Realising functional polymorphs: temperature, pressure and chemistry in pursuit of multiferroics

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The synthesis of a phase combining electrical polarisation P and spontaneous magnetisation M is hard because of the distinct electronic structure requirements for the main mechanisms producing each property e.g., the closed-shell d^0 Ti^{4+} and s^2 Pb^{2+} cations which produce polarisation in the ferroelectric perovskite oxide $PbZr_{1-x}Ti_xO_3$ do not have the unpaired electrons needed for magnetisation. In addition to this fundamental scientific challenge to the control of properties by designed substitution, it is technologically important to efficiently combine these two long-range orders: multiferroic or magnetoelectric information storage offers the possibility to overcome the drawbacks of ferroelectric memory (slow writing) and magnetic random access memory (high power density) and opens the possibility of four state memory with reduced energy consumption.

Several methods can by used to overcome this the most straight forward in the synthesis of metastable phases at high temperature and pressure and their quenching to room temperature, this will be, discussed in terms of the synthesis of metastable perovskite related phases such as : Bi_2ZnTiO_6,(1) Bi_2CoTiO_6, $ScFeO_3$(2) and $GaFeO_3$.

Alternatively the control of symmetry braking by using crystal chemistry and symmetry arguments will be introduced and exemplified by two practical examples in the area of improper ferroelectrics and potentially multiferroics has recently received significant attention. The prediction that a combination of $a^-a^-c^+$ tilting and layered ordering of the A site cations along [001]perov in perovskite ABX_3 systems or in the even n Ruddleston Popper (RP) phases ($A_{n+1}B_nX_{3n+1}$), leads to non-centrosymmetric structures which are predicted to have significant switchable polarisations. Two practical examples will be discussed:

Suitable doping of the RP phase $SrLn_2Fe_2O_7$ can induce a polar tilted ground state where weak ferromagnetism and magnetocelecricity are induced by the appearance of the polar tilted state. The transition temperatures and phase sucession is dependant on the degree of doping.(3)

The oxide heterostructure $[(YFeO_3)_5(LaFeO_3)_5]_{40}$,which is magnetically ordered and piezoelectric at room temperature,(4) has been constructed from two weak ferromagnetic $AFeO_3$ perovskites with different A cations using RHEED-monitored pulsed laser deposition.1 Here we elaborate a superspace description of cation ordering in tilted perovskites that allows the prediction of the symmetry of arbitrary cation ordered superlattices, along <100>perov, <110>perov and <111>perov and ordering of both A and B cations, of the various tilted perovskites, which also rationalizes the observed domain structures. This approach is expaned to include magnetic symmetry and the potential for finding other suitable structural distortions in non-perovskite systems will be discussed.

References:

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