Poster Presentation

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Structural modulations in multiferroic tetragonal tungsten bronze $K_xMn_xFe_{1-x}F_3$

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Multiferroic materials showing coupling of the different order parameters (ferroelectric, ferromagnetic, ferroelastic) are interesting not only from a fundamental perspective, but also from a technological point of view, e.g. for to the development of new storage technologies. However, the coexistence of (ferro)magnetism and ferroelectricity is considered a rare phenomenon. Whilst this may be true for perovskite oxides, where empty *d* shells favor the off-centering of ions but counteract magnetism, this intrinsic limitation can be avoided by moving to different structure types, and/or away from oxides. An example of non-perovskite, non-oxide multiferroic systems are the tetragonal tungsten bronze (TTB) fluorides $K_xM^{2+}_xM^{3+}_{1-x}F_3$ (x = 0.4 – 0.6), which show coexistence of electric and magnetic ordering [1]. Here we present a detailed structural study on a series of TTB fluorides, $K_xMn_xFe_{1-x}F_3$ (x = 0.4 – 0.55). $KMnFeF_6$ has been previously described as tetragonal $P4_2bc$ and orders ferrimagnetically below T = 148 K [2]. Additional satellite reflections were found in transmission electron microscopy experiments and attributed to ferroelastic domains arising from tilting of MF_6 octahedra, but the reported bulk powder XRD measurements indicated only tetragonal symmetry [3]. We used high-resolution powder diffraction techniques to reinvestigate the crystal structure as a function of temperature in comparison with DSC data. Our results reveal a structural distortion to orthorhombic symmetry (*Ccc*2) at room temperature, which diminished when moving to the end members of the series ($x \rightarrow 0.4$ and $x \rightarrow 0.6$). Although structurally subtle, this distortion may indicate a ferroelectric state, similar to K_xFeF_3, where ferroelectricity is observed only in the orthorhombic phase. On heating, an anomaly in the *c*-axis lattice parameter accompanies a phase transition to centrosymmetric $P4_2/mbc$ around 320 – 350 K, marking the transition from ferroelectric – paraelectric state.

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