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Dual ferroic properties of hexagonal ferrite ceramics $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$

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ABSTRACT

Dual ferroic properties of a strong magnetism and large ferroelectricity have been observed in barium $BaFe_{12}O_{19}$ and strontium $SrFe_{12}O_{19}$ hexaferrite ceramics. The samples were fabricated by a modified ceramic technique from highly purified raw materials with addition of boron oxide allowing the control of grain size and enhancement of bulk resistivity. Whereas the samples of $PbFe_{12}O_{19}$ fabricated by the same technological method did not have sufficient electric resistivity to support an electric field and did not exhibit the ferroelectric properties. The structure of the samples examined by X-ray diffraction is consistent with a single hexagonal phase. The grains are randomly oriented with the average grain size of 300–400 nm coated with boron oxide. The magnetic properties are characterised by standard ferrimagnetic behavior with the Neel temperature of about 450 °C. Large spontaneous polarization was observed with the maximal values of 45–50 $\mu C/cm^2$ under an applied electric field of 100–300 kV/m. A strong coupling between magnetic and electric ordering was confirmed by measuring the magnetoelectric (ME) parameter and magnetodielectric ratio. These ME characteristics are more advanced than those for well-known room temperature multiferroic $BiFeO_3$. Furthermore, by applying an electric field, the manipulation of magnetization in the range of up to 9% was observed, which is even greater than in some substituted hexaferrites with a non-collinear magnetic structure. The obtained results on electrical polarization are similar to the values reported for the corresponding hexaferrites sintered by polymer precursor technique. This suggests a promising potential of M-type hexaferrite ceramics in devices utilizing magnetoelectric coupling.

1. Introduction

Magnetoelectric and multiferroic materials that provide coupled magnetic and electrical polarizations and/or ferroelasticity are of considerable interest as they have numerous potential applications [1–5], such as dual field read–write data storage, active responsive materials, four-state logic devices, sensors, controlled microwave absorption materials. Single-phase materials with multiferroics properties would be preferable in order not to dilute either magnetic or electric ordering; however, such materials are rare because the conditions that result in good ferromagnetic properties are in conflict with those leading to a strong ferroelectricity. In many cases, single-phase multiferroic materials exhibit the corresponding properties only at low temperatures (lower than 50 K) or very high applied fields (more than 1 T).

Multiferroics can be classified into several groups based on the physical mechanism of their inversion symmetry breaking, such as charge ordering, magnetism induced ferroelectricity, lone-pair electron effects, octahedral distortion, geometrical frustration. Among them, magnetically induced ferroelectrics are of special interest since they can show very large magnetoelectric (ME) effects. In the case of collinear magnetic structures, a symmetric exchange interaction (also known as exchange striction) may result in ferroelectricity due to shifted bonds caused, in turn, by magnetic ordering. This mechanism explains multiferroic behavior of orthorhombic $ReMnO_3$ (Re denotes a heavy rare earth element, equal to or heavier than Ho) which has antiferromagnetic ordering at rather low temperatures [6,7]. Recently, it was experimentally demonstrated that the occurrence of a large electric polarization in epitaxial $YMnO_3$ films is directly related to E-type antiferromagnetic ordering below 35 K [8]. However, very low antiferromagnetic transition temperatures prevent practical applications of these materials.

Complex non-collinear magnetic structures such as spirals with a cycloid component also can induce the electric polarization due

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Table 1
Basic electro-physical parameters of fabricated hexaferrite ceramics $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$ and $PbFe_{12}O_{19}$.

Samples	Magnetization saturation $4\pi M_S$, G	Remanent magnetization $4\pi M_r$, G	Coercivity (for magnetization) $_MH_C$, Oe	Density γ, g/cm^3	Resistivity ρ, Ω cm	Neel temperature, T_N, °C	Magnetoelectric parameter, α_{ME}, V/A	Magnetodielectric ratio, %
$BaFe_{12}O_{19}$	4760–4775	3640–3700	1900–2000	4.89–4.92	$(1–2) \cdot 10^{10}$	447	0.031–0.033	4.12–4.25
$SrFe_{12}O_{19}$	3450–3570	2420–2650	3400–3500	4.95–4.99	$(8–9) \cdot 10^{9}$	456	0.030–0.031	4.08–4.17
$PbFe_{12}O_{19}$	2450–2700	1600–1800	2200–2600	5.00–5.10	$(5–9) \cdot 10^{6}$	437	–	–

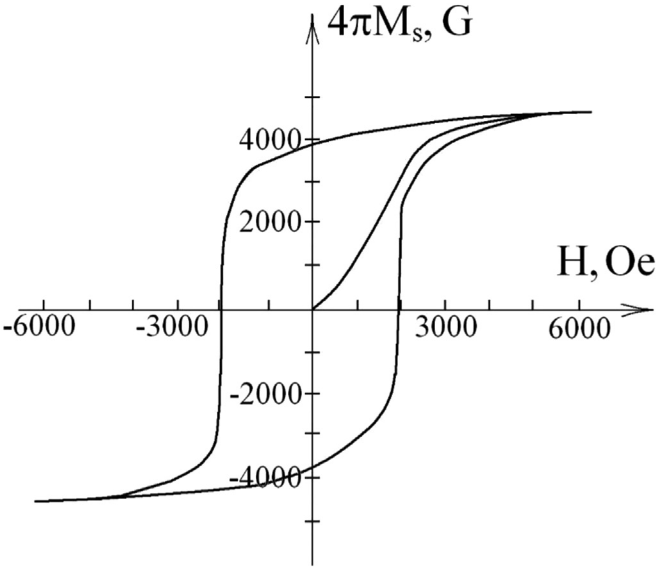

Fig. 1. Hysteresis curve of hexagonal ferrite ceramics $BaFe_{12}O_{19}$.

to the inverse Dzyaloshinskii–Moriya interaction [9]. This mechanism explains multiferroic properties in substituted hexaferrites [10,11]. A non-collinear magnetic structure in hexaferrites typically has a lower transition temperature in comparison with that of a conventional ferromagnetic phase, correspondingly, the temperature of the ferroelectricity onset is also low. Some substituted hexagonal ferrites do show multiferroic properties and a relatively large ME effect at room temperature and weak magnetic fields [12–17]. This generated a practical interest in hexaferrite ferroelectrics which can be promising candidates for multiferroics operating at room temperature and low fields. On the other hand, co-existence of large ferroelectricity and strong ferrimagnetism have been reported for single-phase $SrFe_{12}O_{19}$, $BaFe_{12}O_{19}$, $PbFe_{12}O_{19}$ hexaferrites synthesized by a polymer precursor method [18–20] and for $SrFe_{12}O_{19}$ hexaferrite synthesized by a modified ceramic technique [21]. All these systems belong to M-type hexaferrites having a collinear ferrimagnetic structure (see review in [22]) so the Dzyaloshinskii–Moriya mechanism could not be responsible for dual ferroic properties. It was proposed that the electrical polarization in this case is ascribed to a geometrical structural transition occurring due to the O-octahedral distortion below the electric Curie temperature [18–21]. In the present work, a modified ceramic technique was used to sintering $BaFe_{12}O_{19}$, $PbFe_{12}O_{19}$, and $SrFe_{12}O_{19}$ M-type hexaferrites with enhanced electrical resistivity in order to investigate their electric and magnetic ordering and ME coupling.

Typically, the electric resistivity in hexaferrites is relatively low, which is a highly restricting factor to support an electric field and observe the ME effects. The addition of boron oxide at the stage of wet milling makes it possible to restrict the grain size (with the average value of 300–400 nm) and also to increase the bulk resistivity. In Ba and Sr hexaferrites the resistivity was increased by about 5 orders of magnitude by this technique. In these materials, large spontaneous polarization and large change in magnetization up to 9% in the presence of electric field were observed. The electrical control of magnetization achieved in pure hexaferrites was stronger than in substituted non-collinear systems such as $SrCo_2Ti_2Fe_8O_{19}$ [23]. Tailoring the magnetization with an electric field is of high practical interest for reducing the power consumption and realising spintronic device miniaturization. It is possible that in single-phase hexaferrites some contribution to the electric polarization comes from the spatial distribution of magnetization at the magnetic domain walls, which, causes large ME effects.

In the case of $PbFe_{12}O_{19}$ ferrites prepared by the same method, the increase in resistivity was not sufficient to detect the electric polarization. These results demonstrate that traditional ferromagnetic oxides with a perovskite-like structure could be good multiferroic candidates if their electrical resistivity is strongly enhanced.

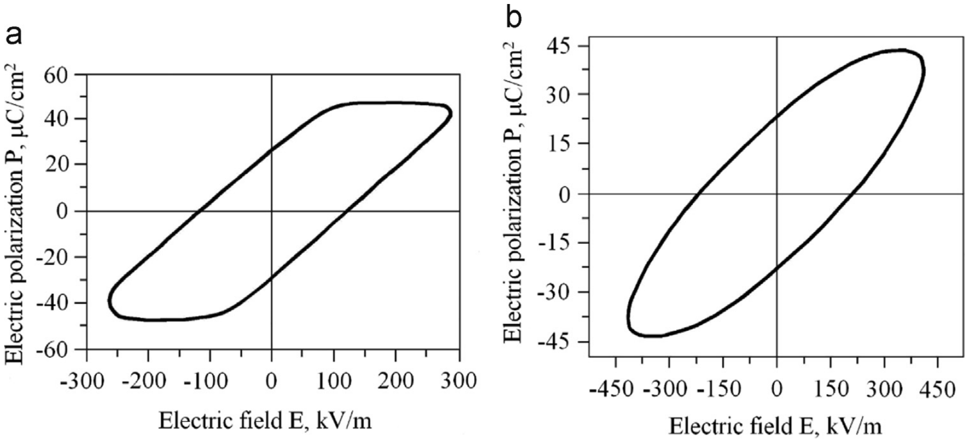

Fig. 2. Ferroelectric hysteresis loops of hexagonal ferrite ceramics $BaFe_{12}O_{19}$ (a) and $SrFe_{12}O_{19}$ (b).

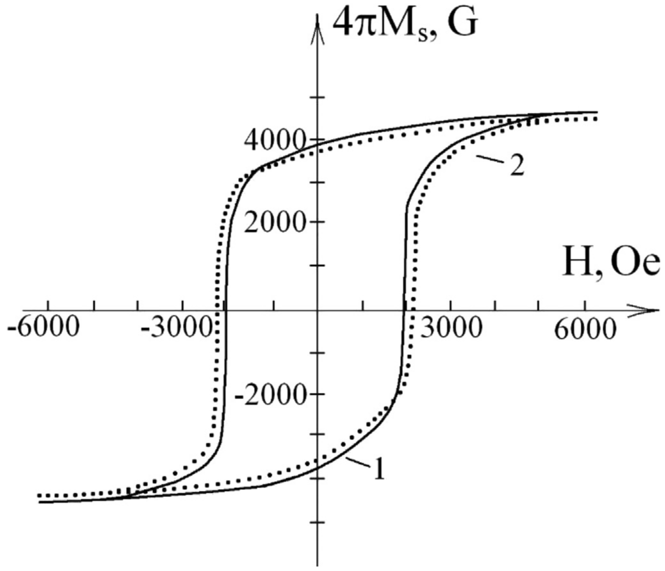

Fig. 3. Comparison of magnetization curves of hexagonal ferrite ceramics $BaFe_{12}O_{19}$ in the presence of electric field (2) and without a field (1). Electric field *E* of 20 kV/cm is applied perpendicular to the magnetic field.

2. Sample fabrication

A modified ceramic technique was used to prepare the hexagonal ferrites $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$ and $PbFe_{12}O_{19}$ (BaM, SrM, and PbM, for short, respectively). As raw materials, powders of highly purified barium carbonate $BaCO_3$, strontium carbonate $SrCO_3$ and oxides PbO and Fe_2O_3 were mixed in the required proportion and pressurized. The obtained pellets were then heated in the rotating oven. The sintering regimes for BaM, SrM and PbM samples were: 1.5 h at 1300 °C, 2 h at 1150 °C and 2 h at 1000 °C, respectively. As a result of the solid state reaction during heating, the ceramic products were stoichiometric compounds of $BaO \cdot 6Fe_2O_3$, $SrO \cdot 6Fe_2O_3$ and $PbO \cdot 6Fe_2O_3$. The samples were cooled in deionized water and then milled, powdered and wet-milled to produce a finer material. Wet-milling was made in the presence of highly purified boron oxide B_2O_3 in mass concentration of 0.5–1.5%, which helped to obtain a fine grain structure with the average grain size of 0.3–0.5 μm, separated by insulating layers. The melting temperature of boron oxide is 450 °C, and when heated upon this temperature it transforms into a liquid state and coats the ferrite grains limiting their growth. More importantly, filling the intergrain space with a good insulating material may increase the bulk resistivity of the ferrite samples up to several orders of magnitude. After wet-milling, the samples were pressed under a pressure of 350 kg/cm^2 to form plates ($15 \times 15 \times 1$ mm^3) and cubes (6 mm). This was followed by drying the samples for 12 h at a temperature of 40 °C in a normal atmosphere. Finally, the samples were sintered in oxygen atmosphere (5 h at 1200 °C, 6 h at 1100 °C and 4–5 h at 900 °C, respectively for BaM, SrM and PbM) and cooled down to room temperature. For investigations, 10 samples of each type were selected and their sides were polished (14th class of purity).

3. Experimental

All the measurements were done at room temperature. The structures of the hexaferrite ceramics were analyzed by x-ray diffraction (XRD) using Rigaku diffractometer with Fe anode tube as a radiation source (tube current – 25 mA, voltage – 25 kW). The radiation wavelength was 0.193728 nm. The Bragg–Brentano geometry with two Soller slits and a Mn filter was used to detect the spectra.

The magnetic parameters and magnetic hysteresis loops were measured with the help of vibrating sample magnetometer (EG&G PARC, USA). The samples in the form of a sphere with a diameter of 4–4.5 mm were prepared for controlling the magnetic measurements. The amplitude of the magnetizing field was up to 10 kOe.

For electrical measurements, the electrodes were made from silver paste or (In, Ga)-eutectic and the both provided good electric contacts. The resistivity was found by two-probe method from voltage–current characteristics. Small currents were measured by electrometer (Keithley 6514). The type of electrodes did not affect the results.

For the investigation of the electrical polarization *P*, ME effect and electrical control of the magnetization, the samples were coated with a silver paste to form capacitors. The ME parameter α_{ME} was found from the measurements of voltage *U* induced across the sample under the application of an alternating magnetic field *H*: $\alpha_{ME} = dU/hdH$, where *h* is the sample thickness. Helmholtz coils were used to generate the field *H* of a frequency of 50 kHz and an amplitude of 500 A/m. The ME voltage was measured with the help of lock-in-amplifier (SR-530) by a dynamic method described in [24].

The magnetodielectric (MD) effect or magnetocapacitance includes the variation of the dielectric constant $\varepsilon(H)$ in the presence of a magnetic field *H*. The corresponding MD ratio defined as $MD = (\varepsilon(H) - \varepsilon(0))/\varepsilon(0)$ was deduced from the dielectric constant measurements in a dc magnetic field of 3 kOe with the help of LCR meter at a frequency of 100 kHz.

A modified Sawyer-Tower circuit method was used to measure the polarization hysteresis *P–E* loops. The voltage source had an amplitude of 2000 V and a frequency of 50 Hz. A compensation capacitor of 0.1 μF in parallel with the sample was used.

We also investigated the effect of electric field *E* on the magnetization measured with the help of VSM by applying *E* on the sample-capacitor perpendicular to the magnetizing field.

4. Results and discussion

XRD analysis has demonstrated that the samples were polycrystalline and XRD-patterns were consistent with the corresponding single-phase hexagonal ferrites with two crystalline lattice parameters: *a*, the width of the hexagonal plane, and *c*, the height of the crystal. The lattice parameters were , for BaM, , for

Table 2
Multiferroic properties of obtained BaM and SrM ceramics in comparison with those of $BiFeO_3$ films.

Material	Property			
	Remanent magnetization $4\pi M_r$, G,	Maximal polarization P_m, μC/cm^2	ME parameter α_{ME}, mV/cm Oe	Magnetodielectric ratio, %
$BiFeO_3$ film	107 [26]	55–100 [27,28]	3.04 [29]	1.0 [29,30]
$BaFe_{12}O_{19}$	3670	50	25.6	4.18
$SrFe_{12}O_{19}$	2535	44	24	4.12

Table 3
Comparison of ferroelectric properties of M-type hexaferrites $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$ and $PbFe_{12}O_{19}$ prepared by modified ceramic and by polymer precursor techniques.

Hexaferrite	Modified ceramic technique		Polymer precursor technique (sintering temperature is 1200 °C)	
	Remanent polarization P_r, μC/cm^2	Electric coercivity E_c, kV/m	Remanent polarization P_r, μC/cm^2	Electric coercivity E_c, kV/m
$BaFe_{12}O_{19}$	29.0	117.5	11.8 [18]	6.0 [18]
$SrFe_{12}O_{19}$	23.5	213.0	15.0 [19]	14.6 [19]
$PbFe_{12}O_{19}$	–	–	33.5 [20]	96.0 [20]

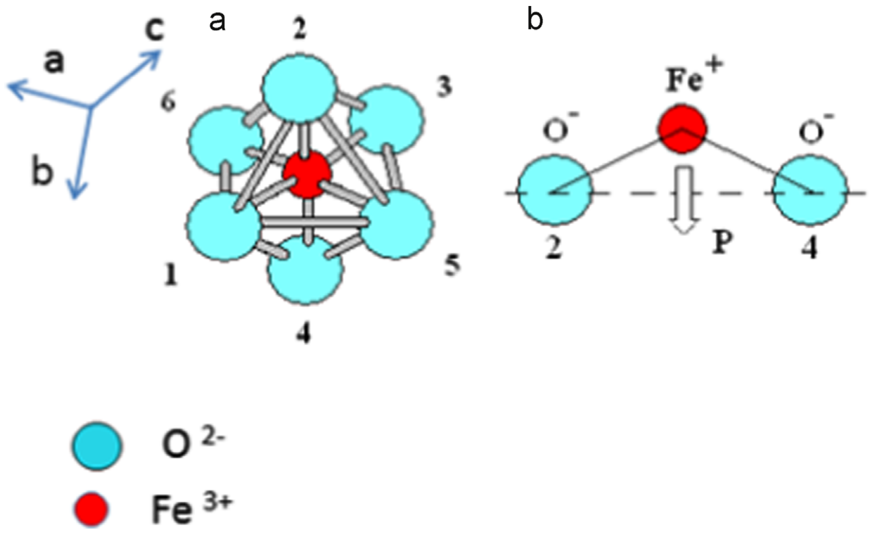

Fig. 4. Illustration of the occurrence of the polarization due to a distorted oxygen octahedron. In (a) – a normal octahedron with small Fe-cation in the center position (Fe-cation and oxygen anions in positions 2 and 4 are in the plane $(1\bar{1}0,\ 001)$); in (b) – a distorted O–Fe–O bond with an open angle.

SrM and , for PbM.

Table 1 lists the main physical parameters of the samples. BaM resembles SrM in most physical properties, and they differ greatly from PbM by resistive properties: for PbM the resistivity is much smaller (more than 3 orders of magnitude). PbM has also the highest density since the lead atom is much heavier. We think that such small resistivity of PbM in comparison with SrM and BaM is caused by non-stoichiometry occurring due to high volatility of Pb ions during ferrite synthesis and annealing processers [25]. This is also consistent with large variations in many physical parameters of $PbFe_{12}O_{19}$ samples: resistivity, density, magnetic parameters and lattice parameters, as seen in Table 1. Higher density of PbM could also result in lower resistivity.

Fig. 1 shows the magnetic hysteresis plots of $BaFe_{12}O_{19}$ samples. The loop shape and magnetic parameters are very similar to those of bulk materials obtained by standard ceramic technology [22]. Samples of $SrFe_{12}O_{19}$ and $PbFe_{12}O_{19}$ had also similar magnetic hysteresis properties. This confirms that the samples had collinear ferrimagnetic structure.

Fig. 2 shows the ferroelectric hysteresis loops for $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ samples.

Maximal polarization of P_m=(48.0–49.5) μC/cm^2 was observed in $BaFe_{12}O_{19}$ samples for fields higher 100 kV/m. These values are slightly larger than P_m for $SrFe_{12}O_{19}$ samples, which were in the range of (43.0–45.5) μC/cm^2. The remanent polarizations for these samples were P_r=(28.0–29.5) μC/cm^2 and (22.5–24.5) μC/cm^2, and the electric field coercivities were E_c=(115–120) kV/m and (210–216) kV/m, respectively.

The ferroelectric behavior in $PbFe_{12}O_{19}$ was not possible to detect. These samples are characterized by rather small resistivity (three orders of magnitude smaller than that of $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ samples, as seen from Table 1). Large leakage currents make it impossible to measure the electric polarization in this case.

The possibility to change the magnetization by applying an electric field is of high interest since this directly demonstrates the coupling between the two ordering. This also makes it possible to realize an electrical control of the magnetization, which is important for device miniaturization. In [21], a large change in magnetization loop of SrM hexaferrite ceramics caused by the applied electric field was reported. Similar results for $BaFe_{12}O_{19}$ are shown in Fig. 3. In the presence of the electric field of 20 kV/cm the remanent magnetization decreases by 5–6% whereas the coercivity increases by 6–8%. Even greater decrease in remanent magnetization by 8–9% was observed for $SrFe_{12}O_{19}$ samples in consistence with the results given in our previous work [21]. The observed changes in magnetization in single-phase Ba and Sr hexaferrites caused by an electric field are larger than those reported for substituted M-type hexaferrites $SrCo_2Ti_2Fe_8O_{19}$ with non-collinear magnetic structure and magnetically induced spontaneous polarization [23].

The obtained results clearly demonstrate room-temperature multiferroic properties of a single-phase $SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ hexaferrites prepared by modified ceramic technique allowing the electrical resistivity to be greatly enhanced. It is interesting to compare the obtained electric and magnetic parameters with those typical of $BiFeO_3$ which is one of the best room-temperature multiferroic materials. This comparison is given in Table 2. $BiFeO_3$ has antiferromagnetic (at about 370 °C) and ferroelectric (at about 830 °C) orders and the corresponding ordering parameters couple to each other [26–30]. Bulk $BiFeO_3$ has a very small magnetization due to an incommensurate cycloidal spin ordering which averages out the canted antiferromagnetic spins. Thin-films of $BiFeO_3$ demonstrate weak magnetism but their remanent magnetization is dozen times smaller than that of hexaferrites (for example, it is smaller than the magnetization of $BaFe_{12}O_{19}$ by more than 30 times). The maximum electric polarization of the fabricated BaM and SrM-samples is up to two times smaller, however, their magnetoelectric parameter is higher up to 8 times and magnetodielectric ratio is up to 4 times higher. Therefore, in terms of the magnetic and electric order coupling, the properties of the synthesized hexaferrite ceramics are much greater.

The obtained values of the magnetoelectric parameter of about 25 mV/cm Oe are surprisingly high and can be compared with those for composite systems consisting of magnetostrictive and ferroelectric phases [31,32].

The success in realizing room temperature multiferroic properties in hexagonal ferrites $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ is attributed to the technological modifications, thus, allowing the BaM and SrM samples with relatively high resistivity in the range of 10^{10} Ω cm to be prepared. The low resistivity of traditional hexagonal ferrites is known to be a problem in the measurements of the electric polarization and electric control of the magnetization. Due to low resistivity of hexaferrites $SrFe_{12}O_{19}$, $SrCo_2Fe_{16}O_{27}$, $Sr_2Co_2Fe_{12}O_{22}$, $Sr_3Co_2Fe_{12}O_{22}$, $Sr_2Co_2Fe_{28}O_{46}$, sintered by standard ceramic technology, it was not possible to detect their ferroelectric behavior, as was reported in [17]. The other example is ferroelectric properties of composites $xSrFe_{12}O_{19}$–$(1-x)$ $BaTiO_3$ prepared by sol–gel method and microwave sintering [33]. It was found that the polarization decreased with increasing the ferrite content. The measurements indicated that with increasing x, the effect of leakage currents on polarization became more and more significant. At $x=0.7$ the maximal polarization was about 3 μC/cm^2. With further increase in the ferrite phase the polarization detection became impossible.

Hexaferrites $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$ and $PbFe_{12}O_{19}$, prepared by polymer precursor method also demonstrate strong room temperature multiferroic properties [18–20]. Table 3 compares the ferroelectric properties of BaM and SrM hexaferrites prepared in this work by modified ceramic technique and by polymer precursor technique with sintering temperature of 1200 °C.

It is seen that the remanent polarization of SrM and BaM obtained by both methods is in the same range (11.8–33.5) μC/cm^2 but the electric coercivity is considerably higher for the samples obtained by ceramic technique. However, in the case of polymer precursor method, an increase of up to 1300 °C in the sintering temperature resulted in quick reduction of the remanent polarization down to 1.2 μC/cm^2 for BaM due to the increase in the densification and grain size. We may suggest that this drop in the polarization occurred owing to enhanced conductivity in samples sintered at higher temperatures.

The ferroelectric behavior of SrM and BaM hexaferrites can be attributed to the following. M-type hexaferrites have a perovskite-like crystal structure with one distorted FeO6 oxygen octahedron in a sub-unit cell as shown in Fig. 4 [18]. In a normal octahedron, a small Fe cation is located in the center having straight line bonds with oxygen anions (for example, in the plane $(1\bar{1}0,\ 001)$ with O2, O4 in Fig. 4). Below the electric Curie temperature, Fe-cation shifts along the *b*-axis, and the oxygen anions in positions 2 and 4 shift along the *a*-axis in opposite directions. Then, the bond O2–Fe–O4 is no longer a straight line forming an open angle and inducing the spontaneous polarization. In addition, a non-uniform magnetization within the magnetic domain walls can also serve as a source of electric polarization similar to spatially modulated spin structures [34]. The 180°-domain walls are pinned at the ferrite grain boundaries by non-magnetic insulator. For the Neel type walls, the magnetization distribution forms a cycloid inducing a local electric polarization in the direction perpendicular to the modulation vector and spin rotation vector, that is along the wall surface. This contribution may be responsible for large ME effects, in particular, for the change in the magnetization coercivity by the perpendicular electric field. The role of the domain wall magnetization and local polarization in bulk ceramics samples should be further investigated.

5. Conclusion

We have demonstrated that hexagonal ferrites $SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ obtained by modified ceramic technology from highly purified raw materials with addition of boron oxide at sintering in oxygen atmosphere possess impressive multiferroic properties at room temperatures. Therefore, the obtained results are of high practical importance for advancing the devices based on magnetoelectrical coupling.

The fabricated samples demonstrated a maximal electric polarization of about 45 μC/cm^2, the magnetoelectric parameter of about 25 mV/cm Oe and magnetocapacitance of more than 4%. The magnetoelectric parameter is greater than that in $BiFeO_3$ and is comparable with the values typical of composite systems consisting of magnetostrictive and ferroelectric phases. The mechanisms of the spontaneous electrical polarization due to distorted oxygen octahedron was proposed. Large magnetoelectric effects could be explained by non-uniform magnetization within the domain walls but the role of this mechanism in ferroelectricity of granular ceramic materials requires further investigations.

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