Preparation of ytterbium substituted BiFeO₃ multiferroics by mechanical activation

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Abstract

Samples in the system Bi_{1-x}Yb_xFeO₃ (0.02 ≤ x ≤ 0.07) have for the first time been prepared by mechanical activation followed by sintering. XRD and DSC measurements show that the solubility limit of ytterbium in the R3c Bi_{1-x}Yb_xFeO₃ system is reached at x ~ 0.03. Higher ytterbium contents lead to a two-phase mixture of a main R3c phase of approximate composition Bi_{0.97}Yb_{0.03}FeO₃ and ytterbium enriched secondary phases that cannot be readily indexed or quantified due to their small amount. DSC and temperature-dependent XRD showed that while the magnetic ordering temperature, T_N, was unaffected by Yb substitution, the ferroelectric ordering, T_C, declined. Temperature-dependent XRD patterns show that all samples exhibit rhombohedral R3c to orthorhombic Pnma phase transitions. Diffuse reflectance spectroscopy suggests the potential use of the samples in photocatalytic applications due to their low band gap energy. Impedance spectroscopy and magnetic measurements show that samples are electrically homogenous and highly insulating, exhibiting antiferromagnetic behaviour at room temperature.

Keywords: Yb substituted BiFeO₃; Multiferroic BiFeO₃; Mechanical activation; Structure identification; Solid-solution.

1. Introduction

BiFeO_3 is one of the most promising and widely studied multiferroic materials (those which exhibit at least two of the so-called “ferroic” properties) because it presents spontaneous magnetic and electric ordering at room temperature [1-4]. BiFeO_3 has a rhombohedrically distorted perovskite structure belonging to the space group $R3c$ and exhibits G-type antiferromagnetic order below $T_N = 633$ K and ferroelectric behaviour below $T_C = 1103$ K [5-7]. On warming, the first phase transition that this material presents is second order, from an antiferromagnetic to a paramagnetic state, whereas the second transition at higher temperature is a first order phase transition from the ferroelectric to the paraelectric state [5]. Due to these relatively high transition temperatures, this material is a potential candidate to be used in several practical applications such as multistate memory devices for storing binary data or in magnetoelectric sensors [8]. Moreover, BiFeO_3 has a small optical band gap (2.1-2.8 eV), which implies a possible use as a photocatalyst for water splitting application and the degradation of organic pollutants [5, 9-10].

Despite the obvious potential of BiFeO_3 , there are several issues that are slowing down its implementation in practical applications. The most pressing of these problems is the difficulty in synthesising phase pure BiFeO_3 as the presence of undesired phases, normally $\text{Bi}_{25}\text{FeO}_{39}$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$, considerably deteriorates its electrical and magnetic properties [11-12]. Additionally, BiFeO_3 exhibits only a very weak spontaneous ferromagnetism at room temperature, and samples can have high leakage currents and dielectric losses due to the presence of Fe^{2+} ions, oxygen vacancies and bismuth deficiency due to the synthesis methods employed [13-14]. Therefore, the synthesis of BiFeO_3 and related materials has been widely explored in an attempt to enhance its physical properties.

One of the most widely adopted approaches for improving the properties of BiFeO₃ is cation substitution at the A or B positions of the ABO₃ perovskite, or by forming solid solutions with other perovskites phases [15-17]. A great number of transition metals (Mn, Co, Ti, Ni, W, Nb) have been employed as Fe substituents and rare earth elements (Sm, La, Y, Er, Dy, Gd) as Bi substituents [16-32]. Special attention has been focused on rare earth elements as it has been shown that the partial substitution of Bi for these elements can enhance the magnetoelectric properties of BiFeO₃ and related materials [14, 33-35]. Substitution of bismuth with small rare earth cations such as Yb³⁺ is attractive as the small ionic radius of ytterbium may lead to an enhanced lattice distortion and consequently an increase in the ferroelectric polarization of the materials [19]. However, only just a few attempts to prepare Bi_{1-x}Yb_xFeO₃ phases have been made and none of them provide a full characterization of the system in terms of structural analysis and electrical and magnetic properties [10, 19, 36-37].

In contrast to solution based approaches, the mechanochemical synthesis and mechanical activation of BiFeO₃ and related materials have been much less explored [38-45]. We have previously reported that BiFeO₃ and substituted Bi_{1-x}La_xFeO₃, can be readily prepared as phase-pure and highly insulating compounds using this approach [46-48]. Hence, exploring the preparation of the partial substitution of BiFeO₃ with ytterbium by mechanical activation is an obvious next step.

2. Materials and methods

Commercially available oxides were used as raw materials for the preparation of Bi_{1-x}Yb_xFeO₃ (nominal x = 0.02, 0.05, 0.07 compositions), without any further purification treatment: Bi₂O₃ (Sigma-Aldrich 223891-500G, 10 μm, 99.9% purity), Fe₂O₃ (Sigma-

Aldrich 310050-500G, $<5\ \mu\text{m}$, $\geq 99\%$ purity) and Yb_2O_3 (Sigma Chemical Company Y-3250-10G, $\geq 99\%$ purity). Suitable stoichiometric ratios of the starting materials were weighted and mechanically milled for 6 h at room temperature and under 7 bar of O_2 pressure using a Pulverisette 7 planetary mill (Fritsch, Idar-Oberstein, Germany), which has been modified for this purpose [48]. A hardened steel jar ($80\ \text{cm}^3$ volume) and balls (9 balls, 15 mm diameter) were used. The powder-to-ball mass ratio was set at 1:20 and the spinning rate of the supporting disc and the superimposed rotation in the opposite direction of the jars was set at 700 rpm. After milling, the collected powder was pressed into cylindrical pellets, with a diameter of 6 mm and thickness of approximately 2 mm, by applying an uniaxial pressure of 0.93 GPa. Subsequently, the pellets were sintered at 1098 K for 6 min in air, the cooling and heating rates were both set at $10\ \text{K min}^{-1}$. The density of the pellets was measured by the Archimedes' method, using distilled water at room temperature as the immersion liquid.

The crystal structure and the phase purity of the samples were characterized by X-ray diffraction (XRD). XRD patterns were collected with a Panalytical X'Pert Pro diffractometer working at 45 kV and 40 mA, using $\text{CuK}\alpha$ radiation and equipped with an X'Celerator detector and a graphite diffracted beam monochromator. Rietveld refinements were carried out with FullProf software [49]. The background was refined using a six order polynomial function, and a pseudo-Voigt profile function with axial divergence asymmetry was used to refine peak shapes. Peak shapes, lattice parameters, and scale were refined simultaneously. Atomic positions and isotropic temperature factors were subsequently included in the refinement. Temperature dependent X-ray diffraction patterns were recorded in $100\ \text{cm}^3\text{min}^{-1}$ airflow using Philips X'Pert Pro diffractometer equipped with a high temperature Anton Par camera working at 45 kV

and 40 mA, using CuK α radiation and equipped with an X'Celerator detector and a graphite diffracted beam monochromator.

The microstructure of the samples was analysed by scanning electron microscopy (SEM) using a Hitachi S-4800 microscope, equipped with an energy dispersive X-ray spectrometer (EDX). Differential scanning calorimetry (DSC) curves were recorded on a simultaneous TG/DSC Instrument (Q600 SDT, TA Instruments, Crawley, UK). The samples were placed in open alumina pans, and under an airflow of 10 cm³ min⁻¹. The heating and cooling rates were set both at 10 Kmin⁻¹ from 373 K to 1098 K. UV-Vis measurements were recorded in a UV-Vis spectrophotometer (Perkin-Elmer Lambda 35, Massachusetts, USA) equipped with an integrating sphere and were taken over a wavelength range from 400 nm to 800 nm. Barium sulphate was used as coated standard pattern. The energy band gap (E_g) values were calculated by means of Tauc's plot:

$$\alpha(h\nu) = A(h\nu - E_g)^{n/2} \quad (1)$$

Where α is the absorption coefficient, $h\nu$ is the photon energy, A is a constant and n depends on the type of optical transition [50]. For BiFeO₃ and related materials the band gap is direct and n equals 1 [51-52].

The electrical properties of the samples were characterized by impedance spectroscopy, taking into account the blank capacitance of the conductivity jig and the overall pellet geometry, whose opposite faces were previously Au sputter-coated using an Emitech K550 Sputter Telstar (Barcelona, Spain). The impedance measurements were taken with a Newtons4th Ltd impedance analyser (Loughborough, UK) over a frequency range from 1 Hz to 5 MHz, with an ac measuring voltage of 0.1 V and in the temperature range from 573 K to 673 K.

Magnetisation data were collected from powder samples using a Quantum Design MPMS SQUID magnetometer in the temperature range from 5 K to 300 K or 350 K in an applied field of 100 Oe. In addition, magnetization data were also recorded at 5 K and 350 K in an applied magnetic field ranging between +50000 Oe and -50000 Oe.

3. Results and discussion

Samples in the nominal compositional range $\text{Bi}_{1-x}\text{Yb}_x\text{FeO}_3$ ($x = 0.02, 0.05$ and 0.07) were prepared by mechanical activation followed by sintering as described above. Figure 1 shows the XRD patterns of the powders obtained for each composition after 6 h of milling. The starting oxides suffer an initial amorphization during the milling treatment, followed by the crystallization of the new phases as grinding proceeds up to 6 h. In terms of milling time, the same behaviour was observed for each composition prepared. Further mechanical treatments did not produce modifications in the powders, as inferred from XRD measurements. Due to the nanometric size of the crystallites obtained after milling, the XRD peaks are quite broad, which made it difficult to obtain detailed crystallographic information.

Figure 1. XRD patterns of powders obtained after milling during 6 h stoichiometric amounts of the single oxides in oxygen (7 bar) for different nominal compositions: a) $x = 0.02$, b) $x = 0.05$, c) $x = 0.07$.

SEM micrographs for nominal $x = 0.05$ composition after different milling times are shown in Figure 2. After short milling times (0.25 h, Figure 2a), the morphology of the powders is plate-like, due to delamination of bismuth oxide into single platelets, mixed with ytterbium oxide and iron oxide particles. As milling proceeds (3 h, Figure 2b), the morphology changes to highly aggregated powders and after 6 h of mechanical treatment the obtained powder is composed of aggregated nanometric subunits as it can be observed in Figure 2c). Similar SEM micrographs were obtained for nominal $x = 0.02$ and $x = 0.07$ compositions (See Supporting information, Figure S1).

Figure 2. SEM micrographs of powders of the sample with nominal $x = 0.05$ composition at different milling times: a) 0.25 h, b) 3 h and c) 6 h.

The milled powders of each nominal composition were pressed into pellets and sintered at 1098 K for 6 min. These sintering conditions were considered optimal after studying their influence on the purity and density of the ceramics. The resulting pellets density was 7.3 g cm^{-3} (89%), 6.9 g cm^{-3} (83%) and 6.8 g cm^{-3} (82%) for the samples with nominal $x = 0.02$, 0.05 and 0.07 compositions, respectively. Figure 3 shows the XRD patterns of the sintered samples. Although the main phase can be indexed in the R3c space group, small reflections corresponding to other phases are observed in the samples with nominal $x = 0.05$ and $x = 0.07$ compositions. Moreover, the intensity of these reflections increases with the ytterbium content of the samples, which suggests that the solubility limit of ytterbium in the BiFeO_3 lattice has been reached.

Figure 3. XRD patterns of the samples obtained after sintering the mechanically activated powders of the nominal compositions: a) $x = 0.02$, b) $x = 0.05$, c) $x = 0.07$. The intensity is represented in square root in order to make the secondary phase more noticeable.

Differential scanning calorimetry curves were recorded with the objective of estimating the solubility limit of ytterbium in BiFeO_3 (and therefore the stoichiometry of the main phase for the nominal $x = 0.05$ and $x = 0.07$ compositions) since a linear relationship between the Curie Temperature (T_C) and the real composition (x) of bismuth substituted samples have been reported [28]. Two endothermic peaks are observed in the DSC traces for all samples (Figure 4). The first one appears at approximately 643 K and corresponds to the Néel temperature (T_N), (Figure 4a), associated with the second order phase transition (antiferromagnetic-paramagnetic) and remaining constant for all compositions. The second peak (Figure 4b), is more intense and corresponds to the T_C (ferroelectric-paraelectric transition) [5, 34]. The sample with composition $x = 0.02$ presents the T_C at 1069 K while for nominal $x = 0.05$ and $x = 0.07$ compositions the T_C appears at 1056 K and 1053 K, respectively, these two last values being very close to each other. The similarity of T_C for the samples with nominal $x = 0.05$ and $x = 0.07$ compositions suggests that the Yb solubility limit has been reached somewhere between $x=0.02$ and 0.05 . For pure BiFeO_3 prepared by mechanochemistry, the T_C is observed at 1103 K [47]. Considering the linear relationship between T_C and composition, by extrapolation it can be estimated that the solubility limit of ytterbium in the system $\text{Bi}_{1-x}\text{Yb}_x\text{FeO}_3$ is reached at approximately $x = 0.03$, and therefore the secondary phases observed in Figure 3 may correspond to ytterbium rich compounds, whose concentration increases with the ytterbium content of the system.

Figure 4. DSC traces for nominal $x = 0.02$, 0.05 and 0.07 compositions milled for 6 h and sintered at 1098 K: a) temperature range from 573 K to 673 K, b) temperature range from 773 K to 1098 K. The dashed line in a) is a guide to the eye.

Rietveld analysis was carried out to obtain crystallographic information of the phases. X-ray diffraction data from composition $x = 0.02$ can be successfully fitted in a rhombohedral R3c structure with good reliability factors (See Supporting Information, Figure S2), which indicates that this compound is essentially phase pure. On the other hand, analogous data from nominal $x = 0.05$ and $x = 0.07$ compositions exhibit the main R3c phase together with small reflections (that increase with ytterbium content as stated above) at the values of 2θ of 23.2° , 26° , 33° , 34° and 35.6° . Figure 5 shows the Rietveld refinement for the nominal $x = 0.05$ composition. The diffraction pattern was refined considering a real composition of $x = 0.03$, as estimated from the T_C data

obtained by DSC, and a rhombohedral R3c structure. The small peaks of the secondary phase were not considered in the refinement. As may be seen, rhombohedral R3c phase accounts for all the main peaks and the diffraction pattern can be refined with good confidence factors (Table 1). Unfortunately, the secondary phase, which would correspond to an ytterbium enriched phase, cannot be identified due to the low intensity of the diffraction peaks contributed by this phase. A very similar refinement is obtained for the nominal $x = 0.07$ composition (See Supporting Information, Figure S3), considering again that the main phase corresponds to a rhombohedral R3c structure with composition $x = 0.03$. Moreover, the values of the structural parameters extracted from the Rietveld analysis are comparable with those obtained for nominal $x = 0.05$ composition.

Therefore, we conclude that the diffraction data show that while composition $x = 0.02$ forms a single $\text{Bi}_{0.98}\text{Yb}_{0.02}\text{FeO}_3$ phase, the compositions $x = 0.05$ and $x = 0.07$ form two-phase mixtures of a majority rhombohedral phase of approximate composition $\text{Bi}_{0.97}\text{Yb}_{0.03}\text{FeO}_3$ and an unidentified, ytterbium rich phase. This result is in agreement with the DSC data analysis. Table 1 lists the structural parameters extracted from the Rietveld analysis of all three samples. Additionally, a slight tendency of volume decrease with x is observed up to the solubility limit $x = 0.03$, which can be attributed to the difference in ionic radii of bismuth and ytterbium. Figure 6 shows the perovskite crystal structure of the sample of composition $x = 0.02$.

Table 1. Rietveld refinement structural parameters obtained from the XRD patterns for the samples with nominal $x = 0.02$, $x = 0.05$ and 0.07 compositions milled for 6 h and sintered at 1098 K.

Nominal composition	$x = 0.02$	$x = 0.05$	$x = 0.07$
Real composition	$\text{Bi}_{0.98}\text{Yb}_{0.02}\text{FeO}_3$	$\text{Bi}_{0.97}\text{Yb}_{0.03}\text{FeO}_3$	$\text{Bi}_{0.97}\text{Yb}_{0.03}\text{FeO}_3$
Space group	R3c	R3c	R3c
a (Å)	5.5771(1)	5.5759(2)	5.5759(1)
b (Å)	-	-	-
c (Å)	13.8648(1)	13.8603(2)	13.8597(2)
Volume (Å ³)	373.48	373.20	373.20
Atomic positions			
Bi	0.00, 0.00, 0.00	0.00, 0.00, 0.00	0.00, 0.00, 0.00
Yb	0.00, 0.00, 0.00	0.00, 0.00, 0.00	0.00, 0.00, 0.00
Fe	0.00, 0.00, 0.22131(3)	0.00, 0.00, 0.22120(2)	0.00, 0.00, 0.22179(7)
O (1)	0.44481(2), 0.01524(4), 0.95134(3)	0.44520(5), 0.02460(5), 0.94920(6),	0.43758(3), 0.02510(5), 0.94949(6)
Confidence factors			
R_{wp}	11.7	9.57	11.1
χ^2	4.21	3.58	4.63

Figure 7 presents temperature-dependent XRD patterns, recorded from 1039 K to 1073 K in the 2θ range from 30° to 34° , for the samples milled for 6 h and sintered at 1098 K. As temperature increases the samples suffer a phase transformation from R3c to Pnma (ferroelectric-paraelectric transition), which is reflected in the double peak, at approximately $31.5\text{--}32^\circ$, appearing to become three overlapping peaks very close together. Additionally, the temperature range at which the phase transformation takes place is consistent with the obtained transition in the DSC data (Figure 4) confirming the decrease of T_C as the concentration of ytterbium increases. A similar behaviour has been observed for other substituents [28, 48]. It is worth noting that the T_C of the nominal $x = 0.05$ and $x = 0.07$ compositions, observed in the diffraction data, are very close to each other, in common with the DSC data, supporting the suggestion that these samples are two-phase mixtures of an $x = 0.03$ phase and an ytterbium rich phase.

Figure 7. Temperature dependent XRD patterns of the samples milled for 6 h and sintered at 1098 K: a) $x = 0.02$, b) nominal $x = 0.05$ composition, c) nominal $x = 0.07$ composition.

SEM micrographs of the different samples, milled for 6 h and sintered at 1098 K, are shown in Figure 8. Pellets were thermally etched for 30 min at 90% of the sintering temperature to reveal the grain boundaries. The microstructure is granular in all the samples. The grain size is higher in the sample $x = 0.02$ (Figure 8a), with typical values between approximately 1 and 4 μm . When the amount of ytterbium increases the grain size decreases to values smaller than 2 μm . Moreover, the porosity also increases with the amount of substituent, in agreement with the calculated densities. An EDX spectrum of the sample with nominal $x = 0.07$ composition is shown in Figure 8d. The elemental composition has been determined by a semiquantitative analysis of the EDX spectra for every composition, as it is presented in Table 2. The experimental results are mostly coincident with the expected values, being an indication that the initial stoichiometry has not been modified during the preparation of the samples. However, slight differences, which can be attributed to the intrinsic errors of the EDX, are observed.

Figure 8. SEM micrographs of the samples milled for 6 h and sintered at 1098 K: a) $x = 0.02$, b) nominal $x = 0.05$ composition, c) nominal $x = 0.07$ composition, d) EDX spectrum of the sample with nominal $x = 0.07$ composition.

Table 2. Elemental atomic composition of the samples milled for 6 h and sintered at 1098 K, determined by a semiquantitative analysis of EDX spectra.

		Experimental atomic composition (%)		
Sample (Nominal compositions)	Theoretical atomic composition Fe/Yb/Bi (%)	Fe	Yb	Bi
$\text{Bi}_{0.98}\text{Yb}_{0.02}\text{FeO}_3$	50/1/49	53.62 ± 3.04	1.02 ± 0.28	45.36 ± 3.52
$\text{Bi}_{0.95}\text{Yb}_{0.05}\text{FeO}_3$	50/2.5/47.5	53.94 ± 3.07	2.45 ± 0.34	43.61 ± 3.73
$\text{Bi}_{0.93}\text{Yb}_{0.07}\text{FeO}_3$	50/3.5/46.5	53.56 ± 3.01	2.78 ± 0.77	43.66 ± 1.41

The optical properties of the samples were studied by measuring their UV-Vis diffuse reflectance absorption spectra. In Figure 9, the absorption spectra for the sample with nominal $x = 0.05$ composition is shown (See Supporting Information, Figures S4-S5 for $x=0.02$ and for nominal $x=0.07$ composition). It can be clearly observed that the samples absorb considerable amount of light in the visible region, which suggests their potential use as visible-light photocatalysts. As BiFeO_3 and related materials are

considered direct band gap semiconductors, n is equal to 1 in Tauc's plot (equation 1) and therefore the band gap energy can be estimated from the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$), through the extrapolation of a tangent line from the point of inflection to $(\alpha h\nu)^2=0$ [51-52], as it is shown in the inset of Figure 9. The band gap energy values are 2.06 eV for the sample $x = 0.02$ and 2.04 eV for both samples with nominal $x = 0.05$ and 0.07 compositions, being again another indication that these two samples contain the same $\text{Bi}_{1-x}\text{Yb}_x\text{FeO}_3$ phase. These values of band gap energy are smaller than those previously reported for pure BiFeO_3 [5, 9, 53], or those reported for ytterbium substituted BiFeO_3 [10]. Hence, this suggests that ytterbium substituted samples prepared by mechanical activation may be good photocatalytic materials.

Figure 9. UV-Vis diffuse reflectance spectra of the sample with nominal $x = 0.05$ composition milled for 6 h and sintered at 1098 K. The inset represents $(\alpha h\nu)^2$ versus photon energy for the calculation of the corresponding band gap energy.

Electrical properties of the samples were studied by impedance spectroscopy. Samples were observed to be highly insulating at room temperature, with resistivity values above 1 $\text{G}\Omega\text{cm}$, and presented modest levels of semiconductivity at high temperatures. The

impedance complex plane plots of the samples are constituted by a single distorted arc, as shown in Figure 10a for nominal $x = 0.05$ composition (See Supporting Information, Figures S6-S7 for the samples $x = 0.02$ and nominal $x = 0.07$ composition), and the associated Z''/M'' spectroscopic plots show single peaks with a small displacement between them for the maxima frequencies (Figure 10b). These results suggest that the samples are electrically homogenous due to the absence of any additional peaks at lower frequencies in the Z'' spectrum despite the presence of the small amount of ytterbium enriched secondary phase for the samples with nominal $x = 0.05$ and 0.07 compositions. Figure 11 shows the resistivity values of the samples obtained from the intercept on the real Z' axes of the complex plane plots, in conventional Arrhenius format ($\log \sigma$ against the inverse of temperature). A linear behaviour is clearly observed, with an activation energy of 1.12 eV for sample of composition $x = 0.02$ and 1.03 eV for the samples with nominal $x = 0.05$ and $x = 0.07$ compositions. Although the activation energies are identical for these two samples, a small increase in the conductivity of the sample with nominal $x = 0.07$ composition is observed, which may be attributed to the presence of a slightly higher amount of secondary phase as compared with the sample with nominal $x = 0.05$ composition, as observed by XRD. It is worth pointing out that the conductivity values for all the samples are small and in good agreement with the results previously reported for stoichiometric BiFeO_3 and $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ samples prepared by mechanosynthesis [46, 48, 54]. This is an indication that there are no other significant sources of conductivity, such as mixed valence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ associated with possible oxygen non-stoichiometry, overcoming one of the major issues related to the synthesis of BiFeO_3 .

Figure 10. a) Impedance complex plane and b) Z''/M'' spectroscopic plots for the sample with nominal $x = 0.05$ composition at 653 K .

Figure 1. Bulk conductivity data for $\text{Bi}_{1-x}\text{Yb}_x\text{FeO}_3$.

Impedance measurements under different oxygen partial pressures were performed in order to study the conduction mechanism. Figure 12 shows the impedance complex-plane plots at 653 K in nitrogen, air and oxygen for the sample with nominal $x = 0.07$ composition, suggesting that the conduction may be p-type. This means that samples can pick up O_2 by the nominal mechanism:

and therefore the conductivity increases with increasing the oxygen partial pressure. It has been proposed that the holes can be associated with Fe as Fe^{4+} ions in the sample surface [48, 55]:

Another possibility is that underbonded surface oxide ions may ionise, resulting in O^- ions that become the source of holes [48, 56-57]. Nevertheless, further investigations are needed to clarify the origin of the holes.

Figure 12. Impedance complex-plane plots at 653 K in nitrogen, air and oxygen for the sample with nominal $x = 0.07$ composition.

Although the changes in conductivity with the oxygen content are small, especially for the samples $x = 0.02$ and nominal $x = 0.05$ composition (See Supporting Information, Figures S8 and S9), a tendency is observed about a possible p-type conduction mechanism. It may indicate that conduction is almost intrinsic but slightly dominated by holes.

Detailed magnetic characterisation of the $\text{Bi}_{1-x}\text{Yb}_x\text{FeO}_3$ samples is hampered by the presence of the ytterbium-rich impurity phase, which adds an unknown contribution to the data collected from the samples with nominal $x = 0.05$ and $x = 0.07$ compositions. However, as can be seen in Figure 13, the temperature dependant magnetisation data from all three samples show small absolute values consistent with the bulk phase becoming antiferromagnetically ordered at $T_N \sim 643\text{K}$ as indicated by the DSC data. Magnetisation-field data collected at 300 K (Figure 14a and Table 3) show a nearly linear field-dependent magnetization and do not saturate at this temperature at the maximum field applied, as has been also observed for bulk BiFeO_3 and related compounds [39-40, 48], and confirm the antiferromagnetic nature of the samples. Moreover, the samples show only a modest change to the weak ferromagnetic behaviour on ytterbium substitution.

On cooling data from all three samples exhibit an anomaly at $T \sim 260\text{ K}$. Below this temperature the Zero-Field Cooled (ZFC) and Field Cooled (FC) data diverge weakly. This is consistent with the observation that magnetisation-field data collected at 5 K (Figure 14b and Table 3) show increased remnant magnetizations (M_r) compared to their behaviour at 300 K, and that there is a significant increase in value with increasing ytterbium content of samples. Given the presence of the secondary, ytterbium rich phases in the $x = 0.05$ and $x = 0.07$ samples, the increase in low temperature of the M_r values cannot be definitively attributed to the majority phases.

Figure 13. Zero-Field Cooled (ZFC) and Field Cooled (FC) magnetisation data collected for the samples of $\text{Bi}_{1-x}\text{Yb}_x\text{FeO}_3$ in an applied field of 100 Oe.

Figure 14. Magnetisation data collected as a function of applied field for the samples of $\text{Bi}_{1-x}\text{Yb}_x\text{FeO}_3$ at a) 300 K and b) 5 K.

Table 3. Coercive field (H_C), remanent magnetization (M_r) and 5 Tesla magnetization (M_{5T}) extracted from magnetisation data collected as a function of applied field from samples of $\text{Bi}_{1-x}\text{Yb}_x\text{FeO}_3$ at 300 K and 5 K.

Temperature	300 K			5 K		
Nominal composition	x = 0.02	x = 0.05	x = 0.07	x = 0.02	x = 0.05	x = 0.07
H_c (Oe)	916	1091	1375	1277	3036	2917
M_r (emu/g)	0.022	0.0028	0.0059	0.113	0.465	0.736
M_{5T} (emu/g)	0.3892	0.4381	0.4789	0.701	1.415	1.936

4. Conclusions

In summary, samples of ytterbium substituted BiFeO_3 have been prepared for the first time by mechanical activation followed by sintering, and have been deeply characterized. In contrast to previous studies [10, 19, 36], XRD patterns and DSC data show that the ytterbium solubility in the rhombohedral R3c $\text{Bi}_{1-x}\text{Yb}_x\text{FeO}_3$ system is limited to approximately $x = 0.03$. This suggests that the reports of high Yb solubility are due to loss of Bi under alternative synthesis methods. DSC data confirm the multiferroic behaviour of the samples, showing two phase transition temperatures, related to T_N (ferromagnetic-paramagnetic transition) and T_C (ferroelectric-paraelectric transition). The crystal structures of the samples were analysed by the Rietveld method. The sample with composition $x = 0.02$ was observed to be essentially phase-pure, maintaining the R3c space group of the parent compound BiFeO_3 . On the other hand, the samples with nominal $x = 0.05$ and $x = 0.07$ compositions present the main R3c phase together with ytterbium enriched secondary phases which cannot be indexed or quantified due to their small amount. Temperature-dependent XRD patterns confirmed the Curie temperatures observed by DSC, showing that all samples exhibit rhombohedral R3c to orthorhombic Pnma phase transitions. Moreover, SEM micrographs and EDX analysis indicated that the initial nominal stoichiometry has not been modified during the preparation of the samples. The UV-Vis measurements

suggested their potential use in photocatalytic applications. Finally, impedance and magnetic measurements showed that samples present low conductivity values with a possible p-type conduction mechanism and an antiferromagnetic behaviour at room temperature with an unknown contribution of the secondary ytterbium-rich phases.

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