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Synthesis and multiferroic properties of M-type $SrFe_{12}O_{19}$ hexaferrite ceramics

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ABSTRACT

The coexistence of strong ferromagnetism and large ferroelectricity has been observed in pure strontium hexaferrite $SrFe_{12}O_{19}$ fabricated by a modified ceramic technological method from highly purified initial materials with addition of boron oxide in mass concentration of less than 1.5%. The structure of the samples confirmed by X-ray diffraction patterns is consistent with a single hexagonal phase. The samples were polycrystalline with the grain size of 300–400 nm and the intergrain space was field with B_2O_3. The use of boron oxide resulted in enhanced resistivity enabling proper electric polarisation measurements. The magnetic properties are characterised by a standard ferrimagnetic behaviour with the Neel temperature of about 450 °C. Large electric polarisation was observed with the remnant value of 22 μC/cm^2 and the maximal value of 45 μC/cm^2 under the electric field of 300 kV/m. A strong coupling between magnetic and electric ordering was confirmed by measuring the magnetoelectric parameter and the electric field-controlled magnetic hysteresis. The change in magnetization by applying an electric field was in the range of 9–10%, which is even greater than that observed in some substituted hexaferrites with a magnetically induced electric polarisation. The combination of room-temperature multiferroic properties and electrically tuneable magnetization is promising for applications in magnetoelectric devices.

1. Introduction

Magnetic oxide materials make an essential contribution to modern technology. Among them, M-type hexagonal ferrites $AFe_{12}O_{19}$ (A = Sr, Ba, Pb) have been a subject of continuous interest. They have a rather complicated crystal structure resulting in a large magnetocrystalline anisotropy, coercivity and complex internal magnetic structure (see, for example, review in [1]). The combination of these properties with a high saturation magnetization and a high temperature of the ferrimagnetic ordering transition around 450 °C makes the hexaferrites attractive for various applications as data storage materials, permanent magnets, and electronic components operating at microwave frequencies [1–3]. Recently it has been reported that some hexagonal ferrites show multiferroic properties and a relatively large magnetoelectric (ME) effect at room temperature and low magnetic fields [4–8]. This discovery raised expectations that these materials may provide novel device applications based on the ME effect such as multiple state logic, non-volatile memory and magnetoelectric sensors.

On the contrary, many other magnetically induced ferroelectrics do not show combined large electric and magnetic polarisations at room temperature, which greatly restricts their practical use. For example, the perovskite BiFeO [9] demonstrates coexistence of magnetic and ferroelectric orders at ambient conditions but its weak ferromagnetism could be a problem for device applications.

Magnetically induced ferroelectricity typically requires a non-collinear magnetic structure which has a lower ordering transition temperature in comparison with that of a conventional collinear phase. This is why the ferroelectricity in such systems often exists at rather low temperatures. In hexagonal ferrites the ferroelectric effects are observed at elevated temperatures, up to room temperature. M-type hexaferrites have a collinear ferromagnetic ordering at ground state but conical magnetic structures are well known for a number of substituted systems [10–12] where the ferroelectric ordering induced by a magnetic field has been recently reported [13].

On the other hand, combined large ferroelectricity and strong ferrimagnetism have been observed in pure single-phase hexaferrite ceramics synthesized by a polymer precursor method [14–16]. The origin of dual ferroic properties in this case could be related with a geometrical structural transition occurring below

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the Curie temperature. In this paper, we report on a large multiferroic effect in pure $SrFe_{12}O_{19}$ prepared by a modified ceramic synthesis technique. Small addition of boron oxide was used to increase the balk resistivity and to ensure proper polarisation properties. A large effect of the electric field on the magnetization behaviour was observed which could be of interest for novel information storage technology and four-state logic device.

2. Sample preparation and measurement methods

Strontium ferrites were prepared by a modified ceramic method. The obtained samples were stoichiometric compounds of $SrO{\cdot}6Fe_2O_3$ as a result of the solid state reaction between oxides of Sr and Fe during thermal treatment. Highly purified strontium carbonate $SrCo_3$ and iron oxide Fe_2O_3 were mixed together in the required composition and pressurised into pellets. They were fired in the rotating oven at a temperature of 1150 °C during 2 h to synthesise a ferrite phase. The samples then were cooled down in deionised water. This followed by rough crashing, dry milling and ultra-fine wet milling. After the dry-milling stage, highly pure boron oxide B_2O_3 in the mass concentration of 0.5–1.5% was added with the aim to obtain a fine-grain structure with highly resistive intergrain streaks. The boron oxide has the melting temperature of 450 °C, therefore, during heating it transforms into a liquid state and coats the ferrite grains suppressing their growth. The presence of B_2O_3 also enhances the bulk resistivity of the ferrite samples.

After wet milling, the average grain size was 0.3–0.5 μm. The powders were pressurised (under pressure of 650 kg/cm^2) to obtain stripe-formed samples ($15 \times 15 \times 1$ mm) and cube-formed samples with a side of 6 mm. This followed by placing the samples in the drying chamber at a temperature of 40 °C and normal atmospheric pressure for 12 h. Finally, the samples were fired at a temperature of 1100 °C during 6 h in oxygen at normal atmospheric pressure and left cooling down to room temperature. Altogether, 10 samples of $SrFe_{12}O_{19}$ were fabricated by these processes. For further investigations, the samples were polished (14th class of purity). All the measurements were done at room temperature.

The structures of the sintered samples were examined by X-ray diffraction (XRD) using Dron-3M diffractometer with Cu Kα radiation source and Rigaku diffractometer with Fe anode tube as a radiation source (current – 25 mA, voltage – 25 kW). The radiation wavelength was 0.193728 nm. The spectra were detected using a Mn filter. The Brag-Brenton focusing scheme with two Soller slits was used.

For electrical measurements, the surfaces of the samples were coated with silver paste to form a capacitor. The electrodes from (In,Ga)-eutectic were also used. The both types of electrodes provided good Ohmic contacts. The resistivity was found from voltage–current characteristics and by two-probe method. Small currents were gathered by electrometer (Keithley, model 6514). The polarisation hysteresis P–E loops were measured with a home-made instrumentation based on a modified Sawyer-Tower circuit at 50 Hz using a compensation capacitor of 0.1 μF in parallel with the sample. The polarisation was found by digital integration of the current. The voltage varied within 0–2 kV.

The magnetization loops $M-H$ and magnetic parameters were measured with the help of a vibrating sample magnetometer (VSM, EG&G PARC, USA) in the external magnetic field up to 10 kOe. For control measurements, the samples in the form of a sphere with a diameter of 4–4.5 mm were also prepared. The effect of the electric field E on the magnetization was measured with a VSM by applying E across the sample-capacitor perpendicular to the magnetic field H and the induced M was detected by pick up coils.

The magnetoelectric (ME) effect was deduced from the measurements of voltage U occurring across the sample-capacitor of thickness h under the application of an alternating magnetic field. The magnitude of ME effect is characterised by the parameter α_{ME} found from

$$\alpha_{ME} = \frac{dE}{dH} = \frac{dU}{hdH} \quad (1)$$

The alternating magnetic field having a frequency of 50 kHz and an amplitude up to 550 A/m was created by Helmholtz coils. The induced ME signal was measured by a dynamic method [17] with the help of lock-in-amplifier (SR-530) with the input resistance of 100 MΩ and capacitance of 25 pF. The magnetic field amplitude was fixed at 500 A/m.

The variation of dielectric constant $\varepsilon(H)$ with a magnetic field H is known as the magnetodielectric (MD) effect or magnetocapacitance. The measure of MD is defined as:

$$\mathrm{MD} = \frac{\varepsilon(H) - \varepsilon(0)}{\varepsilon(0)} \quad (2)$$

Here $\varepsilon(H)$ and $\varepsilon(0)$ are the values of the dielectric constant in the presence of a magnetic field and without the field, respectfully. The measurements were performed with LCR metre at a frequency of 100 kHz in a dc magnetic field of 3 kOe.

3. Results and discussions

The XRD patterns of the fabricated samples are shown in Fig. 1 which are consistent with single phase strontium hexaferrites with the lattice parameters $a = 5.88$ Å, $c = 23.3$ Å. They also reveal that the fabricated samples had a polycrystalline structure.

Table 1 lists the main magnetic, electric and magnetoelectric parameters of the ceramic samples. The obtained resistivity of the order of 10^{10} Ω cm is sufficiently high to support an electric field and ensures proper electric and magnetoelectric measurements. In many single phase hexaferrites the resistivity is much lower and special methods should be used to increase the resistivity. In the present case, small addition of boron oxide lowers the conductivity. In substituted hexaferrites the resistivity can be greatly enhanced. For example, substituting Fe^{3+} with (Co^{2+}/Ti^{4+}) may increase the resistivity by up to five orders of magnitude to 4.36×10^{10} Ω cm for $SrCo_2Ti_2Fe_8O_{19}$ [18]. Small addition of Mg or Al also helps to increase the resistivity [8,13,19]. M-type hexaferrite ceramics prepared by polymer precursor technics also have an enhanced resistivity [14–16].

The obtained ME parameter of about 25 mV/Oe is considerably higher than its typical value for single phase materials. This can be compared with the ME effect in composites consisting of magnetostrictive and ferroelectric phases [20,21].

Fig. 2 shows the magnetization loop of the fabricated $SrFe_{12}O_{19}$ ceramics. The loop shape and magnetic characteristics are typical of strontium hexaferrites produced by a standard ceramic technique [1,22].

Fig. 3 demonstrates the polarisation hysteresis loops of $SrFe_{12}O_{19}$ under applied electric field. The loop is fully enclosed and its shape indicates the absence of leakage currents, which was possible to achieve due to enhanced resistivity. In many cases, low resistivity of ferrites makes it difficult to measure the electrical polarisation. Thus, in composites x $SrFe_{12}O_{19}$–$(1-x)$ $BaTiO_3$ the polarisation decreases with increasing the ferrite content and at $x = 0.7$ the maximal polarisation is about 3 μC/cm^2 [23]. On the contrary, a very large maximal polarisation of about 45 μC/cm^2 is observed in Fig. 3. The remnant polarisation is about 23 μC/cm^2 and the electric coercivity is about 210 kV/m. Similar values of the remnant and maximal polarisations are obtained for M-type hexagonal ferrites $AFe_{12}O_{19}$ prepared by polymer precursor technology [14–16].

We have also studied the effect of an applied electric field on the magnetization behaviour. The possibility of tuning the magnetization with electric field is of interest for new information storage technology and four-state logic devices. Furthermore, it can help to realize the device miniaturization in planar technology since it is easier to incorporate a miniature capacitor to generate an electric field than a coil generating a magnetic field. The change in the magnetization loop of hexaferrite ceramics $SrFe_{12}O_{19}$ caused by electric field is shown in Fig. 4. In the presence of the electric field of 20 kV/cm the remnant magnetization decreases by 9–10% and the coercivity increases by 6–8%. The observed electric field effect on the magnetization is larger than that reported for substituted M-type hexaferrite $SrCo_2Ti_2Fe_8O_{19}$ [18].

The obtained results clearly demonstrate room-temperature multiferroic properties of a single-phase strontium hexaferrite ceramics fabricated from highly pure initial materials with addition of boron oxide. It is interesting to compare the obtained parameters with those typical of $BiFeO_3$ which is shown in Table 2. $BiFeO_3$ is one of the mostly studied multiferroics which has coupled antiferromagnetic and ferroelectric orders at a corresponding temperatures (about 370 °C and 830 °C) well above room temperature [9,24–26]. Thin films of $BiFeO_3$ demonstrating weak magnetism have a potential for developing practical devices

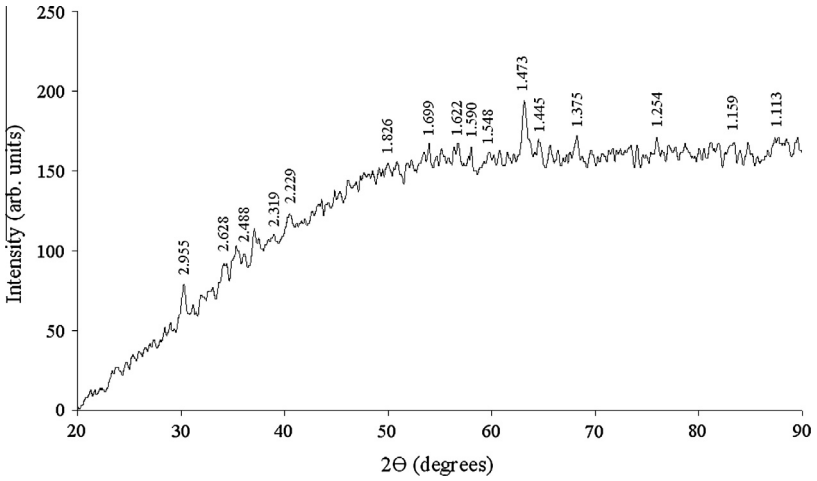

Fig. 1. XRD patterns of sintered $SrFe_{12}O_{19}$ ferrite ceramics.

Table 1
Characteristics of fabricated hexagonal ferrite ceramics $SrFe_{12}O_{19}$.

Density γ, g/cm^3	Resistivity ρ, Ω cm	Remnant magnetization, emu/g	Coercivity (magnetization), Oe	Neel temperature, T_N, °C	ME parameter α_{ME}, mV/Oe cm	MD ratio, %
4.95–4.99	$(8–9)\cdot10^9$	37.5–38.5	3600–3700	456	24–25	4.08–4.17

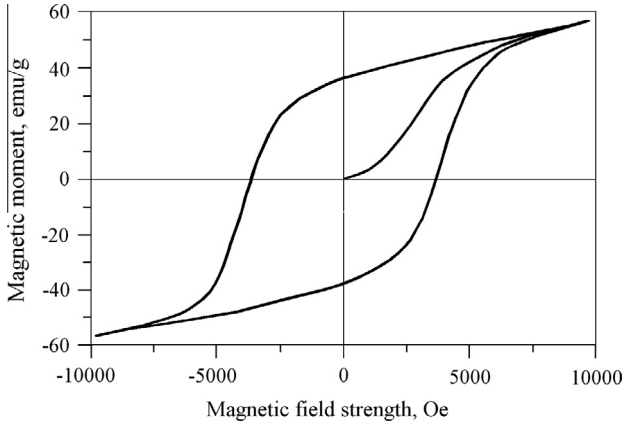

Fig. 2. Magnetization loop of the fabricated single-phase hexagonal ferrite ceramics $SrFe_{12}O_{19}$.

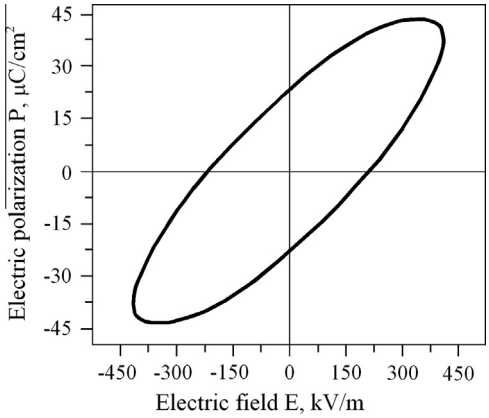

Fig. 3. Electric polarisation loop of the fabricated single-phase hexagonal ferrite ceramics $SrFe_{12}O_{19}$ with addition of boron oxide.

exploiting the magnetoelectric effect. The magnetization of bulk $BiFeO_3$ is very small and thin-film remnant magnetization is smaller than that of $SrFe_{12}O_{19}$ by 4.4 times. The maximum polarisation of the fabricated samples is up to two times smaller, however, the magnetoelectric parameter is higher up to 8 times and the magnetodielectric ratio is 4 times higher. Therefore, in terms of the magnetic and electric order coupling the properties of the synthesised hexaferrite ceramics are much greater.

The ferroelectric behaviour of strontium ferrites can be attributed to the following. The 180°-domain walls are pinned at the ferrite grain boundaries but the electric polarisation occurs in the direction perpendicular to the wall surface. The existence of the distorted octahedron FeO_6 in hexagonal elementary cell of $SrFe_{12}O_{19}$ results in the occurrence of electrical dipole moments inducing the spontaneous polarisation. The observed large ME effect needs further investigation.

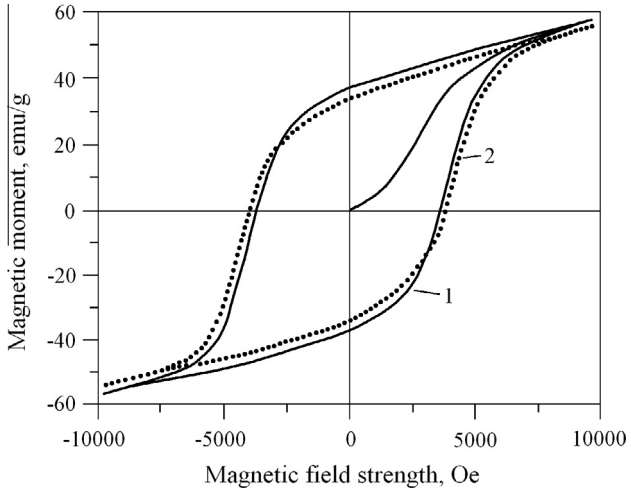

Fig. 4. Effect of the applied electric field on the magnetization loop of strontium hexaferrite $SrFe_{12}O_{19}$. Loop 1-no field is applied. Loop 2-an electric field of 20 kV/cm is applied perpendicular to the magnetic field.

Table 2
Comparison of multiferroic properties of fabricated single-phase $SrFe_{12}O_{19}$ ceramics and $BiFeO_3$ films.

Material	Property			
	Remnant magnetization emu/g	Maximal polarisation μC/cm^2	ME parameter – α_{ME}, mV/Oe cm	MD ratio, %
$BiFeO_3$ films	8.7 film [24]	55–100 [25]	3.1 [26]	1.0 [27]
$SrFe_{12}O_{19}$	38	44	24.5	4.12

4. Conclusion

We have demonstrated that hexagonal ferrite ceramics $SrFe_{12}O_{19}R$ obtained by modified ceramic technology from highly purified initial materials with addition of boron oxide during sintering in oxygen possess multiferroic properties at room temperatures which are more advanced than those of $BiFeO_3$ – one of the mostly studied multiferroics. The ME properties can be compared with the corresponding parameters reported for composite systems. The fabricated samples demonstrated a maximal electric polarisation of 45 μC/cm^2, the magnetoelectric parameter of 25 mV/Oe and magnetodielectric ratio of more than 4%. The electrical control of the magnetization of about 9–10% is larger than in substituted ferrites giving a valuable contribution to the development of magnetoelectric devices. The mechanism of the spontaneous electrical polarisation and large magnetoelectric effect is proposed but requires further investigations.

The obtained results open up the potential of utilizing hexaferrites in devices based on magnetoelectrical coupling.

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References

[1] R.C. Pullar, Hexagonal ferrites: a review of the synthesis, properties and applications of hexaferrite ceramics, Prog. Mater. Sci. 57 (2012) 1191–1334.
[2] O. Gutfleisch, M.A. Willard, E. Bruck, C.H. Chen, S.G. Sankar, J.P. Liu, Magnetic materials and devices for the 21st century: stronger, lighter, and more energy efficient, Adv. Mater. 23 (2011) 821–842.
[3] U. Ozgur, Y. Alivov, H. Morkoc, Microwave ferrites, J. Mater. Sci.: Mater. Electron. 20 (2009) 789–834.
[4] Y. Kitagawa, Y. Hiraoka, T. Honda, T. Ishikura, H. Nakamura, T. Kimura, Low-field magnetoelectric effect at room temperature, Nat. Mater. 9 (2010) 792–802.
[5] S. Ishiwata, Y. Taguchi, H. Murakawa, Y. Onose, Y. Tokura, Low-magnetic-field control of electric polarization vector in a helimagnet, Science 319 (2008) 1643–1646.
[6] A.P. Pyatakov, A.K. Zvezdin, Magnetoelectric and multiferroic media, PHYS-USP 55 (2012) 557–581.
[7] T. Kimura, Magnetoelectric hexaferrites, Annu. Rev. Condens. Matter Phys. 3 (2012) 93–110.
[8] O.Yu. Dyakonitsa, V.Ya. Shkuratov, K.E. Kamentsev, A.A. Bush, Synthesis and investigation of hexaferrite phases in CoO–SrO–Fe_2O_3, in: Proceedings of International Conference INTERMATIC-2014, part 2, 2014, pp. 7–10.
[9] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajanet, Epitaxial $BiFeO_3$ multiferroic thin film heterostructures, Science 299 (2003) 1719–1722.
[10] J. Kreisel, H. Vincent, F. Tasset, M. Pate, J.P. Ganne, An investigation of the magnetic anisotropy change in BaFeTiCoO single crystals, J. Magn. Magn. Mater. 224 (2001) 17–29.
[11] N. Koga, T. Tsutaoka, Preparation of substituted barium ferrite BaFe (Ti Co) O by citrate precursor method and compositional dependence of their magnetic properties, J. Magn. Magn. Mater. 313 (2007) 168–175.
[12] G.B. Teh, N. Saravanan, D.A. Jefferson, A study of magnetoplumbite-type (M-type) cobalt–titanium-substituted barium ferrite, BaCo Ti Fe O (x = 1–6), Mater. Chem. Phys. 105 (2007) 253–259.
[13] Y. Tokunaga, Y. Kaneko, D. Okuyama, S. Ishiwata, T. Arima, S. Wakimoto, K. Kakurai, Y. Taguchi, Y. Tokura, Multiferroic M-type hexaferrites with a room-temperature conical state and magnetically controllable spin helicity, Phys. Rev. Lett. 105 (2010) 257201–257204.
[14] T. Guolong, C. Xiuna, Structure and multiferroic properties of barium hexaferrite ceramics, J. Magn. Magn. Mater. 327 (2013) 87–90.
[15] G. Tan, M. Wang, Multiferroic $PbFe_{12}O_{19}$ ceramics, J. Electroceram. 26 (2011) 170–174.
[16] G. Tan, X. Chen, Synthesis, structures, and multiferroic properties of strontium hexaferrite ceramics, J. Electron. Mater. 42 (2013) 906–911.
[17] G.V. Duong, R. Groessinger, M. Schoenhart, D. Bueno-Basques, The lock-in technique for studying magnetoelectric effect, J. Magn. Magn. Mater. 316 (2007) 390–393.
[18] L. Wang, D. Wang, Q. Cao, Y. Zheng, H. Xuan, J. Gao, Y. Du, Electric control of magnetism at room temperature, Sci. Rep. 2 (2012) (Article number: 223).
[19] A.M. Balbashev, V.Yu. Ivanov, A.A. Mukhin, L.D. Iskhakova, Yu.F. Popov, G.P. Vorob'ev, M.E. Voronchikhina, Magnetic and magnetoelectric properties of substituted M-type hexaferrites $TSc_xFe_{12-x}O_{19}$ (T = Ba, Sr), Zh. Eksp. Teor. Fiz. Pisma 101 (2015) 542–549.
[20] P. Guzdek, The magnetostrictive and magnetoelectric characterization of $Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4$–$Pb(FeNb)_{0.5}O_3$ laminated composite, J. Magn. Magn. Mater. 349 (2014) 219–223.
[21] P. Guzdek, M. Sikora, L. Gora, Cz. Kapusta, Magnetic and magnetoelectric properties of nickel ferrite–lead iron niobate relaxor composites, J. Eur. Ceram. Soc. 32 (2012) 2007–2011.
[22] L.M. Letyuk, V.G. Kostishin, A.V. Gonchar, Technology of Ferrite Materials for Electronics, MISIS, 2005.
[23] S. Katlakunta, P. Raju, S.S. Meena, S. Srinanth, R. Sandhua, P. Kuruva, S.R. Murthy, Multiferroic properties of microwave sintered $BaTiO_3$–$SrFe_{12}O_{19}$ composites, Physica B 448 (2014) 323–326.
[24] V.G. Kostishin, N.N. Krupa, V.V. Nevdacha, L.V. Panina, D.N. Chitanov, V.M. Trukhan, N.A. Yudanov, Magnetic properties of multiferroics $BiFeO_3$, (BiLa) FeO_3, (BiNd) FeO_3 electrets formed by corona discharge, Eng. J. Don 3 (2013) 1–7.
[25] J. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruette, A.P. Pyatakov, A.K. Zvezdin, D. Viehland, Dramatic enhanced polarization I (001), (101) and (111) $BiFeO_3$ thin films due to epitaxial enduced transitions, Appl. Phys. Lett. 84 (2005) 5261–5264.
[26] A.A. Amirov, I.K. Kamilov, A.B. Batdalov, I.A. Verbenko, O.N. Razumovskaya, L.A. Reznichenko, L.A. Shilkina, Magnetoelectric interactions in $BiFeO_3$, $Bi_{0.95}Nd_{0.05}FeO_3$ and $Bi_{0.95}La_{0.05}FeO_3$, Tech. Phys. Lett. 34 (9) (2008) 760–762.
[27] A.A. Amirov, A.B. Batdalov, S.N. Kallaev, Z.M. Omarov, I.A. Verbenko, O.N. Razumovskaya, L.A. Reznichenko, L.A. Shilkina, Specific features of the thermal, magnetic, and dielectric properties of multiderroics $BiFeO_3$ and $Bi_{0.95}La_{0.05}FeO_3$, Phys. Solid State 51 (6) (2009) 1189–1192.