Final report to Belgian Federal Science Policy Office

Nanoscale magnetism tuned by local electrical fields in multiferroics

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Controlling the magnetic properties is usually done via external magnetic fields, a technology which is not always easy to integrate into modern electronics. If it would be possible to tune the magnetic properties via electrical fields (as used in modern electronics applications), great progress can be achieved. Multiferroic materials exhibit simultaneously ferroelectric and ferro- or antiferromagnetic order and possibile coupling between them, allowing the manipulation of magnetism by applied electric fields and vice versa. This coupling offers interesting new perspectives for the design of ferroelectric memories with a non-destructive magnetic reading or magnetic random access memories (MRAM) with an electrical writing procedure (MERAM). But still there are open questions: why only a few materials with simultaneous ferroelectric and magnetic order are known, how to explain the coupling of magnetic and ferroelectric order, etc.

Among the several classes of multiferroics, $BiFeO_3$ (BFO) is still the only known room temperature multiferroic magnetoelectric (ferroelectric Curie temperature T_C~1100 K and an antiferromagnetic Nèel temperature T_N~640 K). Magnetic ordering in BFO is quite complex because of Dzyaloshinsky-Moriya (DM) interaction which results in a canted AFM ordering of the Fe^{3+} spins in the system. The weak ferromagnetic moment originating from the canting (green in Fig 1), however, averages to zero over a period of the incommensurate spiral modulated spin structure (SMSS), superimposed onto G-type antiferromagnetic spin ordering in BFO. This spiral spin structure cancels the macroscopic magnetization and prevents the observation of linear ME effect. However, the transition from the spiral spin structure to the homogeneous magnetic state in $BiFeO_3$-based compounds can be induced by the application of high magnetic fields (>18 T), by doping and by epitaxial constraint. That is why the main aim of the project is to find out the optimal synthesis and composition parameters of $BiFeO_3$-based multiferroics and to understand the coexistence conditions of ferroelectric and magnetic ordering. The research objectives are the synthesis and investigation of optical,

dielectric, magnetic and magnetoelectric properties of $BiFeO_3$-based multiferroics.

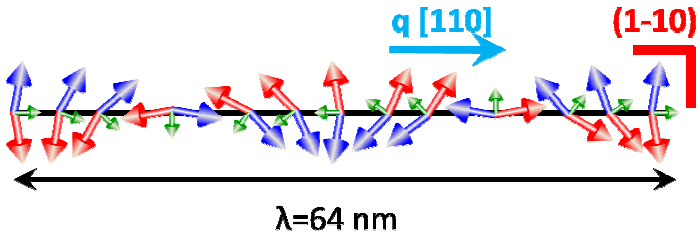

Figure 1. Scheme of the canted antiferromagnetic structure of $BiFeO_3$ where the two AF sublattices are organized along a cycloidal spiral. The propagation vector q is along the direction [110] and the plane of spin-rotation is (1-10).

First, the $Bi_{1-x}La_xFeO_3$, $Bi_{1-x}Nd_xFeO_3$, $Bi_{1-x}Gd_xFeO_3$, $Bi_{0.8}(LaGd)_{0.2}FeO_3$ (x=0-0.2) ceramic samples were prepared by a solid-state reaction technique. Then these ceramic samples were used as a targets for thin films preparation using thermal chemical vapor deposition and pulsed laser deposition (PLD).

To study aforesaid multiferroic ceramic samples and thin films, modern experimental techniques were used. The magnetization hysteresis (M-H) loops were measured using an automated vibrating sample magnetometer (VSM, Oxford Instruments). Magnetic properties of thin films were investigated by more sensitive superconducting quantum interference device (SQUID). For transport and magnetoelectric measurements the Physical Property Measurement System equipped with a 9 T superconducting magnet (PPMS: Model 6000, Quantum design) was used. The optical reflectivity spectras R(ω) at room temperature in the infrared range (IR) were recorded with a FTIR spectrometer (Bruker Corporation, Vertex 80V).

Results and Conclusions

A. Bulk multiferroics

The phase composition and structural transformations in ceramic samples have been investigated by XRD. A representative XRD pattern of doped BFO samples is shown in Fig. 2. The presence of non-perovskite $Bi_2Fe_4O_9$ secondary phase [peaks marked by * in Fig. 2] were routinely observed in undoped $BiFeO_3$. The increasing doping level prevents the formation of the second phase. Rietveld refinement of the X-ray powder diffraction patterns showed a continual structural transformation with ion substitution of rare-earth elements at the Bi site of BFO, while nonperovskite secondary $Bi_2Fe_4O_9$ phase, found in pure BFO, disappears completely at x=0.1.

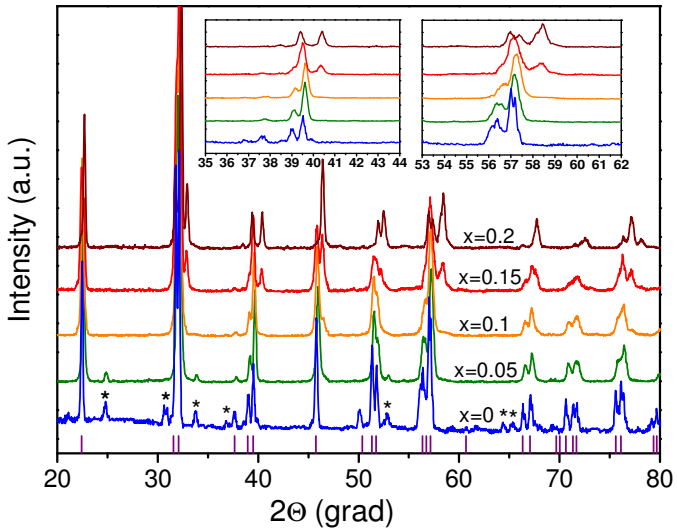

Figure 2. XRD patterns of $Bi_{1-x}Gd_xFeO_3$ as a function of x illustrating the clear change in crystal structure at x>0.1. The lower ticks are given for the $BiFeO_3$ bragg reflections taken from JCPDS Card No.86-1518. The peaks from the impurity phase $Bi_2Fe_4O_9$ are marked with *.

The optical reflectivity spectras R(ω) at room temperature in the infrared range (IR) were recorded with a FTIR spectrometer (Bruker Corporation, Vertex 80V). The IR spectras contain information about the values of ionic polarizability, limit frequencies of longitudinal ω_L and transversal ω_T optical phonons. The $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ components of complex dielectric constant were obtained from R(ω) through the Kramers-Kronig transformation. Their features in the infrared region indicate the predominance of the ionic bonding in BGFO compounds and the presence of dielectric polarization mechanisms, related to the elastic displacement of electrons and ions.

In order to study magnetic properties, the temperature dependence of magnetization M(T) and M(H) loops at different temperatures were measured. All of the M vs. T curves for BFO ceramic samples show a constant magnetization at high temperatures and an Curie-like upturn at low temperatures (below 40-100 K depending on composition). The undoped compounds exhibit a linear field dependence of magnetization typical for antiferromagnets, as expected for an antiferromagnetic alignment of the Fe^{3+} magnetic moments. A weak net magnetization in doped BFO starts to develop at low concentrations (5%) of the substituting element. Due to the transformation of crystal structure, the SMSS in BFO-based samples collapses continuously with increasing x, showing a noticeable enhancement of magnetic properties. Among chosen rare-earth substituting elements the most enhanced magnetic properties were obtained for Gd-containing compounds (see Fig. 3). This can be explained by the fact that the Gd^{3+} ions are magnetically active and possess their own large magnetic moments which tend to align in the same direction as the weak ferromagnetic component of iron sublattice, thus providing a significant rise to the magnetization.

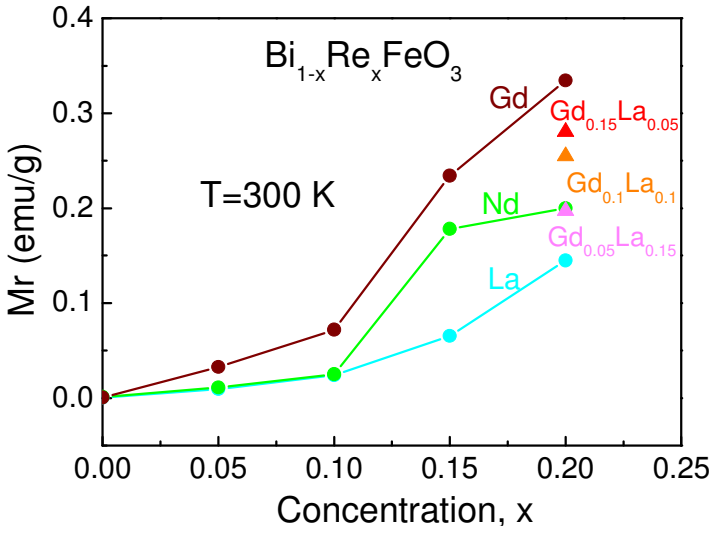

Figure 3. Variation of remanent magnetization Mr with the content of sustituting elements ; Re=Gd, Nd, La, $(GdLa)_{0.2}$

The magnetoelectric effect (ME), that is a polarization response to an applied magnetic field, was studied in present work. The most critical indicator of the magnetoelectric coupling in multiferroics is the ME coefficient α_{ME}. Practically, α_{ME} is determined by measuring the electric field generated across the sample when an AC magnetic field and DC bias are applied. In order to perform such measurements the commercial sample puck for transport measurements using Quantum Design PPMS have been modified in our laboratory (see Fig 4a). The AC field was generated by sending an AC current (Keithley 6221) through a coil (1290 turns of AWG 36 phosphor bronze wire, with a diameter of 18 mm) which was assembled on the standard sample puck for PPMS electrical transport measurements. The DC magnetic field was produced by the PPMS-internal superconducting magnet. Samples were mounted in longitudinal geometry, i.e. magnetoelectric voltage is parallel to the direction of AC and DC magnetic fields (Fig. 4b). Through these measurements we expect to explore the underlying physics of magnetoelectric coupling in BFO multiferroics.

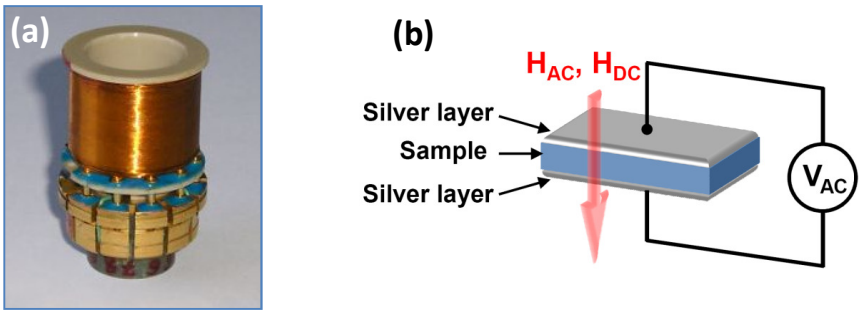

Figure 4. (a) The sample puck for ME measurements ; (b) schematic view of the ME measurement circle

The variation of ME coefficient with DC bias magnetic field at room temperature is shown in figure 5. For rhombohedral BGFO compounds with x<0.15, ME coefficient increases with increasing magnetic field and exhibits maximum around H=0.3 kOe. In case of orthorhombic Gd-doped BFO, ME coefficient increases with increasing magnetic field up to 1.2 kOe and attains a maximum value of 9.15 mV/(cm•Oe) for x=0.2. Further increase in magnetic field up to 10 kOe does not bring about any significant variation in the output.

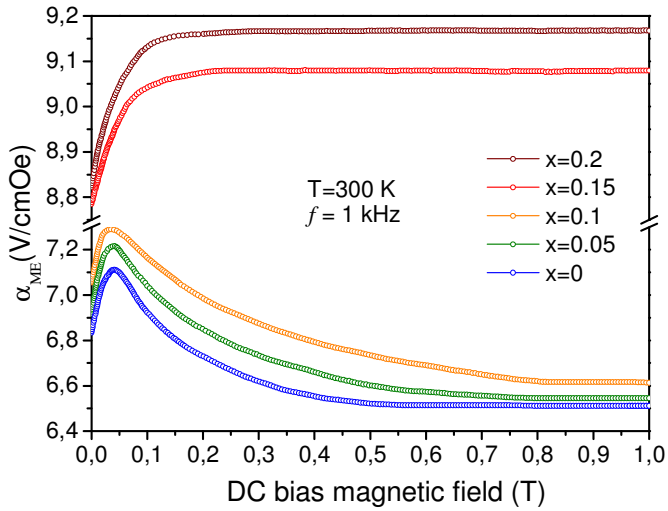

Figure 5. Magnetoelectric coefficient α_{ME} dependence on on DC bias magnetic field at room temperature at an AC magnetic field H_{ac}=10 Oe for BGFO compounds.

These data present clear evidence for the magnetoelectric coupling in BGFO ceramic compounds, providing an opportunity to control the polarization by the magnetic field. The observed ME coupling could be explained through the piezoeffect. In a piezomagnetic BFO an applied magnetic field induces mechanical strain, which, in turn, can induce an electric polarization via piezoelectric effect.

B. Multiferroic thin films

Not many multiferroics compounds are known, and most of them are antiferromagnetic ferroelectrics. It is known that the ME response is limited by the relation $\alpha_{ij}^2 < \chi_{ij}^{e}\chi_{ij}^{m}$, where χ_{ij}^{e} and χ_{ij}^{m} are the electric and magnetic susceptibilities. Consequently, ferromagnetic ferroelectrics are prime candidates for displaying giant ME effects. Though the symmetry of the BFO system permits the existence of a weak ferromagnetic moment, originating from the Dzyaloshinsky–Moryia interaction, the SMSS prevents the observation of any net magnetization. Growing BFO in thin film form can suppress this spiral spin structure which leads to the appearance of weak ferromagnetism.

Therefore, $Bi_xLa_{1-x}FeO_3$ (BLFO) thin films (x=0.0; 0.3; 0.5) of 90 nm thickness were grown on SiO_2-glass substrates using a thermal chemical vapor deposition method. The monoclinically distorted crystal structure of the films was revealed by X-ray diffraction at room temperature, while corresponding bulk samples crystallize in rhombohedral symmetry. The dc magnetization of the films was measured as a function of temperature and magnetic field.

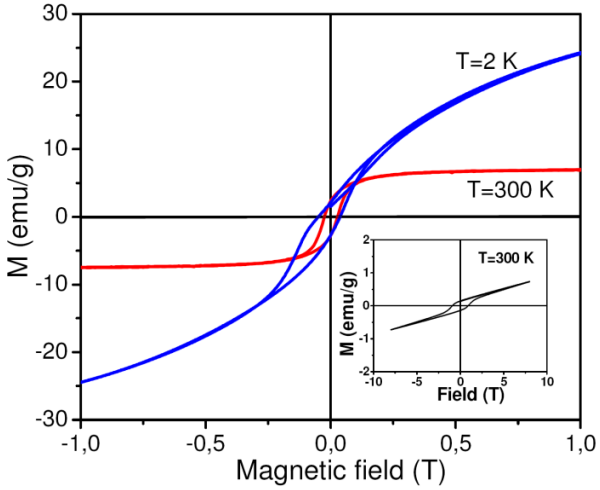

Figure 6. Field dependence of the magnetization obtained for the BLFO (x=0.5) thin film. Inset shows the M-H curve of corresponding bulk sample at room temperature

The observed M-H curves reveal weak ferromagnetism in LBFO thin films even at room temperature. As seen from Fig. 6, the value of the remanent magnetization Mr at room temperature for BLFO (x=0.5) film is about 5 emu/g which is consistent with the value observed previously by Wang et al. (Science 299, p. 1719, 2003) for the PLD deposited BFO films. The magnetization at corresponding temperatures is an order of magnitude higher in comparison to that of the bulk BLFO samples (see inset of Fig. 5). Besides, the saturation magnetization at room temperature is ~7 emu/g at relatively low applied magnetic field. In BLFO thin films grown on glass substrate, the epitaxial strain induced by the substrate and film lattice mismatch cannot be responsible for the enhanced magnetism. Neutron diffraction measurements, performed by Béa et al. (Phil. Mag. Lett. 87, p. 165, 2007), revealed that right monoclinically distorted BFO films show G-type antiferromagnetic ordering with no indication of any cycloidal modulation. Thus, the observed M(H) nonlinearity, finite coercitivity and the enhancement of M_r and M_s for BLFO thin films can be explained as due to suppression of the cycloidal spin structure and the release of the locked magnetization.

Magnetic force microscopy (MFM) scans were also performed on the BLFO films in order to study their magnetic domain structure. Figure 7 demonstrates the MFM images of $Bi_{0.5}La_{0.5}FeO_3$ thin film obtained at room temperature.

The periodic magnetic structure with a period of 1.5 μm is clearly seen in Fig. 7c, which differs significantly from the topography structure (Fig. 7a). This periodicity reflects the presence of magnetic stripe domains in the BLFO thin films.

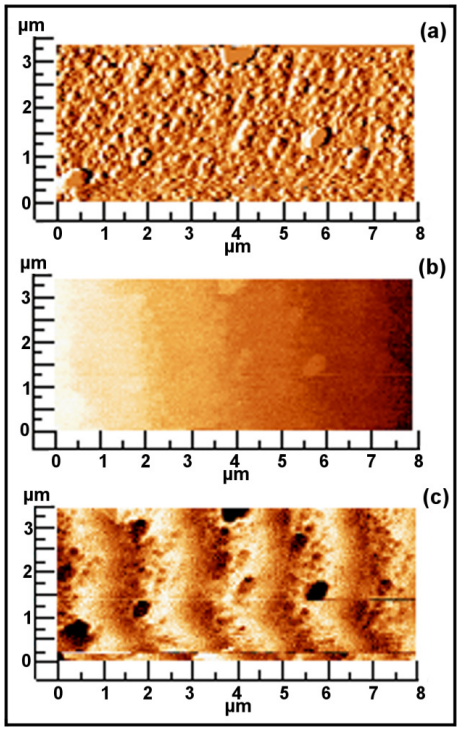

Figure 7. MFM images of the BLFO (x=0.5) film: (a) topography, (b) phase and (c) amplitude

In conclusion, our results demonstrate the weak ferromagnetic nature of the monoclinically distorted thin films perepared by thermal chemical vapor deposition method. Therefore, these films are good candidates for the observation of a linear magnetoelectric effect, prohibited in the bulk due to the spiral modulation of the G-type spin ordering.

C. Epitaxial strained multiferroic thin films

Using epitaxial growth, the properties of multiferroic thin films can be engineered by tuning the strain imposed by the substrate. Biaxial strain, developing due to lattice mismatch between the film and the substrate, leads to the structural changes in the growing film such as the formation of misfit dislocations. The epitaxial strain in $BiFeO_3$ thin films has been described as one of the way to supress the SMSS and, therefore, enhance magnetic and ferroelectric properties.

Among the known multiferroics, the $BiFeO_3$ is a very interesting candidate for epitaxial growth onto $SrTiO_3$ (STO) substrates because of the small lattice mismatch (misfit strain is 1.5%). In the present work, the polycrystalline BFO-based thin films (Fig. 8) have been grown onto STO using. Pulsed Laser Deposition (PLD). Pulsed laser deposition has emerged as a relatively simple and highly precise technique for the growth of thin films of variety of materials and especially oxides.

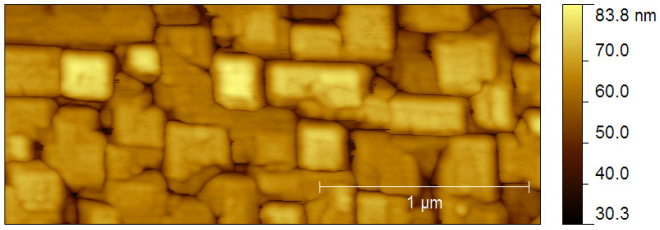

Figure 8. AFM image of BFO/STO film surface

Single phase thin films grown by pulsed laser deposition can only be obtained in a narrow window of deposition pressure and temperature. Out of the stability window Fe-

or Bi-rich impurity phases form, which has a strong impact on the physical and structural properties of the films.

Structural characterization of the BFO/STO films was performed usin X-ray diffraction (XRD). Figure 9 shows the diffraction patterns of the films grown under varying oxygen deposition pressures with only (00l) peaks revealed. The position of the peakes shift to larger angles with increasing oxygen pressure. This data indicate that that the highly (001)-oriented single phase BFO thin films were obtained.

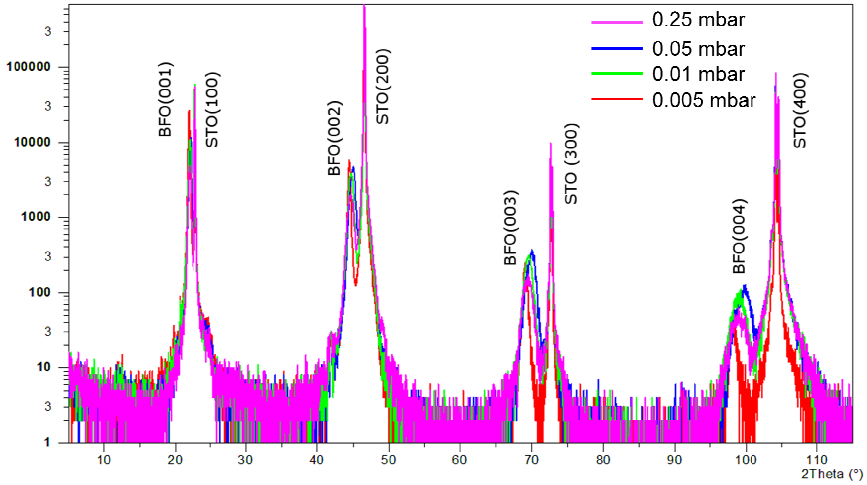

Figure 9. XRD pattern of BFO/STO thin films grown under varying oxygen deposition pressures

Figure 10 shows in-plane magnetic hysteresis loop measured for BFO thin film using SQUID magnetometer in comparison with field dependence of magnetization for bulk ceramic sample. Thin film exhibits saturated weak ferromagnetic loop at room temperature, contrary to antiferromagnetism of bulk samples. This increased magnetization may be attributed to a suppressed inhomogeneous antiferromagnetic spin structure through the epitaxial strain induced by the substrate.

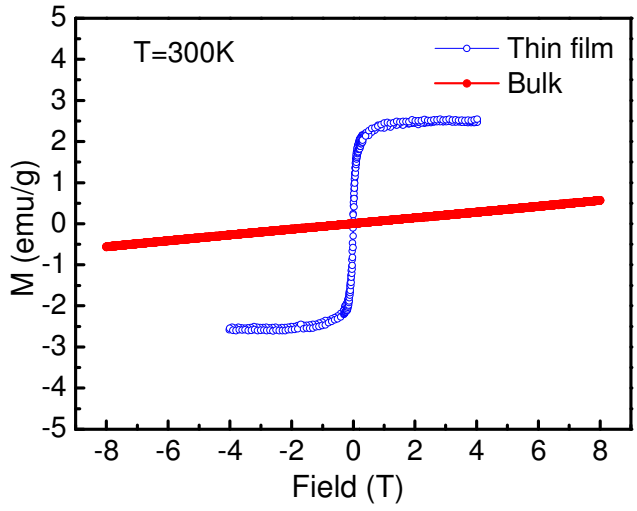

Figure 10. Field dependences of the magnetization obtained for epitaxially strained BFO thin films and for bulk ceramic BFO.

To further systematically study the stress enhancement effect in thin films, we grew a $BiFeO_3$ film samples with a continuously changing thickness. The results of structural and magnetic measurements are under way.

Furthermore, it has been shown that strained epitaxial BFO thin films are good quality ferroelectrics with greatly enhanced polarization (90-100 $\mu C/cm^2$). And they can be used in fabrication of ferroelectric/superconductor heterostructures. Interfacial couplings in such heterostructures can lead to new very interesting phenomena. The critical temperature of superconductor can be changed via the application of an electric field. The carrier density modulation is induced by switching the polarization of a ferroelectric layer upon the application of a voltage pulse. This effect allows changing the T_C in a nonvolatile and reversible way. Therefore, epitaxial BFO/MoGe thin film heterostructures were fabricated on $SrTiO_3$ (100) substrate and are under investigation.

In summary, the $Bi_{1-x}Re_xFeO_3$ (Re=Gd, La, Nd) ceramic samples were prepared by a solid-state reaction technique. Using them as targets, the BFO thin films were deposited onto glass substrate by thermal chemical vapor deposition method and epitaxial BFO films onto STO(100) substrates by PLD. We found that in bulk samples due to the transformation of crystal structure, the spiral antiferromagnetic spin structure in BFO-based samples collapses continuously with increasing the concentration of the doping element, showing a noticeable enhancement of magnetic properties. Among chosen rare-earth substituting elements the most enhanced magnetic properties were obtained for Gd-containing compounds. Through studying the temperature/magnetic field dependence of the magnetoelectric coefficient, we have revealed the effect of Gd^{3+} ions substitution on the magnetoelectric properties, and have demonstrated the possibility of manipulating the electric state in BGFO multiferroics by applying magnetic field at room temperature.

A significant enhancement of magnetization, compared to that of corresponding bulk ceramics, was observed in thin films. Our results demonstrate room-temperature weak ferromagnetism of BFO thin films, making them good candidates for the observation of a linear magnetoelectric effect, prohibited in the bulk due to the spiral modulation of the G-type spin ordering. Further investigations are under way, especially the effect of film thickness, epitaxial strain and doping type and level on the magnetic properties of BFO thin films.

In the framework of this project a **new collaboration** was started with PLD workgroup, Institut für Experimentelle Physik II, Fakultät für Physik und Geowissenschaften, UNIVERSITÄT LEIPZIG.

Publications

1. V.V. Lazenka, G. Zhang, J. Vanacken, I.I. Makoed, A.F. Ravinski, and V.V. Moshchalkov. Structural transformation and magnetoelectric behavior in Gd-modified $BiFeO_3$ multiferroics. J. Phys. D: Appl. Phys. 45 (2012) 125002.

2. V.V. Lazenka, A.F. Ravinski, I.I. Makoed, G. Zhang, J. Vanacken and V.V. Moshchalkov Weak ferromagnetism in $Bi_{1-x}La_xFeO_3$ thin films. Submitted to J. Appl. Phys.

3. F. Ravinski, I.I. Makoed, K.I. Janushkevich, A.I. Galyas, O.F. Demidenko, V.V. Lazenka,and V.V. Moshchalkov. Dielectric and optical properties of gadolinium substituted bismuth ferrite. Bulletin of the Russian Academy of Sciences: Physics, accepted.

4. A.F. Ravinski, I.I. Makoed, K.I. Janushkevich, A.I. Galyas, O.F. Demidenko, V.V. Lazenka, V.V. Moshchalkov. Magnetic properties of $BiFeO_3$-based multiferroic compounds. Proceed. of 3rd International meeting on Multiferroics, Rostov-on-Don – Loo, Russia, September 4-8, 2011.