ESRF	**Experiment title:** **X-ray and temperature induced phase transitions in ternary fluorides with tungsten bronze structure**	**Experiment number**: CH3361
Beamline: ID31	**Date of experiment**: from: 8/6/2011 to: 14/6/2011	**Date of report**: 31/8/2011
Shifts: 12	**Local contact(s)**: Adrian Hill	*Received at ESRF:*

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Report:

The aim of the proposed experiment was to study the structural behaviour of selected members of the family of transition metal fluorides adopting a distorted tungsten bronze structure (TTB) as a function of temperature and X-ray illumination. Such materials are prototypical multiferroic systems where charge and magnetic ordering can couple with ferroelectricity and ferroelasticity. The most prominent example of TTB ferroelectric/ferroelastic fluoride is $K_{0.6}FeF_3$ which has been extensively studied over the last 30 years. At room temperature it crystallizes in an orthorhombic distortion of the fundamental TTB lattice (polar space group *Pba2*) displaying doubling of the *c* axis which is driven by a particular charge ordered (CO) pattern. Ferroelectricity and ferroelasticity were explained in terms of atomic coordinates relationships and atomic displacements along the polar axis [1]. It is important to notice here that the *Pba2* structural model gives 10 Fe^{2+}, 6 Fe^{3+}, and 4 $Fe^{2.5+}$ ions and implies only partial charge order with some sites statistically occupied by both Fe^{2+} and Fe^{3+}. $K_{0.6}FeF_3$ shows an interesting structural phase diagram; a first structural transition around 570 K from tetragonal to orthorhombic, a second transition at 490 K where partial Fe^{2+}/Fe^{3+} CO occurs, and a third transition around 290 K to a ferroelectric monoclinic phase (FES) which was observed by electron diffraction [2,3]. This last transition is driven by the tilting of the $[FeF_6]$ octahedral. Recent theoretical work on $K_{0.6}FeF_3$ proposed that charge order is the real driving force behind ferroelectricity with polarization induced by electronic degrees of freedom [4].

To get a further insight into this new type of mechanism for ferroelectricity, we synthesised the analogous compound $K_{0.6}CrF_3$ with the aim of unveiling for the first time its structural and magnetic phase diagram and draw analogies with the well studied $K_{0.6}FeF_3$. Magnetic measuraments have revealed that the presence of magnetically ordered phases below 30 K. Rietveld refinements of the room temperature diffraction profile were first initiated assuming a orthorhombic structural model (**o**) similar to $K_{0.6}FeF_3$ (*Pba2*; $a = 13.14861(5)$, $b = 12.55887(4)$, $c = 7.84013(2)$). The analysis of the Cr-F bond distances for the six symmetry independent Cr atoms suggests a charge ordering scheme where Cr^{2+} and Cr^{3+} tend to alternate along the *c* axis as displayed in Fig1. In the layer at $z = 0.25$, the extra-perovskite site Cr1 is occupied by $Cr^{2+,}$ whereas Cr^{2+} and Cr^{3+} alternate around the perovskite cage in the Cr3 and Cr5 sites, respectively. At $z = 0.75$ the extraperovskite site Cr2 is occupied by $Cr^{3+,}$ whereas around the perovskite cages Cr4 and Cr6 are occupied statistically and by Cr^{2+}, respectively. As previously mentioned within the *Pba2* model only partial charge order is possible. While the results of the Rietveld refinements were satisfactory the presence of a statistically occupied site was not convincing given the electronic differences between the JT active Cr^{2+} and Cr^{3+}. A more detailed investigation of the RT diffraction profile (data were collected over 4 hours) revealed the presence of superlattice peaks clearly indicating a further distortion to lower symmetry (Fig 2). Such a distortion must be driven by a full charge ordering and model were tested by considering different types of charge ordering schemes on the z = 0.75 layer. Rietveld refinements clearly indicated that at RT the structure is monoclinic in the space group *P112* where Cr^{2+} and Cr^{3+} at z = 0.75 are also alternating around the perovskite cage (Fig 1). This type of charge ordering was never observed before in related TTB structure but was predicted theoretically for $K_{0.6}FeF_3$ as one of the possible charge ordering patterns that induce ferroelecticity.

The fully CO monoclinic structure is robust upon cooling and no structural phase transitions are observed down to 5 K. However, a striking feature of the data at 100 K was that with increasing X-ray exposure time the diffraction peaks continuously shifted and within 30 min a new phase was stabilized. The diffraction profile of the newly formed phase was indexed in a orthorhombic cell (**o'**) with lattice constants $a_{o'} = \sqrt{2}a_o$, $b_{o'} = \sqrt{2}b_o$ $c_{o'}= 1/2c_o$ in the space group *Cmm2* (Fig 3). This new structure is related to the ferroelastic/ferroelectric (FES) superstructure reported for $K_{0.6}FeF_3$ and $Ba_2NaNb_5O_{15}$ [2,3]. Detailed Rietveld refinements showed that X-ray irradiation induces a melting of the charge ordering where all the Cr sites are now statistically occupied by $Cr^{2+/}Cr^{3+}$ with a phenomenology similar to the CO manganites. The loss of CO could have tremendous implication on the physical properties and most probably a shift to a different ferroelectric mechanism. We performed a number of different experiments in order to get a better insight on the nature of such X-ray induced transition. At 5 K the transition is very fast and the charge disordered phase is formed within 5 min. The phase transition is reversible and switching off the X-ray light at 5 K for one hour leads to the recovery of the CO structure. In addition the X-ray effect occurs only below 150 K and illumination at higher temperature does not induce any change. Data were also collected at 20, 50, 100 and 150 K to study the kinetics of the X-ray induced transition. Refinements of all these sets of data are still in progress.

Heating $K_{0.6}CrF_3$ above room temperature leads to two different phase transitions occurring at 500 and 850 K respectively, linked to the gradual loss of charge ordering which occurs in two consecutive steps. (fully CO monoclinic → partially CO orthorhombic *Pba2*– tetragonal TTB).

We were also interested in understanding what would be the effect of changing the nature of the transition metals on the complex phase diagram showed by $K_{0.6}CrF_3$. Exchanging the JT active Cr^{2+} with the non-active Mn^{2+} leads to the isolation of $K_{0.5}Mn_{0.5}Cr_{0.5}F_3$ which is a ferrimagnetic transition at 27 K. The room temperature diffraction profile shows that this systems crystallises in the acentric tetragonal space group $P4_2bc$ (a = 12.65302(1), c = 7.93842(1)) and implies partial charge ordering with the perovskite-cage sites statistically occupied by Mn^{2+} and Cr^{3+} (Fig 3). While this material should still be ferroelectric (measurements of the dielectric constants and polarization are currently in progress), the structural behaviour of $K_{0.5}Mn_{0.5}Cr_{0.5}F_3$ is profoundly different from $K_{0.6}CrF_3$. No X-ray or temperature induced phase transitions are observed between 5 and 823 K and the structure remains strictly tetragonal. A discontinuity in the temperature evolution of the lattice parameters is observed at 400 K and it's linked to a strong reduction of the tilting of the CrF_6/Mn_6 octahedra. Rietveld refinements of the neutron data are currently under progress to define the magnetic structure.

Our results clearly demonstrate the richness of the structural/electronic and magnetic phase diagram of the family of TTB fluorides and pushes for more investigations. Small changes in compositions by varying the relative amounts of 2+/3+ ions and the nature of the transition metal leads to completely different charge ordering patterns and multiferroic properties. Revealing the electronic and magnetic behaviour and determining the performance limits of these families of TTB transition metal fluorides will greatly enhance our current understanding strongly correlated systems. It should be noticed that high-resolution/high-intensity instrumental characteristics of ID31 with access to excellent quality data at high Q have been pivotal for the success of our work.

References : [1] Abrahams, S. C. *et al. Ferroelectrics* **1992**, *135*, 21761. [2] Mezzadri F. *et al. Phys. Rev. B.* **2008***, 78,* 06411. [3] Fabbrici *et al. Chem Mater.* **2004***, 16, 3007.* [4] Yamauchi K. *et al. Phys Rev Lett* **2010**, *105*, 107202.

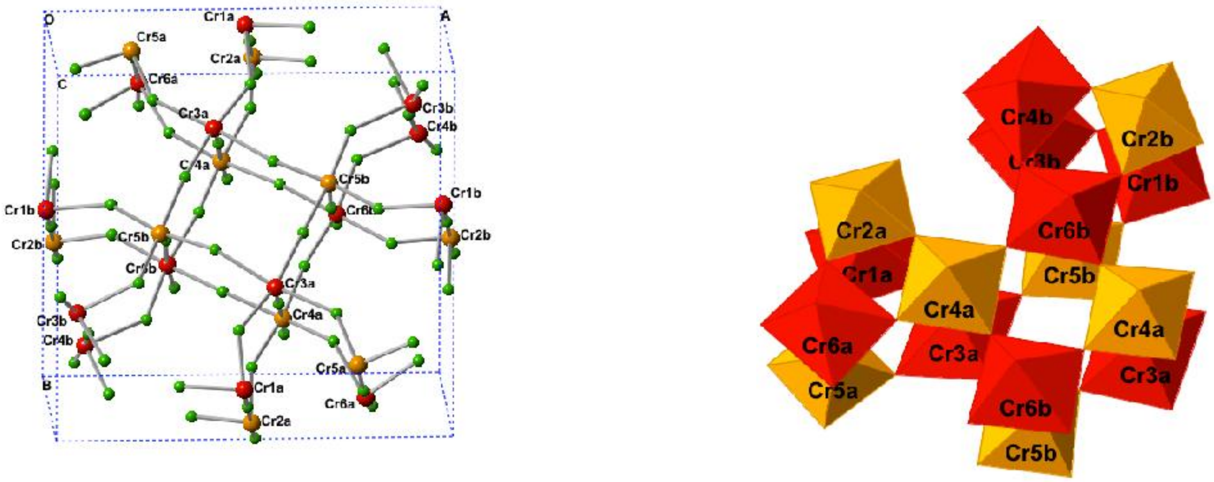

Fig.1. Refined crystal structure of $K_{0.6}CrF_3$ in the space group *P* 112. Yellow spheres/octahedra indicate Cr^{3+} and red spheres/octahedra indicate Cr^{2+}. In the orthorhombic *P* ba2 model the Cr positions indicated as 4a and 4b are statistically occipied.

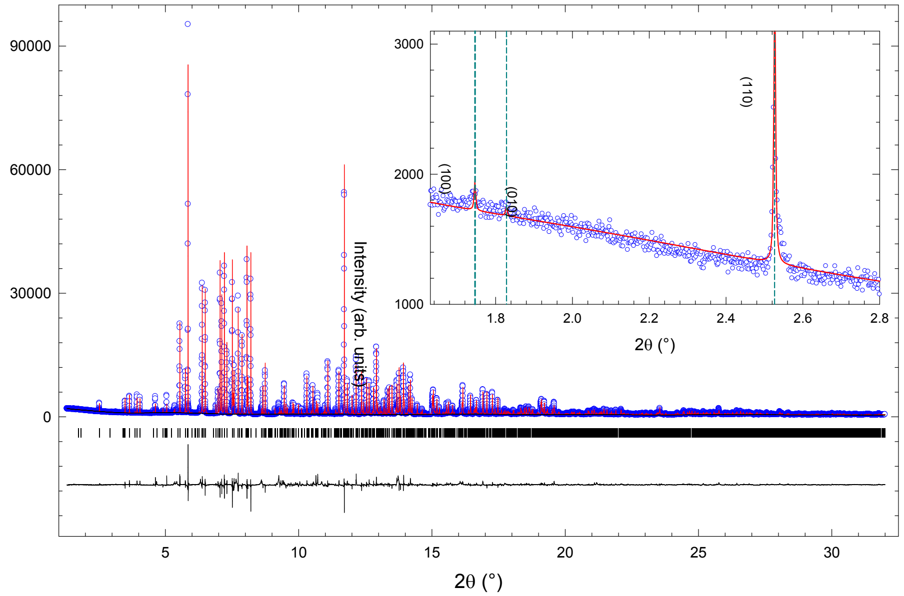

Fig.2. Rietveld refinement of the 300 K data of $K_{0.6}CrF_3$. Inset: superlattice peaks indicating the monoclinic distortion. Data were collected at λ= 0.4 Å

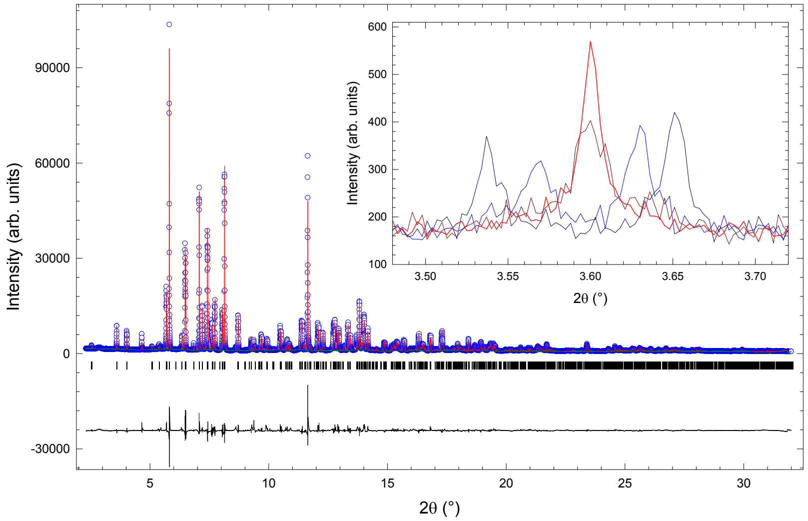

Fig.3. Rietveld refinement of the X-ray induced phase of $K_{0.6}CrF_3$ at 5 K (orthorhombic- *C mm2*). Inset Evolution of the diffraction profiles at with X-ray illumination time at 5 K (black: 1 min, blue: 6 min, dark red: 11 min and red: 20 min). Data were collected at λ= 0.4 Å