Supplement: Ferroelectricity in corundum derivatives

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The properties of FE materials are sensitive to atomic displacements and strain, so it is essential to start our calculation with accurate structural parameters. The lattice constants and Wyckoff positions obtained from our calculations are summarized in the Tables I and II, with experimental results provided for reference. Our structure parameters are very close to the experimental results.

To investigate the magnetic structures of Mn_2FeWO_6 and Mn_3WO_6, four different types of unit cell are considered in the calculation. We adopt a notation like "*udu*" to describe the possible spin structure, where "*u*" is spin-up, "*d*" is spin-down, and the spins are given on atom β, δ and γ, in that order. The four possible states (not counting those that are trivially related by a global spin reversal) are *uuu*, *uud*, *udu*, and *udd*. The energy of each fully-relaxed magnetic structure is listed in Table III. Of those, the most stable state for both Mn_2FeWO_6 and Mn_3WO_6 is *udu*. However, for Mn_3WO_6, the energy difference between the *uud* and *udu* states is tiny, so we considered the polarization reversal for both magnetic states.

The magnetic ground states of Mn_2FeWO_6 and Mn_3WO_6 can be understood by analyzing the super-exchange interactions between A_1, A_2 and B cations (also shown as β, γ and δ cations). The magnetic moments are coupled through the oxygen octahedra, and there are three independent coupling constants. The moments on A_2 and B sites are coupled through face-sharing and corner-sharing oxygen octahedra with strength J_{A_2B}; the A_1 and B moments are coupled through edge-sharing octahedra with strength J_{A_1B}; and the A_1 and A_2 moments are coupled through corner-sharing octahedra with strength $J_{A_1A_2}$. Then the magnetic energy E_{mag} can be written as

$$E_{\mathrm{mag}} = J_{A_1B}\hat{S}_{A_1}\cdot\hat{S}_B + J_{A_2B}\hat{S}_{A_2}\cdot\hat{S}_B + J_{A_1A_2}\hat{S}_{A_1}\cdot\hat{S}_{A_2}\,, \tag{1}$$

where $\hat{S}$ represent the spin on each site. Substituting the energy of different magnetic orderings in Table III into Eq.(1), we find that the coupling constants are all positive. This result implies that the three magnetic moments all favor AFM coupling. However, it is impossible to make three collinear spins couple antiferromagnetically, and this frustration implies that one pair must be ferromagnetically coupled.

In Table IV we list the relative spin orientations of the magnetic ions. Since the face-sharing coupling J_{A_2B} is the strongest, it is not surprising that the A_2 and B moments couple antiferromagnetically; the competition between J_{A_1B} and $J_{A_1A_2}$ then determines the magnetic ground state. In Mn_3WO_6, these two couplings are comparable, so the energy difference between the *uud* and *udu* states is tiny. In the case of Mn_2FeWO_6, the magnetic moment on the B cation is smaller, so the coupling J_{A_1B} is weaker than $J_{A_1A_2}$. Therefore, the lowest-energy state is *udu*.

For the ordered-LNO materials the two A cations are inequivalent, and one of them is already closer to the oxygen plane in the ground state ($\xi_{1\mathrm{S}} \neq \xi_{2\mathrm{S}}$). Therefore it is energetically favorable for this particular A cation to migrate first in the reversal path, which causes either the B or B' cation to be sandwiched between two A cations in the midpoint structure. If $\xi_{1\mathrm{S}} > \xi_{2\mathrm{S}}$, the sandwiched cation is B; otherwise it is B'. By calculating the energy difference $\Delta E = E_B - E_{B'}$ between the B and B' sandwiched midpoint structures, we find that the cations that are sandwiched in the midpoint structures are Zr for Li_2ZrTeO_6, Hf for Li_2HfTeO_6, W for Mn_2FeWO_6 and Mn_3WO_6, and Os for Zn_2FeOsO_6. These results are consistent with the analysis of $\xi_{1\mathrm{S}}$ and $\xi_{2\mathrm{S}}$, as shown in Table V. We find that the energy difference between the two distinct midpoint structures is mainly due to the difference $\Delta E^{\mathrm{M}} = E^{\mathrm{M}}_B - E^{\mathrm{M}}_{B'}$ between the Madelung energies of the two structures in a simple point-ion model, as shown in Table. V.

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TABLE I. Rhombohedral structural parameters of LNO-type ABO_3 corundum derivatives $LiNbO_3$, $LiTaO_3$, $ZnSnO_3$, $FeTiO_3$ and $MnTiO_3$ from first-principles calculations and experiments. The Wyckoff positions are 2a for A and B cations, and 6c for oxygen anions (note that $A_x = A_y = A_z$ and $B_x = B_y = B_z$). The origin is defined by setting the Wyckoff position B_x to zero.

		Lattice constants		Wyckoff positions				
		a (Å)	α (°)	A_x	B_x	O_x	O_y	O_z
$LiNbO_3$	Calc.	5.486	56.0	0.282	0.000	0.360	0.719	0.112
	Exp.[1]	5.494	55.9	0.280	0.000	0.359	0.720	0.111
$LiTaO_3$	Calc.	5.476	56.2	0.284	0.000	0.365	0.726	0.119
	Exp.[2]	5.473	56.2	0.291	0.000	0.368	0.732	0.124
$ZnSnO_3$	Calc.	5.584	56.5	0.283	0.000	0.392	0.709	0.104
	Exp.[3]	5.569	56.4	0.286	0.000	0.381	0.721	0.111
$FeTiO_3$	Calc.	5.434	56.5	0.290	0.000	0.364	0.721	0.104
	Exp.[4]	5.458	56.0	0.287	0.000	0.364	0.720	0.109
$MnTiO_3$	Calc.	5.481	56.6	0.279	0.000	0.348	0.721	0.120
	Exp.[5]	5.455	56.8	0.276	0.000	0.345	0.731	0.128

TABLE II. Rhombohedral structure parameters of ordered-LNO $A_2BB'O_6$ corundum derivatives Li_2ZrTeO_6, Li_2HfTeO_6, Mn_2FeWO_6, Mn_3WO_6 and Zn_2FeOsO_6 from first-principles calculations and experiments. Wyckoff positions are 1a for A_1, A_2, B and B' cations, and 3b for O_1 and O_2 anions. The origin is defined by setting the Wyckoff position B'_x to zero. For ordered-LNO Mn_3WO_6 and Zn_2FeOsO_6, no experimental results are available.

		Magnetic order	Lattice constants		Wyckoff position									
			a (Å)	α (°)	A_{1x}	A_{2x}	B_x	B'_x	O_{1x}	O_{1y}	O_{1z}	O_{2x}	O_{2y}	O_{2z}
Li_2ZrTeO_6	Calc.	—	5.526	56.1	0.291	0.781	0.504	0.000	0.366	0.745	0.111	0.628	0.219	0.895
	Exp.[6]	—	5.497	56.1	0.298	0.768	0.507	0.000	0.390	0.729	0.133	0.621	0.235	0.893
Li_2HfTeO_6	Calc.	—	5.480	56.3	0.289	0.781	0.504	0.000	0.366	0.743	0.115	0.629	0.222	0.889
	Exp.	—	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mn_2FeWO_6	Calc.	*udu*	5.531	57.3	0.286	0.787	0.506	0.000	0.356	0.744	0.109	0.632	0.207	0.884
	Exp.[7]	NA	5.562	56.9	0.278	0.785	0.493	0.000	0.347	0.745	0.102	0.631	0.197	0.885
Mn_3WO_6	Calc.	*udu*	5.607	56.7	0.287	0.790	0.508	0.000	0.356	0.742	0.102	0.631	0.199	0.893
	Calc.	*uud*	5.613	56.6	0.283	0.779	0.493	0.000	0.384	0.693	0.124	0.595	0.234	0.848
	Exp.[8]	NA	5.605	56.7	0.283	0.788	0.510	0.000	0.351	0.744	0.104	0.631	0.190	0.901
Zn_2FeOsO_6	Calc.	FiM	5.410	56.7	0.284	0.783	0.504	0.000	0.376	0.732	0.114	0.619	0.223	0.885
	Exp.	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

TABLE III. Magnetic energy of different magnetic states relative to the lowest-energy state in Mn_2FeWO_6 and Mn_3WO_6, in units of meV per formula unit (f.u.).

	Energy (meV/f.u.)			
	uuu	*uud*	*udd*	*udu*
Mn_2FeWO_6	90.2	32.1	39.5	0.0
Mn_3WO_6	101.8	1.0	19.2	0.0

TABLE IV. Relative spin direction between different magnetic ions in Mn_2FeWO_6 and Mn_3WO_6.

	uuu	*uud*	*udd*	*udu*
A_1 and B	FM	AFM	FM	AFM
A_2 and B	FM	AFM	AFM	FM
A_1 and A_2	FM	FM	AFM	AFM

TABLE V. Ground state and midpoint structures of ordered-LNO candidates and the energy differences between B and B' sandwiched midpoint structures. The distances between A cations and the oxygen planes in the ground state are characterized by ξ_{1S} and ξ_{2S}. The energy difference between the B and B' sandwiched midpoint structures is ΔE. The Madelung energy difference between the B and B' sandwiched midpoint structures is ΔE^{M}.

Ordered-LNO	B	B'	Sandwiched cation	ξ_{1S} (Å)	ξ_{2S} (Å)	ΔE^{M} (meV)	ΔE (meV)
Li_2ZrTeO_6	Zr	Te	Zr	0.607	0.559	−186	−48
Li_2HfTeO_6	Hf	Te	Hf	0.582	0.550	−94	−29
Mn_2FeWO_6	Fe	W	W	0.623	0.707	2085	225
uud Mn_3WO_6	Mn	W	W	0.635	0.799	1666	266
udu Mn_3WO_6	Mn	W	W	0.642	0.790	1499	290
Zn_2FeOsO_6	Fe	Os	Os	0.565	0.574	382	102