


**Experiment title:**

Structural investigation of Pb-based perovskite-like ferrites with crystallographic shear planes

**Experiment number:**

HS-4395

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**Report:**

The experiment was devoted to a comprehensive structural study of the perovskite-based materials modulated by periodically spaced parallel translational interfaces (crystallographic shear (CS) planes). According to the (3+1)D structure model [1], the diffraction patterns of such compounds can be interpreted with a basic monoclinic unit cell with  $a \approx b \approx c \approx a_p$  ( $a_p$  - perovskite subcell parameter), modulation vector  $\mathbf{q} = \alpha\mathbf{a}^* + \gamma\mathbf{c}^*$  and the superspace group  $X2/m(\alpha 0\gamma)$ , where  $X = [1/2, 1/2, 1/2, 1/2]$  is the centering vector. The chemical composition of the compounds is related to the components of the modulation vector as  $\text{Pb}_{6\gamma+2\alpha}\text{Bi}_{1-7\gamma-\alpha}\text{Fe}_{1+\gamma-\alpha}\text{O}_{3-3\gamma-\alpha}$ . Five compounds in the Pb-Bi-Fe-O system with the compositions listed in the Table 1 were investigated in the temperature range from 80K to 900K (above the AFM transition temperature). High resolution and signal-to noise ratio of the ID31 beamline allowed us to determine the components of the modulation vector (Table 1) and collect the diffraction data with the satellites up to third order clearly discerned.

 Table 1. Chemical compositions, unit cell parameters and the components of the modulation vector for the  $\text{Pb}_{6\gamma+2\alpha}\text{Bi}_{1-7\gamma-\alpha}\text{Fe}_{1+\gamma-\alpha}\text{O}_{3-3\gamma-\alpha}$  compounds.

Composition	$a$ , Å	$b$ , Å	$c$ , Å	$\beta$ , deg.	$\alpha$	$\gamma$
$\text{Pb}_{0.866}\text{Bi}_{0.096}\text{Fe}_{1.038}\text{O}_{2.567}$	3.9377(1)	3.9337(1)	4.0047(1)	92.6028(9)	0.06736(3)	0.11586(2)
$\text{Pb}_{0.772}\text{Bi}_{0.193}\text{Fe}_{1.035}\text{O}_{2.615}$	3.92801(3)	3.92638(3)	4.05172(3)	92.2254(4)	0.05789(2)	0.10362(1)
$\text{Pb}_{0.678}\text{Bi}_{0.290}\text{Fe}_{1.032}\text{O}_{2.662}$	3.92111(3)	3.91931(2)	4.09271(3)	91.9044(4)	0.05003(1)	0.09132(1)
$\text{Pb}_{0.547}\text{Bi}_{0.430}\text{Fe}_{1.023}\text{O}_{2.725}$	3.91413(4)	3.91176(4)	4.13833(5)	91.5549(5)	0.04121(2)	0.07491(1)
$\text{Pb}_{0.442}\text{Bi}_{0.541}\text{Fe}_{1.017}\text{O}_{2.781}$	3.91163(5)	3.90815(4)	4.16777(6)	91.2980(7)	0.03403(2)	0.06055(2)

The Rietveld refinement of the modulated structures was performed using saw-tooth functions for modelling the displacement of the perovskite blocks due to crystallographic shear operation and the precise atomic arrangements at the interfaces between the perovskite block. The pattern of antiferroelectric displacements of the Pb, Bi and Fe atoms was obtained by adding orthogonalized harmonic displacement modulation functions on top of the linear displacements of the saw-tooth functions. Fig. 1 demonstrates the

resulting structure of a commensurate approximant ( $a = 117.35\text{\AA}$ ,  $b = 3.9081\text{\AA}$ ,  $c = 125.03\text{\AA}$ ,  $\beta = 91.2980(7)^\circ$ ) of the  $\text{Pb}_{0.442}\text{Bi}_{0.541}\text{Fe}_{1.017}\text{O}_{2.781}$  compound.

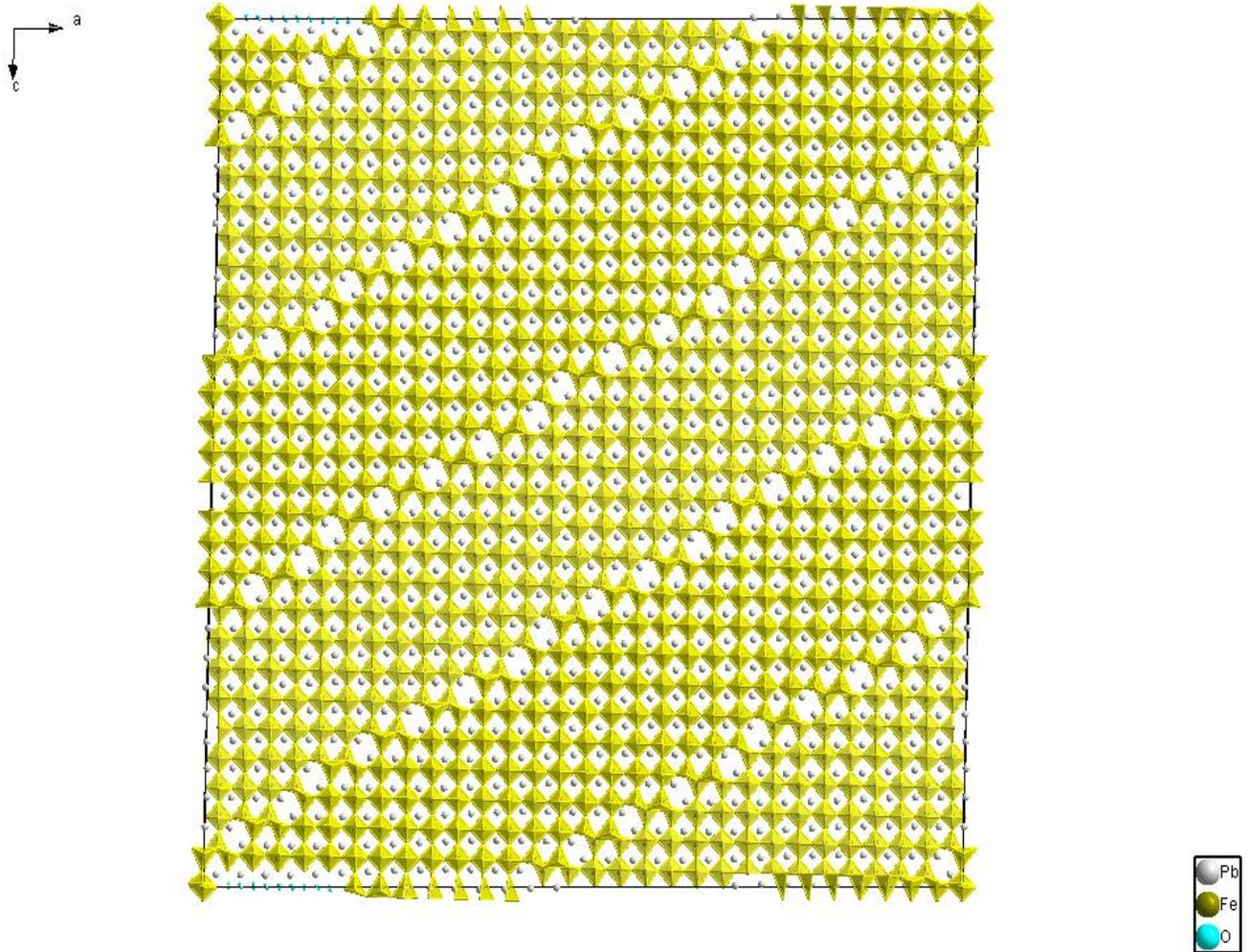


Figure 1. A commensurate approximant of the  $\text{Pb}_{0.442}\text{Bi}_{0.541}\text{Fe}_{1.017}\text{O}_{2.781}$  structure. The Fe atoms are situated at the yellow octahedra and distorted tetragonal pyramids. The Pb and Bi atoms are shown as spheres.

The CS planes in the  $\text{Pb}_{6\gamma+2\alpha}\text{Bi}_{1-7\gamma-\alpha}\text{Fe}_{1+\gamma-\alpha}\text{O}_{3-3\gamma-\alpha}$  compounds keep nearly constant  $\sim (509)_p$  orientation and changing the chemical composition occurs due to variation of the thickness of the perovskite blocks between the CS planes. The  $\text{FeO}_6$  octahedra of the perovskite block are transformed into distorted  $\text{FeO}_5$  tetragonal pyramids at the interfaces between the perovskite blocks. Changing the linkage of the polyhedra from corner-sharing in the parent perovskite structure to the edge-sharing at the interfaces reduces the oxygen content thus adopting the structure to different Pb/Bi ratio. The Pb, Bi and Fe atoms demonstrate polar displacements which are arranged in an antiparallel manner on both sides of the interfaces resulting in an antiferroelectric type structure.

Phase transition in the  $\text{Pb}_2\text{Ba}_2\text{BiFe}_5\text{O}_{13}$  compound with the  $(-101)$  CS planes have been investigated. The compound transforms from the high temperature orthorhombic  $Ammm$  structure to the low temperature monoclinic  $A2/m$  structure. The transformation is accompanied by a gradual evolution of the anisotropic broadening of the reflections and appearance of broad shoulders due to monoclinic distortions (Fig. 2). Such extremely complex diffraction profile makes Rietveld refinement impossible without taking into account the defect structure of the material. Using HRTEM it was realized that the low temperature phase consists of nano-sized monoclinic twinned lamellae also containing numerous antiphase boundaries. The synchrotron diffraction profiles will be used for the refinement of the crystal and defect structure of the material with the DISCURS program package.

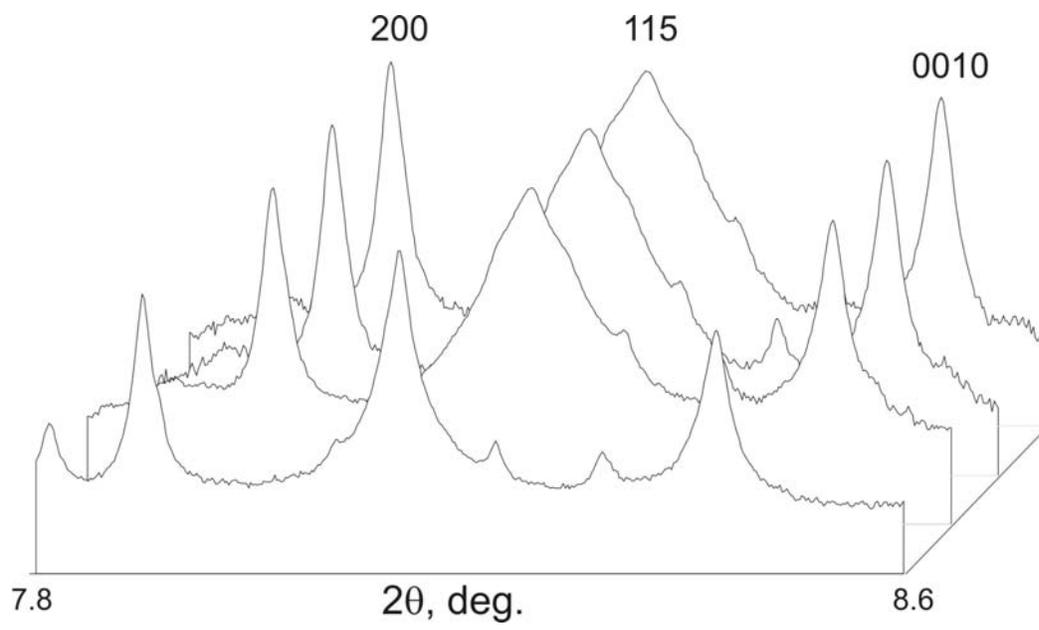


Figure 2. Changing the shape of the reflections at the  $Ammm$ - $A2/m$  phase transition in  $\text{Pb}_2\text{Ba}_2\text{BiFe}_5\text{O}_{13}$ .

**References.**

1. A.M. Abakumov et al., *Chem. Mater.*, v. 23, pp 255–265 (2011).