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# Synthesis, structural and magnetic characterisation of the fully fluorinated compound 6H–$BaFeO_2F$

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ABSTRACT

The compound 6H-$BaFeO_2F$ ($P6_3/mmc$) was synthesised by the low temperature fluorination of 6H-$BaFeO_{3-d}$ using polyvinylidenedifluoride (PVDF) as a fluorination agent. Structural characterisation by XRD and NPD suggests that the local positions of the oxygen and fluorine atoms vary with no evidence for ordering on the anion sites. This compound shows antiferromagnetic ordering at room temperature with antiparallel alignment of the magnetic moments along the *c*-axis. The use of PVDF also allows the possibility of tuning the fluorine content in materials of composition 6H-$BaFeO_{3-d}F_y$ to any value of $0 < y \leq 1$. In addition, the oxygen content, and therefore the iron oxidation state, can be tuned by applying different partial pressures of oxygen during the reaction.

## 1. Introduction

Perovskite type $A^{[12]}B^{[6]}X_3$ compounds are widely used for a variety of applications, such as fuel cell cathodes, solid electrolytes, and gas sensors [1–3].

In the perovskite structure, the $AX_3$ subsystem forms a close packed lattice, where the stacking sequence can differ [4] from purely cubic (c… e.g. for $SrFeO_2F$ [5–9] and $BaFeO_2F$ [7,10–12] (both space group $Pm\overline{3}m$) to purely hexagonal (h… e.g. for $BaCoO_3$ [13]) and can also form lattices in between those two extremes (e.g. cchcch… for 6H–$BaFeO_{3-d}$ [14–19] or chcch… for 15R–$BaFeO_{3-d}F_{0.2}$ [20–22]). For a fully filled anion lattice $X_3$, all the B cations are octahedrally coordinated and the connection to the neighbouring octahedrons is determined from the stacking sequence. For a cation between cc layers, the octahedron is connected by corners to 6 neighbouring octahedra (3 in the layer above, 3 in the layer below), whereas for a cation between hc layers, it is connected by faces to one octahedron via the h layer and by corners to 3 octahedra via the c layer. For a cation between hh layers the connection is to 2 octahedra by faces (1 in the layer above, one in the layer below).

A range of factors can be responsible for the type of structure adopted. In addition to electronic and electrostatic reasons the average oxidation state of the B cation and therefore the relative average size of the ions, numerically expressed in the tolerance factor *t* [4], strongly influences the structure adopted.

The pure oxide $BaFeO_{3-d}$ can be prepared via a simple high temperature solid state reaction from the metal-oxides or -carbonates. For this system the oxygen partial pressure has been shown to be of crucial importance in determining the type of structure adopted [7,14,23,24] particularly at higher temperatures. These phases and others can be fluorinated by a variety of fluorination agents [25], and prior studies have reported either a partially fluorinated $BaFeO_{3-d}F_y$ [20–22] in a 15R perovskite structure (chcch…) or fully fluorinated cubic $BaFeO_2F$ [7,10–12] where the latter contains only $Fe^{3+}$ and can be prepared by low temperature fluorination of the precursor oxide $BaFeO_{2.5}$ (space group $P2_1/c$, vacancy ordered distorted cubic perovskite) using PVDF.

Low temperature treatments of perovskite phases have, for many years, been known to be suitable to modify the average transition metal oxidation states and therefore allow for the synthesis of different modifications of the same product, e.g. cubic and hexagonal $SrMnO_3$ [26]. Recently, Hayashi et al. showed that cubic $BaFeO_3$ can be made by low temperature oxidation of $BaFeO_{2.5}$ ($P2_1/c$) [23]. Formation of the different modifications is supported by the good ionic conductivity of the anions, whilst the Ba/Fe substructure remains immobile at low temperatures [20]. The PVDF route [7,25,27] has also been shown to be a “chimie douce” route allowing the formation of kinetically stable products which decompose at higher temperatures to the thermodynamically most stable products.

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The reaction mechanism for the PVDF method depends on the material which is to be fluorinated [25]. For the fluorination of $BaFeO_{2.5}$ to cubic $BaFeO_2F$, two $F^-$ ions replace one $O^{2-}$ ion (and the carbon residues of the polymer are burnt off by the oxygen from the air) [7,10,11], whereas for the fluorination of $SrFeO_3$ to cubic $SrFeO_2F$ one $F^-$ ion replaces one $O^{2-}$ ion (supported by the stability of the trivalent oxidation state of iron and/or the reductive potential of PVDF) [5,6]. Hence the filling of vacancies and/or the substitution of oxygen ions are the possible reaction mechanisms for this method of fluorination (for nonstoichiometric compounds (e.g. $Sr_{0.5}Ba_{0.5}FeO_{2.77}$ [7]) the reaction mechanism would be a combination of vacancy filling and substitution of oxygen).

Recent work has shown that perovskite phases with nearly single valent $Fe^{3+}$ show a high stability in their magnetic ordering even at elevated temperatures. $BaFeO_2F$ (space group $Pm\overline{3}m$) is a G-type antiferromagnet [10] and $SrFeO_2F$ [6] also shows antiferromagnetic ordering at ambient temperature. 15R–$BaFeO_{3-d}F_y$ (space group $R\overline{3}m$, $0.15 \leq y \leq 0.30$) and 6H–$Ba_{0.8}Sr_{0.2}FeO_{3-d}F_y$ (space group $P6_3/mmc$, $0.15 \leq y \leq 0.25$) were also shown to be antiferromagnetically ordered, where the magnetic moments align in different directions with respect to the direction along which the $AX_3$ layers lie [22]. All these phases show magnetic ordering above room temperature, whereas fluorine-free mixed valent 6H–$BaFeO_{3-d}$ (space group $P6_3/mmc$, $d \sim 0.15$) orders below 130 K [16].

In this paper, we report the first synthesis of hexagonal 6H–$BaFeO_2F$ (space group $P6_3/mmc$) by low temperature fluorination of 6H–$BaFeO_{3-y}$ using polyvinylidenedifluoride (PVDF) as a fluorination agent. We report on the characterisation of the sample by neutron diffraction and magnetic measurements as well as by high temperature XRD to investigate the thermal stability towards decomposition. We also describe preliminary results on the synthesis of partly fluorinated samples 6H–$BaFeO_{3-d}F_y$ ($0 < y < 1$) and use lattice volume relationships to provide an estimation of their oxygen content (and consequent iron oxidation state).

## 2. Experimental

### 2.1. Sample synthesis

The precursor oxide 6H–$BaFeO_{3-d}$ was prepared by a solid state reaction. Stoichiometric mixtures of high purity $BaCO_3$ and $Fe_2O_3$ powders (Sigma Aldrich, $\geq 99.9\%$) were ground using a planetary ball mill (Fritsch pulverisette 7, 350 rpm, 1.33 h) and heated to 970 °C for 12 h under flowing $O_2$. The samples were slowly cooled to room temperature (20 °C/h) to increase the oxygen uptake and ensure the formation of the pure 6H–$BaFeO_{3-d}$ phase and the procedure was repeated a second time.

For the preparation of the oxide fluorides of composition $BaFeO_{3-d}F_y$($y=0.2$, 0.4, 0.8, 1), stoichiometric amounts of the as prepared 6H–$BaFeO_{3-d}$ and polyvinylidenedifluoride (PVDF) were thoroughly ground in *n*-pentane (for the synthesis of $BaFeO_2F$, $y=1$, a 4% excess of PVDF was used). The mixtures were then slowly heated to 370 °C (20 °C/h) under air and kept at this temperature for 20 h; slow heating was found to be beneficial to minimise the amount of $BaF_2$ impurity formed during the reaction (~ 1 wt%). The as prepared oxide fluoride materials were subsequently heated to 370 °C for 4 h under flowing $O_2$ to allow uptake of oxygen, and hence maximise the Fe oxidation state.

Structural studies focused on the 6H–$BaFeO_2F$ phase, which was shown to be metastable and its thermal decomposition was confirmed by studying the high temperature decomposition products arising from heating at 1000 °C for 5 min in air.

### 2.2. Diffraction experiments

XRD patterns were recorded with a Bruker D5005 diffractometer with Bragg-Brentano geometry and a fine focus X-ray tube with Cu anode. No primary beam monochromator was attached. A PSD detector and a fixed divergence slit were used. The total scan time was 16 h for the angular range between 5 and 140° $2\theta$.

High temperature XRD of 6H–$BaFeO_2F$ was performed with a Bruker D8 diffractometer with Bragg-Brentano geometry and a fine focus X-ray tube with Cu anode in a $2\theta$-range from 20 to 60° and at temperatures between 30 and 750 °C in steps of 30 °C. A primary beam monochromator was attached and a LYNX eye detector and fixed divergence slit were used. The total scan time was 1 h for the angular range between 20 and 60° $2\theta$ for each temperature step.

Time of flight powder neutron diffraction (NPD) data were recorded on the newly upgraded Polaris medium resolution diffractometer at the ISIS pulsed spallation source (Rutherford Appleton Laboratory, UK). 4 g of 6H–$BaFeO_2F$ powder was loaded into a 8 mm diameter thin-walled, cylindrical vanadium sample can and data collected at ambient temperature for 250 μA h proton beam current to the ISIS target (corresponding to $\sim 1^3/_4$ h beamtime).

Structure refinement of both the XRD and NPD data was performed using the Rietveld method with the program TOPAS 4.2 (Bruker AXS, Karlsruhe, Germany) [28]. For the room temperature XRD data the whole $2\theta$-range was used, while for the NPD data only those data collected in the highest resolution backscattering detector bank (bank 5, average $2\theta = 146.7°$, $d_{max} \sim 2.65$ Å) were used. The instrumental intensity distribution for the X-ray data was determined empirically from a sort of fundamental parameters set [29] using a reference scan of $LaB_6$, and microstructural parameters were refined to adjust the peak shapes for the XRD data. For the neutron diffraction data, a modified pseudo Voigt function plus a Gaussian crystallite size function was used to model the time-of-flight dependence of the peak width. Lattice parameters were constrained to be the same for neutron and XRD data and the same positional parameters were used and refined for both data sets. Independent thermal displacement parameters were refined for each atom type, but the values for O and F were constrained to the same value. While these parameters were also constrained to be the same both for X-ray, and neutron, powder diffraction data, an additional B overall value was refined for XRD data accounting for further effects such as absorption or surface roughness. Reflections that showed a large magnetic scattering contribution were omitted for the initial crystallographic refinement. Furthermore, the intensities of the XRD and NPD patterns were normalised to values between 0 and 1 to give each pattern similar weight in the Rietveld analysis.

Refinement of the magnetic structure of 6H–$BaFeO_2F$ was performed with the program GSAS [30,31] using the NPD data collected in one of the Polaris low angle detector banks (bank 3, average $2\theta = 52.2°$, $d_{max} \sim 7.02$ Å). The magnetic contribution to the diffraction pattern was modelled by introducing a second phase in triclinic space group *P1* containing just Fe atoms (to allow refinement of the magnetic structure without any symmetry restrictions), and calculating only its magnetic scattering. Unit cell, atomic positions and thermal vibration parameters in this second phase were set to the refined values determined above and then fixed to ensure that the triclinic (*P1*) cell remained geometrically and symmetrically hexagonal. Different orientations of the magnetic moments were investigated, including those previously reported for the similar compounds [22].

### 2.3. Magnetic measurements

DC susceptibility measurements were performed over the temperature range 5–300 K using a Quantum Design MPMS