential is known, the change of the CBM can be calculated for a given phonon amplitude as $\Delta E_C = d_m \delta_m$. An analogous expression can be defined for the valence band maximum (VBM), which can then be added to the expression for the CBM to give the change in the band gap. However, because we set the VBM to zero in our calculations, we only consider the CBM. The larger the deformation potentials for the CBM and VBM are for a given phonon mode, the larger the change in the band gap under atomic displacements.

LBO and CBO Pockels tensors

The five largest components of the Pockels tensor for LBO, broken into electronic, ionic, and piezoelectric contributions, are listed in Table 2. The predicted values are extremely small.

Comparing the components, we see that the ionic contribution is of the same order as the electronic and piezoelectric contributions, despite the extraordinary anharmonicity of the LBO crystal. Recall from Eq. (4), however, that the ionic contribution is inversely proportional to phonon frequencies at Γ , squared. The large phonon frequencies in LBO (Table S1), an order of magnitude larger than those in perovskite titanates^{18–20}, suppress the EO response. How do these high phonon frequencies coexist with the large thermal anharmonicity? A high-temperature

Table 2. EO tensor components of LBO, CBO, and strained STO.

Crystal	EO tensor component	r^{el} (pm/V)	r^{ion} (pm/V)	r^{piezo} (pm/V)	r^{σ} (pm/V)
LBO	r_{42}	−0.574	−0.019	0.000	−0.593
	r_{51}	0.484	−0.367	−0.330	−0.213
	r_{13}	0.504	−0.210	0.304	0.598
	r_{23}	−0.563	0.391	0.190	0.017
	r_{33}	0.083	−0.108	2.505	2.480
CBO	r_{41}	0.878	2.554	—	—
	r_{63}	0.861	0.600	—	—
	r_{52}	0.928	0.069	—	—
STO (−1.2%)	r_{33}	−0.085	−236.469	−28.90	−265.454

Largest components of the EO tensor of LBO and CBO, broken down into electronic, ionic contributions. Piezoelectric contributions and the unclamped (stress-free) Pockels tensor are also given for LBO. The Cs atoms are $\sim 19\times$ heavier than the Li atoms, leading to much softer phonon modes (Table S1), as expected. However, the Pockels response remains small. This is due to a small Raman susceptibility (Fig. 2c). For comparison, the largest component of the Pockels tensor of STO at the critical strain¹⁸ is also presented.

Fig. 2 Raman susceptibilities and mode polarities of LBO and CBO. For the ten softest optical modes of LBO, **a** the magnitude of the largest component of the Raman susceptibility, and **b** the magnitude of the mode polarity. The same quantities are plotted for CBO in **c** and **d**, respectively. The Raman susceptibilities of LBO (**a**) are much larger than those of CBO (**c**), while the mode polarities (**b**, **d**) are roughly the same (because the atoms have Born effective charges of roughly the same magnitude). The Raman susceptibilities of LBO (**a**) are comparable in magnitude to those of STO at 1% biaxial compressive strain (Fig. 3a), while the mode polarities are much smaller and the phonon frequencies are much larger¹⁸.

X-ray powder diffraction study⁴¹ of the thermal expansion of LBO found the driving mechanisms behind the thermal expansion in LBO to be large oscillations of the Li atom along the a -axis, the increasing separation of the B_3O_7 chains comprising the c -oriented helices (leading to the large thermal expansion in the a - and b -directions), and the collapse of a B–O–B angle linking different chains (leading to the compression in the c -direction). Furthermore, the frequency of oscillation is proportional to $1/\sqrt{m}$. The heaviest atom in LBO is oxygen, which is tightly bonded to the B atoms. In contrast, in perovskite titanates^{18–20}, the most anharmonic mode (and the mode responsible for the large Pockels responses) is associated with a ferroelectric phase transition and involves displacement of a much heavier Ti atom. The mechanism underlying the anharmonicity of perovskite titanates is therefore quite different from LBO. Therefore, when the phonon mode

driving the thermal expansion is a high-frequency mode, the simple association between strong Pockels response and anharmonicity breaks down.

Given these differences between LBO and the perovskite titanates, can the LBO crystal's Pockels response be enhanced? We calculate the Grüneisen parameters of the ten softest optical modes of LBO and find mode 9 is the most anharmonic (Fig. S1). This phonon mode primarily consists of motion of the Li atoms (Fig. S2). Owing to its relatively large Raman susceptibility and mode polarity (Fig. 2), it has a relatively high contribution to r^{ion} (specifically, $r_{23}^{\text{mode } 9} = 0.32$ pm/V and $r_{33}^{\text{mode } 9} = -0.19$ pm/V). Only the high frequency ($\omega_0 = 154.9$ cm^{-1}) of the mode keeps the contribution of this mode to the Pockels tensor small. If we can soften this mode, we would expect the already (relatively) large contribution of this mode to increase.

Fig. 3 Raman susceptibilities and mode polarities of strained STO. Raman susceptibilities and mode polarities for all 12 optical modes of STO (see Hamze and Demkov¹⁸ for calculation details). The magnitude of the largest component of the Raman susceptibility and the magnitude of the mode polarity under biaxial compressive strain of 1.0% are shown in **a** and **b**, respectively. The same values are plotted for STO at the critical strain in **c** and **d**, respectively. The magnitudes of the mode polarity are essentially unchanged under the different strains (**b**, **d**), but the Raman susceptibility increases by an order of magnitude at every mode (**a**, **c**). The frequency of the softest mode, the primary contributor to the Pockels response in STO, is also approximately halved from -1.0% strain to -1.2% strain.

To soften the mode, we replace the Li atoms in the crystal with Cs atoms. Cs is ~ 19 times heavier than Li, and because the ionic contribution to the Pockels tensor is inversely proportional to the phonon frequency squared, which is in turn inversely proportional to the atomic mass, we expect a significant reduction in the phonon frequencies from this replacement. However, a simple replacement of Li with Cs in LBO leads to a dynamically unstable crystal, so we instead consider the related CBO crystal. Its space group is $P2_12_12_1$, and like LBO, CBO has a network of B_3O_7 rings, but in CBO they share four of their external oxygen atoms with other B_3O_7 rings^{57,58}. The Cs atoms sit in the voids of this network, which run along the a - and b -axes instead of just along one axis as in LBO. The phonon frequencies in CBO (Table S1) are indeed much lower than in LBO, but the Pockels tensor (Table 2) remains extremely small. To understand why, we now turn to the numerator of the ionic contribution to the Pockels tensor (Eq. (4)) that is the product of the Raman susceptibility (Eq. (6)) and the mode polarity (Eq. (7)). In Fig. 2, we plot the magnitude of the Raman susceptibilities and mode polarities of the ten softest optical modes of LBO and CBO. The mode polarities of LBO and CBO (Fig. 2b, d) are roughly of the same magnitude, which we expect because the atoms in LBO and CBO have similar Born effective charges. The Raman susceptibilities (Fig. 2a, c), however, are an order of magnitude smaller in CBO. This cancels out all the gains made from reducing the phonon frequencies and keeps the net EO response small.

To understand the role of the Raman susceptibility in the Pockels response, we first consider its role in the extreme enhancement of the Pockels response in strained STO¹⁸, and second, to gain physical intuition of the underlying mechanism, we introduce a simple tight-binding model. In Fig. 3, we plot the Raman susceptibility and mode polarity of STO under two biaxial compressive strains, -1.0% in **a** and **b** and -1.2% in **c** and **d**. Hamze and Demkov¹⁸ showed that at -1.2% strain (hereafter referred to as the critical strain), the Pockels tensor exhibits a large peak with the largest ionic component reaching $r_{33} = -236.469$ pm/V. This is caused by the proximity of the crystal at this strain to a phase transition from the centrosymmetric tetragonal $P4/mmm$ phase to the noncentrosymmetric tetragonal

$P4mm$ phase. The phonon mode responsible for this transition goes extremely soft at this strain, leading to the large Pockels response. However, there is an additional contribution to the large response. Comparing the Raman susceptibilities at -1.0% strain and -1.2% strain (Fig. 3a, c, respectively), we see that the magnitude of the Raman susceptibility increases by an order of magnitude at the critical strain. In contrast, the mode polarities (Fig. 3b, d) are effectively unchanged between strains because, like in the LBO and CBO case, the Born effective charges are identical between the cells.

DISCUSSION

To gain further insight, we calculate the derivative of the electronic susceptibility with respect to atomic displacements, $\partial\chi^{(1)}/\partial\tau$, which is the key component of the Raman susceptibility (see Eq. (6)), in a simple tight-binding model^{59,60} of a 1-D diatomic chain with lattice constant a and distance between the atoms of $a/2$. One atom has a $1s$ orbital and the other has a $2p$ orbital. We assume the hopping interaction is proportional to $1/d^2$ with constant of proportionality A , where d is the distance between the atoms, which is a good approximation for many materials⁶¹. The linear electronic susceptibility in an insulating crystal is given by⁶¹

$$\chi^{(1)} = \frac{2\hbar^4 e^2}{m_e \Omega} \sum_{n,n'} \frac{|\langle \psi_{n'} | \partial/\partial x | \psi_n \rangle|^2}{(\epsilon_{n'} - \epsilon_n)^3}, \quad (11)$$

where n and n' are band indices for occupied and unoccupied bands, respectively, ψ_n is the wave function with eigenvalue ϵ_n , and the band sum implicitly contains a sum over the entire Brillouin zone. Note that the susceptibility goes as the inverse cube of the transition energy, a detail that will be important later. Considering only nearest neighbor interactions, we calculate a numerical derivative of the susceptibility as a function of atomic displacement in the optical mode (see Eq. (12) and the “Methods” section for more details). For $A = 1$ eV $\cdot \text{\AA}^2$, $a = 1$ $\text{\AA}$, $\epsilon_s = 0$ eV, $\epsilon_p = 3$ eV, and a displacement amplitude of $\delta = 0.01a$, we obtain $\chi^{(1)} = 97.96$ and $\partial\chi^{(1)}/\partial\tau = -180.95$ $\text{\AA}^{-1}$. In other words, a 2%

Fig. 4 Transition energies vs phonon amplitudes. Smallest transition energies as a function of amplitude of phonon mode displacements for **a** STO at the critical compressive strain¹⁸, **b** LBO, and **c** CBO. The smallest transition energy of the ground state structure for each material is set to 0. Changes in the transition energy due to phonon modes that have large Raman susceptibilities and contribute strongly to the Pockels response (Pockels-active modes) are plotted in black, and changes in the transition energy due to phonon modes with small Raman susceptibilities and weakly contribute (or do not contribute) to the Pockels response (Pockels-inactive modes) are plotted in red.

change in the bond length amounts to a $\sim 20\%$ change in $\chi^{(1)}$, showing $\partial\chi^{(1)}/\partial\tau$ is large.

The connection between the change in the Raman susceptibility, the electronic structure, and phonons can be understood as follows. Because of the third power in the denominator of Eq. (11), the smallest electronic transition energy is the dominant contribution to the susceptibility; hence, phonon modes that strongly affect the band edges should have large Raman susceptibilities. If those modes are soft, that in turn should ensure a large contribution to the Pockels tensor. In Fig. 4, we plot the smallest transition energy as a function of the amplitude of two different phonon modes for STO, LBO, and CBO (Fig. 4a–c, respectively). The two phonon modes for each material are chosen such that one (labeled the “active” mode) has a large Raman susceptibility and a significant contribution to the Pockels tensor, while the other (labeled the “inactive” mode) does not. It is clear that in STO the active phonon causes a large change in the direct band gap, while in CBO the active mode has nearly no effect. This is because the band gap in STO, a charge transfer oxide, is controlled by the p – d bonding–antibonding separation, and the active phonon changes the Ti–O interatomic distance. This makes the differences between these three materials clear: STO has soft phonons and the soft modes strongly affect the band edges, which leads to a large Raman susceptibility and EO response. The active mode in LBO also has a significant effect on the gap and therefore the Raman susceptibility is relatively large, but the high phonon frequencies suppress the EO response. In CBO, this is reversed with very soft modes having very little impact on the band gap, which therefore suppresses the Raman susceptibility and the EO response.

This aspect of electron–phonon interactions is commonly described using deformation potentials^{54–56}, which we list for STO, LBO, and CBO in Table S2 (we also provide the band structure of LBO and CBO in Fig. S3). We see that the deformation potential for every material is larger when the ions are displaced according to the Pockels active mode than when they are displaced according to the inactive mode (except in CBO, in which the deformation potentials for both modes are ~ 0 eV/Å), indicating that large deformation potentials are associated with large Raman susceptibilities and therefore could indicate the potential for strong Pockels responses in such materials.

To summarize, soft phonons inducing substantial changes in the band gap (in other words those with strong electron–phonon couplings) cause large changes in the electronic susceptibility, as the tight-binding model above illustrates. Large changes in the electronic susceptibility in turn imply large Raman susceptibilities, to which the ionic contribution to the EO response is proportional. Therefore, noncentrosymmetric materials with soft phonons and strong electron–phonon interaction will likely be strong Pockels materials. This explains why LBO and CBO have weak EO responses, and why perovskite titanates are special and have such strong EO responses.

We explore the relationship between the microscopic properties such as lattice anharmonicity and strength of electron–phonon coupling and the Pockels effect using LBO as a test case because of its extraordinarily large thermal expansion coefficients. Despite the correspondence between large thermal expansion coefficients and large EO responses many EO materials, we found that LBO has a very small Pockels response. The small Pockels response is caused by the extremely small masses of the constituent atoms resulting in high optical phonon frequencies.

Guided by the Grüneisen parameter analysis of the ten softest optical phonon modes, we tested this assertion by studying the related CBO crystal to see if simply increasing the atomic masses would lead to a large Pockels response by softening the modes. This approach was found to be too simplistic—in CBO, the small Raman susceptibility results in a weak Pockels response despite the presence of much softer phonon modes. A simple tight binding model provides an intuitive physical description of the underlying mechanism at play behind the Raman susceptibility. Borrowing from the methods used to study semiconductors, this can be explained in terms of the deformation potential, which quantifies the strength of the electron–phonon coupling of the near-edge states. Modes with large Raman susceptibilities are shown to have large deformation potentials. Hence, we formulate a refined design rule for strong Pockels materials: materials with strong electron–phonon couplings (and therefore large Raman susceptibilities), that are noncentrosymmetric, and that have soft phonons will be strong Pockels materials. We thus show the most important components of the ionic Pockels response are the phonon frequency softness (for which the thermal expansion and Grüneisen parameters are proxies) and Raman susceptibility

(strong electron–phonon coupling). Our results will hopefully guide materials scientists and engineers in searching for new EO materials with even stronger responses.

METHODS

DFT calculations

All DFT and density functional perturbation theory calculations were performed using the ABINIT software package^{45–51}. Troullier–Martins norm-conserving pseudopotentials⁶² generated with the `fh98PP` package⁶³ were used for all calculations. The valence electron configurations were $2s^1$ for Li, $2s^2 2p^1$ for B, $2s^2 2p^4$ for O, and $6s^1$ for Cs. The exchange–correlation energy was calculated in the local density approximation^{64,65}. An $8 \times 8 \times 8$ Monkhorst–Pack^{66,67} k -point grid and a plane wave cut-off energy of 50 Ha was used for all calculations. The lattice parameters used for all the LBO calculations are $a = 8.444 \text{ \AA} = 15.957 \text{ Bohr}$, $b = 7.378 \text{ \AA} = 13.942 \text{ Bohr}$, and $c = 5.146 \text{ \AA} = 9.725 \text{ Bohr}$, which are experimental lattice parameters measured at room temperature by Shepelev et al.⁴¹. The atomic positions are fully relaxed from the initial experimental coordinates until the forces were smaller than $2 \times 10^{-5} \text{ Ha/Bohr}$.

For calculations of CBO, we use the experimental structure determined by Krogh-Moe⁵⁷, which has lattice parameters $a = 6.213 \text{ \AA} = 11.741 \text{ Bohr}$, $b = 8.521 \text{ \AA} = 16.102 \text{ Bohr}$, and $c = 9.170 \text{ \AA} = 17.329 \text{ Bohr}$.

To calculate the piezoelectric contribution to the Pockels tensor, we need to calculate the photoelastic tensor (see Eq. (4)). We do this by straining the unit cell to isolate the component of the tensor we want, calculating the dielectric tensor, inverting it, and taking a numerical derivative with respect to strain^{18,53,68}.

In Eq. (11), we calculate the matrix element in the numerator following Graf and Vogl⁶⁹. For a given k^* , it can be calculated as⁶⁹

$$\langle \psi_n | \partial / \partial x | \psi_n \rangle = \frac{m_e}{\hbar} \sum_{\alpha, \alpha'} C_{\alpha}^*(n k^*) \sum_L i(R_{\alpha', L} - R_{\alpha, 0}) e^{i k^* (R_{\alpha', L} - R_{\alpha, 0})} t_{\alpha', \alpha} (R_{\alpha', L} - R_{\alpha, 0}) C_{\alpha}(n' k^*), \quad (12)$$

where α is a compound index that labels the atomic orbital and the position of the atom in the cell, L (and 0) label the unit cell, n is a band index, the C_{α} are the coefficients in the expansion of the eigenfunctions of the tight-binding Hamiltonian, and $t_{\alpha', \alpha} (R_{\alpha', L} - R_{\alpha, 0}) = \langle \alpha', L | H | \alpha, 0 \rangle$.

DATA AVAILABILITY

Requests for data should be addressed to A.A.D., demkov@physics.utexas.edu.

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AUTHOR CONTRIBUTIONS

A.K.H. did all the calculations and data analysis. M.R., J.G.-K., and A.K.H. made Table 1. All authors contributed to writing the manuscript. A.A.D. supervised and lead the study.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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