

Supplementary data

CASTEP calculations: We used an energy cutoff for the plane waves of 380 eV, and a k -point grid (generated according to the Monkhorst-Pack scheme¹) that matched the precision of the plane-wave cut-off. The cell parameters and atomic positions were relaxed and optimised by energy minimization using a conjugate-gradient algorithm with a maximum force tolerance and maximum stress component of 0.05 eV/Å and 0.1 GPa respectively.

SIESTA calculations: The pseudopotentials used were generated with the following atomic configurations and cutoff radii (au) for the s , p , d and f components respectively: Li: $2s^{0.3}$, 4×2.40 ; F: $2s^2 2p^5$, 4×1.00 ; Na: $3s^{0.3}$, 3.50, 4.00, 3.50, 3.50; Mg: $3s^{1.5}$, 3.50, 4.00, 3.50, 3.50; K: $4s^{0.3}$, 3.25, 3.50, 2.00, 2.00; Ca: $4s^1$, 3.25, 3.50, 2.00, 2.00. Ni: $4s^1 3d^9$, 2.25, 2.25, 1.50, 1.50. In the pseudopotential generation for Na, K and Ni use was made of non-linear partial-core corrections for the exchange-correlation energy and potential.² Additionally, for Ni a relativistic pseudopotential was generated. We used a split-valence double- ζ basis set including a set of polarization functions for all atoms, as obtained with an energy shift of 250 meV³. In order to obtain the Hamiltonian matrix elements, the electron integrals of the self-consistent terms are computed with the help of a regular space grid in which the electron density is projected. The grid spacing is determined by the maximum kinetic energy of the plane waves that can be represented in that grid. For all systems we used cutoffs close to 200 Ry, namely, distances between grid point smaller than 0.16 Å. In all computations, the Brillouin zone (BZ) was sampled using a (5×5×5) grid, corresponding to 75 k -pointsⁱ. The cell parameters and atomic positions were relaxed and optimised by energy minimization using a conjugate-gradient algorithm with a maximum force tolerance and maximum stress component of 0.02 eV/Å and 0.5 GPa respectively.

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SIESTA CALCULATIONS:

AMF ₃ structure	LiMgF ₃	LiCaF ₃	LiNiF ₃	
Phase (Space Group)	LiNbO ₃ (161, <i>R3c</i>)	Orthorhombic Inverse (62, <i>Pbnm</i>)	LiNbO ₃ (161, <i>R3c</i>)	
Volume (Å ³ /formula unit)	57.35	61.16	54.88	
Energy (eV/formula unit)	-2013.14	-2026.64	-3307.15	
<i>a</i>	5.295	5.381	5.208	
<i>b</i>	5.295	5.966	5.208	
<i>c</i>	14.168	7.616	14.019	
A	(0, 0, 0.7957)	(½, 0, ½)	(0, 0, 0.7856)	
M	(0, 0, 0.5021)	(0.5240, 0.5933, ¼)	(0, 0, 0.4935)	
F	(0.0419, 0.6866, 0.5729)	(0.3708, 0.9517, ¼)	(0.0590, 0.7152, 0.5714)	
F		(0.1798, 0.1863, 0.5631)		
AMF ₃ structure	NaMgF ₃	NaCaF ₃	KMgF ₃	KCaF ₃
Phase (Space Group)	Orthorhombic (62, <i>Pbnm</i>)	LiNbO ₃ (161, <i>R3c</i>)	Cubic (221, <i>Pm-3m</i>)	Orthorhombic (62, <i>Pbnm</i>)
Volume (Å ³ /formula unit)	61.53	76.71	67.22	81.23
Energy (eV/formula unit)	-2012.48	-2125.48	-2079.45	-2192.48
<i>a</i>	5.482	5.869	4.066	6.013
<i>b</i>	5.726	5.869	4.066	6.256
<i>c</i>	7.844	15.429	4.066	8.628
A	(0.5184, 0.5632, ¼)	(0, 0, 0.7901)	(0, 0, 0)	(0.5157, 0.5614, ¼)
M	(½, 0, ½)	(0, 0, 0.4967)	(½, ½, ½)	(½, 0, ½)
F	(0.4011, 0.9539, ¼)	(0.0473, 0.6884, 0.5662)	(½, ½, 0)	(0.4056, 0.9657, ¼)
F	(0.1951, 0.2010, 0.5624)			(0.1904, 0.1972, 0.5568)

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Phase (Space Group)	LiNbO ₃ (161, <i>R3c</i>)	Orthorhombic Inverse (62, <i>Pbnm</i>)	LiNbO ₃ (161, <i>R3c</i>)	
Volume (Å ³ /formula unit)	52.66	56.24	52.13	
Energy (eV/formula unit)	-3170.57	-3197.66	-3242.76	
<i>a</i>	5.092	5.263	5.053	
<i>b</i>	5.092	5.747	5.053	
<i>c</i>	14.067	7.438	14.142	
A	(0, 0, 0.7779)	(½, 0, ½)	(0, 0, 0.7832)	
M	(0, 0, 0.4915)	(0.5189, 0.5861, ¼)	(0, 0, 0.4911)	
F	(0.0268, 0.6759, 0.5654)	(0.3898, 0.9636, ¼)	(0.0341, 0.6890, 0.5699)	
F		(0.1888, 0.1850, 0.5561)		
AMF ₃ structure	NaMgF ₃	NaCaF ₃	KMgF ₃	KCaF ₃
Phase (Space Group)	Orthorhombic (62, <i>Pbnm</i>)	LiNbO ₃ (161, <i>R3c</i>)	Cubic (221, <i>Pm-3m</i>)	Orthorhombic (62, <i>Pbnm</i>)
Volume (Å ³ /formula unit)	59.37	69.21	66.79	84.95
Energy (eV/formula unit)	-4287.49	-4314.21	-3761.73	-3788.64
<i>a</i>	5.454	5.665	4.057	6.154
<i>b</i>	5.598	5.665	4.057	6.294
<i>c</i>	7.779	14.942	4.057	8.773
A	(0.5091, 0.5488, ¼)	(0, 0, 0.7855)	(0, 0, 0)	(0.5106, 0.5424, ¼)
M	(½, 0, ½)	(0, 0, 0.5017)	(½, ½, ½)	(½, 0, ½)
F	(0.4050, 0.9670, ¼)	(0.0447, 0.6752, 0.5652)	(½, ½, 0)	(0.4148, 0.9692, ¼)
F	(0.2011, 0.2037, 0.5496)			(0.2064, 0.2082, 0.5444)

Polarization computations with SIESTA:⁴

We used the same computational parameters as for the optimization (see above). The ferroelectric phase (FE) is the lowest energy optimized structure. In order to obtain the paraelectric phase (PE), we displaced the Li (Na) atoms to the fluoride planes and the Mg (Ca) atoms midway between those planes (see Figure 1 in text) for LiMgF₃ (NaCaF₃). Since the Berry's phase is defined modulo 2π , the spontaneous polarization or the total change in polarization per unit volume, $\Delta\mathbf{P}$, for a crystal is determined to within a factor of $(fe/\Omega)\mathbf{R}$, where f , e , Ω and \mathbf{R} are the occupation number of states in the valence band (in spin degenerate systems $f = 2$, as in the systems treated in this work), the electron charge, the cell volume and a lattice vector in real space, respectively. In practice the arbitrary factor of $(fe/\Omega)\mathbf{R}$ can often be eliminated by inspection because one is usually interested in polarization changes where $|\Delta\mathbf{P}| \ll |(fe/\Omega)\mathbf{R}_1|$, with \mathbf{R}_1 the shortest nonzero real-space lattice vector⁵. Therefore we subtracted when necessary $n(2ec/\Omega)$ from the values obtained for the macroscopic polarization, being c the lattice parameter along z . In order to check the reliability of the calculations, we computed $|\Delta P_z|$ along the distortion coordinate x , so that $z(x) = x z^{\text{PE}}(\text{B}) + (1 - x) z^{\text{FE}}(\text{B})$, being z and B respectively the fractional coordinate in the c axis and atom labels for Li(Na) and Mg(Ca) atoms in LiMgF₃(NaCaF₃). The "adiabatic" transformation from the FE to the PE phase was computed with values $0 \leq x \leq 1$, with a step of 0.1 units and a linear relation was found for $|\Delta P_z|$ against x after subtracting the appropriate "quanta" in the c direction, thus confirming the calculation for the spontaneous polarization (Figure 2). z^{PE} and z^{FE} correspond to the fractional z coordinate of Li (Na) and Mg (Ca) atoms in the PE and FE phases respectively. Figure 2 below shows the computed $|\Delta P_z|$ versus x for LiMgF₃ and NaCaF₃; the FE and PE phases correspond to $x=0$ and $x=1$ respectively.

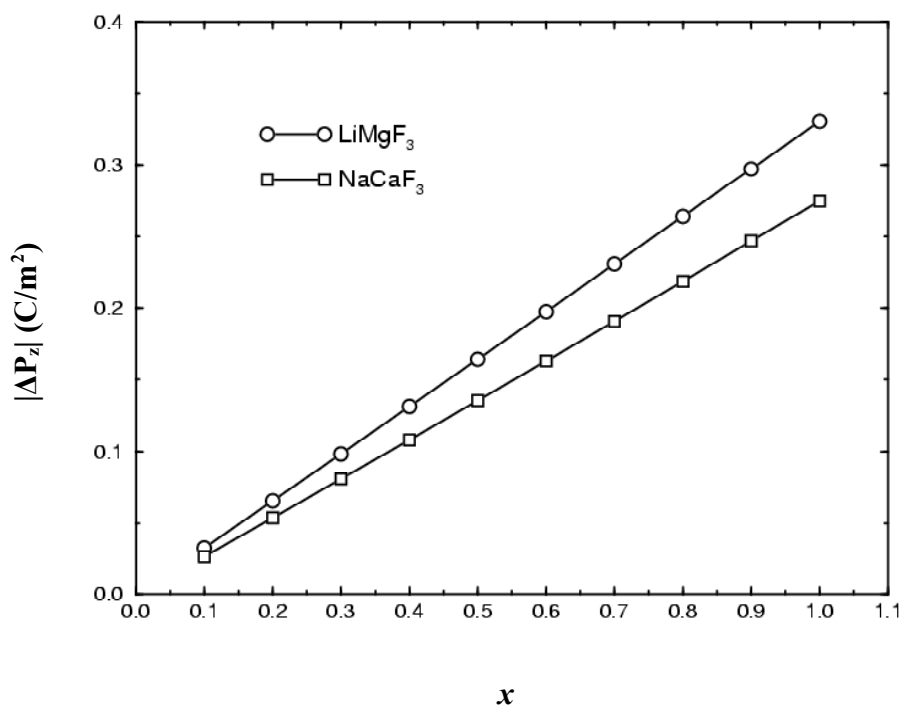


Fig 2 Plot of $|\Delta P_z|$ versus x , the distortion coordinate for Li (Na) and Mg (Ca) atoms from the FE ($x=0$) to PE ($x=1$) phase in LiMgF₃ (NaCaF₃).

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References

- ¹ H.J. Monkhorst and J.D. Pack, *Phys. Rev. B* 1976, **13**, 5188.
² S.G. Louie, S. Froyen, M.L. Cohen, *Phys. Rev. B*, 1982, **26**, 1738.
³ E. Artacho, D. Sánchez-Portal, P. Ordejón, A. Garcia, J.M. Soler, *Phys. Stat. Solidi B*, 1999, **215**, 809.
⁴ D. Sánchez-Portal, I. Souza and R.M. Martin, *Fundamental Physics of Ferroelectrics 2000*, AIP Conf. Proc. Vol. 535, ed R. Cohen, Melville AIP, pp 111-120.
⁵ R.D. King-Smith and D. Vanderbilt, *Phys. Rev. B*, 1993, **47**, 1651.