Electronic properties of $NaCdF_3$: A first-principles prediction

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Based on first-principles total energy calculations, we predict that $NaCdF_3$ could be formed in a ferroelectric crystal structure. Using a symmetry guided search with structure optimization, we found two ferroelectric structures, nearly degenerate in energy, competing for the ground state: a rhombohedral structure with space group $R3c$ and an orthorhombic structure with space group $Pna2_1$. The energies of both structures are $\approx$60 meV lower than the sum of those of the constituents, NaF and CdF_2, implying chemical stability.

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Perovskite and perovskitelike crystal structures are prevalent in many areas of scientific and technological importance. This is especially true in the area of ferroelectrics where oxide perovskites dominate applications in electronics and optics. While halide-based perovskites form an interesting class of materials, with many structural instabilities, until now, only one, $NaCaF_3$ has been predicted to have a ferroelectric ground state.[1] Results of subsequent calculations[2] and the lack of success in forming this compound experimentally, indicate the components NaF and CaF_2 have sufficiently lower energy to prohibit compound formation by standard methods. Fabrication of new halide-based ferroelectrics is of general scientific interest because they are rare and may be desirable for certain applications in technology. The nonperovskite fluoride, $BaMgF_4$, has been considered for use in nonvolatile memories because of its low fatigue rate.[3] The oxide, $LiNbO_3$, finds many applications owing to its nonlinear optical properties. The fluoride compounds considered here have structures isomorphous with $LiNbO_3$, but with a much larger band gap, which would allow components to operate at much higher frequencies.

In this Brief Report we revisit $NaCaF_3$ and consider another compound, $NaCdF_3$, which, as we will see, has predicted properties similar to those of $NaCaF_3$, but with more favorable energetics for compound formation. We explore the candidate structures for these hypothetical compounds using a two stage method. In the first stage, we do an approximate calculation of the ''instability tree.'' Specifically, an approximate density-functional theory (DFT) based model, capable of rapid total energy calculations, is applied to compute the instabilities of the undistorted cubic perovskite structure. Here we use an automated procedure to follow the instabilities to lower symmetry structures that are isotropy subgroups of the parent group.[4] All symmetry points of the Brillouin Zone are considered. The process is repeated for the new parent groups, etc., until we find all stable structures that resulted originally from instabilities of the cubic perovskite structure. In the final stage, we further relax and refine the approximate structures using a highly accurate DFT method. The same accurate DFT method is applied to the constituent compounds NaF and CdF_2 (CaF_2) for comparison with total energy results for $NaCdF_3$ ($NaCaF_3$).

Several alkaline cadmium fluoride compounds $M\mathrm{CdF}_3$ (M=K, Rb, Cs, Tl) have been synthesized experimentally,[5–7] however none of them exhibit ferroelectricity. Let us consider the possibility that $NaCdF_3$ would be ferroelectric in the context of the tolerance factor of perovskite compounds ABX_3,[8] $\tau=(R_A+R_X)/\sqrt{2}(R_B+R_X)$, where R_A, R_B, and R_X are the effective ionic radii of *A*, *B*, and *X*, respectively, and $\tau=1$ is regarded the most stable perovskite structure from purely geometrical point of view. Adopting the Shannon radii,[9] we find the τ value of $NaCdF_3$ (0.84) is much smaller than those of $M\mathrm{CdF}_3$ (M=K, Rb, Cs, Tl) and very close to that of $NaCaF_3$ (0.83). This implies that it is relatively easier to distort $NaCdF_3$ from the ideal cubic structure, which has higher symmetry and no polarization, to a structure with much less symmetry. The trend of τ values for these compounds correlates with their structural phase transitions and lack thereof. Specifically, $KCdF_3$ ($\tau=0.92$) has three phase transitions[7] ($Pm3m\rightarrow P4/mbm\rightarrow Pbnm\rightarrow Pbn2_1$). As the value gets higher, it is found that there exist small distortions at low temperature in $RbCdF_3$ ($\tau=0.98$) and $TlCdF_3$ ($\tau=0.94$), but no distortion was observed in $CsCdF_3$ ($\tau=1.00$).[7] A similar trend is seen for the $M\mathrm{CaF}_3$ (M=K, Rb, Cs) compounds.[10–13]

Previous studies[14–16] have shown that the structural and vibrational properties of $M\mathrm{CaF}_3$ are rather well predicted by the electron-gas model of Gordon and Kim (GK).[17] However, when anions overlap with cations having filled *d* shells, as in $NaCdF_3$, the GK model significantly overestimates the repulsive force—in this case, between Cd and F. Thus, for Cd-F interactions we scale the repulsive part of the GK potential, i.e., that arising from the Thomas-Fermi approximation for electronic kinetic energy, by an amount (0.86) chosen to give the experimental lattice constant of CdF_2. The instability trees obtained using the GK models for $NaCdF_3$ and $NaCaF_3$ are summarized as follows. First of all, the results for both compounds are qualitatively the same. In each case, the two lowest-energy structures originate from the most unstable mode of the cubic structure, which has R_5^-

TABLE I. Predicted structure parameters for compounds considered in this paper. GK model values are identified, where appropriate, by parentheses. Lattice parameter lengths are in Bohr and angles are in degrees.

Compound	Space Group	Lattice parameters	Wyckoff notation	Coordinates x	y	z	atom
NaF	$Fm3m$	a=8.88(8.75)					
CaF_2	$Fm3m$	a=10.41(10.17)					
$NaCaF_3$	$R3c$	r=11.74(11.38)	a	0.289(0.285)	0.289(0.285)	0.289(0.285)	Na
		β=56.17(56.88)	a	0(0)	0(0)	0(0)	Ca
			b	0.879(0.875)	0.617(0.623)	0.212(0.217)	F
$NaCaF_3$	$Pna2_1$	a=11.42(11.10)	a	0.964	0.495	0.770	Na
		b=11.17(10.85)	a	0.520	0.500	0.003	Ca
		c=16.05(15.60)	a	0.148	0.334	0.551	F
			a	0.724	0.199	0.921	F
			a	0.071	0.878	0.747	F
$NaCdF_3$	$R3c$	r=11.60(11.42)	a	0.286	0.286	0.286	Na
		β=56.81(56.81)	a	0	0	0	Ca
			b	0.878	0.619	0.215	F
$NaCdF_3$	$Pna2_1$	a=11.31(11.12)	a	0.966	0.496	0.772	Na
		b=11.06(10.88)	a	0.524	0.500	0.003	Ca
		c=15.93(15.61)	a	0.139	0.338	0.549	F
			a	0.730	0.201	0.916	F
			a	0.076	0.875	0.746	F

symmetry. One branch leads to a stable crystal with space group $R3c$ and involves the Γ_2^- ferroelectric instability of the $R\overline{3}c$ structure. Another branch leads to a stable crystal with $Pna2_1$ symmetry and involves a Γ_4^- ferroelectric instability of the $Pnma$ structure, preceded by an X_4^- instability of the $Imma$ structure. The GK models find the $R3c$ structure 12 and 15 meV lower in energy than the $Pna2_1$ structure for $NaCdF_3$ and $NaCaF_3$, respectively, and the energy of the constituent compounds are 295 and 204 meV per formula unit below the $R3c$ energies, respectively. A third branch originating from the second most unstable mode (M_2^+ symmetry) was considered and found to lie $\sim$125 meV above the $R3c$ structures.

Ab initio band structure and total energy calculations were carried out for $NaCdF_3$ and $NaCaF_3$ in three space groups, $R3c$, $Pbn2_1$, and $Im3$ using the FLAPW method[18] and the GGA.[19] The factor RK_{max} is set to be 9. The upper limit of the angular momentum $l_{\max}$=10 is adopted in the spherical-harmonic expansion of the Kohn-Sham functions inside the atom spheres. Twenty k points in the irreducible part of the Brillouin zone are used in the self-consistent calculation. The convergence obtained is up to 0.1 meV of the total energy. The same methods were applied to calculate total energies for NaF, CaF_2, and CdF_2. Based on our tests on RK_{max}, we are able to set an uncertainty of $\pm$10 meV on our calculated energies.

The relaxed structures and total energies are listed in Tables I and II. The $Im3$ structure, originating from the second most unstable mode (M_2^+ symmetry) of the cubic perovskite structure, has substantially higher energy than the

TABLE II. Calculated energies for the instability tree structures of $NaBF_3$ relative to the energy of the constituent compounds: specifically, $E(NaBF_3)$-E(NaF)-$E(BF_2)$, where B=Ca or Cd, in units of meV. GK model results are shown in parentheses.

Compound	Tree 1 Group	Mode	Energy	Tree 2 Group	Mode	Energy	Tree 3 Group	Mode	Energy
$NaCaF_3$	$Pm3m$	R_5^-	889(930)	$Pm3m$	R_5^-	889(930)	$Pm3m$	M_2^+	889(930)
	$R\overline{3}c$	Γ_2^-	205(282)	$Imma$	X_4^-	—(304)	$Im3$	Γ_4^-	—(354)
	$R3c$		146(204)	$Pnma$	Γ_4^-	157(227)	$Imm2$		—(332)
				$Pna2_1$		131(219)			
$NaCdF_3$	$Pm3m$	R_5^-	792(1087)	$Pm3m$	R_5^-	792(1087)	$Pm3m$	M_2^+	792(1087)
	$R\overline{3}c$	Γ_2^-	75(384)	$Imma$	X_4^-	—(408)	$Im3$	Γ_4^-	130(463)
	$R3c$		-59(295)	$Pnma$	Γ_4^-	−16(321)	$Imm2$		113(437)
				$Pna2_1$		−52(308)			

other two structures, so we do not consider it to be a candidate for the ground state. The FLAPW calculations using GK structure parameters give lower total energies, relative to the combined total energy of the constituent compounds, than the corresponding GK values. Relaxation of the lattice parameters rendered significantly lower energies. On the other hand, the GK model Wyckoff parameters were found to be already very near the minimum energy values. For both compounds the relaxed Wyckoff parameters agree with those of the GK model to within ~0.01. Compare values in Table I for $NaCaF_3$ in the $R3c$ structure. We did not attempt more precise refinements for the remaining compounds/structures. For $NaCdF_3$, the total energy of the rhombohedral phase is lower than that of the orthorhombic phase by only 7 meV per formula unit. Considering the accuracy of our method, either structure could be the ground state.

In Fig. 1 we show the calculated energy band structures for the two phases of $NaCdF_3$. The theoretical energy gaps of the rhombohedral and orthorhombic phases are 3.6 and 3.4 eV at the Γ point, respectively. Partial density of states analysis reveal quite similar pictures of both band structures: the upper part of the valence states consists mainly of the F $2p$ electron states. The Cd $4d$ electron states lie around -5 eV of the valence bands. The bottom of conduction bands is dominated by Cd $5s$ states and F $2p$ electron states. The Na $3s$ electron states appear apparently only from 8 eV above the Fermi level. It shows that the interaction between Cd^{2+} and F^- ions is much larger than that between Na^+ and F^- ions. The valence-band dispersion is small compared to the case of $LiNbO_3$.[20]

The rhombohedral phases of $NaCaF_3$ and $NaCdF_3$ have the same symmetry as the $LiNbO_3$ structure. Thus we apply the same method to compute the electronic structure and lattice parameters of $LiNbO_3$, as well as NaF, CaF_2, CdF_2, for comparison with available experimental results (Table III). We see the calculated lattice constants agree well with observations. Discrepancies are within 2%. Of the three perovskite-type compounds, $LiNbO_3$ has the smallest lattice constants, whereas $NaCaF_3$ has the largest. The close agreement between the theoretical and experimental lattice constants of $LiNbO_3$ supports our prediction of the theoretical structure of $NaCdF_3$.

We found that the total energies of both structures of $NaCdF_3$ are about 60 meV per formula unit lower than the sum of that of the constituents. This renders the fabrication of $NaCdF_3$ more promising than that of $NaCaF_3$. The calculated energy gaps of NaF and CdF_2 are much lower than experimental values, consistent with the common trend in density-functional methods of underestimating the energy gap. By adjusting accordingly for this expected error, we estimate the experimental energy gap for $NaCdF_3$ would be around 8.5 eV.

We have applied the self-consistent atomic deformation (SCAD) method[27] to determine monopole and dipole moments of ions in the predicted ferroelectric structures of $NaCaF_3$ and $NaCdF_3$. The SCAD eigenvalues compare favorably with the band structure. The predicted monopole moments are the full ionic charges, and these do not change when the structures are distorted from paraelectric to ferroelectric. Thus the change in polarization is simply given by the sum of contributions from monopole displacements and the induced dipole moments.[28] Since the F^- ion is not very polarizable, a reflection of the fact that the fluorine bands have low dispersion, polarization values for the ferroelectric structures are dominated by the monopole displacement contributions. Dipolar contributions are only a few percent of the total and in the direction to reduce the total polarization. Specifically, we find 0.23 C/m^2 for $NaCdF_3$ in the $R3c$ structure and 0.11 C/m^2 in the $Pna2_1$ structure. For $NaCaF_3$ the corresponding values are 0.26 and 0.10 C/m^2. For comparison, we have applied this method to compute the polar-

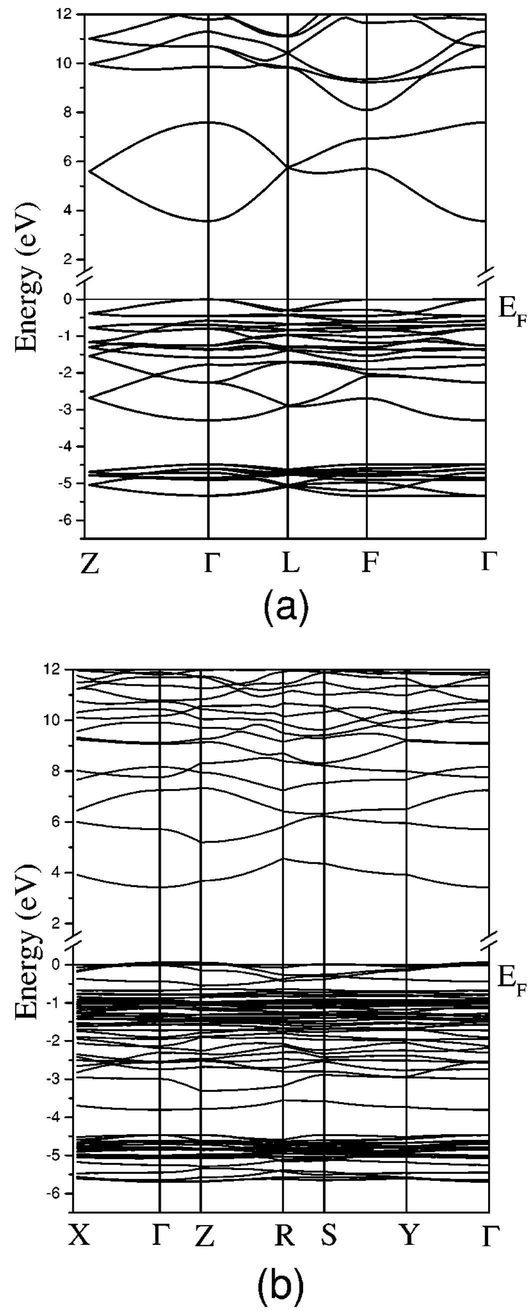

FIG. 1. Calculated band structures of $NaCdF_3$: (a) rhombohedral phase, (b) orthorhombic phase.

TABLE III. Calculated GGA-DFT lattice constants, a/c ratios and energy gaps E_g of NaF, CaF_2, CdF_2, $NaCdF_3$, $NaCaF_3$, and $LiNbO_3$. Available experimental values are shown in parentheses.

	NaF	CaF_2	CdF_2	$NaCdF_3$	$NaCaF_3$	$LiNbO_3$
a (Å)	4.70(4.63 [a])	5.51(5.46 [a])	5.49(5.39 [a])	5.84	5.85	5.18(5.15 [b])
c (Å)				15.39	15.64	14.09(13.86 [b])
a/c				0.379	0.374	0.368(0.371 [c])
E_g (eV)	6.1(11.7 [b])	7.4(12.4 [d])	3.5(8.4 [e])	3.6	6.6	3.2(3.78 [f])

[a]Reference 21.
[b]Reference 23.
[c]Reference 22.
[d]Reference 24.
[e]Direct gap, Ref. 25.
[f]Reference 26.

ization $LiNbO_3$ using the experimental structure. Again, the monopole charges are the full ionic values. We find a ferroelectric polarization of 0.77 C/m^2, in good agreement with the room temperature value (0.71).[29] However, in this case the dipolar contributions are about 20% of the total and serve to enhance the monopole contribution.

In conclusion, our *ab initio* calculations predict that $NaCdF_3$ could be formed in a ferroelectric structure having an energy substantially lower than its constituents. We estimate an experimental energy gap of about 8–9 eV at the Γ point. This indicates that this compound might be a good candidate for a frequency conversion material working in the ultraviolet region.

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