

Ab initio predictions of ferroelectric ternary fluorides with the LiNbO₃ structure†

Frederik Claeysens,^a Josep M. Oliva,^a Daniel Sánchez-Portal^b and Neil L. Allan^{*a}

^a School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS.

E-mail: n.l.allan@bristol.ac.uk

^b Centro Mixto CSIC-UPV/EHU and Donostia International Physics Center, P^o Manuel de Lardizábal 4, E-20018 Donostia, Spain

Received (in Cambridge, UK) 29th July 2003, Accepted 22nd August 2003

First published as an Advance Article on the web 8th September 2003

First-principles periodic density-functional theory calculations suggest ternary fluorides LiMgF₃, NaCaF₃ and LiNiF₃ should adopt the ferroelectric LiNbO₃ structure at low temperatures; LiMgF₃ and LiNiF₃ are predicted to have negative enthalpies of formation from the binary fluorides.

There remains intense interest in the search for new ferroelectric materials.¹ In particular, lithium niobate is one of the most technologically relevant ferroelectric oxides because of its remarkable optical anisotropy,¹ large spontaneous polarization,² and electro-optical and nonlinear optical activity.³ In parallel, solid inorganic fluorides are playing increasingly important roles in areas ranging from novel glasses to thin-film solid electrolytes.

A surprisingly unanswered question is the absence of ferroelectric AMF₃ systems, analogous to LiNbO₃. Why is there apparently no fluoride analogue of lithium niobate? We have thus carried out a set of periodic *ab initio* calculations to address the question of the thermodynamic stability of ternary fluorides AMF₃ and whether they might be ferroelectric. We consider here (i) the set of compounds AMF₃ (A = Li, Na, K; M = Mg, Ca), which includes, for validation purposes, several known systems (*cf.* an earlier molecular mechanics study⁴). These are NaMgF₃, KMgF₃ and KCaF₃. Recently, thin films of metastable NaCaF₃ with a *perovskite* structure have also been synthesized by pulsed laser deposition,⁵ (ii) LiNiF₃, which is unknown and which we have included for purposes of comparison with LiMgF₃ bearing in mind the similar size of Mg²⁺ and Ni²⁺.

The first-principles DFT^{6,7} calculations were carried out using (i) plane waves and (ii) periodic numerical atomic orbitals, as implemented in the CASTEP⁸ and SIESTA⁹ codes respectively. In either calculations the generalized-gradient approximation (GGA) to DFT was used, and the exchange-correlation functionals of Perdew–Wang¹⁰ and Perdew–Burke–Ernzerhof¹¹ were used respectively in CASTEP and SIESTA calculations. Only valence electrons are considered explicitly, the core electrons being replaced by suitable pseudopotentials: in the CASTEP and SIESTA calculations use was made respectively of the ultra-soft Vanderbilt potentials,¹² and norm-conserving scalar pseudopotentials,¹³ factorised in the Kleinman–Bylander form.¹⁴ Full details of the pseudopotential generation, energy cutoffs, basis sets and other technical details are available in the ESI.†

Possible structures for the AMF₃ fluorides fall into two classes:

(i) the first class comprises perovskite structures found when A is large enough for the formation of close-packed layers AF₃. The simplest such structure is the well-known cubic perovskite structure in which AF₃ layers are cubic close packed. The larger univalent ion is 12-coordinate and the divalent ions 6-coordinate. An 'inverse perovskite' structure, in which the univalent and divalent cations exchange positions is also observed, as for BaLiF₃¹⁵ when the 2+ ion is larger than the 1+. When the A cation is too small to touch the anions in the cubic structure, the

M–M bridges linking the MF₆ octahedra bend and such orthorhombic perovskites are common.

(ii) The second class of structures arises when A and M are the same size and the size is suitable for octahedral coordination. In these both cations are 6-coordinate. Examples are the lithium niobate (Fig. 1) and ilmenite structures, both of which contain hexagonally packed anion layers. They differ solely in the distribution of the cations between the octahedral holes.

For each AMF₃ system we have used first principles periodic DFT calculations to determine the energies and corresponding optimised lattice parameters and basis atom positions for each of these possible structures: cubic, orthorhombic, 'inverse' cubic, 'inverse' orthorhombic, lithium niobate and ilmenite. For each system the predicted low temperature phase (*i.e.*, that with the lowest energy) is listed in Table 1. Structural parameters and atomic positions for all optimised structures are given in the ESI.†

Where experimental data are available (marked with an asterisk) the predicted structures are those observed at low temperatures, Table 1 lists optimised lattice parameters obtained using SIESTA (CASTEP results are similar — see ESI†). The agreement between computed lattice parameters and experimental values where available is good. Typical errors are ≈ 1–3 %.

Three compounds in which the univalent and divalent cations are of comparable size, LiMgF₃, NaCaF₃, and LiNiF₃ are predicted to adopt the lithium niobate structures. We have therefore calculated the enthalpy of formation, Δ*H*, of these three systems from the corresponding binary fluorides. For LiMgF₃ and LiNiF₃ the values of Δ*H* are negative (−18 kJ mol^{−1} and −12 kJ mol^{−1} respectively). For NaCaF₃, a positive value is obtained (+40 kJ mol^{−1}). Of course, experimental synthesis of LiMgF₃ and LiNiF₃ from the binary fluorides could

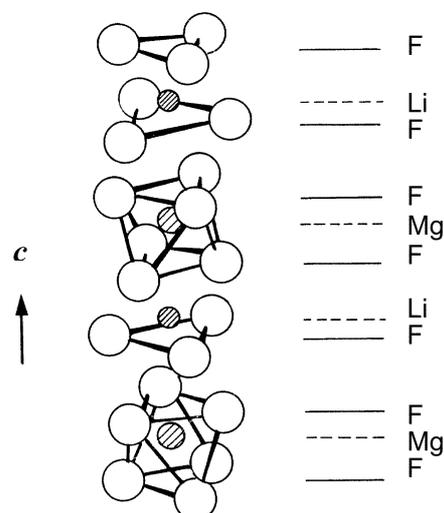


Fig. 1 Predicted low-temperature ferroelectric LiMgF₃ crystal structure, isomorphous with LiNbO₃.

† Electronic supplementary information (ESI) available: CASTEP and SIESTA calculations. See <http://www.rsc.org/suppdata/cc/b3/b309000k/>

Table 1 First-principles DFT calculated low-temperature phases and optimised lattice parameters (Å) in AMF₃ compounds (SIESTA values). * denotes compounds for which experimental crystallographic data are available. Experimental lattice parameters are shown in parentheses^a

		Ion M		
		Mg ²⁺	Ca ²⁺	Ni ²⁺
Ion A	Li ⁺	LiNbO ₃ <i>a</i> = 5.296 <i>b</i> = 5.296 <i>c</i> = 14.168	Orthorhombic Perovskite (Inverse) <i>a</i> = 5.381 <i>b</i> = 5.966 <i>c</i> = 7.616	LiNbO ₃ <i>a</i> = 5.208 <i>b</i> = 5.208 <i>c</i> = 14.019
	Na ⁺	Orthorhombic Perovskite* <i>a</i> = 5.482 (5.350) <i>b</i> = 5.726 (5.474) <i>c</i> = 7.844 (7.652)	LiNbO ₃ <i>a</i> = 5.869 <i>b</i> = 5.869 <i>c</i> = 15.429	
	K ⁺	Cubic Perovskite* <i>a</i> = 4.066 (3.989) <i>b</i> = 4.066 (3.989) <i>c</i> = 4.066 (3.989)	Orthorhombic Perovskite* <i>a</i> = 6.013 (6.164) <i>b</i> = 6.256 (6.209) <i>c</i> = 8.628 (8.757)	

^a NaMgF₃¹⁷ KMgF₃¹⁸, KCaF₃.¹⁷

lead to phases with compositions different from those considered here. For the known fluorides considered in this work, we obtain negative enthalpies of formation for the orthorhombic perovskite NaMgF₃ (−30 kJ mol^{−1}) and the cubic perovskite KMgF₃ (−53 kJ mol^{−1}). Experimental data for comparison are scarce; a recent experiment reports a value of −16 kJ mol^{−1} for the enthalpy of formation of NaMgF₃¹⁶ at room temperature from the binary fluoride. For LiCaF₃ and KCaF₃ small positive enthalpies of formation are obtained (+4 kJ mol^{−1} and +14 kJ mol^{−1} respectively).

Finally we turn to the question of ferroelectricity in those systems predicted to adopt the LiNbO₃ structure at low temperatures. The change of polarization in solids can be computed by means of the geometric Berry phase approach,¹⁹ implemented in the SIESTA code within the periodic first-principles DFT formalism²⁰. For the lithium niobate phases of LiMgF₃ and NaCaF₃ we computed the total change in polarization per unit volume — spontaneous polarization — $\Delta P_z = P_z^{(1)} - P_z^{(0)}$ along the *c* axis, using the model shown in Fig. 1. The Li/Na and Mg/Ca atoms are displaced along *c* from the more symmetric (high temperature) paraelectric phase (1) (in which the 1+ ions are three-fold coordinate and the 2+ lie in the centre of the MF₆ octahedra, midway between adjacent F planes) to the lower symmetry (lower temperature) ferroelectric phase (0) respectively. The details of these calculations can be found in the supplementary information. The first-principles DFT computed spontaneous polarization calculations using the geometric phase approach yield values of 0.33 C m^{−2} and 0.27 C m^{−2} for LiMgF₃ and NaCaF₃ respectively; for comparison similar computations on LiNbO₃ give 0.85 C m^{−2}, in good agreement with the reported¹ experimental value of 0.70 C m^{−2}.

We thus suggest the ternary fluorides LiMgF₃, LiNiF₃ and NaCaF₃ should adopt the lithium niobate structure at low temperatures. The Li compounds are predicted to have negative enthalpies of formation from the binary fluorides and LiMgF₃ and NaCaF₃ are predicted to be ferroelectric. It is hoped that an

experimental study of these compounds is stimulated by the present work.

This work was made possible by computing resources available through two JREI (HEFCE) awards. Help from Javier Junquera with the polarization calculations is gratefully acknowledged.

Notes and references

- 1 Y. Xu, *Ferroelectric Materials and their Applications*, Elsevier Science Publishers, Amsterdam, 1991.
- 2 S. Kim and V. Gopalan, *Appl. Phys. Lett.*, 2002, **80**, 2740.
- 3 D. Xue and S. Zhang, *J. Phys. Chem. Solids*, 1997, **58**, 1399.
- 4 N. L. Allan, M. J. Dayer, D. T. Kulp and W. C. Mackrodt, *J. Mater. Chem.*, 1991, **1**, 1035–1039.
- 5 R. W. Smith and J. S. Horwitz, Patent No. US 6,372,306 B1, Apr. 16, 2002.
- 6 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, 864.
- 7 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, 1133.
- 8 *CASTEP 4.2 academic version*, licensed under the UKCP-MSI agreement, 1999; *Rev. Mod. Phys.*, 1992, **64**, 1045.
- 9 J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, *J. Phys: Condens. Matter*, 2002, **14**, 2745.
- 10 J. P. Perdew, K. Burke and Y. Wang, *Phys. Rev. B*, 1996, **54**, 16533.
- 11 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 12 D. Vanderbilt, *Phys. Rev. B*, 1990, **41**, 7892.
- 13 N. Trouiller and J. L. Martins, *Phys. Rev. B*, 1991, **43**, 1993.
- 14 L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 15 W. L. W. Ludekens and A. J. E. Welch, *Acta. Crystallogr.*, 195, **5**, 841.
- 16 L. Topor, A. Navrotsky, Y. Zhao and D. J. Weidner, *J. Solid State Chem.*, 1997, **132**, 131.
- 17 *Inorganic Solid Fluorides – Chemistry and Physics*, ed. P. Hagenmuller, Academic Press, London, 1985.
- 18 R. C. DeVries and R. Roy, *J. Am. Chem. Soc.*, 1953, **75**, 2459.
- 19 R. D. King-Smith and D. Vanderbilt, *Phys. Rev. B*, 1993, **47**, 1651.
- 20 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.