Structural, spectroscopic, magnetic and electrical characterisation of polycrystalline

$\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ ($x \leq 0.1$)

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Abstract

The crystal structure and physical properties of multiferroic polycrystalline Ca^{2+} -doped BiFeO_3 samples have been investigated. The present experimental investigation suggests that $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ ($x \leq 0.1$) can be considered as a solid solution between BiFeO_3 and $\text{CaFeO}_{2.5}$. The oxidation state of Fe in these materials is +3 and charge balance occurs through the creation of oxygen vacancies. For each composition, two structural phase transitions are revealed as anomalies in the variable-temperature *in-situ* X-ray diffraction data which is consistent with the well-established high-temperature structural transformation in pure BiFeO_3 . All compositions studied show antiferromagnetic behaviour along with a ferromagnetic component that increases with Ca^{2+} doping. The resistivities of the $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ samples at room temperature are of the order of $10^9 \Omega\text{cm}$ and decrease with increasing Ca^{2+} content. Arrhenius plots of the resistivity show two distinct linear regions with activation energies in the range of 0.4-0.7 and 0.03-0.16 eV. A correlation has been established between the critical temperatures associated with the structural phase transitions

and the multiferroic properties. A composition of $x = 0.085$ is predicted to show maximum magneto electric coupling.

Introduction:

Over the past few decades BiFeO_3 has emerged as the most studied multiferroic material. [1-5] The antiferromagnetic and ferroelectric ordering temperatures of BiFeO_3 are ~ 640 K and 1103 K respectively. Since both transitions are above room temperature BiFeO_3 may have potential applications in devices. [3, 4] Owing to its high spontaneous electrical polarisation ($\sim 100 \mu\text{C cm}^{-2}$) BiFeO_3 is also considered as a practical lead-free ferroelectric material [6-8]. On the other hand, the low thermal stability of BiFeO_3 provides an obstacle towards conventional ceramics processing of this material, as the processing window is very narrow. The formation of impurity phases such as $\text{Bi}_{25}\text{FeO}_{39}$, $\text{Bi}_2\text{Fe}_4\text{O}_9$ provide an additional difficulty in the physical characterisation of the paraelectric high temperature phase. [9] Since part of the problem lies in the volatility of bismuth, doping the Bi-site in BiFeO_3 is a key strategy, and there have been plenty of studies on the effect of replacement of Bi^{3+} with different substituents. [10-16] The doping experiments with Ca^{2+} are of particular interest because they can be exploited to control the band-filling in insulating BiFeO_3 thin films thereby triggering an insulator-metal transition with varying composition. [17] In polycrystalline samples, we have shown recently that the effect of Ca^{2+} doping can be compared to that of hydrostatic pressure on BiFeO_3 , [18] raising the Neel temperature. The doping-induced convergence between the magnetic Neel temperature and the ferroelectric Curie temperature should lead to increased magneto-electric coupling, and $\text{Bi}_{0.7}\text{Ca}_{0.3}\text{FeO}_3$ ceramic powder shows a converse magneto electric effect. [19]

As regards the crystal structure of Ca^{2+} doped BiFeO_3 , Chen *et al.* refined the $0.1 \leq x \leq 0.2$ materials as a mixture of a rhombohedral and a disordered cubic phase. [20] While Schiemer *et al.* have observed the appearance of an ordered perovskite related phase using transmission electron microscopy. [21] It is also interesting to note that $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$ with $x = 0.1$ has been described by Kothari *et al.* as triclinic [22] whereas Khomchenko *et al.* have found that up to $x = 0.3$ a rhombohedral structure can adequately describe single-phase material. [13], [23], [24]

Here we provide a detailed investigation of structure-property relationship in $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ ceramic powders. We show that doping with Ca^{2+} in polycrystalline BiFeO_3 affects the high-temperature structural phase transition of polycrystalline BiFeO_3 in a manner which is in consistent with that observed in epitaxial thin films. Doping with Ca^{2+} on the A-site of BiFeO_3 reduces the number of Bi^{3+} ions which will in turn reduce the collective number of stereo-chemically active $6s^2$ lone pairs. Simultaneously, charge balance occurs through the creation of oxygen vacancies. These affect the degree of off-centering of the FeO_6 octahedra and thus also the multiferroic properties of BiFeO_3 .

Experimental:

Synthesis: Polycrystalline samples of $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ were synthesised using a tartaric acid based sol-gel process. This technique is particularly useful since it provides better control over the chemical homogeneity of the samples. The synthesis was performed by drying the gel with subsequent calcinations at 600°C followed by sintering at 700°C in the form of a pellet. The processing temperature was kept low in order to prevent thermal decomposition of the BiFeO_3 . Details of the synthesis process can be found elsewhere. [18] [25]

Characterisation: For powder X-ray diffraction (PXRD) analysis, the sintered pellets were ground into fine powder. PXRD data were collected at room temperature using a Bruker D8 Advance X-ray diffractometer operating with $\text{CuK}\alpha_1$ ($\lambda = 1.5406 \text{ \AA}$) radiation and a Sol-X energy discriminating detector. *In-situ* variable temperature PXRD patterns were collected using a Bruker D8 Advance set up for high-temperature measurement, with an MSI furnace and $\text{CuK}\alpha$ X-ray source in θ - θ geometry. Data were collected with a Vantec 1-D position sensitive detector, allow rapid data acquisition. Rietveld refinement of the PXRD data was performed using the GSAS-EXPGUI package [26, 27]. Raman spectroscopy data on polished pellets were recorded at room temperature using a Renishaw inVia Raman Microscope equipped with an Ar⁺ Laser with a wavelength of 514.5 nm. Magnetisation versus temperature (M v T) and applied magnetic field (M v H) data were collected over the temperature range 5 - 400 K in applied magnetic fields of up to 10000 Oe using a Quantum Design Magnetic Property Measurement System (MPMS) squid magnetometer. In an attempt to remove any surface-adsorbed molecular oxygen, the samples were first heated to 400 K in the magnetometer and the sample chamber was then purged and backfilled with helium gas several times. M v T data were collected while zero-field cooled warming (ZFCW) and on field cooled cooling (FCC). X-ray Absorption Near Edge Structure (XANES) experiments were performed using the B18 beamline of the Diamond Light Source, UK. B18 provides X-ray energies in the range 2.05 - 35 keV using a fixed-exit, double-crystal monochromator.[28] Typically, ~20 mg of each $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ samples was mixed with ~80 mg of polyethylene powder and then pressed into 13 mm diameter pellet of ~1 mm thickness. XANES data were collected at the Bi L_{III} and Fe K_{III} edges in transmission mode, with ion chambers before and after the sample filled with appropriate mixtures of inert gases to optimise sensitivity. The spectra were measured with a step size equivalent to less than 0.5 eV. Data were normalised

using the Athena program [29] with a linear pre-edge and polynomial post-edge background subtracted from the raw $\ln(I_t/I_0)$ data.

The resistivity of the samples was measured from room temperature up to the thermal decomposition temperature of the materials inside a quartz tube furnace. Four platinum wires were attached to the sintered ceramic samples using silver paste, and the resistance was measured using the four-probe method using a Keithley D500 multimeter.

Results and Discussion:

At ambient conditions BiFeO_3 is a rhombohedrally distorted perovskite polymorph which can be described in different settings of the rhombohedral space group $R\bar{3}m$ (no. 160) or $R3c$ (no. 161), although Lebeugle [30] and Schmid [31] have emphasized that, though metrically rhombohedral, the known presence of a magnetic cycloid should strictly lower the symmetry to monoclinic due to magnetostriction. Figure 1 shows least-square Rietveld refinement results of the PXRD patterns of $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$. The rhombohedral peak splitting in the PXRD patterns (*e. g.* between the $(0\bar{1}\bar{1})$ peak at around $31.965^\circ 2\theta$ and the $(10\bar{1})$ peak at approximately $32.130^\circ 2\theta$) gradually decreases with increasing Ca^{2+} doping. This is consistent with observations of Chen *et al.* and Kothari *et al.* [20, 22] Bearing in mind the observations of Khomchenko *et al.* [13, 14] we have refined the PXRD patterns of the $x = 0.05$ - 0.1 samples using both rhombohedral and cubic structural models. The atomic coordinates used in this study for space groups $R\bar{3}m$ and $Pm\bar{3}m$ have been taken from [32] and [33] respectively. Interestingly, both the cubic and the rhombohedral models give equally good fits (as judged by the goodness of fit parameters in Table 1) for the calcium doped

samples with $x = 0.05-0.1$. In Table 1 we show the refined lattice parameters along with the goodness of fit parameters for the different structural models employed in this study. In Figures 2a and b we compare the pseudo-cubic unit cell parameter (a_p) and volume (V_p), of the $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ samples ($0 \leq x \leq 0.2$) with three different independent studies in the literature. [20] [21] [24] Figures 2a and 2b reveal that the lattice parameters and cell volume of the present samples, although determined using laboratory PXRD data, correlate well with those obtained using neutron and synchrotron diffraction techniques. The decrease in the lattice parameter and unit cell volume is almost linear for $x \leq 0.2$ as expected due to the stoichiometric replacement of Bi^{3+} with a smaller ionic radii substituent (in this case Ca^{2+}). A comparison of the lattice parameters themselves reveals a single-phase solid solution for $0 \leq x \leq 0.2$. We note that a high solubility limit of Ca^{2+} in single phase $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ samples is expected. Indeed, $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{FeO}_{2.75}$ is known to be stabilised as a perovskite structure under certain synthesis conditions [34]. The effect of Ca^{2+} doping is further reflected in the Raman spectra of the $x = 0.0 - 0.1$ samples as shown in Figure 3. It is clear that increasing x gives rise to broad and less intense Raman bands associated with the normal modes in pure BiFeO_3 , while there is no appearance of extra bands in the doped samples. Thus, it appears that doping with Ca^{2+} in BiFeO_3 affects the perovskite-related phonon modes which are associated with a tilting of the FeO_6 octahedra, the motion of oxygen atoms associated with Bi site, and the off-centering of the Fe from its special crystallographic position. [35] A similar effect is also observed when BiFeO_3 is doped with rare-earth ions like, Nd^{3+} , Sm^{3+} and Gd^{3+} . [36] Thus, a combination of the Raman spectroscopy and the PXRD data suggest that our samples are single-phase members of a solid solution between BiFeO_3 and $\text{CaFeO}_{2.5}$ [21, 34]

The determination of oxidation state of Fe is important as this can provide indirect evidence of the oxygen stoichiometry in doped BiFeO_3 . Figure 4 shows that the Fe K-edge

XANES spectra obtained for the Ca^{2+} doped samples are very similar to the spectra of Fe_2O_3 . There is no noticeable difference in the position of the absorption edge among samples with varying doping concentration. The edge position for all the samples is around 7124 eV (determined from the first derivative of the absorption with respect to energy or the inflection point in Figure 4b) which is characteristic of Fe^{3+} [37-38] and is related to the 1s to 4s transition. The pre-edge feature (denoted as P in Figure 4b) that arises from a dipole-forbidden transition (1s to 3d) in Fe is weak although more pronounced in the $x = 0.1$ sample. A considerable post-edge feature (C) is seen which is associated with a 1s to 4p transition. We note that any change in the oxidation state of Fe is expected to give a detectable shift in the absorption edge. [39] Thus, the Fe in these samples is in the 3+ oxidation state. The increase in the number of dipole forbidden transitions in the $x = 0.1$ sample may be due to an increase in the number of oxygen vacancy related distortions of FeO_6 octahedra. Interestingly, the lattice distortion due to the steric effect of the A-cation (reduction of average ionic radius) is reduced, as reflected in progressive reduction of rhombohedral distortion in the doped samples as discussed above. A similar but more pronounced effect is observed in Ta-doped BiFeO_3 [40] and in epitaxial BiFeO_3 thin films [41]. Additionally, Bi_{LIII} XANES spectra analysis of these doped samples, show that all Bi atoms are in 3+ oxidation state suggesting Ca^{2+} doping in BiFeO_3 create oxygen vacancies to maintain the charge balance.

Figure 5 shows the DC magnetisation versus temperature behaviour for $x = 0.0 - 0.1$ samples in an applied magnetic field of 10000 Oe. The nearly temperature-independent magnetisation behaviour seen between 300 K and 50 K is expected of antiferromagnetic $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ samples well below their Néel temperatures (T_N). A small rise in the magnetisation below 50 K is observed for the $x = 0.0$ and 0.03 samples, and is attributed to an

unidentified paramagnetic impurity phase. [42] The formation of paramagnetic impurities is suppressed with calcium doping since samples within $0.05 \leq x \leq 0.1$ shows almost no rise in magnetic moment in the low-temperature region. There is also a subtle magnetic anomaly at ~ 50 K which has also been seen in previous reports. [20] One possible explanation for this type of anomaly in the temperature region of 50-70 K could be an antiferromagnetic transition of adsorbed molecular oxygen on the surface of small-grain samples. Another possibility worth mentioning is that this type of feature may arise from $\text{CaFeO}_{2.5}$ impurities, which exhibit a similar magnetic anomaly due to a change in the easy axis of magnetisation between 40 K and 60 K. [43] [44] However, it is unlikely that the system is phase separated into $\text{CaFeO}_{2.5}$ and BiFeO_3 at such low Ca^{2+} doping levels.

Figure 6 shows M vs. H loops collected at 5 K. A significant hysteresis develops with increasing mole fraction of Ca^{2+} . The difference between the ZFCW and FCC curves also increased with x . This can be understood as a suppression of the magnetic spin spiral arrangement of BiFeO_3 , which leads to a weak (canting) ferromagnetic moment caused by the Dzyaloshinskii-Moriya interaction. The unwinding of the spiral and appearance of a canted moment has previously been reported as a function of pressure, strain or chemical doping. [45] In our case, it is not clear whether the key factor is the reduction of the stereochemical activity of the Bi site, or the “chemical pressure” effect of the substitution for a smaller ion; the chances are that both factors are at play here.

The high temperature structural phase transition in these Ca^{2+} doped BiFeO_3 samples has been investigated using the variable temperature *in-situ* PXRD technique. Figures 7 and 8 show the variation of the pseudo cubic lattice parameter and rhombohedral angle (α), respectively for samples within $x = 0.0$ -0.1. Clearly the rhombohedral angle is almost 90° for $x = 0.07$ and 0.1 indicating that the rhombohedral distortion in these samples is negligible.

Additionally, variations in the pseudo cubic lattice parameter and the rhombohedral angle as a function of temperature reveal the existence of at least two structural phase transitions. The associated transition temperatures, defined as T_{C1} and T_{C2} , are given in Table 2. Both T_{C1} and T_{C2} in BiFeO_3 decrease linearly with calcium doping but with noticeably different rates. A linear fitting reveals that the rates of change of T_{C1} and T_{C2} are ~ 50.5 K per mole% Ca^{2+} and ~ 1.8 K per mole% Ca^{2+} , respectively. An extrapolation of the fitted lines to $x = 0.0$ (pure BiFeO_3) gives $T_{C1} = 1072(18)$ K and $T_{C2} = 1142(26)$ K. The structural phase transition temperature T_{C1} has been regarded as the ferroelectric Curie temperature T_C in BiFeO_3 for many years [17]. Present analysis shows that T_{C1} reduces drastically with Ca^{2+} doping. Our results are quite similar to those of Chaigneau *et al.* [46] and Levin *et al.* [47] who studied Pb^{2+} and Nd^{3+} doped BiFeO_3 . This indicates that doping with Pb^{2+} and/or Ca^{2+} in BiFeO_3 reduces the ferroelectric ordering temperature. Furthermore, the effect of doping on the different rate of changes of the two critical temperatures is consistent with the known behaviour of the α - β and β - γ phase transitions of pure BiFeO_3 . The α - β (ferroelectric-paraelectric) transition changes the symmetry of the system and is associated with a very large volume contraction [48] [49], while the β - γ (metal-insulator) phase transition is isostructural and has a much smaller volume contraction. [50] Additionally, with increasing Ca^{2+} doping level, one should expect that the concentration of oxygen vacancies increases. Self-ordering of a large number of vacancies in the perovskite oxides can cause a structural phase transition (for example this is well known in the perovskite to brownmillerite structural phase transition in $\text{CaFeO}_{2.5}$ [51]). Thus, the recent observation of the emergence of a brownmillerite-type phase in heavily Ca^{2+} doped BiFeO_3 by Schiemer *et al.* [21] is easily understood. In the present lightly-doped system ($x \leq 0.1$) the vacancies created by doping can be considered to remain as uncorrelated clusters. There is a possibility that migration of these

clusters also plays a role in reducing the structural phase transition temperature in this system. Combining the above discussion with our previous report (increase of T_N with Ca^{2+} doping [18]) it follows that a doping concentration of approximately 8.5 mole% of Ca^{2+} in BiFeO_3 will result in the same critical temperature for both ferroelectric and antiferromagnetic ordering. Thus, one should expect the maximum magneto-electric coupling in $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ at this composition. We attempted to measure the ferroelectric hysteresis loops, but all the doped samples exhibit poor P - E hysteresis loops due to large leakage currents. This is in agreement with Chen *et al.*[20] Thus, high frequency (GHz) magneto-dielectric measurements on this system may be used to test the above hypothesis.

The large room temperature conductivity of Ca^{2+} -doped BiFeO_3 has already been reported for thin films [17]. The resistivity (ρ) values measured for our Ca^{2+} -doped polycrystalline samples are 3.49×10^{10} ($x = 0.00$), 3.18×10^{10} ($x = 0.03$), 3.01×10^{10} ($x = 0.05$) and 2.72×10^{10} ($x = 0.05$) 0.795×10^{10} ($x = 0.1$) Ωcm , at room temperature. It is interesting to note that the resistivity reduces by almost an order of magnitude within 10 mole % Ca^{2+} doping (Figure 10). Given the underlying coupling between structure, extrinsic defect (oxygen vacancies) concentration, and conductivity in these materials (including a metal-insulator transition at the high-temperature beta-gamma transition of pure BiFeO_3 [2], [48]) and in view of the large structural changes induced by doping in our samples, we measured the resistance as a function of temperature for all our samples in the high temperature region. Figure 11 shows the resistivity behaviour as a function of temperature. No clear anomaly is observed in the temperature region where the structural and magnetic phase transitions take place. This is in partial agreement with Selbach *et al.* [52] For each composition, in the temperature range of 573 – 1173 K, plots of $\ln \rho$ as a function of $1/T$ exhibit two separate temperature regions where a linear dependence is observed. The linearity is characteristic of a

system with a well defined band gap such that $\rho(T) \sim \exp(E_a/k_B T)$, where E_a is the thermal activation energy and k_B is the Boltzmann constant. The two straight lines yield two E_a values as shown in Figure 11. The E_a values in the low- and high-temperature regions are estimated to be 0.4-0.7 and 0.03-0.16 eV, respectively. This suggests that the conduction in Ca^{2+} doped BiFeO_3 is mainly governed by thermally-activated hopping of electrons between oxygen vacancy related defects which is inconsistent with the vacancy-assisted electronic conduction mechanism observed in epitaxial thin films recently. [17].

Conclusions:

We have shown that samples of composition $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ form a solid solution for $x \leq 0.1$, with the octahedral cation remaining Fe^{3+} throughout and charge compensation achieved through oxygen vacancy substitution. The introduction of oxygen vacancies and of Ca on the A-site appears to be stochastic, with no indication of long-range ordering. It therefore stabilises the high-symmetry high-temperature polymorphs of $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ with transition temperatures for the α - β phase transition dropping in temperature with increased Ca-content. Magnetic measurements demonstrates that these samples are all antiferromagnetic, but that increased Ca-incorporation leads to weak canted ferromagnetism. Finally, electrical conduction in these samples occurs via oxygen vacancy hopping, as revealed by the thermally-activated behaviour shown in our data.

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Table 1. Refined pseudo cubic unit cell lattice parameters of polycrystalline $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ where $x = 0.0 - 0.01$ obtained using different structural models. The goodness of fits of the refinement is also presented.

Table 2. Two structural phase transition temperatures, T_{C1} and T_{C2} , respectively evaluated from in-situ XRD analysis. T_C : ferroelectric Curie temperature determined by Yang *et al.* [17] x : mole fraction of Ca^{2+} in $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$.

Figure captions:

Figure 1. Results from the Rietveld refinement of laboratory PXRD patterns of $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$. Samples with $x = 0.0 - 0.7$ are refined with space group $R\bar{3}m$ while cubic space group $Pm\bar{3}m$ is used for $x = 0.1$. Tick marks correspond to the expected reflection positions of respective structures.

Figure 2. Variation of the lattice parameter a_p and unit cell volume V_p with x in $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ derived from PXRD analysis and compared with literature reported values obtained from analysis of powder neutron diffraction (PND) and synchrotron x-ray diffraction (SXR) by Chen *et al.* [20], PXRD by Khomchenko *et al.* [23] and Schiemer *et al.* [21]

Figure 3. Raman spectra recorded on polycrystalline $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ using a 514.5 nm laser.

Figure 4. (a) The normalised Fe K-edge XANES spectra and (b) its first derivative with respect to energy for polycrystalline $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ samples compared with suitable standards. Features in the post edge, edge and pre-edge regions are marked with C, B and P.

Figure 5. Variation of magnetisation with temperature in polycrystalline $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$. In each case DC magnetisation data were recorded with an applied magnetic field of 10 kOe.

Figure 6. Magnetic hysteresis loops for polycrystalline $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ samples measured at 5 K

Figure 7. Variation of the pseudo cubic lattice parameter as a function of temperature for $x = 0.03 - 0.1$ in $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ determined by Rietveld refinement of in-situ powder XRD patterns. Both the cubic space-group $Pm\bar{3}m$ and the rhombohedral space group $R\bar{3}m$ were used as starting models depending on the temperature regions and samples of interest. The cubic model was used between 300 - 1175 K (for $x = 0.05, 0.07, 0.1$) and 1000 - 1175 K (for $x = 0.03$). The rhombohedral model was used between, 300 K and 1175 K (for $x = 0.03$ and 0.05), 300 - 870 K (for $x = 0.07$) and 300 - 720 K for ($x = 0.1$). All data were recorded during heating in air.

Figure 8. Variation of the rhombohedral angle (α) with temperature for different compositions. The angle was determined employing the rhombohedral space group $R\bar{3}m$ as a starting model to refine the lattice parameter.

Figure 9. Variation of the structural phase transition temperatures (T_{C1} and T_{C2}) with mole fraction of Ca^{2+} in polycrystalline $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ determined by in-situ XRD analysis. For comparison, the ferroelectric T_C of Ca-doped BiFeO_3 thin films reported in Figure 1 of [17] has been incorporated. All T_{C1} values (from the present work and [17]) were used to fit a straight line.

Figure 10. Variation of resistivity with mole fraction (x) of calcium measured at room temperature on sintered pellets.

Figure 11. Arrhenius plots of resistivity of $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_{3-x/2}$ samples for $x = 0.03 - 0.1$. E_a is the activation energy as described in the text. The structural and antiferromagnetic phase transition temperatures are indicated with arrows.

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	$x = 0.00$		$x = 0.03$		$x = 0.05$		$x = 0.07$		$x = 0.1$	
	$R\bar{3}m$		$R\bar{3}m$		$R\bar{3}m$		$R\bar{3}m$		$R\bar{3}m$	$Pm\bar{3}m$
$a_p(\text{\AA})$	3.96109(23)		3.95740(10)		3.95055(12)		3.9489(6)		3.94656(16)	3.94422(19)
$\alpha(^{\circ})$	89.435(7)		89.4811(29)		89.544(4)		90		89.711(7)	90
$V_p(\text{\AA})^3$	62.141(6)		61.9693(26)		61.6499(33)		61.580(17)		61.467(4)	61.360(5)
Rp	0.091		0.09		0.0847		0.1186		0.0844	0.1157
							0.0964			0.0961
χ^2	1.173		1.432		1.461		2.801		1.331	2.364
									1.509	1.448

Atomic co-ordinates for $R\bar{3}m$ and $Pm\bar{3}m$ were taken from references [32] and [33], respectively.

Table 1

$x^{(a)}$	T_{C1} / K	$T_C^{(b)} / K$	T_{C2} / K
0.03	985	982	1061
0.05	911	900	1061
0.07	799	756	1076
0.1	678	600	1045

Table 2

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11