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Direct and inverse magnetoelectric effect in orthorhombic single crystals of $\text{Dy}_{1-x}\text{Ho}_x\text{MnO}_3$

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In this work, the magnetoelectric response in a series of $\text{Dy}_{1-x}\text{Ho}_x\text{MnO}_3$ crystals with substitution x from 0 to 0.4 was investigated. The measurement results showed that, as x increases, a decrease in both the polarization P_a and the magnitude of the susceptibility of the inverse magnetoelectric effect α_{ba} is observed. In addition, the field H_b increases, at which the $P_c \rightarrow P_a$ transition is observed, and the temperature range of the existence of the magnetoelectric response decreases. Thus, an increase in the substitution x suppresses the magnetoelectric effect in this series of compounds. The measurement results also indirectly indicate the prolongation of the P_a state and, consequently, of the magnetic state with a cycloid lying in the ab -plane by an external electric field E_a . The reported study was funded by Russian Foundation for Basic Research, Government of Krasnoyarsk Territory, Krasnoyarsk Regional Fund of Science to the research project No.20-42-243008.

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1. Introduction

For the last two decades the fast growth of number of publications, related to multiferroics, is observed. Multiferroics are compounds, which include at least two of the three following types of spontaneous ordering: magnetic, ferroelectric and ferroelastic [1]. Multiferroics, in which magnetic and ferroelectric ordering are simultaneously implemented, draw attention due to presence of magnetoelectric effect, that entails in connection of magnetic subsystem with electrical. It means, that by impacting the crystal with magnetic field, it is possible to change its electric polarization $P = P(H)$ and vice versa, at crystal putting into external electric field its magnetic moment $M = M(E)$ changes. Recently, the terminology has been established in literature, according to which the first effect is called a direct magnetoelectric effect (ME_H -effect), while the second — a reverse magnetoelectric effect (ME_E -effect). Simultaneous presence of ferroelectric and magnetic ordering in the crystal results in appearance of new interesting phenomena, that are also promising in terms of application.

Magnetoelectric effect manifests itself completely different in different compounds. For instance, the effect is also observed in compounds, which are not multiferroics at all. The great example of this are monocrystals of paramagnetic borates, where gigantic magnetoelectric effect is observed [2,3]. Monocrystals of $\text{HoAl}_3(\text{BO}_3)_4$ have a symmetry group $R32$, that prevents from piezoelectricity, but allows piezoelectric effect. Due to strong single-ion

anisotropy, magnetic field results in lattice deformation due to magnetostriction, which impacts a sample polarization by means of piezoelectric effect. At the same time, temperatures, at which the effect is observed, correspond to paramagnetic state.

However, according to general conceptions, the maximum effects are expected from compounds, for which the values of dielectric and magnetic permittivity are the highest, i.e. from multiferroics with ferromagnetic and ferroelectric ordering [4,5].

Multiferroics are usually divided into two types. Compounds, in which ferroelectric transition and transition into an ordered magnetic state happen independent from each other, are referred to multiferroics of the first type, but if ferroelectric transition is not-intrinsic and caused by magnetic structure change, these compounds are referred to multiferroics of the second type. In non-intrinsic ferroelectrics a primary parameter of the order is a lattice distortion mode with non-zero wave vector, while spontaneous polarization appears as a parameter of the secondary order, induced by lattice distortion. Spontaneous magnetostriction, appearing at magnetic phase transition, can be the reason for lattice distortion. Multiferroic type indirectly reflects the value of magnetoelectric response. Indeed, in compounds, where magnetic structure itself produces appearance of non-compensated electric dipole moment, the strong influence of magnetic subsystem on polarization, and vice versa, should be expected. Orthorhombic perovskite-like manganites of some rare earth elements belong to this multiferroic class.

Orthorhombic manganites of RMnO_3 (spatial group $Pbnm$) draw huge interest of researchers due to large amount of phase transitions in it. At temperature of Mn^{3+} ions ordering the rare earth subsystem ordering is not observed, it is in paramagnetic state, however the type of rare earth ion exercises a decisive influence on type of Mn^{3+} ions ordering. In series of rare earth elements with R^{3+} ionic radius reduction, three regions are implemented, corresponding to three different types of Mn^{3+} ordering. For instance, for $R = \text{La-Eu}$ ($Z = 57-63$) the antiferromagnetic ordering of A-type is implemented, magnetic moments of Mn^{3+} ions are ferromagnetically ordered in ab -plane and along c axis. In HoMnO_3 ($Z = 67$) the antiferromagnetic order of E-type appears, when magnetic structure in ab -plane is built as per „up-up-down-down“ type [6], that destroys inverse symmetry in this plane.

In interval $Z = 65-66$ in manganites with rare earth element Tb and Dy the series of magnetic transitions is observed with temperature decrease. At Neel temperature T_N (41 K for TbMnO_3 and 39 K for DyMnO_3) the incommensurate sinusoidally modulated collinear antiferromagnetic ordering of magnetic moments of Mn^{3+} ions with wave vector $(0, k, 1)$ is observed, where $k \sim 0.29$ for TbMnO_3 and $k \sim 0.39$ for DyMnO_3 [7,8].

As was shown in the work [6], with decrease of rare earth element ionic radius the evolution of lattice distortion of GdFeO_3 -type happens, which consists in tightening of MnO_6 octahedra. As a result, it changes a path length, and, consequently, energy of superexchange interactions in ab -plane between the closest neighbors along the path of Mn-O-Mn (ferromagnetic ordering), as well as interaction along two other superexchange paths through two oxygen ions of Mn-O-O-Mn , one of which is antiferromagnetic (along b -axis), and another is weak ferromagnetic (along a -axis). When reaching a certain degree of GdFeO_3 -type lattice distortion (which is defined with ionic radius of rare earth element), the competition appears between ferromagnetic contribution from closest neighbors and antiferromagnetic from the next closest neighbors. The latter results in spin frustration and appearance of incommensurate sinusoidal magnetic ordering and antiferromagnetism of E-type.

In TbMnO_3 and DyMnO_3 compounds the spontaneous polarization is not observed in sinusoidal magnetic phase. However, with the further increase of temperature, the wave number k reduces until temperature T_S , below which it remains almost the same. In this point the transition happens, that is accompanied with spontaneous electric polarization, directed along c axis. Ferroelectric phase appears at temperature $T_S = 28$ K for TbMnO_3 and 19 K for DyMnO_3 . In the work [9] the study of neutrons diffraction on TbMnO_3 crystal is performed, which showed, that magnetic ordering, corresponding to ferroelectric phase, is elliptically modulated cycloid spiral magnetic structure, and this conclusion is confirmed with the work [10]. The third magnetic transition is observed at temperatures ~ 7

and ~ 5 K in TbMnO_3 and DyMnO_3 , respectively, when rare earth subsystem is ordered. Measurements of magnetic characteristics are also performed in the work [11].

Below temperature T_S the spontaneous polarization in these compounds is described with expression $\mathbf{P} \propto [(\mathbf{r}_{i+1} - \mathbf{r}_i) \times [\mathbf{S}_i \times \mathbf{S}_{i+1}]]$, where \mathbf{r}_i and \mathbf{S}_i — radius-vector, drawn to i -th ion of Mn^{3+} and its spin, respectively [12]. As seen from this expression, polarization is different from zero only in the case, when magnetic moments of neighbouring Mn^{3+} ions are noncollinear, that corresponds to a spin cycloid. At the same time, the direction of the resulting polarization is perpendicular to direction of modulation of magnetic moment b and cycloid plane. In zero magnetic field the spontaneous polarization, directed along c axis, appears in both compounds, i.e. the spin cycloid is within bc plane. However, the sharp change of spontaneous polarization direction $P_c \rightarrow P_a$, related to tripping of cycloid of Mn^{3+} moments to ab plane, is observed at application of external magnetic field in ab plane. The latter is confirmed experimentally in the work [13]. Effect of direction change of spontaneous polarization vector under external magnetic field exposure is very attractive, since polarization susceptibility to external magnetic field in $P_c \rightarrow P_a$ transition point is very high, therefore it can be of interest for applications.

In our previous work [14] we performed study of direct and reverse magnetoelectric effect in DyMnO_3 . In this work we focused on evolution of magnetoelectric response with Dy^{3+} ions substitution with Ho^{3+} ions in monocrystals of $\text{Dy}_{1-x}\text{Ho}_x\text{MnO}_3$ composition with $x = 0-0.4$.

2. Experimental part

Monocrystals of $\text{Dy}_{1-x}\text{Ho}_x\text{MnO}_3$ with substitution value $x = 0-0.4$ were obtained using spontaneous crystallization method from solution in melt. The average size of obtained monocrystals was $\sim 1 \times 1 \times 1.5 \text{ mm}^3$. X-ray diffraction analysis showed, that the obtained monocrystals of $\text{Dy}_{1-x}\text{Ho}_x\text{MnO}_3$ belong to rhombic spatial group $Pbnm$. Total of four samples with substitution $x = 0, 0.2, 0.3$ and 0.4 were studied in the work.

For measurements of direct and reverse magnetoelectric effects the samples were prepared as flat capacitors by means of grinding. Coats of current-conducting paste based on epoxide with silver filler were applied on the prepared monocrystal facets, perpendicular to crystallographic axis a .

Measurements of electric polarization (ME_H -effect) were performed by measuring an electric charge, flowing from the sample coats, using Keithley 6517B electrometer. Before measurements the samples were preliminary polarized by cooling in constant electric field $E_0 = 7.4 \text{ kV/cm}$, applied along a axis of the crystal to temperature of 4.2 K. After that the applied electric field was removed and the measurements process started. Measurements of temperature $P(T)$ and field $P(H)$ dependencies of polarization P_a along a axis

were performed. Magnetic field H during polarization measurements was applied along b direction.

Measurements of reverse magnetic effect (ME_E -effect) were performed at experimental setup, made by the authors. Detailed description of the experimental setup and measurement methods are presented in the works [2,15,16]. As in the case of ME_H -effect, before measurements of ME_E -effect the sample was preliminary polarized by cooling in constant electric field $E = 7.4 \text{ kV/cm}$, applied along a axis of the crystal. After cooling the polarized field was removed, and alternating electric field $\mathbf{E} = e_0 \cos(\omega t)$ with amplitude $e_0 = 3.7 \text{ kV/cm}$ and frequency $f = 1 \text{ kHz}$ was applied to the sample. Due to magnetoelectric effect the applied alternating electric field E changes magnetic moment of the sample as per periodic law. As a result, voltage is induced in a removable coil, and later this voltage is interpreted as magnetic moment oscillations amplitude of the sample, based on calibration data.

Exciting electric field was applied only along a -axis, while change of magnetic moment ΔM was registered along b axis (transverse ME_E -effect). Synchronous amplifier SR830, registering both the first oscillation harmonic of magnetic moment $\Delta M'$ and the second one $\Delta M''$, was used for signal measurement. The first one corresponds to magnetic moment oscillation at frequency of exciting electric field ω , while the second one — to magnetic moment oscillation at double frequency 2ω . As was shown in the work [16], $\Delta M' = \alpha e_0$, $\Delta M'' = \beta e_0^2/2$, where α and β — susceptibilities of linear and quadratic terms of reverse magnetoelectric effect in terms of electric field, e_0 — oscillations amplitude of the applied electric field. This work presents results on measurement of the first harmonic only, but it should be noted, that in $\text{Dy}_{1-x}\text{Ho}_x\text{MnO}_3$ compounds the second harmonic of the reverse magnetoelectric effect was also excited, that is a topic for the study in the future.

3. Results and discussion

Spontaneous polarization appears in orthorhombic manganite of DyMnO_3 at temperature T_S , directed along c axis. Since a shape and a size of the grown crystals prevented from preparation of samples in the form of flat capacitor with a plane, perpendicular to c axis, we performed measurements of magnetoelectric properties along a direction. Despite the fact, that spontaneous polarization in this compound appears along c , it can be tripped in direction a by external magnetic field H_b . Clear marker of $P_c \rightarrow P_a$ transition is a sharp increase of dielectric permittivity ε_a at spontaneous polarization P_a appearance. Figure 1, a shows dependencies of relative dielectric permittivity ε_a on value of the applied magnetic field H_b . Obvious anomalies are observed for $\text{Dy}_{1-x}\text{Ho}_x\text{MnO}_3$ compounds with substitution value $x = 0.2$ and 0.3 , for $x = 0.4$ the anomaly is almost not noticeable, for $x = 0$ the data are presented in the work [8]. With increase of substitution x in the compound, the magnetic field, resulting in reorientation of polarization

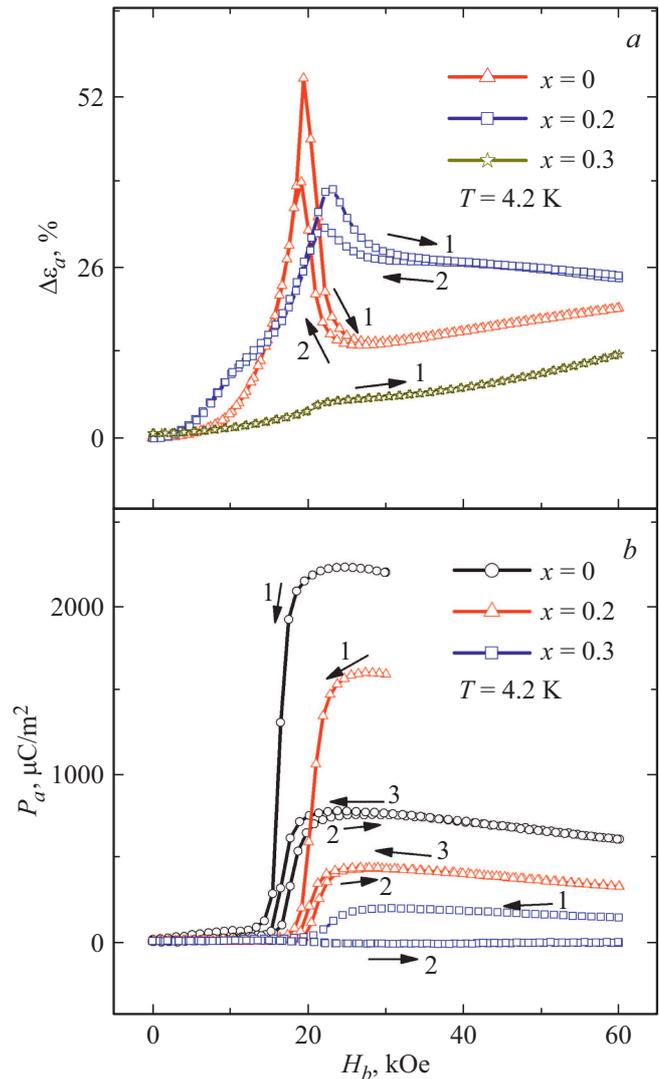


Figure 1. Dependence of relative change of dielectric permittivity $\Delta\varepsilon$ (a) and polarization P_a (b) on external magnetic field H_b for various compositions of $\text{Dy}_{1-x}\text{Ho}_x\text{MnO}_3$ ($x = 0-0.4$) at temperature $T = 4.2 \text{ K}$.

vector, increases. At $x = 0$ $H_c \sim 13 \text{ kOe}$ ($T = 2 \text{ K}$) [8], for $x = 0.2, 0.3$ the field, at which the anomaly is observed, is $H_c \sim 19, 22 \text{ kOe}$ ($T = 4.2 \text{ K}$), respectively. For $x = 0.4$ the field H_c is also about 22 kOe . Also the hysteresis, related to a sequence of $P_c \rightarrow P_a \rightarrow P_c$ transitions, is also observed on diagrams of dependence $\Delta\varepsilon_a(H_b)$. Arrows in the figure indicate direction of the field change. Anomalies of dielectric permittivity correspond to transition, consisting in tripping of a plane of cycloid of Mn^{3+} ionic spins from bc to ba with simultaneous rotation of spontaneous polarization vector $P_c \rightarrow P_a$.

Figure 1, b shows dependencies of electric polarization on external magnetic field H_b . Part of the presented data was already published by us earlier [14] for pure crystal of DyMnO_3 , and in this work we complement them and present a fuller picture with Dy substitution with

Ho. As seen from dependencies of $P(H)$, with increase of substitution x the polarization value decreases, while magnetic field of $P_c \rightarrow P_a$ transition also increases. In general, it can be said, that polarization diagrams totally correspond with dependencies of $\varepsilon(H)$. As for polarization for $x = 0.4$, we performed such measurements, but values of the measured polarization were too small to confirm the effect presence with certainty.

Sample polarization with $x = 0.3$ is noticeable. Initial curve course was made, as for all other curves, with precooling in magnetic and electric fields. Magnetic field H_b at precooling was applied for initiation of transition to P_a state, electric field E_a was applied for ferroelectric state P_a to be a single-domain before the start of polarization measurements. Measurement process started from magnetic field reduction in a start point, corresponding to magnetic field, applied at precooling, and this course is designated with number 1 in diagrams of Fig. 1, *b*. It is not unexpected, that with magnetic field reduction the sharp drop of polarization happens in $P_a \rightarrow P_c$ transition point, and with the further increase of magnetic field the P_a state initiates again, but polarization value is not so high, since during this $P_c \rightarrow P_a$ transition the external electric field, contributing to a single-domain state, was not applied already. But in case of $x = 0.3$ the polarization value not only decreases at repeated initiation of P_a state, but its sign also changes. The latter indicates, that there is some preferable polarization direction along a in this sample, opposite to electric field, applied during precooling. Probably, this feature of a certain sample is not applied to all $\text{Dy}_{1-x}\text{Ho}_x\text{MnO}_3$ compounds with $x = 0.3$. For instance, gradient of internal stresses in the crystal can act as one of the possible reasons for that. According to phase transition theory, formation of order parameter is equally probable in direction $+a$, as in direction $-a$, but additional polar external factors can result in lower energy of one of the directions. Of course, the latter does not guarantee a single-domain state, since it is necessary to also consider the surface energy of a ferroelectric, that is minimized by a crystal volume separation into domains with different direction of ferroelectric polarization.

In case of reverse magnetoelectric effect, when the exciting alternating electric field was applied to the crystal and magnetic moment oscillations were measured, dependence on sample cooling history was also observed. At excitation of ME_E -effect the alternating electric field is applied to the crystal, and piezoelectric effect appears, which sign is defined with mutual direction of a vector of spontaneous polarization and external exciting electric field. If crystal is divided into ferroelectric domains, the formation of both positive and negative piezoeffects in various crystal regions is inevitable. Without going deep into deformation type, the latter means, that both positive and negative deformations appear, which impact the macroscopic magnetic moment differently and, probably, oppositely. Therefore, the resulting ME_E -effect is small, when measurements were performed without procedures, resulting in single-domain state P_a .

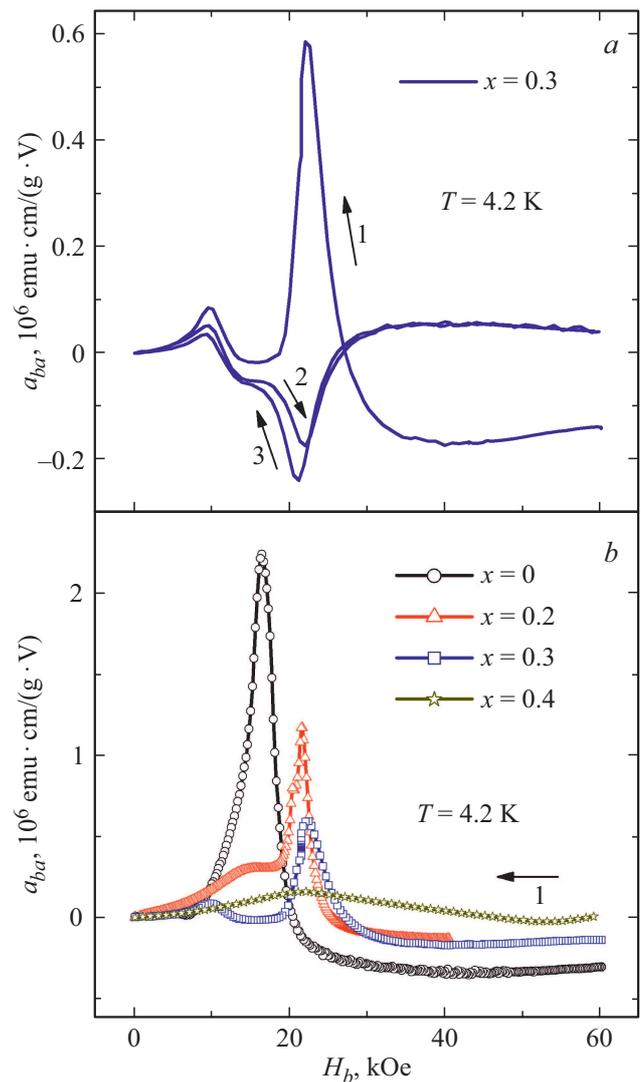


Figure 2. Susceptibility of linear term of magnetoelectric effect α_{ba} depending on external magnetic field H_b in $\text{Dy}_{1-x}\text{Ho}_x\text{MnO}_3$ with $x = 0.3$ (*a*) and other compositions (*b*) at $T = 4.2$ K.

Sample with $x = 0.3$ demonstrates the most interesting dependence on history. As was mentioned earlier, the repeated initiation of $P_c \rightarrow P_a$ transition in this sample results in polarization P_a , which sign is opposite to the one, that was initially set by external field. Figure 2, *a* shows dependence of $\alpha_{ba}(H_b)$ for $x = 0.3$, that also demonstrates change of a sign of reverse magnetoelectric effect at repeated induction of P_a state. Susceptibility α was defined as a ratio of magnetization oscillation amplitude ΔM and amplitude of exciting electric field E , $\alpha = \Delta M/E$. Only magnetization oscillations, that oscillate with the same frequency (1 kHz), as the applied electric field, were registered. As seen from the figure, in initial course 1 the magnetoelectric effect has maximum near 20 kOe, that corresponds to $P_a \rightarrow P_c$ transition, and disappears in the field $H = 0$. But with increase of magnetic field in

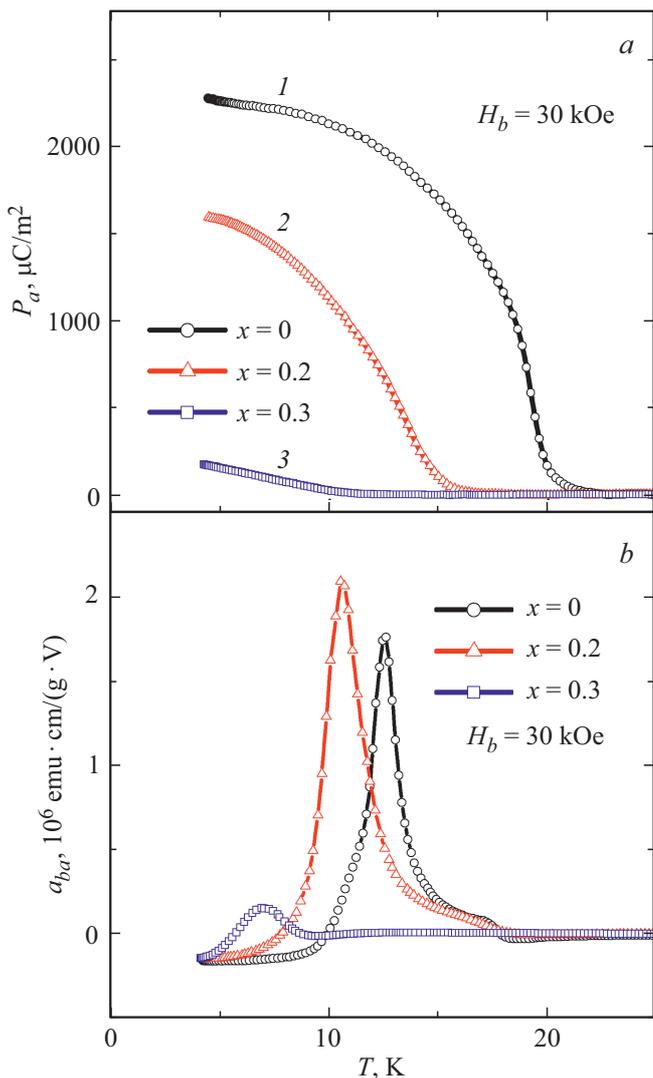


Figure 3. Dependence of electric polarization P_a (a) and susceptibility of the linear term of magnetoelectric effect α_{ba} (b) on temperature for various substitutions x in the field of 30 kOe.

$P_c \rightarrow P_a$ transition point the susceptibility α_{ba} changes its sign and minimum appears. With the further cycling over magnetic field the negative nature of the dependence remains.

Figure 2, b shows dependencies of susceptibility of a term of magnetoelectric effect, linear in electric field, α on magnetic field H_b , measured for various values of substitution x at $T = 4.2$ K. As in case of polarization, the strongest effect appears for unsubstituted sample of $DyMnO_3$. Results of measurements of ME_E -effect confirm, that with substitution x increase the magnetoelectric response reduces, and $P_c \rightarrow P_a$ transition field increases, that corresponds with the results of measurements of $P(H)$. We also registered a valid signal, related to ME_E -effect for a sample with $x = 0.4$, that was not achieved at measurement of ME_H -effect, and it indicates the higher sensitivity of the method.

Temperature dependencies of polarization $P_a(T)$ and reverse magnetoelectric effect $\alpha_{ba}(T)$ are shown in Fig. 3, a and b, respectively. These measurements were performed for various values of substitution x in magnetic field $H_b = 30$ kOe. With substitution increase the polarization formation temperature decreases, thus indicating the temperature shift of T_s transition, corresponding to magnetic ordering of cycloid type. As known, at $x = 1$ ($HoMnO_3$) the ordering of magnetic moments of manganese subsystem of E-type [17] appears, so the presented data naturally reflect the process of coherent cycloid phase suppression.

Such dependence also appears in ME_E -effect, as seen from Fig. 3, b, but effect for the sample with substitution $x = 0.2$ completely disappears at the same temperatures, as in unsubstituted sample. The latter contradicts with $P_a(T)$ data and, apparently, is caused by presence of exciting electric field, that is present during measurement of ME_E -effect ($e = 3.7$ kV/cm, $f = 1$ kHz). Indeed, it is well known, that magnetic phase transition is dissolved in presence of magnetic field, the similar dissolving can also happen for ferroelectric in external electric field. In presence of spontaneous polarization the ferroelectric energy includes a term, proportional to a product of spontaneous polarization and electric field stress, $-(\mathbf{P}\mathbf{E})$, therefore it is energetically favorable for the system to maintain polarization, if electric field is not zero. This also means, that with reduction of exciting electric field amplitude the maximum temperature, at which ME_E -effect is observed, can reduce. Moreover, due to connection of magnetic and ferroelectric orders, it may be expected, that electric field E_a maintains magnetic ordering, corresponding to a spin cycloid within ab plane.

As was mentioned above, the linear dependence of magnetization oscillation amplitude ΔM on the applied electric field e at its fixation at excitation frequency was assumed at susceptibility α_{ba} determination. Such approach is based on assumption, that the value of susceptibility α_{ba} itself does not depend on electric field amplitude, but due to recent observations it may be not true, especially near phase transition. Therefore in the nearest future we are planning to study the ferroelectric hysteresis loops and regions of possible nonlinearities of α_{ba} for the same compositions. The second harmonic of ME_E -effect, i.e. the term quadratic to electric field, is of separate interest.

4. Conclusion

The work includes study of magnetoelectric response in a series of substitutions of $Dy_{1-x}Ho_xMnO_3$, with x from 0 to 0.4. Temperature and field dependencies of direct and reverse magnetoelectric effect are studied. In general, it can be concluded, that substitution of Dy^{3+} ions with Ho^{3+} exerts suppression influence on magnetoelectric effect in this compound. With increase of substitution x , the reduction of polarization P_a , reduction of susceptibility value of reverse magnetoelectric effect α_{ba} , as well as increase of the field H_b , at which $P_c \rightarrow P_a$ transition

happens, reduction of magnetoelectric response presence temperature range are observed.

Measurement results also indicate, that the applied electric field can extend P_a state, and, consequently, magnetic state with cycloid within ab plane. The observed data also indicate the possible presence on nonlinear effects, related to dependence of susceptibility of linear term of magnetoelectric effect on electric field.

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Conflict of interest

The authors declare that they have no conflict of interest.

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