Supporting Information for "Structural principles of cation ordering and octahedral tilting in A-site ordered double perovskites: ferroelectric $CaMnTi_2O_6$ as a model system."

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I. CRYSTAL STRUCTURES OF THE STUDIED SYSTEMS

The optimized crystal structures of the studied systems are provided as separate files in CIF format.

II. ABSOLUTE ELECTRONIC ENERGIES OF THE STUDIED SYSTEMS

Table I. Absolute energies of studied systems with columnar A-site ordering. The energies are normalized per formula unit (Z).

Tilt System	k-mesh	Absolute Energy/Z (Hartree)	Relative Energy (kJ/mol)
$a^+a^+a^+$	$5\times5\times5$	–3978.559814	31
$a^+a^+c^-$	$4\times4\times4$	–3978.568378	9
$a^-b^+a^-$	$6\times4\times6$	–3978.563829	21
$a^-b^-b^-$	$6\times6\times4$	–3978.551783	52
$a^-a^-a^-$	$6\times6\times4$	–3978.551780	52
$a^0b^+b^+$	$4\times4\times4$	–3978.554731	44
$a^+b^0c^-$	$4\times4\times4$	–3978.563927	20
$a^0b^-b^-$	$4\times6\times6$	–3978.550529	55
$a^0a^0c^+$	$4\times4\times8$	–3978.536814	91
$a^0a^0c^-$	$6\times6\times4$	–3978.538517	87
$a^0a^0a^0$	$6\times6\times8$	–3978.501563	184

Table II. Absolute energies of studied systems with planar A-site ordering. The energies are normalized per formula unit (Z).

Tilt System	k-mesh	Absolute Energy/Z (Hartree)	Relative Energy (kJ/mol)
$a^+a^+a^+$	$4 \times 4 \times 4$	–3978.546794	65
$a^+a^+c^-$	$4 \times 4 \times 4$	–3978.553181	49
$a^-b^+a^-$	$4 \times 4 \times 4$	–3978.561826	26
$a^-b^-b^-$	$6 \times 6 \times 4$	–3978.555895	41
$a^-a^-a^-$	$4 \times 6 \times 6$	–3978.555924	41
$a^0b^+b^+$	$4 \times 4 \times 4$	–3978.544915	70
$a^+b^0c^-$	$4 \times 6 \times 6$	–3978.557188	38
$a^0b^-b^-$	$4 \times 6 \times 6$	–3978.553096	49
$a^0a^0c^+$	$4 \times 4 \times 4$	–3978.537465	90
$a^0a^0c^-$	$6 \times 6 \times 4$	–3978.540274	82
$a^0a^0a^0$	$8 \times 8 \times 4$	–3978.501764	183

Table III. Absolute energies of studied systems with rock-salt A-site ordering. The energies are normalized per formula unit (Z).

Tilt System	k-mesh	Absolute Energy/Z (Hartree)	Relative Energy (kJ/mol)
$a^+a^+a^+$	$4\times4\times4$	–3978.547783	63
$a^+a^+c^-$	$4\times4\times4$	–3978.554239	46
$a^-b^+a^-$	$4\times6\times6$	–3978.561888	26
$a^-b^-b^-$	$6\times6\times4$	–3978.554775	44
$a^-a^-a^-$	$6\times6\times4$	–3978.554252	46
$a^0b^+b^+$	$4\times4\times4$	–3978.547653	63
$a^+b^0c^-$	$4\times6\times6$	–3978.558367	35
$a^0b^-b^-$	$6\times6\times6$	–3978.556047	41
$a^0a^0c^+$	$6\times6\times4$	–3978.542046	78
$a^0a^0c^-$	$6\times6\times6$	–3978.544687	71
$a^0a^0a^0$	$4\times4\times4$	–3978.501787	183

III. BASIS SET DETAILS FOR CA

For Ca, we used the following SVP level basis set, modified from Karlsruhe def-SVP for periodic calculations,

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20 9
0 0 6 2.0 1.0
35138.713929      0.39482520740E-02
5276.4111348      0.30234243552E-01
1200.4692589      0.14952019681
338.71810542      0.51597345713
109.85385922      1.0339510296
37.608880299      0.76937933526
0 0 3 2.0 1.0
73.107977555     -0.28268525011
8.2407705688      1.6796092142
3.2959812993      1.2803766016
0 0 2 2.0 1.0
5.2341800914     -0.76868604561E-02
0.84187220515     0.25382375978E-01
0 1 1 2.0 1.0
0.35               1.0 1.0
0 1 1 0.0 1.0
0.15               1.0 1.0
0 2 5 6.0 1.0
413.11313893      0.20327135354E-01
96.935786224      0.14730276362
30.372154659      0.54887167322
10.684776830      1.0440659818
3.8821258350      0.68653490684
0 2 2 6.0 1.0
1.7993016295      .75410246871
0.69189056530      1.3409296599
0 3 2 0.0 1.0
5.4979093879      0.73770011433E-01
1.3177128032      0.26052853169
0 3 1 0.0 1.0
0.32188682649     0.45233836380
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