First principles investigation of structural and electronic properties of hexagonal rare-earth ferrite systems, $RFeO_3$ (R = Lu - Er)

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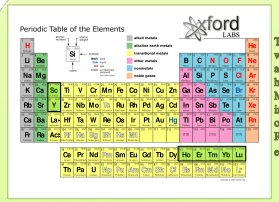
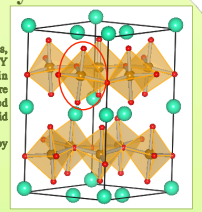
Hexagonal manganite systems



The $RMnO_3$ manganites, with R = Lanthanide , In, Y and Sc, crystallize in hexagonal structure, where Mn^{+3} ions are situated inside trigonal bipyramid oxygen environment and R^{+3} ions are coordinated by eight oxygen ions.



Most of the hexagonal manganite compounds are ferroelectric with a high ferroelectric transition temperature and order magnetically around 100 K

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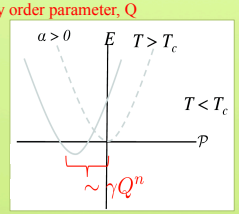
Multiferroic materials

Origin of Ferroelectricity

Polarization is a slave to the primary order parameter, Q

$$\mathcal{F}(P,Q) = \frac{1}{2}|\alpha|P^2 + \frac{1}{4}\beta P^4 + \frac{1}{2}\alpha_q Q^2 + \frac{1}{4}\beta_q Q^4 + \gamma P Q^n$$

n = faintness index

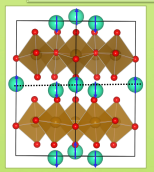


Once primary order parameter becomes non zero, a polarization is induced

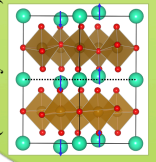
Craig J. Fennie and Karin M. Rabe, Phys. Rev B 72, 100103(R) (2005)
vanAken, Palstra, Fillipetti, Spaldin, Nature Materials 2004.

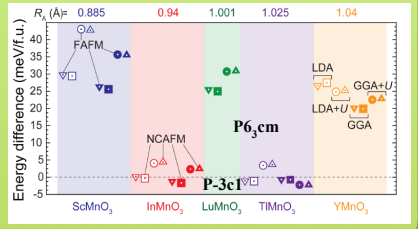
In case of hexagonal manganites the primary order parameter is a zone boundary (K_3) phonon mode

P6_3cm (185) (Polar)



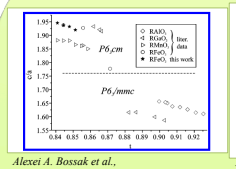
P-3c1 (165) (Centrosymmetric)



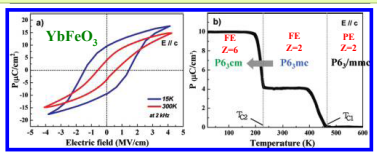


Yu Kumagai et. al, arXiv:1109.1448v1, 2011

Hexagonal ferrite systems



Alexei A. Bossak et al., Chem. Mater. 2004, 16, 1751.

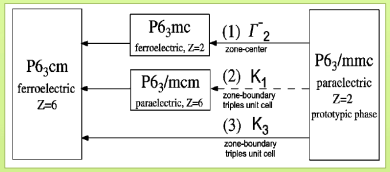


Young Kyu Jeong et al., J. Am. Chem. Soc. 134, 1450 (2012).

- **Stabilized via the epitaxy on the $ZrO_2(Y_2O_3)$ (111) substrate.**
- **Lattice mismatch is 3-4.5%**

Motivation

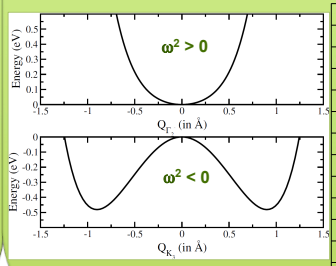
Possible transition paths from high temperature centrosymmetric P6$_3$/mmc state to the polar P6$_3$cm state



- The above mentioned experimental results on $YbFeO_3$ show that the transition from the high temperature paraelectric (PE) P6$_3$/mmc state to the trimarized polar P6$_3$cm state is mediated via an intermediate polar P6$_3$mc state. On the other hand so far no such intermediate phase has been reported for its manganite counterpart. In particular a direct transition from P6$_3$/mmc state to the trimarized polar P6$_3$cm (following path (3)) state has been recently confirmed for the prototype system $YMnO_3$ [*I.-K. Jeong et al. J. Appl. Crystall, 40, 730-735 (2007), A. S. Gibbs et al. Phys. Rev. B 83, 094111 (2011)*]. This indicates that the underlying energetics of the hexagonal ferrite systems are different compare to their manganite counter part, which is investigated in details in the present study.

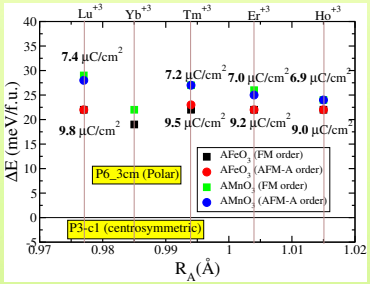
Results

Computed phonon frequencies



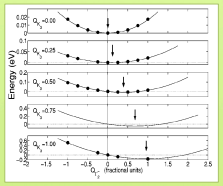
System	Phonon frequencies (cm^{-1})		
	Γ_2^-	K_1	K_3
$HoFeO_3$	73	276	114 i
$ErFeO_3$	75	271	113 i
$TmFeO_3$	78	268	112 i
$YbFeO_3$	115	298	97i
$LuFeO_3$	84	263	108 i
$HoMnO_3$	65	249	125 i
$ErMnO_3$	61	245	128 i
$TmMnO_3$	56	240	130 i
$YbMnO_3$	117	266	127i
$LuMnO_3$	54	232	132 i

Ground state structure



- The hexagonal phase of $RFeO_3$ (R = Lu-Er) is stabilized in the polar P6$_3$cm state.
- The net polarization of the ferrite systems is comparable with their manganite counterparts.

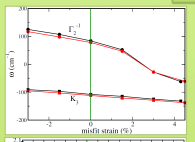
Contribution of zone center polar mode

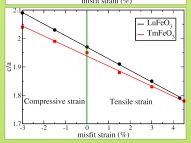


System		HoFeO$_3$	ErFeO$_3$	TmFeO$_3$	LuFeO$_3$
Polarization (μC/cm^2)	With Γ_2^-	9.0	9.2	9.5	9.8
	With out Γ_2^-	0.04	0.01	0.02	0.09
System		HoMnO$_3$	ErMnO$_3$	TmMnO$_3$	LuMnO$_3$
Polarization (μC/cm^2)	With Γ_2^-	6.9	7.0	7.2	7.4
	With out Γ_2^-	-0.04	-0.27	0.05	0.23

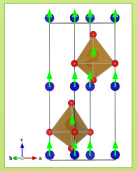
Polarization is developed through the coupling of K_3 mode with polar Γ_2^- mode.

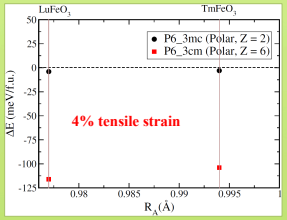
Effect of epitaxial strain





Γ_2^- mode





Conclusions

- From first principles density functional investigation we have shown that similar to hexagonal rare-earth manganite systems hexagonal ferrites are ferroelectric with comparable magnitude of polarization.
- Large polarization is driven by quadratic coupling between K_3 mode and the polar Γ_2^- mode.
- Our results indicate a direct transition from the PE P6$_3$/mmc to FE P6$_3$cm phase.