Hexagonal ABC semiconductors as ferroelectrics

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We use a first-principles rational-design approach to identify a previously-unrecognized class of ferroelectric materials in the $P6_3mc$ LiGaGe structure type. We calculate structural parameters, polarization and ferroelectric well depths both for reported and as-yet hypothetical representatives of this class. Our results provide guidance for the experimental realization and further investigation of high-performance materials suitable for practical applications.

A rapidly developing paradigm for the rational design of functional materials is based on the first-principles study of large families of known and as yet unreported compounds. First-principles calculations of structure and properties are used first to explore the microscopic origins and establish design principles for the functional properties of interest, and then to screen a large number of both equilibrium and metastable phases to identify promising candidate systems [1–4]. One recent study showed the semiconducting members of the ABC half-Heusler family to be piezoelectric, with a range of piezoelectric properties comparable to the much-studied ABO_3 perovskite oxides [4].

A ferroelectric is a material with a polar phase produced by a structural transition from a nonpolar high-symmetry paraelectric state, with an electric polarization that can be switched between two or more symmetry-related variants by application of an electric field [5]. The rational design of new ferroelectric materials is motivated both by fundamental scientific interest and by potential technological applications [6]. New materials can offer better performance, including reduction in switching time, in coercive field and in fatigue, operation at higher or lower temperatures, and the possibility of better integration with other materials based on structural or chemical compatibility. New ferroelectrics with lower band gaps for photoactive applications [7–9] are also of interest. Additional practical advantages could include decreased toxicity, for example Pb-free [10], and possible multifunctionality.

Any polar structure (if insulating) could potentially support ferroelectricity if the barrier to switching is low enough [11–13]. We therefore can search for new ferroelectric semiconductors by targeting intermetallic compounds in polar space groups and screening both reported and hypothetical compounds to find insulating representatives with a low barrier to uniform switching through a nonpolar reference phase, which provides an indication of the barrier to realistic switching. ABC compounds with polar space group $P6_3mc$ in the LiGaGe structure type [14–17] are a promising target class. This structure, shown in Figure 1, is a hexagonal variant of the half-Heusler structure and can be described as a wurtzite structure "stuffed" with a third cation [18]. The *Inorganic Crystal Structural Database* (ICSD) [19] includes 18 ABC compounds in this structure type that do not contain an f-block element. We can classify these combinations into the following groups: I-III-IV (LiGaGe), I-II-V (LiBeSb), I-XII-V (LiZnSb), XI-III-IV (CuYSn), XI-II-V (AgCaBi) and II-XII-IV (CaZnSn). In addition, we find that six entries (CuScSn, CuYSn, AuYSn, AgCaBi, CaZnSn and CaHgSn) are also reported with nonpolar $P6_3/mmc$ symmetry in the ZrBeSi structure type, which we identify as the nonpolar reference phase. It has been previously noted that the $P6_3/mmc$ ZrBeSi structure can be obtained by a symmetry-restoring distortion of the LiGaGe structure in which the buckling of the atomic planes in the wurtzite structure is eliminated; this relationship is analogous to that of the wurtzite structure to the metastable hexagonal structure of ScN [20, 21].

In this paper, we use first-principles methods to establish a new class of ferroelectrics in the LiGaGe structure type and to identify promising candidate materials for further investigation. Specifically, we compute the structural parameters, band gap, polarization, and barrier to uniform switching of the eighteen reported and 70 as-yet-hypothetical ABC compounds in the LiGaGe structure type. We identify several insulating combinations with polarization comparable to or greater than that of $BaTiO_3$, and uniform switching barriers comparable to or less than that of $PbTiO_3$. For all insulating combinations studied, we find that the band gaps are in the semiconducting range; the lower band gaps could be useful for photoactive applications [7–9]. These candidate ferroelectrics offer promise for experimental investigation and for the future development of new high-performance materials for practical applications.

First principles computations were performed with the ABINIT package [22]. The local density approximation (LDA) and a $4 \times 4 \times 4$ Monkhorst-Pack sampling of the Brillouin zone [23] were used for all calculations, except for the Berry phase polarization [24, 25] calculations, for which a $8 \times 8 \times 8$ grid was used. All atoms were represented by norm-conserving optimized [26] designed nonlocal [27] pseudopotentials, generated with the OPIUM code [28]. All calculations were performed with a plane wave cutoff of 50 Ry.

We first consider the eighteen non-rare-earth compounds that have been experimentally reported in the LiGaGe structure type in the ICSD [31]. For each combination, we optimized the structural parameters for each of the three structural variants $\underline{A}BC$, $A\underline{B}C$, and $AB\underline{C}$, where the underscore indicates the element at Wyckoff position $2a$, which stuffs the wurtzite structure comprised by the other two elements. The results for the lowest energy structural variant are reported in Table I. The computed structural parameters generally show good agreement with experimental values, with the underestimate of lattice constants characteristic of LDA calculations, about 1-2 % for a and as large as 3-4 % for c.

There are only two insulating compounds in the set of reported LiGaGe-type compounds: LiBeSb (I-II-V) and LiZnSb (I-XII-V); in each the stuffing atom is the monovalent element Li. The total of 8 s and p valence electrons is expected to improve the likelihood of band gap formation [29]. The band gap for LiBeSb is 1.71 eV (indirect) and for LiZnSb it is 0.67 eV (direct). The computed polarizations of 0.59 C/m^2 (LiBeSb) and 0.56 C/m^2 (LiZnSb) are larger than that of $BaTiO_3$. To assess switchability, we compute the energy difference between the polar state and the nonpolar high-symmetry reference state. While we recognize that ferroelectrics do not switch by uniform change of the polarization through the high-symmetry state, the energy barrier for uniform switching can be used to assess the possibility of realistic switching by comparing with the values for known ferroelectrics: 0.2 eV for $PbTiO_3$ and 0.02 eV for $BaTiO_3$ [30]. In the present case, this comparison suggests that the nominal barriers in LiBeSb and LiZnSb (0.58 eV and 0.80 eV) are too high for switchability to be likely.

To search for candidate LiGaGe-type ferroelectrics with lower barriers, we consider equiatomic combinations of three distinct constituent elements ABC with valences given by I-II-V or I-XII-V, with I=(Li, Na, K), II=(Be, Mg, Ca, Sr, Ba), XII=(Zn) and V=(P, As, Sb, Bi). This generates a total of 72 candidate combinations to be searched, only two of which are included in Table I. We optimize the structural parameters for each of the three variants corresponding to the three choices of element for the $2a$ position.

We find that 6 of the 72 combinations are found to be metallic in the lowest-energy structural variant: the computed structural parameters and ΔE, the energy relative to the relaxed high-symmetry $P6_3/mmc$ phase, for these are given in Table II. For the remaining 66 of the 72 combinations, the predicted lowest-energy variant is insulating, with computed band gap ranging from 0.04 eV to 1.81 eV; since DFT tends to underestimate band gaps, we expect that the actual fraction of insulating compounds will be slightly higher than our calculations would indicate. Of these 66 compounds, 49 have relaxed to the higher non-polar $P6_3/mmc$ symmetry; results for these compounds are given in the supplementary material. For the 17 polar insulating compounds, we also compute the spontaneous polarization; results for these compounds are given in Table III.

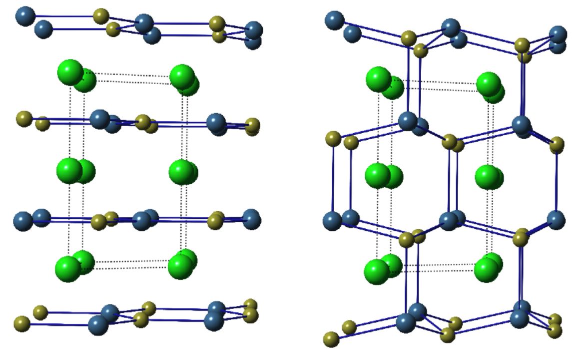
Thus, we have narrowed the search for new LiGaGe-type ferroelectrics to seventeen polar insulating combinations. For this set, we see in Figure 2 that ΔE has a positive correlation with polarization, as would be expected in a simple double-well model. The eight compounds LiBeP, LiCaBi, NaMgP, NaMgAs, NaZnSb, NaMgBi, KMgSb, and KMgBi have polarizations comparable to that of $BaTiO_3$ and ΔE <0.25 eV, in the range favorable for ferroelectric switching, and therefore are promising candidates for ferroelectricity.

The ferroelectric double well for NaMgP, shown in the inset of Figure 2, is representative of this group. The key to the switchability of the polarization is that the wurtzite substructure is not characterized by ideal sp^3 bonding like in ZnO, which would require breaking and reforming of rigid bonds to switch. Rather, the structure should be understood as the buckling of the flat planes of the $P6_3/mmc$ structure, with sp^2 bonding. We define a buckling parameter, d, as the distance along the c-axis between the inequivalent atoms in the buckled plane. We find that d decreases as the size of the stuffing ion increases from Li to Na to K, weakening the interplanar bond so that the barrier to switching is reduced most for compounds containing K. This structural trend directly affects the polarization, which arises from a combination of the buckling and the displacement of the planes relative to the stuffing cation. Since changing the sense of the buckling does not involve breaking and reforming of bonds, the barrier to switching can be low enough for ferroelectricity.

A key question is that of the prospects for synthesis of the candidate compounds in the desired structure. Of the eight compounds we have identified as candidate ferroelectrics, six have reported structures in ICSD. Five are reported in space group $P4/nmm$ (LiBeP, NaMgAs, NaZnSb, KMgSb, KMgBi), and one in space group $Pnma$ (LiCaBi). Of the two for which there is no reported structure, results from a recent theoretical study [3] predict them to be of $P4/nmm$ (NaMgP) or $P2_1/c$ (NaMgBi) symmetry.[32] However, it could still be possible to synthesize at least some of our candidate LiGaGe-type ferroelectrics as metastable phases, in cases in which the LiGaGe structure type is sufficiently close in energy to the ground state. In particular, for NaZnSb the LiGaGe phase is only 0.04 eV per f.u. higher in energy than the $P4/nmm$ ground state, which makes the metastable phase quite accessible. Furthermore, for NaZnSb the energy difference between the lowest energy variant and the next (with Zn as the stuffing atom) is 0.51 eV, suggesting that it will be possible to obtain full chemical ordering.

If these compounds are grown as epitaxial films, this would provide an additional route to engineering the polarization, the switching barrier, and the relative stability of the LiGaGe phase. For example, first-principles calculations show that 3% tensile strain in the (0001) plane reduces the ΔE of the reported compounds LiZnP by 0.11 eV, LiZnAs by 0.12 eV and LiMgAs by 0.08 eV, to 0.57 eV, 0.60 eV and 0.36 eV, respectively. Strain could also promote a polar instability in the insulating nonpolar $P6_3/mmc$ compounds. Of the forty-nine compounds we have identified as nonpolar insulators, six are reported in ICSD with $P6_3/mmc$ symmetry (see supplemental Table 1), and the previously mentioned theoretical study found five additional compounds with this structure. First principles calculations of the zone-center phonon frequencies for six selected compounds (LiBaSb, NaBeSb, NaCaBi, KZnAs, KZnSb, and KBaSb) show that in each case the frequency of the lowest frequency polar mode is below 100 cm^{-1}. However, the coupling of this mode to (0001) epitaxial strain is not strong enough to produce an instability in the range ± 4 % in any of the six compounds we tested.

In conclusion, we have used first-principles methods to establish a new class of ferroelectrics in the LiGaGe structure type and to identify promising candidate materials for further investigation. Through targeted synthesis, LiGaGe-type compounds could potentially be developed as a valuable class of ferroelectric and piezoelectric materials; other structure types with substructures related to wurtzite could similarly yield systems with switchable polarization. This is a specific application of a larger-scale strategy to identify new ferroelectrics by targeting polar insulating compounds not previously recognized as ferroelectric and tuning the composition and other control parameters, such as epitaxial strain, and/or modifying the structure by intercalation of atoms to reduce the barrier to polarization switching. The identification of ferroelectricity in classes of materials in which it was previously unrecognized offers the possibility of optimizing properties and combining polarization with other functional properties, including magnetism, to produce multifunctional behavior of fundamental scientific interest and for groundbreaking technological applications.



(a) $P6_3/mmc$ (b) $P6_3mc$

FIG. 1: The $P6_3/mmc$ ZrBeSi structure shown in a) is the nonpolar high-symmetry reference structure for the polar $P6_3mc$ LiGaGe structure shown in b). The two structures are related by a buckling of the planes formed by atoms at Wyckoff positions $2b$ (dark blue) and $2b'$ (gold) and displacements of the planes relative to the stuffing atom at $2a$ (green).

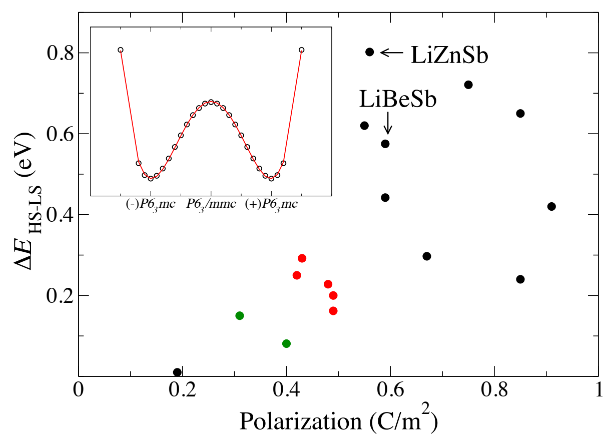


FIG. 2: Difference in energy between the low ($P6_3mc$) and high ($P6_3/mmc$) symmetry ABC structures vs polarization for all polar insulating combinations. Combinations with A=Li (black circles) are less likely to be switchable than those with A=Na (red circles) or A=K (green circles). The two reported compounds LiBeSb and LiZnSb are labeled. The inset shows the characteristic ferroelectric double well energy of NaMgP as a function of polar distortion obtained by linear interpolation between the polar $P6_3mc$ and nonpolar $P6_3/mmc$ structures.

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Competing Financial Interests

There are no competing financial interests.

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	a (Å)	c (Å)	z_{2b}	z'_{2b}	ΔE (eV)
LiGaGe	4.14 (4.18)	6.71 (6.78)	0.31 (0.31)	0.70 (0.70)	0.80
ScCuSn	4.35 (4.39)	6.80 (6.83)	0.33 (0.33)	0.73 (0.73)	0.45
YCuSn	4.48 (4.54)	7.15 (7.27)	0.32 (0.32)	0.73 (0.73)	0.32
YCuPb	4.51 (4.56)	7.19 (7.33)	0.32 (0.32)	0.73 (0.73)	0.34
YAgSn	4.63 (4.68)	7.24 (7.37)	0.31 (0.31)	0.70 (0.72)	0.39
ScAuGe	4.26 (4.31)	6.68 (6.85)	0.30 (0.30)	0.71 (0.70)	0.61
ScAuSn	4.51 (4.59)	7.07 (7.20)	0.35 (0.34)	0.73 (0.73)	0.75
YAuSi	4.25 (4.29)	7.36 (7.55)	0.27 (0.27)	0.72 (0.73)	0.05
YAuGe	4.36 (4.41)	7.08 (7.31)	0.28 (0.28)	0.71 (0.72)	0.26
YAuSn	4.61 (4.64)	7.29 (7.37)	0.33 (0.32)	0.73 (0.73)	0.70
LiBeSb	4.09 (4.15)	6.64 (6.74)	0.35 (0.34)	0.73 (0.73)	0.58
LiZnSb	4.38 (4.43)	7.08 (7.16)	0.29 (0.30)	0.67 (0.69)	0.80
LiZnBi	4.46 (4.58)	7.23 (7.38)	0.28 (0.28)	0.66 (0.66)	0.62
CaAgBi	4.73 (4.81)	7.56 (7.83)	0.32 (0.31)	0.72 (0.72)	0.36
CaZnSn	4.60 (4.66)	7.33 (7.63)	0.31 (0.30)	0.72 (0.72)	0.32
CaHgSn	4.75 (4.80)	7.55 (7.76)	0.31 (0.30)	0.71 (0.72)	0.53
SrHgSn	4.88 (4.89)	7.80 (8.22)	0.29 (0.30)	0.69 (0.72)	0.36
SrHgPb	4.89 (5.00)	8.05 (8.17)	0.29 (0.30)	0.69 (0.72)	0.19

TABLE I: First-principles results for the eighteen LiGaGe-structure compounds reported in ICSD. The computed ground state structural parameters are compared to experimental values, given in parentheses (in some cases, a transformation has been applied to facilitate comparison). The origin is chosen so that the atom at position $2a$ (underlined) is at z=0. ΔE is the energy difference between the polar state and the relaxed nonpolar high-symmetry reference state.

ABC	a (Å)	c (Å)	z_{2b}	$z_{2b'}$	d	E_{gap} (eV)	ΔE (eV)	P (C/m^2)
LiBeP	3.634	5.833	0.295	0.686	0.11	1.51(i)	0.24	0.85
LiMgP	4.134	7.211	0.413	0.773	0.14	1.81(i)	0.42	0.91
LiZnP	3.924	6.365	0.341	0.722	0.12	1.33(i)	0.65	0.84
LiBeAs	4.091	6.636	0.265	0.647	0.12	1.71(i)	0.30	0.67
LiMgAs	4.292	7.483	0.414	0.774	0.14	1.48(d)	0.44	0.59
LiZnAs	4.108	6.673	0.335	0.715	0.12	0.97(d)	0.72	0.75
LiBeSb	4.094	6.645	0.267	0.650	0.12	1.13(i)	0.58	0.59
LiZnSb	4.376	7.081	0.288	0.669	0.12	0.67(d)	0.80	0.56
LiBeBi	4.179	6.806	0.262	0.643	0.12	0.45(i)	0.62	0.55
LiCaBi	4.679	7.503	0.287	0.731	0.06	0.16(i)	0.01	0.19
NaMgP	4.424	6.877	0.310	0.716	0.09	1.17(d)	0.20	0.49
NaMgAs	4.549	7.262	0.314	0.715	0.10	0.67(d)	0.23	0.48
NaMgSb	4.868	7.584	0.307	0.705	0.10	0.69(d)	0.29	0.43
NaZnSb	4.558	7.332	0.285	0.677	0.11	0.20(d)	0.16	0.49
NaMgBi	4.957	7.584	0.302	0.704	0.10	0.14(i)	0.25	0.42
KMgSb	5.017	7.789	0.290	0.697	0.09	0.59(d)	0.08	0.40
KMgBi	5.092	8.005	0.291	0.698	0.09	0.15(i)	0.15	0.31

TABLE III: First-principles results for the lowest-energy variant of each of the 17 polar insulating ABC combinations in the LiGaGe structure type. The structure is specified by the lattice constants and the internal structural parameters for two of the atoms; the origin is chosen so that the atom at position $2a$ (underlined) is at z=0. The buckling parameter d is described in the text. The computed values for the band gap $E_{\rm gap}$ (d=direct and i=indirect), ΔE (as in Tables I and II), and polarization P are included.

ABC	a (Å)	c (Å)	z_{2b}	$z_{2b'}$	d	ΔE (eV)
LiMgSb	4.501	6.979	0.301	0.715	0.09	0.10
LiMgBi	4.602	7.051	0.300	0.718	0.08	0.42
LiZnBi	4.461	7.233	0.277	0.658	0.12	0.62
NaZnBi	4.653	7.479	0.283	0.675	0.11	0.13
KSrBi	5.757	7.044	0.250	0.750	0	0
KZnBi	4.582	10.135	0.250	0.750	0	0

TABLE II: First-principles results for the lowest-energy variant of each of the 6 metallic ABC combinations in the LiGaGe structure type. The buckling parameter d is described in the text. ΔE, as in Table 1.

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