$BiFeO_3$ PEROVSKITES: THEORETICAL AND EXPERIMENTAL INVESTIGATIONS

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Introduction

From the technological point of view, the mutual control of electric and magnetic properties is an attractive possibility, but the number of candidate materials is limited. One of them, $BiFeO_3$, has critical conditions for synthesizing single phase since the temperature stability range of the phase is very narrow. Hence, various aspects of $BiFeO_3$ system have to be studied. $BiFeO_3$ is one of the most studied multiferroic materials. $BiFeO_3$ – BFO – is known to be the only material that exhibits multiferroism at room temperature. It is a rhombohedrally (R3c) distorted ferroelectric perovskite with Tc ~ 827 ° C (1100 K) and shows G – type antiferromagnetism up to 370 ° C (643 K) - T_N .

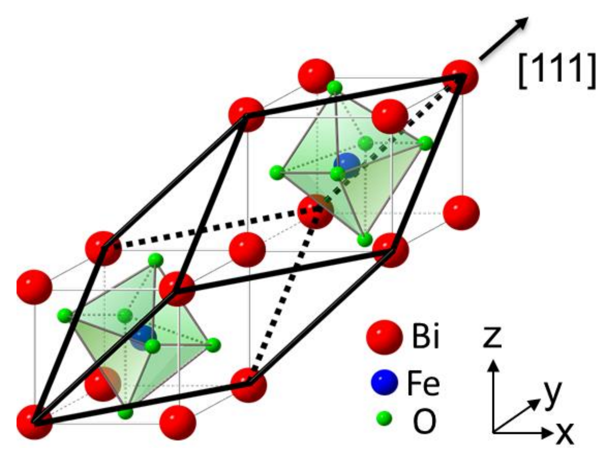

Figure 1. Schematic drawing of the crystal structure of perovskite $BiFeO_3$.

Idea

The goal was to find the easiest way to obtain the pure $BiFeO_3$. To synthesize $BiFeO_3$ ceramics and gain insight into its properties and to improve the properties of BFO to be more applicable and to explore a new era of multiferroic applications. Hydrothermal synthesis is a cheap and easy way to get a BFO. The aim of the research is to find new structures and perform their characterization.

Sample preparation

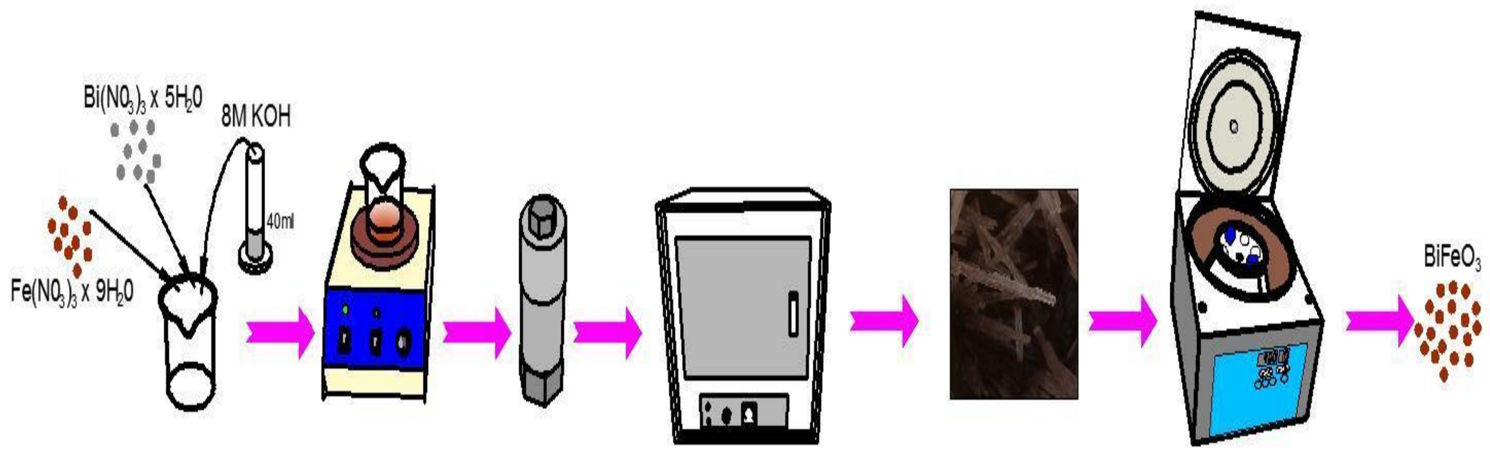

Figure 2. Hydrothermal synthesis

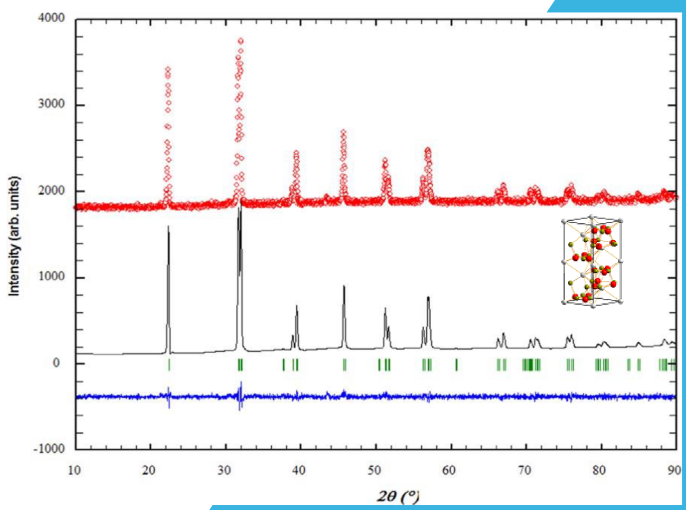

Figure 7. XRD pattern after structural refinement procedure using Rietveld's method

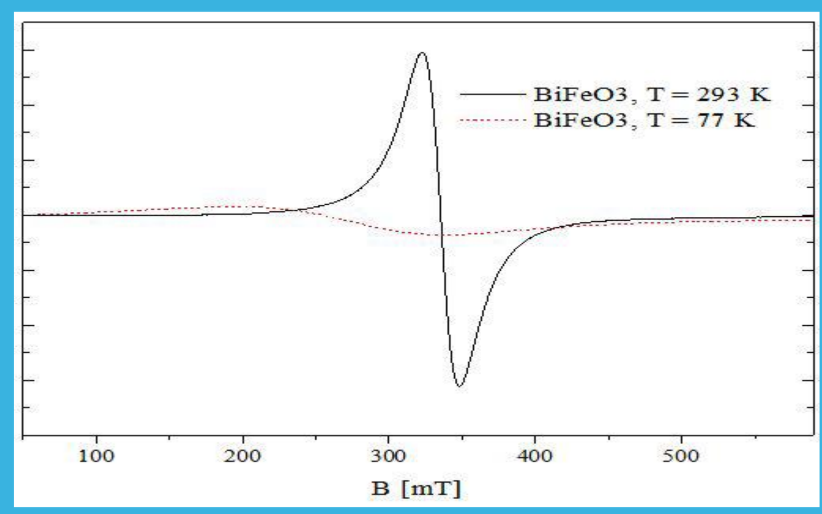

Figure 8. EPR spectra of the BFO powder measured at T = 293K and T = 77K

Results

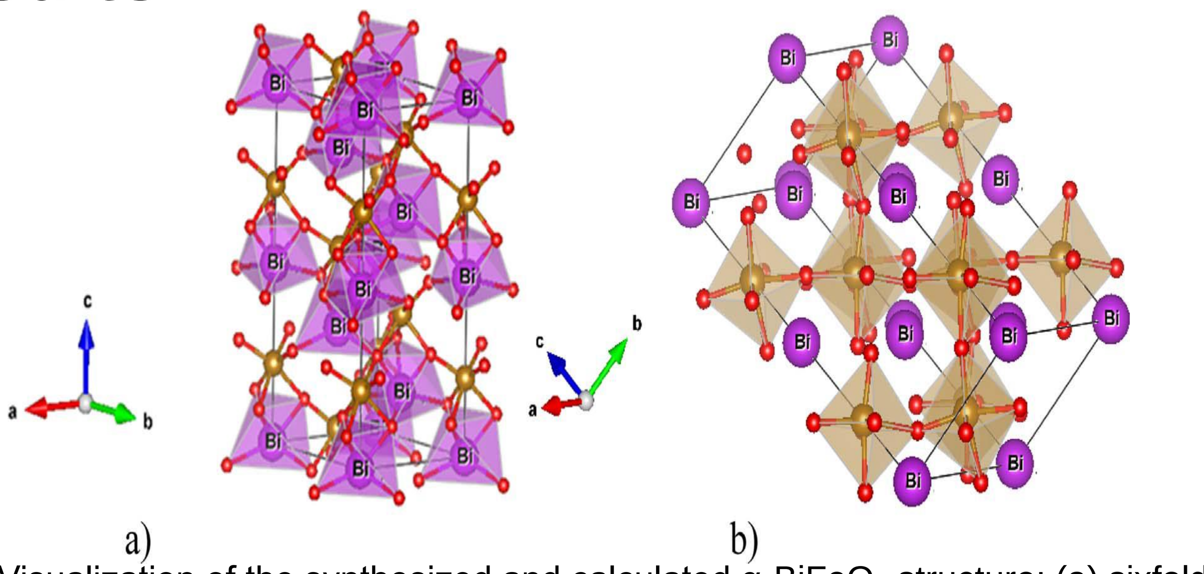

Figure 3. Visualization of the synthesized and calculated α-$BiFeO_3$ structure: (a) sixfold coordination (CN=6) of the Bi atom by O atom; (b) sixfold coordination (CN=6) of the Fe atom by O atom

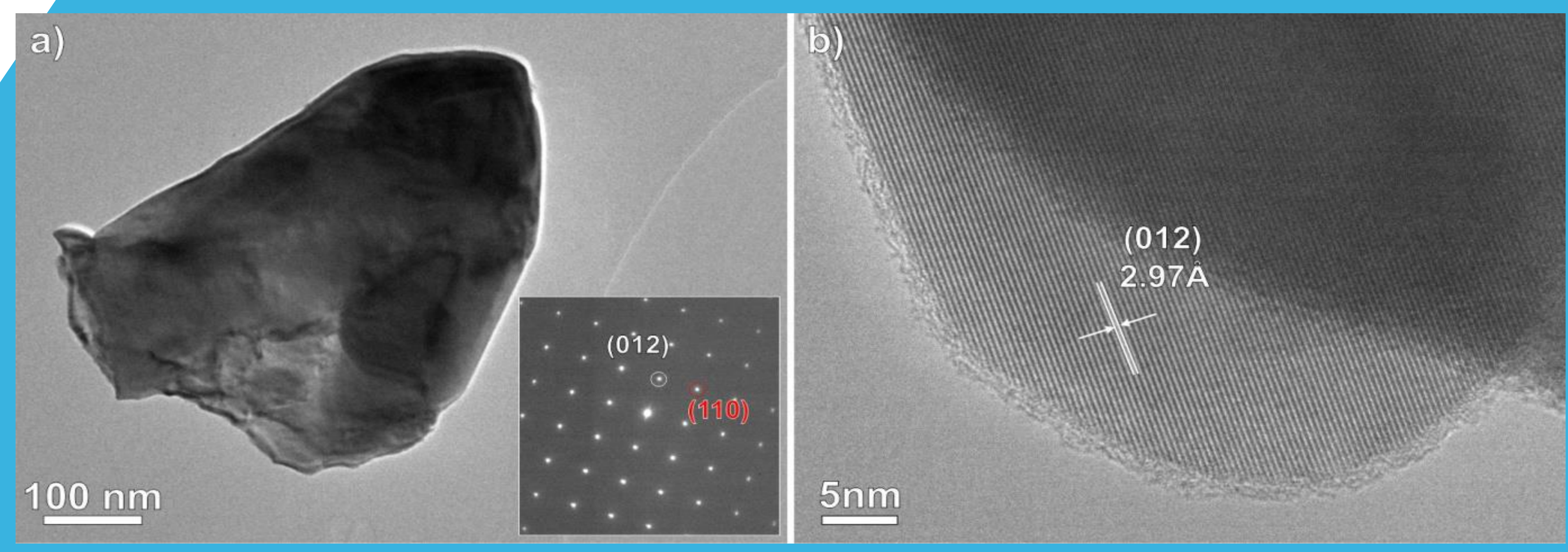

Figure 9. TEM image of a typical BFO particle (insert - SAED pattern over one grain) (a) and HRTEM image with characteristic d-spacing value (b)

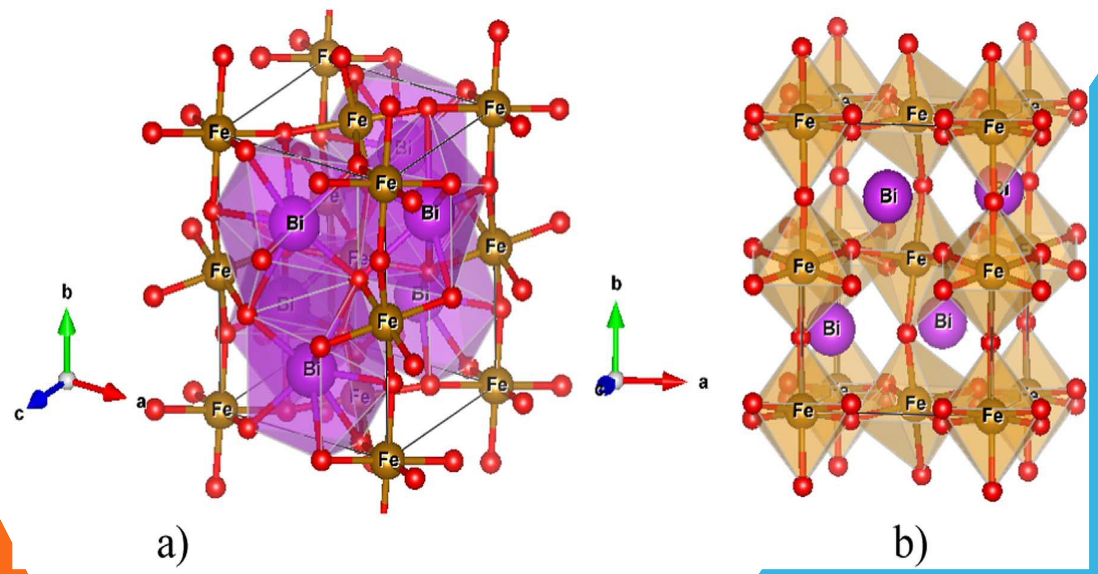

Figure 4. Visualization of the calculated β-$BiFeO_3$ structure: (a) eight fold coordination (CN=8) of the Bi^{3+} cation by O^{2-} anion; (b) six fold coordination (CN=6) of the Fe^{3+} cation by O^{2-} anion.

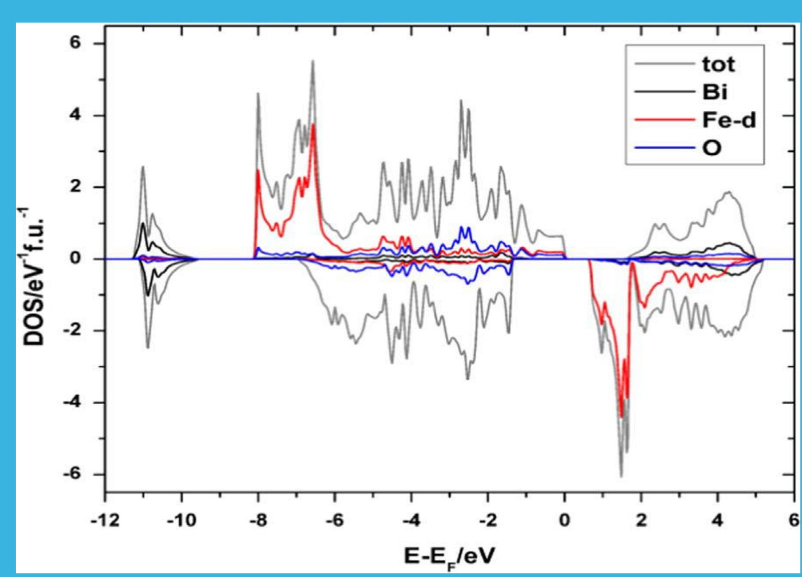

Figure 10. Spin-polarized total and partial density of states for the ferromagnetic $BiFeO_3$;spin-up states shown as positive and spin-down states shown as negative.

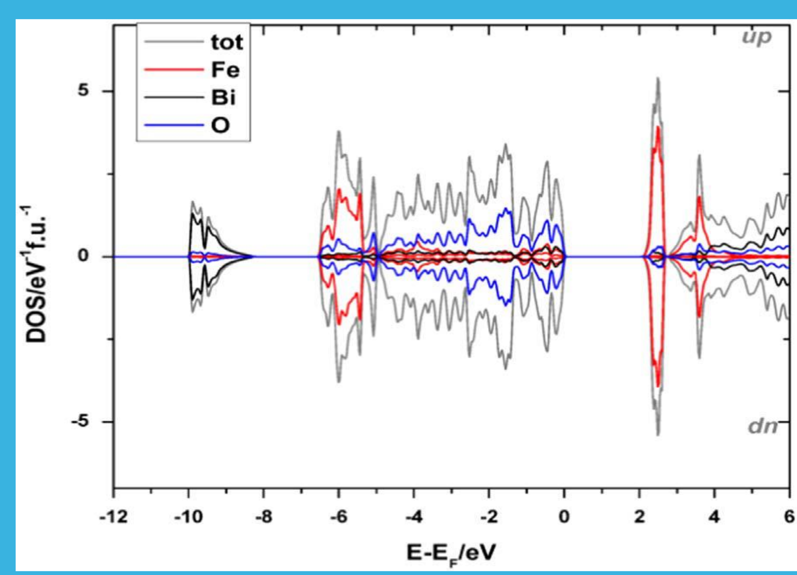

Figure 11. Spin up (positive) and spin-down (negative) total and partial density of states for the antiferromagnetic $BiFeO_3$.

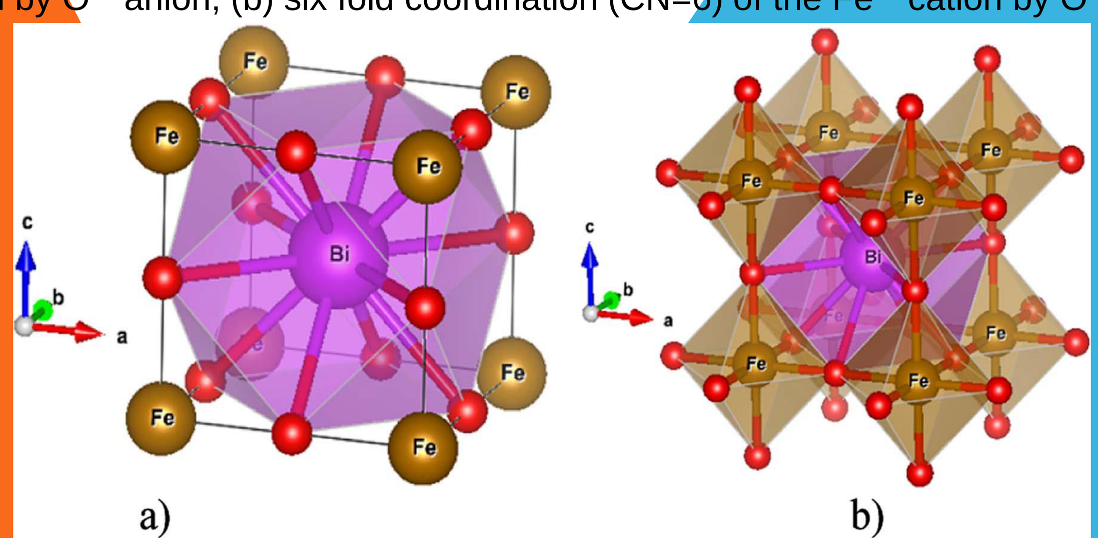

Figure 5. Visualization of the calculated cubic γ- $BiFeO_3$ structure: (a) twelve fold coordination (CN=12) of the Bi atom by O atom; (b) six fold coordination (CN=6) of the Fe atom by O atom

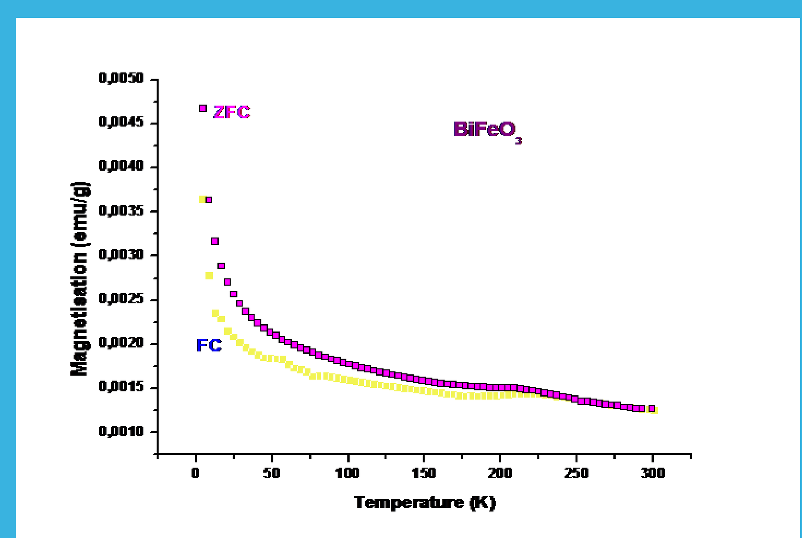

Figure 12. Temperature dependence of magnetization of $BiFeO_3$.

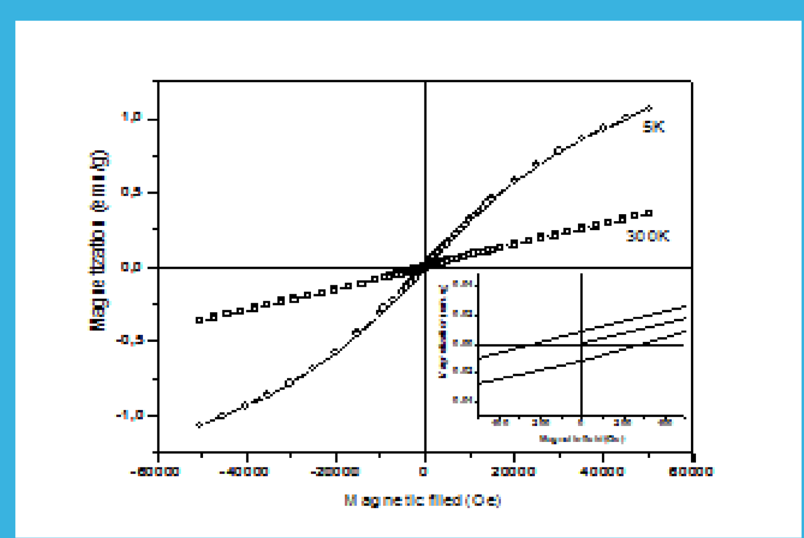

Figure 13. Magnetization curve versus applied magnetic field at 5 K and room temperature. Inset: Details of M(H) behavior at 5K.

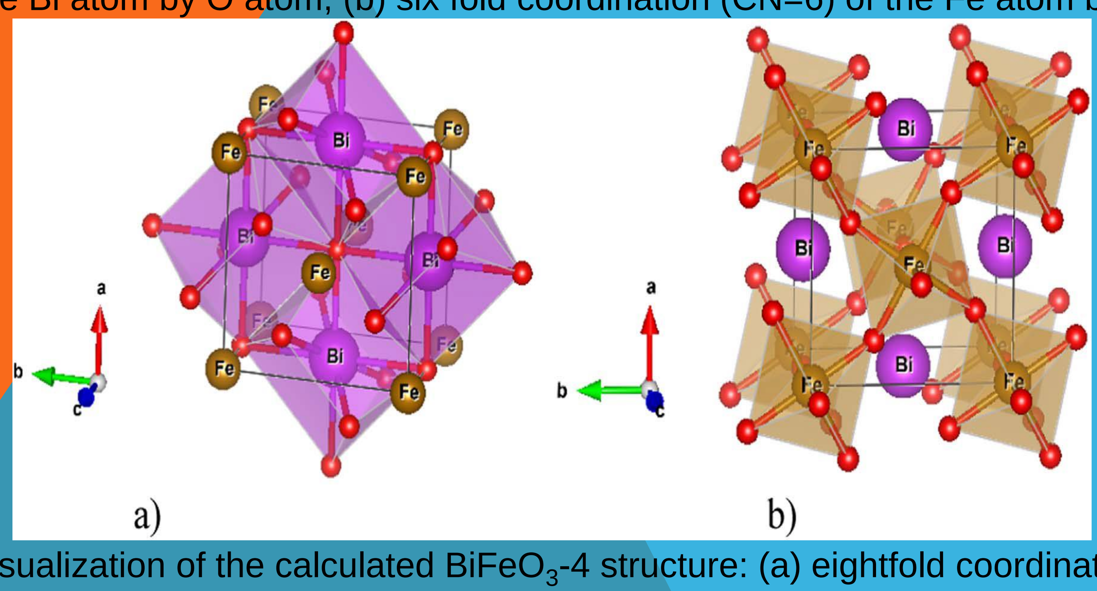

Figure 6. Visualization of the calculated $BiFeO_3$-4 structure: (a) eightfold coordination (CN=8) of the Bi atom by O atom; (b) sixfold coordination (CN=6) of the Fe atom by O atom

Name	Space group	Tilt system	GII (a.u.)
$BiFeO_3$-(1)	*R-3c*	$a^-a^-a^-$	0.00047
$BiFeO_3$-(2)	*Pnma*	a-b+a-	0.01123
$BiFeO_3$-(3)	*Imma*	$a^0b^-b^-$	0.01592
$BiFeO_3$-(4)	P_4/mbm	$a^0a^0c^-$	0.09595
$BiFeO_3$-(5)	I_4/mcm	$a^0a^0c^-$	0.09595
$BiFeO_3$-(6)	$P4_2/nmc$	$a^+a^+c^-$	0.09783
$BiFeO_3$-(7)	C_2/c	$a^-b^-b^-$	0.15273
$BiFeO_3$-(8)	*Cmcm*	$a^+b^0c^-$	0.17060
$BiFeO_3$-(9)	*Im-3*	$a^+a^+a^+$	0.24293
$BiFeO_3$-(10)	I_4/mmm	$a^0b^+b^+$	0.27773
BiFeO3-(11)	*Pm-3m*	$a^0a^0a^0$	0.74669

Table 1. Calculated values of the global instability index (GII) and tilt system for 11 $BiFeO_3$ modifications using SPuDS software

Conclusions

$BiFeO_3$ powders were synthesized using $Bi(NO_3)_3 \cdot 5H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ as starting material and 8 M KOH as mineralizer. It was detected that all reflections can be indexed to a pure rhombohedral α-$BiFeO_3$ crystal phase which crystallizes in R*3*c (no. 161) space group. Refined structure and microstructural parameters show that the crystal size is in the nanometric range at about 30 nm. Further analysis with the HRTEM of individual particles confirmed the evidence of ultra-fine single crystal particles, with characteristic (012) crystal planes. Furthermore, HRTEM confirmed the existence of twin stacking faults, which are responsible for enhanced magnetic properties of synthesized fine particles. The EPR results suggested the existence and participation of electrons trapped by vacancies or defects. It has been proposed that the existence of $Fe^{3+}-O_V$ defect complex could be generated at elevated temperatures followed by formation of trivalent Fe ions, which intensely provide the local 3d moments. Temperature dependence of magnetization shows antiferromagnetic-paramagnetic phase transition at TN=220 K, while below this temperature weak ferromagnetic ordering is detected.The structure prediction method has been used and 11 additional perovskite-related structure candidates in different space groups were obtained. After ab initio optimization equilibrium α-$BiFeO_3$ modification was confirmed by experimental results. Besides, β-$BiFeO_3$ and γ-$BiFeO_3$ modification at elevated temperatures and/or pressures were identified as well as their respective transition route. In addition, a novel tetragonal $BiFeO_3$–4 phase which has never been reported before, was identified in this study. DFT calculations on electronic and magnetic properties of $BiFeO_3$ show good agreement with respective measurements studied here, previous

Acknowledgments

This project was financially supported by the Serbian Ministry of Education, Science and Technological Development on projects III 45012 ;