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Magnetodielectric effect insingle crystals sequence of $Pb_2Fe_{2-x}Mn_xGe_2O_9$ $(x = 0-0.4)$

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In this work, the magnetodielectric response have been studied in a series of single crystals of $Pb_2Fe_{2-x}Mn_xGe_2O_9$ with substitution x from 0 to 0.43. The research results showed that an increase in x leads to a change in the orientation of the antiferromagnetism vector in a zero magnetic field. The application of an external magnetic field leads to spin-flop and spin-reorientation magnetic transitions, which are accompanied by anomalies in the behavior of the permittivity.When Fe^{3+} ions are replaced by Mn^{3+} ions, the response of the magnetic subsystem to an external magnetic field changes, which is naturally reflected in the change in the magnetodielectric response. The permittivity changes stepwise when the magnetic subsystem passes into a state with a nonzero vector of the weakly ferromagnetic moment, or when its magnitude and orientation change due to a spin-flop transition. The latter indicates that a sharp change in polarizability is a consequence of a change in the contribution of the exchange energy, as well as the contribution of the Dzyaloshinskii–Moriya term, due to a change in the skew angle between two interacting magnetic moments.

Keywords: magnetodielectric effect, phase transition, week ferromagnetism.

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1. Introduction

The search for new multifunction materials is one of the bases of development of modern microelectronic devices. Much attention in the last two decades is paid, in particular, to synthesis and study of physical properties of multiferroics — materials with a strong interrelation between magnetic and electric properties.

Pb-containing compounds having a magnetic order arouse much interest within this area. This interest is due to the fact that a possible reason of multiferroics properties is the presence of ions with unusual stereochemical properties in compounds, in addition to $3d$-ions accountable for magnetic properties. Such ions include, for example, Bi^{3+}, Pb^{2+} ions where outer $6s^2$-electrons are not involved in the formation of a chemical bond to neighboring ions, but form the so-called „lone pairs“of electrons. Ions with unsaturated bonds are characterized by a high polarizability, forming local dipole moments. Such a polarized state enhances the structure instability and can lead to formation not only of ferroelectric, but also of nonlinear optical and relaxor properties [1,2]. Moreover, dipoles lead to severe distortions both of their immediate environment and the neighboring octahedra which contain $3d$-ions, thereby directly affecting the state of crystals' magnetic subsystem.

Interesting results of Pb-containing magnetically ordered compounds are shown by crystals with the general formula $Pb_2M_2X_2O_9$, where M is a trivalent $3d$-ion (Fe^{3+}, Mn^{3+} etc.), $X =$ Ge or Si. The studies of magnetic properties of polycrystalline $Pb_2Mn_2Si_2O_9$ (kentrolite) with an orthorhombic structure (space group $P2_122_1$) showed [3] that a transition to the antiferromagnetic state occurs in this compound at Neel temperature $T_N = 67\,K$; this state, in the authors' opinion, with further temperature increase evolves into a disordered spin-glass state where the ferromagnetic and antiferromagnetic phases coexist.

Another representative of this family has been studied in more detail — $Pb_2Fe_2Ge_2O_9$, which is a counterpart of the silicate mineral melanotekite. As in the other crystals of this group, the crystal structure is composed of zigzag chains, elongated along rhombic axis c [001], which in this crystal consist of FeO_6 octahedra connected by edges. The chains are connected to each other via Ge_2O_7 groups formed by tetrahedra. The static magnetic studies showed that a beveled antiferromagnetic order with an antiferromagnetic vector, directed along rhombic axis c and weakly ferromagnetic moment along axis a, settles in this crystal below Neel temperature $T_N = 45.2\,K$ [4,5]. Studies of magnetodielectric properties revealed their strong dependence on magnetic structure of the crystal. In particular, sudden changes of permittivity, induced by a spin-flop transition, were found.

An efficient method for influence on magnetic structure of the crystal is partial or complete substitution of magnetic subsystem ions by other $3d$- or $4f$-ions with differing magnetoanisotropic properties, in particular, doping with ions with a strong magnetic anisotropy. This technique was used to control the magnetic structure of a whole number of crystals with the structure of spinel [6] and garnet [7], orthoferrites [8–10] and rare-earth ferroborates with the huntite structure [11–14].

The same technique was used to control the magnetic structure of $Pb_2Fe_{2-x}Mn_xGe_2O_9$. Partial $(x = 0.43)$ substitution of iron atoms by heavily anisotropic ions of Mn^{3+} has led to a radical change of the magnetic phase diagram [15] in the substituted crystal: the antiferromagnetic vector reoriented to rhombic axis b, while weak ferromagnetism disappeared. Moreover, the result of such doping was a threefold intensification of the magnetodielectric response under a spin-reorientation transition. Such relatively high values of responses of the crystal's dielectric subsystem at a spontaneous or induced change of the magnetic structure cannot be explained by magnetostriction and are, most probably, conditioned by a change of permittivity due to magnon-phonon bond [16,17].

Magnetodielectric anomalies at magnetic phase transitions — both spontaneous and induced by an applied magnetic field — were observed in several crystals, including $Co_4Nb_2O_9$ [18], $Mn_{0.95}Co_{0.05}WO_4$ [19] and $SrNdFeO_4$ [20]. Thus, magnetodielectric properties of such materials can be used to study magnetic phase diagrams.

In the present paper we continue studying the magnetodielectric properties of $Pb_2Fe_{2-x}Mn_xGe_2O_9$ single crystals in a series of substitutions of Fe^{3+} iron atoms by Mn^{3+}. The present paper was complemented with a study of the magnetodielectric effect in intermediate compound $Pb_2Fe_{2-x}Mn_xGe_2O_9$ with $x = 0.2$ and a review of evolution of the magnetodielectric effect in a series of substitutions was made.

2. Samples and study methods

Single crystals $Pb_2Fe_{2-x}Mn_xGe_2O_9$ with $x \approx 0.2$ were drawn by the same technology as the crystals with $x = 0.43$ [15]. Crystals sized up to $1 \times 1 \times 3$ mm of black color with metallic luster were mechanically removed from the platinum crucible. As with $x = 0$ and 0.43, the single crystals are prisms (elongated along rhombic axis c) the side edges of which coincide with diagonal planes 110. The crystal structure is described by space group $Pbcn$ with parameters close to a non-substituted crystal: $a = 7.149(3)$ Å, $b = 11.177(4)$ Å and $c = 10.144(3)$ Å.

The experimental diffraction Laue pattern (Fig. 1), obtained by reflection from crystallographic plane (110), shows no twinning and reflections of extraneous phases, which confirms the high quality of single crystals.

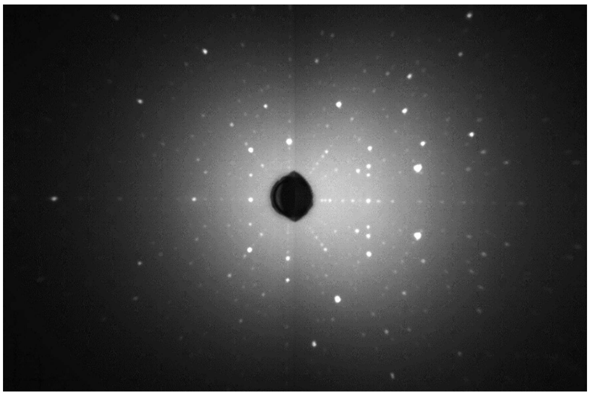

Figure 1. Experimental diffraction Laue pattern obtained by reflection from crystallographic plane (110) of single crystal $Pb_2Fe_{2-x}Mn_xGe_2O_9$.

The actual content of Mn^{3+} ion impurity in crystals was determined using a JEOLJSM-7001F scanning election microscope equipped with an Oxford IncaPentaFet-x3 energy-dispersive X-ray spectrometer. The actual content of Mn^{3+} ion impurity was equal to $x = 0.16$, which is slightly less than the charging content $(x_{\text{init}} = 0.2)$. Thus, the actual chemical formula of the crystal is $Pb_2Fe_{1.84}Mn_{0.16}Ge_2O_9$.

As in our previous papers, for permittivity and magnetodielectric effect measurements the single crystals were ground to the shape of a plate and its opposite planes were coated with epoxy-based conductive adhesive with silver filler. Electric capacitance of the obtained capacitor was measured using an Agilent E4980A instrument.

3. Results and discussion

The results of measurements of the magnetodielectric effect in a series of $Pb_2Fe_{2-x}Mn_xGe_2O_9$ samples with a magnetic field directed along rhombic axis c (H_c) are shown in Fig. 2. As seen from Fig. 2, a, an anomaly is observed for a non-substituted crystal at $T = 4.2$ K in the behavior of permittivity in the are of 40 kOe. Thereat, the anomaly manifests itself in field H_c in two directions simultaneously (ε_a and ε_c), but is of different nature. As magnetic field H_c increases, the component ε_a remains virtually unchanged up to the critical field where it drops sharply, and then the value of ε_a again remains virtually unchanged. Thus, curve $\varepsilon_a(H_c)$ for a pure crystal describes a step the height of which is relatively small; a change of permittivity due to the magnetodielectric is $\sim 0.17\%$. The other component, ε_c, smoothly decreases with an increase of magnetic field H_c, however, in contrast with the behavior of permittivity along direction a, ε_c sharply increases (when the critical magnetic field of ~ 40 kOe is reached) to the initial value observed for this component in the absence of a magnetic field. Magnetodielectric effect $\varepsilon_c(H_c)$ demonstrates v-shaped behavior with a difference $\sim 0.3\%$. A linear dependence in configuration $\varepsilon_a(H_a)$ with a negative

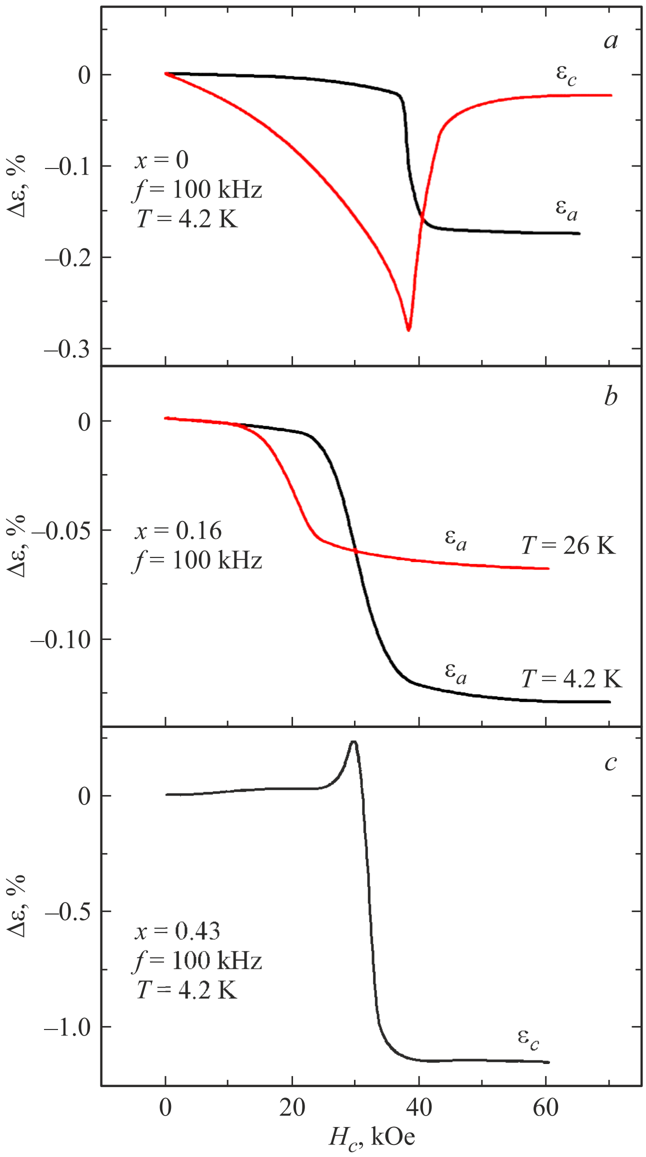

Figure 2. Magnetodielectric effect in a series of substitutions $Pb_2Fe_{2-x}Mn_xGe_2O_9$. Permittivity was measured along directions a and c. A magnetic field was applied along direction c ($H \parallel c$).

inclination angle was also observed in the pure crystal, but the value of this magnetodielectric effect is small, only $\sim 0.03\%$.

The whole range of mutual orientations of the magnetic and electric fields, applied to the studied samples, is given in the table.

Some electric field orientations were not field reproduced, due to the small dimensions of the synthesized crystals, which is shown by a dash „—“.

The obtained curves for a non-substituted crystal correlate well with the data of magnetic measurements, namely, the pure crystal with $x = 0$ in magnetic field $H_c \approx 40$ kOe features a spin-flop transition, accompanied by a turn of the antiferromagnetic vector from direction c towards direction a and, consequently, a turn of the weak ferromagnetism vector from $M_{Da} \rightarrow M_{Dc}$ [5]; spontaneous magnetic moment M_D is conditioned by Dzyaloshinskii–Moriya interaction and single-ion anisotropy. An abrupt change of permittivity is observed exactly in the same field.

The magnetodielectric response changes as iron sites are substituted by Mn^{3+} ions. Indeed, v-shaped behavior is no longer observed in dependence $\varepsilon_c(H_c)$ when substitution value is $x = 0.16$ (Fig. 2, b); the magnetodielectric effect is not observed in this orientation of the magnetic and electric field at all. A step in dependence $\varepsilon_a(H_c)$ remains but becomes smoother than in the sample without substitution. Measurements at two temperatures $T = 4.2$ and 26 K were performed on the sample of this composition and, as seen from the plot, the anomaly in the behavior of permittivity remains at high temperature and shifts towards weak magnetic fields.

Magnetic characteristics also change significantly [21]. According to the obtained magnetic data, the antiferromagnetic vector at substitution $x = 0.16$ in helium temperature is directed not along axis c, as in the case of a pure crystal, but lies in plane bc at the angle of 20° to axis b. However, at a temperature increase the antiferromagnetic vector smoothly turns towards axis c, and the turn is completed at the temperature of $T_c \approx 20$ K. Application of an external magnetic field along axis c causes a turnover of the antiferromagnetic vector in direction a, accompanied by a weakly ferromagnetic moment along the c-axis M_{Dc}. Neel temperature shifts towards low temperatures as the concentration of Mn^{3+} increases, and is $T_N = 45.2$, 42, 39.9 K for the samples with the substitution value of $x = 0$, 0.16, 043 respectively.

The temperature dependences of permittivity also have peculiarities in the temperature range close to the antiferromagnetic ordering temperature. As seen in Fig. 3, the tangent of the inclination angle of dependence $\varepsilon(T)$, taken

Configuration of applied magnetic and electric fields and revealed magnetodielectric effects in $Pb_2Fe_{2-x}Mn_xGe_2O_9$

x	Magnetic field	Dependence type		
		ε_a	ε_b	ε_c
0	H_a	linear	–	no
	H_b	no	–	no
	H_c	step	–	v-shaped
0.16	H_a	no	–	no
	H_b	no	–	no
	H_c	step	–	no
0.43	H_a	–	Frequency-dependent	no
	H_b	–	no	no
	H_c	–	no	step

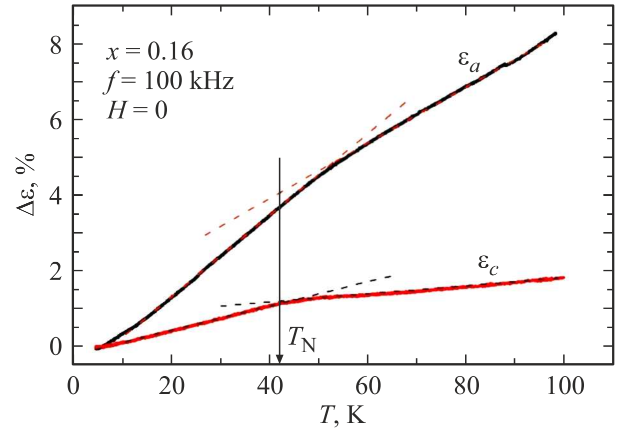

Figure 3. Temperature dependence of permittivity $\varepsilon(T)$ in directions a and c, taken on the crystal with $x = 0.16$ with a zero magnetic field.

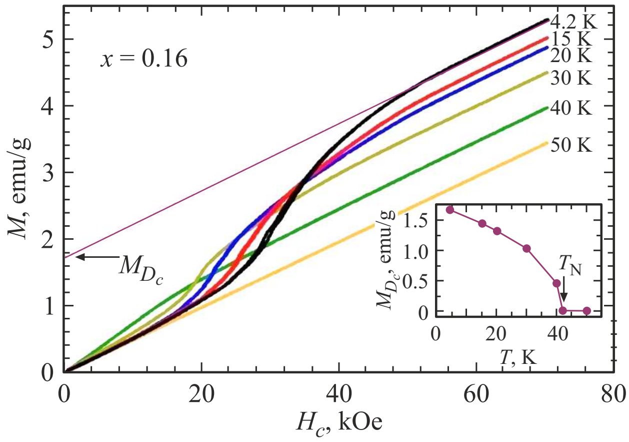

Figure 4. Field dependences of magnetization $M(H_c)$ of the crystal with substitution $x = 0.16$, measured at different temperatures in magnetic field $H \parallel c$.

for the crystal with $x = 0.16$ with no magnetic field applied, varies in the area of Neel temperature T_N. Here we would like to point out that changes in the behavior of permittivity in fact begin at a slightly higher temperature which, in all likelihood, is related to the settling of a short-range order inside octahedra chains of $3d$-elements.

Fig. 4 shows the field dependences of magnetization of the crystal with $x = 0.16$ along axis c, $M_c(H_c)$. A linear increase of magnetization is observed in weak magnetic fields at temperature $T = 4.2$ K, however, increase becomes non-linear beginning with fields of ~ 20 kOe; this interval ends in the area of 50 kOe where dependence $M_c(H_c)$ becomes linear again. It is also noticeable that the angles of inclination of linear areas in weak and strong fields are almost identical; the latter is due to the fact that both these areas are conditioned by transverse susceptibility $\chi_\perp$, when the applied field is perpendicular to the direction of antiferromagnetic's magnetic moments, since the antiferromagnetic vector l rotates in a plane almost perpendicular to the external magnetic field. The formation of spontaneous moment M_{Dc} is related to a rise of component l_a, as shown in [5,15].

The antiferromagnetic vector at high temperatures turns from axis b towards direction c, application of an external magnetic field H_c also leads to a $l_c \to l_a$ turn, but at smaller magnetic fields. This peculiarity also affects the magnetodielectric effect; the latter makes it possible to affirm that the anomaly in dependence $\varepsilon_a(H_c)$ accompanies the turn of the antiferromagnetic vector towards direction a.

The magnetodielectric response in the sample with $x = 0.43$ also demonstrates regular differences from the pure crystal. As magnetic field H_c increases, permittivity remains virtually unchanged up to a certain critical value, at which permittivity value drops abruptly, thus forming a step. Thus, $\varepsilon_c(H_c)$ in the sample with $x = 0.43$ demonstrates a behavior similar to dependence $\varepsilon_a(H_c)$ for the pure non-substituted crystal with $x = 0$, but in the perpendicular direction. Moreover, the magnetodielectric effect value in the sample with $x = 0.43$ is more than three times greater than the effect in a pure crystal and is equal to $\sim 1\%$. Unfortunately, we did not manage to measure permittivity in the sample with $x = 0.43$ in direction ε_a due to the limited sample sizes in the required directions.

The magnetic characteristics are described in [15] and also greatly differ from the pure crystal. Orientation of the antiferromagnetic vector changes at the given substitution value, vector l finally goes to direction b. Field H_c applied in the sample with $x = 0.43$ induces a spin-reorientation transition, accompanied by weakly ferromagnetic moment M_{Dc} directed along axis c, which means a change of antiferromagnetic vector direction $l_b \to l_a$.

Permittivity along direction b was also measured on the sample with $x = 0.43$. The measurement data is given in Fig. 5 and it can be seen that the magnetodielectric effect in this configuration depends on frequency of the exciting electric field. Indeed, it can be seen that permittivity measured at frequencies above 60 kHz remains virtually unchanged with growth of the magnetic field, and a sharp change of ε_b is observed in the area of 10 kHz (see Fig. 5, *b*). Such a low-frequency dependence shows that a change of polarizability in an external magnetic field cannot be explained by electronic contribution and is, in all likelihood, conditioned by polarization caused by ionic displacement (under the electric field action). It should be noted that this frequency dependence occurs only in case of mutual orientation of the electric and magnetic fields E_bH_c.

The directly measured parameter during permittivity measurements is the capacitor capacitance, which generally depends not only on permittivity, but also on capacitor's geometrical parameters. The latter can depend on an external magnetic field, for example, due to magnetostriction. If a plane capacitor model is applicable, we can assume that electric capacitance C is determined by expression $C = \varepsilon s/d$, where ε is the relative permittivity, s is the plate area, d is the distance between plates. A change of electric

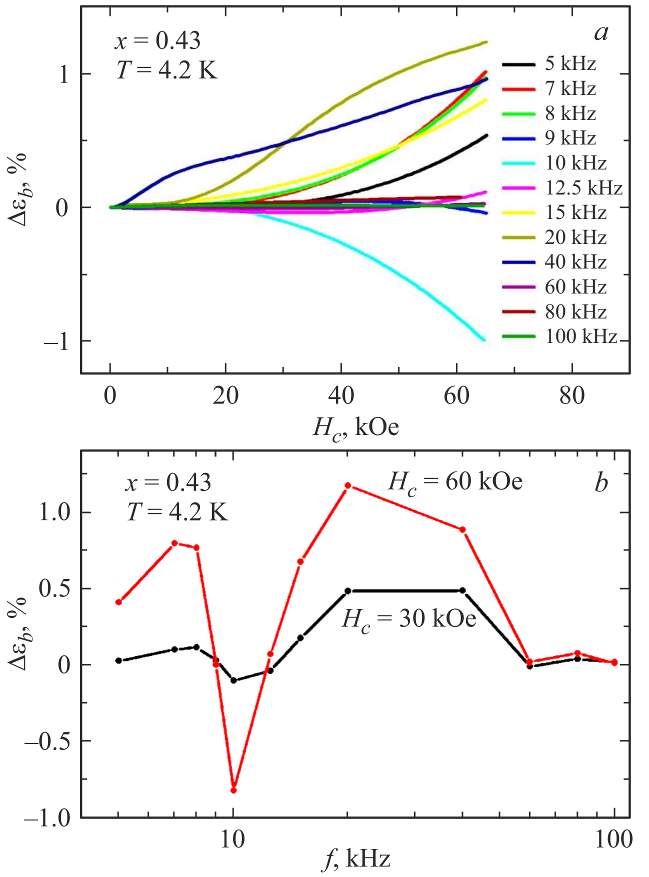

Figure 5. *a*) Permittivity ε_b of the crystal with substitution $x = 0.43$ vs. external magnetic field $H \parallel c$, measured at different frequencies of the exciting electric field; *b*) frequency dependence of permittivity $\varepsilon_b(f)$ at the magnetic field value of 30 and 60 kOe. $T = 4.2$ K.

capacitance can be related to a change of permittivity $\varepsilon(H)$ or geometrical parameters $d(H)$ and $s(H)$, which can be caused by magnetostriction of the capacitor dielectric.

Relative elongation $\lambda = \Delta l/l$ in technical saturation fields for polycrystalline samples of iron and nickel at low and room temperatures is small and equal to $\lambda \approx 10^{-6}$ [22]. Magnetostriction in cobalt and its alloys (e.g., permendur), cobalt ferrite is significantly higher, but usually not higher than 10^{-4}. A similar deformation value is also observed in compounds with rare earth elements $HoGa_3(BO_3)_4$ and $HoAl_3(BO_3)_4$ ($\lambda \approx 10^{-4}$) [23]. Magnetostriction in samples of pure metals of rare earth elements reaches values of 10^{-3}.

When distance between plates changes due to magnetostriction, a change in capacitance $\Delta C/C \approx \lambda/(1+\lambda)$ can be expected, which is equal to 0.0001 and 0.1% for $\lambda = 10^{-6}$ and 10^{-3}, respectively. Capacitance changes by more than 0.1% cannot be explained by magnetostriction. Therefore, we can assume that the observed magnetodielectric effect is not related to magnetostriction artifacts.

A change of electric capacitance can be also noted at a change of conductivity of the capacitor dielectric material, e.g. due to heating or magnetoresistive effects, and this must be taken into account in measurements. Since the measurements were performed at low temperatures and the samples are dielectrics, this contribution is also excluded.

As regards the magnetodielectric effect itself, that is, the dependence of permittivity on an external magnetic field, several possible mechanisms of polarization in a solid body must be considered. Permittivity is determined by expression $\varepsilon = 1 + 4\pi\alpha$, where α is polarizability, it is coefficient of proportionality between polarization (substance unit volume) and an external electric field. Polarizability can be related to a change in orientation of the existing dipole moments, displacement of electron shells or ionic displacement. Polarization related to a turn of the spontaneous polarization vector in ferroelectrics and the associated giant magnetodielectric effect was observed in multiferroic $SmFe_3(BO_3)$ [24], where a change of permittivity in an external magnetic field is about 70%. An increase of ε in the ab plane at a temperature decrease below T_N is conditioned by a contribution made to the permittivity by the rotational component, which is related to a turn of spontaneous polarization (it turns rather easily in an electric field due to the low anisotropy in the ab plane). Application of a magnetic field in this plane suppresses the permittivity, because it freezes the spins perpendicularly to the field and prevents their turn and, consequently, a turn of electric polarization. As a result, permittivity in an external magnetic field decreases considerably.

A magnetic field applied in the $DyMnO_3$ multiferroic along direction b ($Pbnm$) induces a transition, as a result of which the spontaneous polarization vector reorients from direction c to direction a, which is accompanied by a sharp peak of permittivity $\varepsilon(H)$ [25–27].

A spontaneous electric moment is not observed in $Pb_2Fe_2Ge_2O_9$ compounds and, thus, the magnetodielectric effect cannot be related to rotation of the existing dipole moment. A frequency dependence of the magnetodielectric effect $\varepsilon(H, f)$ in the low-frequency region indicates an ionic type of polarization, hence, ionic displacement in different magnetic states must be considered in order to explain the magnetodielectric effect in these compounds. The fact that permittivity differs in different magnetic fields indicates a change of ion mobility in an external magnetic field.

Energy of a magnetic ion is determined by the following main contributions: exchange interaction energy, anisotropy energy, Dzyaloshinskii–Moriya contribution, energy in magnetic and electric fields $W = W_{\text{ex}} + W_{\text{D}} + W_A + W_E + W_{\text{M}}$. Exchange energy is determined by expression $W_{\text{ex}} = A(\mathbf{S}_1\mathbf{S}_2)$, where A is the overlap integral, $\mathbf{S}_1$ and $\mathbf{S}_2$ are spins of interacting ions. Thereat, the scalar product does not depend on spin orientation in space, but is determined by their mutual orientation alone, that's why the scalar product is unchanged at spin-flop or spin-reorientation transitions, except when there is a skew of spins between each other. The latter takes place in case of a weakly ferromagnetic moment. Exchange integral A directly depends on interionic distance and, consequently, will change in case of their displacement. Hence it can be concluded that the contribution of exchange energy to the total energy of the crystal is different in states with a zero and non-zero weakly ferromagnetic moment. As a result, an identical ionic displacement in different magnetic states leads to different changes of exchange interaction energy and crystal's total energy.

A spin-flop transition $l_c \to l_a$ occurs in the crystal with $x = 0$ in a magnetic field directed along axis c; before and after this transition a weakly ferromagnetic moment existed due to a skew of magnetic moments of iron sublattices; however, not only the orientation of spontaneous moment $M_{Da} \to M_{Dc}$ changes under a transition, but also the skew value, namely, moment M_{Dc} is almost two times greater than moment M_{Da}. The orientation of antiferromagnetic vector $l_b \to l_a$ also changes in the crystal with $x = 0.16$ and 0.43 in field H_c when spontaneous moment M_{Dc} arises. In all the three cases there is an abrupt change of permittivity, which accompanies the change or formation of sublattice skew; this indicates a relation between the magnetodielectric effect and the magnetic state.

As is well-known [28,29], weak ferromagnetism arises in antiferromagnetic structures which are even in relation to operations of the symmetry centers and elementary translations. This condition is met in the given compound, the symmetry center and elementary translations transpose the ions which pertain to one and the same antiferromagnetic sublattice, and this is an evenness condition. As regards the mechanisms of formation of weak ferromagnetism, firstly, two noncollinear axes of easy magnetization form when two nonequivalent sites of magnetoactive ions with different crystalline fields are present in the lattice, and this leads to a skew of the magnetic moments of sublattices and a non-compensated weakly ferromagnetic moment. Secondly, weak ferromagnetism arises as a result of Dzyaloshinskii–Moriya interaction from a combination of effects of spin-orbital and indirect exchange coupling. According to [30], weak ferromagnetism in the $Pb_2Fe_2Ge_2O_9$ compound is conditioned by both mechanisms.

Energy of Dzyaloshinskii–Moriya interaction is determined by expression $W_D = \mathbf{D}[\mathbf{S}_1 \times \mathbf{S}_2]$, where $\mathbf{S}_1$ and $\mathbf{S}_2$ are spins of interacting ions, $\mathbf{D}$ is the Dzyaloshinskii vector which becomes zero when a crystalline field has inversion symmetry at the point located in the middle between the interacting ions. Iron ions in a pure compound without manganese ion doping are located at two nonequivalent sites, one of which is centrosymmetric and the other is no, which ensures the condition of presence of term W_D.

When doped with Mn^{3+} manganese ions, some of the iron sites are substituted, while anisotropy of Mn^{3+} can cause additional lattice distortions, which, in all likelihood, leads to an increase of the magnetodielectric effect. Indeed, the maximum magnetodielectric value in the compound with $x = 0$ is $\sim 0.3\%$, while the effect for the crystal with $x = 0.43$ increases threefold and is equal to $\sim 1\%$. However, the values of weakly ferromagnetic moment in the pure and highly substituted crystals are virtually identical along axis c.

4. Conclusion

The magnetodielectric response was studied in a series of $Pb_2Fe_{2-x}Mn_xGe_2O_9$ single crystals, with substitution x from 0 to 0.4. The study results have shown that the peculiarities of the magnetodielectric effect accompany changes in the magnetic subsystem as substitution of Fe^{3+} ions by Mn^{3+} ions increases. An increase of substitution x leads to a change of orientation of antiferromagnetic vector l in the zero magnetic field from l_c to l_b. Application of an external magnetic field leads to spin-flop and spin-reorientation magnetic transitions, accompanied by anomalies in the behavior of permittivity. Substitution of Fe^{3+} ions by Mn^{3+} ions causes a change of magnetic subsystem's reaction to the external magnetic field, which naturally affects the change of the magnetodielectric response.

Permittivity changes stepwise when the magnetic subsystem passes into a state with a non-zero vector of weakly ferromagnetic moment, or when its value and orientation change due to a spin-flop transition. The latter confirms that an abrupt polarizability change is caused by a change of the contribution of exchange energy, as well as the contribution of the Dzyaloshinskii–Moriya term, given a change of the angle of skew between two interacting magnetic moments. In other words, a polarizability change is caused by a change of the scalar and vector products which are included in the expressions for exchange energy and energy of Dzyaloshinskii–Moriya interaction. A frequency dependence of the magnetodielectric effect was found in the sample with $x = 0.43$; it manifests itself at electric field frequencies up to 60 kHz; the latter indicates that the revealed magnetodielectric effect has the nature of ionic polarization.

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Conflict of interest

The authors declare that they have no conflict of interest.

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