Influence of Ho doping on structural and magnetic behaviour of multiferroic $BiFeO_3$

Maria Čebela[1,2], Pavla Šenjug[2], Filip Torić[2], Željko Skoko[2], Dejan Zagorac[1] , Damir Pajić[2]

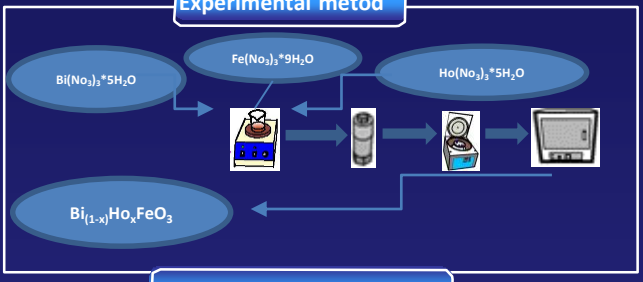
[1] Institute for Nuclear sciences, Centre of Excellence- CextremeLab "Vinča", University of Belgrade, 11000 Belgrade, Serbia

[2] Department of Physics, Faculty of Science, University of Zagreb, Bijenička c. 32, HR-10000 Zagreb, Croatia

Abstract

$BiFeO_3$ is a multiferroic material showing significant promise for future spintronic device applications as well as sensors and actuators. $BiFeO_3$ and $Bi_{1-x}Ho_xFeO_3$ ultrafine nanopowders were synthesized by the hydrothermal method. The diffraction pattern was recorded at room temperature and atmospheric pressure in the absence of any re-heating of the sample. A fitting refinement procedure using the Rietveld method was performed which showed the incorporation of Ho^{3+} ions in the $BiFeO_3$ crystal lattice, where they substitute Bi^{3+} ions. All the samples belong to R3c space group. In addition, theoretical investigation using bond valence calculations have been performed in order to mimic pure and Ho doped $BiFeO_3$ compounds produced in the experiment. Various BFO polymorphs were investigated as function of holmium concentration and final optimization of crystal structures has been performed on ab initio level using Density Functional Theory (DFT). Magnetic behavior of synthesized materials was investigated by SQUID magnetometer in wide temperature interval (2-800 K).

Experimental metod



X-ray Diffraction

$BiFeO_3$

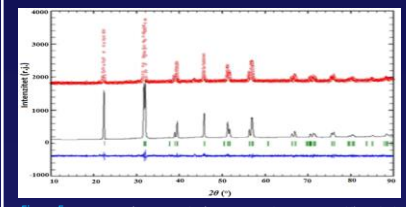
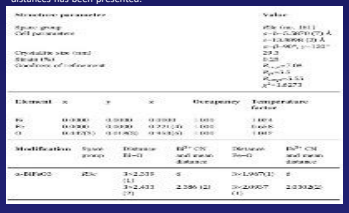


Figure 5. XRD pattern after structural refinement procedure using Rietveld's method

Tabele 5. Space group, cell parameters and atomic positions of α-BiFeO3 refined structure and microstructural parameters after X-Ray Powder Diffraction (XRPD) and Rietveld refinement. In addition, Bi3+ and Fe3+ coordination number (CN), Bi–O and Fe–O distances has been presented.



Ho doped Bi FeO_3

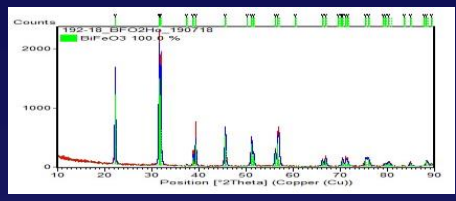


Figure 6. XRD pattern after structural refinement procedure using Rietveld's method

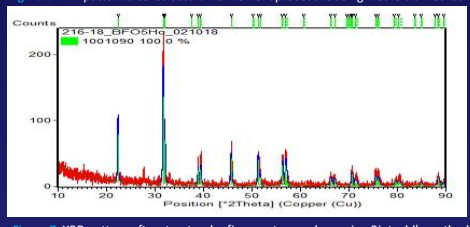


Figure 7. XRD pattern after structural refinement procedure using Rietveld's method

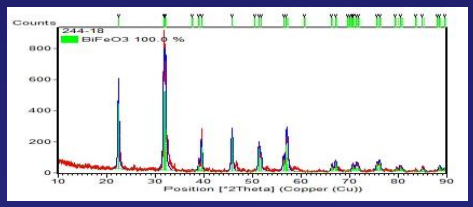


Figure 8. XRD pattern after structural refinement procedure using Rietveld's method

ab initio optimization

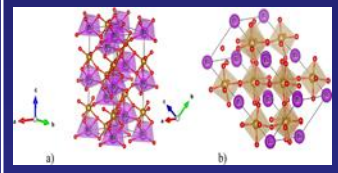


Figure 1. Visualization of the synthesized and calculated α-BiFeO3 structure: (a) sixfold coordination (CN=6) of the Bi atom by O atom; (b) sixfold coordination (CN=6) of the Fe atom by O atom

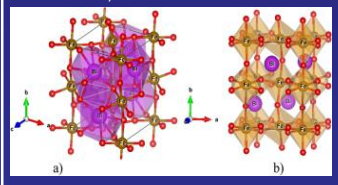


Figure 2. Visualization of the calculated β-$BiFeO_3$ structure: (a) eight fold coordination (CN=8) of the Bi^{3+} cation by O^{2-} anion; (b) six fold coordination (CN=6) of the Fe^{3+} cation by O^{2-} anion.

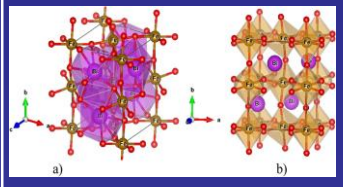


Figure 3. Visualization of the calculated cubic γ- BiFeO3 structure: (a) twelve fold coordination (CN=12) of the Bi atom by O atom; (b) six fold coordination (CN=6) of the Fe atom by O atom

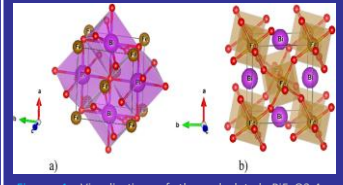


Figure 4. Visualization of the calculated BiFeO3-4 structure: (a) eightfold coordination (CN=8) of the Bi atom by O atom; (b) sixfold coordination (CN=6) of the Fe atom by O atom

Table 1. Calculated values of the global instability index (GII) and tilt system of the most promising $Bi_{0.98}Ho_{0.02}FeO_3$ modifications using bond valence (BVC) method

Modification	Space group	Tilt system	GII
β-$Bi_{0.98}Ho_{0.02}FeO_3$	Pnma	$a^-b^+a^-$	0.03816
R-$Bi_{0.98}Ho_{0.02}FeO_3$	R-3c	$a^-a^-a^-$	0.04284
T_1-$Bi_{0.98}Ho_{0.02}FeO_3$	P4/mbm	a^0a^0c-	0.08938
T_2-$Bi_{0.98}Ho_{0.02}FeO_3$	I4/mcm	a^0a^0c-	0.08938
γ-$Bi_{0.98}Ho_{0.02}FeO_3$	Pm-3m	$a^0a^0a^0$	0.72910

Table 2. Calculated values of the global instability index (GII) and tilt system of the most promising $Bi_{0.95}Ho_{0.05}FeO_3$ modifications using bond valence (BVC) method.

Modification	Space group	Tilt system	GII
β-$Bi_{0.95}Ho_{0.05}FeO_3$	Pnma	$a^-b^+a^-$	0.05815
R-$Bi_{0.95}Ho_{0.05}FeO_3$	R-3c	$a^-a^-a^-$	0.06113
T_1-$Bi_{0.95}Ho_{0.05}FeO_3$	P4/mbm	a^0a^0c-	0.09992
T_2-$Bi_{0.95}Ho_{0.05}FeO_3$	I4/mcm	a^0a^0c-	0.09992
γ-$Bi_{0.95}Ho_{0.05}FeO_3$	Pm-3m	$a^0a^0a^0$	0.73225

Table 3. Calculated values of the global instability index (GII) and tilt system of the most promising $Bi_{0.93}Ho_{0.07}FeO_3$ modifications using bond valence (BVC) method.

Modification	Space group	Tilt system	GII
β-$Bi_{0.93}Ho_{0.07}FeO_3$	Pnma	$a^-b^+a^-$	0.06835
R-$Bi_{0.93}Ho_{0.07}FeO_3$	R-3c	$a^-a^-a^-$	0.07050
T_1-$Bi_{0.93}Ho_{0.07}FeO_3$	P4/mbm	a^0a^0c-	0.10621
T_2-$Bi_{0.93}Ho_{0.07}FeO_3$	I4/mcm	a^0a^0c-	0.10621
γ-$Bi_{0.93}Ho_{0.07}FeO_3$	Pm-3m	$a^0a^0a^0$	0.73434

Table 4. Calculated values of the global instability index (GII) and tilt system of the most promising $Bi_{0.9}Ho_{0.1}FeO_3$ modifications using bond valence (BVC) method.

Modification	Space group	Tilt system	GII
β-$Bi_{0.9}Ho_{0.1}FeO_3$	Pnma	$a^-b^+a^-$	0.08023
R-$Bi_{0.9}Ho_{0.1}FeO_3$	R-3c	$a^-a^-a^-$	0.08226
T_1-$Bi_{0.9}Ho_{0.1}FeO_3$	P4/mbm	a^0a^0c-	0.11480
T_2-$Bi_{0.9}Ho_{0.1}FeO_3$	I4/mcm	a^0a^0c-	0.11480
γ-$Bi_{0.9}Ho_{0.1}FeO_3$	Pm-3m	$a^0a^0a^0$	0.73746

Magnetic properties

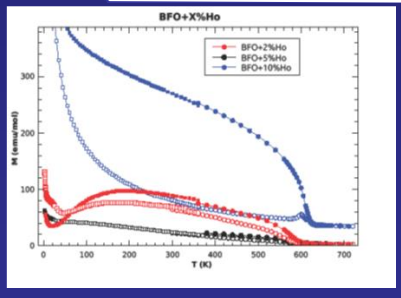


Figure 9. Temperature dependence of magnetization

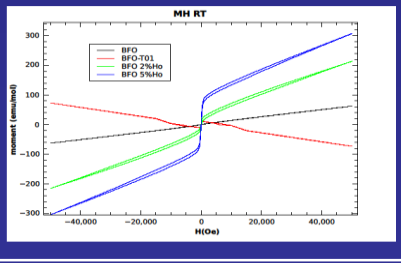


Figure 10. Magnetization curve vs. applied magnetic field.

Conclusion

- *Single-phase multiferroic $BiFeO_3$ and Holmium(Ho) doped $BiFeO_3$ nanopowders have been successfully synthesized with the hydrothermal method.*
- *The phase composition of the synthesized $Bi_{1-x}Ho_xFeO_3$ samples was determined by the x-ray diffraction (XRD) analysis, and the results showed that synthesized material crystallizes in the space group R3c.*
- *Splitting between the zero-field-cooled and field-cooled magnetization curves becomes more pronounced as the Ho concentration is increased, pointing to the development of weak ferromagnetic moment, which is usually connected with uncompensated spins or spin canting. Hysteresis loops show the same fact, attaining higher magnetization with more Ho included, and becoming wider, i.e. magnetically harder.*