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The relationship between magnetoelectric and magnetoelastic properties in single crystals of substituted oxyborates $Sm_{1-x}La_xFe_3(BO_3)_4$ $(x = 0, 0.5, 0.75)$

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In this work, the magnetoelectric effect in a single-crystal substituted oxyferroborate crystal $Sm_{1-x}La_xFe_3(BO_3)_4$ $(x = 0, 0.5, 0.75)$ was investigated. The data obtained in this experiment were compared with the data of the magnetostriction experiment. It was shown that magnetoelastic interaction is the cause of magnetoelectric interaction, but in this series of crystals there is a competing mechanism in the form of an increase in ion mobility, which affects the magnetoelectric properties, but does not affect the magnetostrictive ones.

Keywords: polarization, magnetostriction, substituted single crystal, magnetic anisotropy.

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1. Introduction

Co-existence of magnetic ordering and spontaneous electric polarization in materials known as multiferroics is the subject of research in the field of condensed matter physics. The interest in these systems is caused both by numerous fundamental effects demonstrated by multiferroics [1–5] and by their applicability [6–8]. According to the definition in [9], multiferroics may include compounds that have any two or all three types of ordering: spontaneous magnetic moment, spontaneous dipole moment and spontaneous deformation.

Mechanism responsible for the microscopic-level magnetoelectric effect is still not fully understood. Experimental discovery of linear magnetoelectric interaction [10] gave rise to numerous studies devoted to the search and study of materials demonstrating this effect [11–13]. Materials, in which a magnetoelectric effect is observed, demonstrate a dependence of polarization on the applied magnetic field. It is also recognized that polarization effects may be induced by magnetoelastic interaction [14].

Among the substances demonstrating a magnetoelectric effect, a family of borates, $RM_3(BO_3)_4$, is distinguished, where R is the rare-earth ion or Y, and M is Al, Fe, Ga, Sc, Cr ion. Crystals of this family have space group R32 [15], which defines the absence of the center of inversion. A sublattice of MO_6 octahedra forms a helicoidal chain along the c axis with exchange interaction between 3d-elements, rare earth element ions forming RO_6 prisms are isolated from each other by BO_3 triangles and, consequently, there is no $R{-}O{-}R$ type interaction [16]. Both BO_3 triangles and RO_6 prisms are bound with three MO_6 chains (Figure 1).

In [17] it was shown that a transition element, for example, iron, is not necessary for occurrence of the magnetoelectric effect in huntite-structure oxyborates. It was also shown that the magnitude of magnetoelectric polarization in the $HoFe_3(BO_3)_4$ and $HoAl_3(BO_3)_4$ systems depends mainly on the magnitude of magnetostriction in these compounds [18]. To verify this argument, polarization and magnetostriction shall be measured in a system containing different concentration of a rare-earth ion because this particular subsystem is responsible for the magnitude of magnetostriction [18].

Among ferroborates with one type of rare-earth ion, a $SmFe_3(BO_3)_4$ system is distinguished, the highest magnetoelectric effect [19] and giant magnetodielectric effect [20] were found in these single crystals. To understand the role of Sm^{3+} and Fe^{3+} in formation of magnetic structure, spontaneous polarization, magnetoelectric polarization and magnetostriction in $SmFe_3(BO_3)_4$, investigations and further comparative analysis of ferroborates may be performed with successive samarium substitution with other rare earth elements. In particular, lanthanum is a suitable substituting element. Firstly, it is nonmagnetic and, thus, will not affect the magnetic anisotropy in the $Sm_{1-x}La_xFe_3(BO_3)_4$ crystal. Secondly, it has the largest ionic radius among rare earth elements, and this may affect cation mobility in a local anionic environment, which in turn will cause modification of magnetoelectric properties. Magnetic properties of the studied system were investigated in [21].

This study investigates the magnetoelectric effect and magnetostriction in substituted samarium ferroborates, $Sm_{1-x}La_xFe_3(BO_3)$, where $x = 0$, 0.5 and 0.75.

2. Experiment

To measure the magnetoelectric polarization, epoxy resin electrodes with conducting filler were applied to the faces

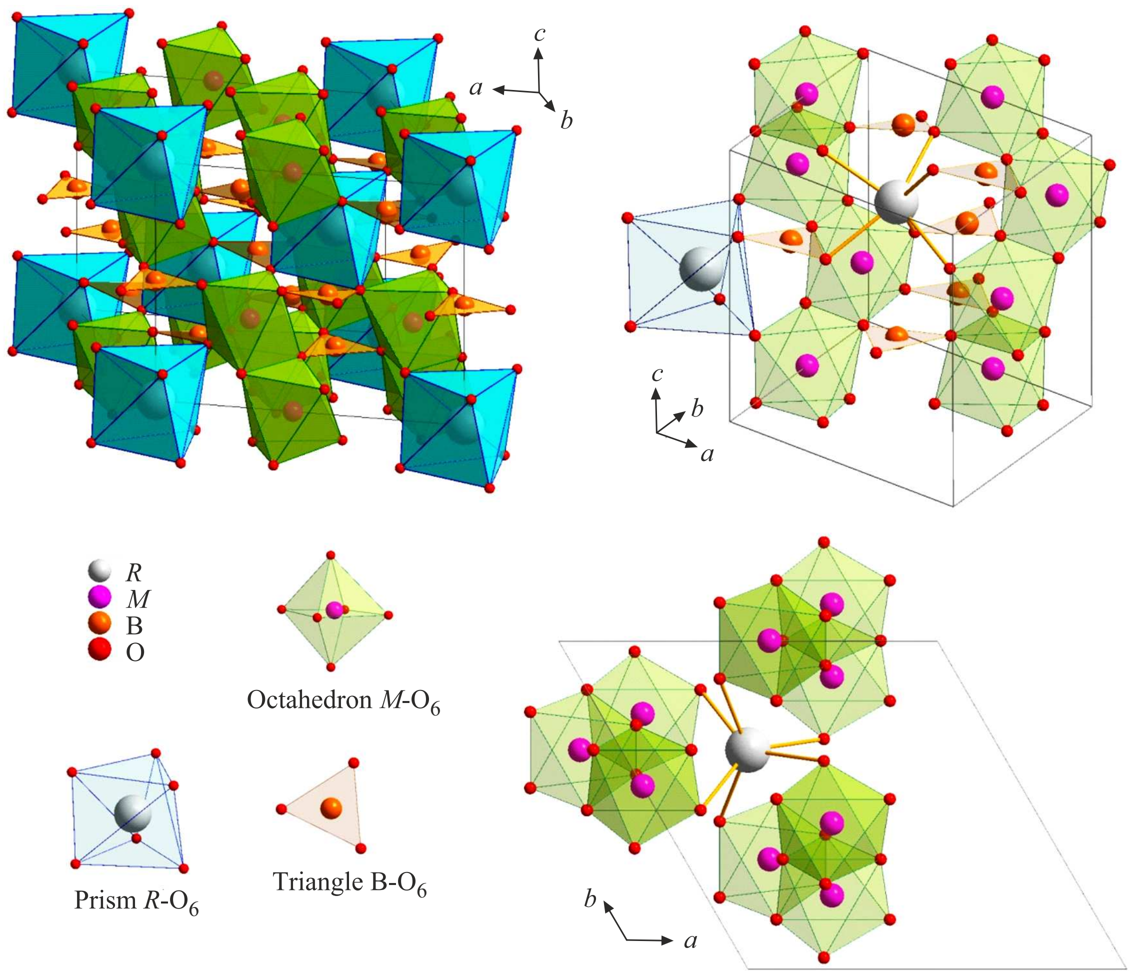

Figure 1. $RM_3(BO_3)_4$ lattice cell and its elements.

of the studied sample prepared in a form of a plane-parallel slice (face planes are perpendicular to the a axis). A charge induced by the magnetoelectric effect on the sample was measured by the Keithley 6517B electrometer. Magnetic field was applied along the twofold crystallographic axis „a axis" (direction x) and alonf the „b axis" (direction y) perpendicular to the „a axis" and „c axis".

Magnetostriction dependences were measured at the laboratory of strong magnetic fields and low temperatures, Wroclaw, Poland, using a system described in [22] in 2016. Crystal orientation for striction tests was the same as for polarization measurement.

3. Results and discussion

Temperature dependences of magnetoelectric polarization of $Sm_{1-x}La_xFe_3(BO_3)_4$ induced along the x direction and measured in different fields with different magnetic field directions are shown in Figure 2. The figure shows that a non-zero electric polarization is observed below the Néel temperature. It is important that the magnitude of spontaneous electric polarization is very different for various compounds (at $T = 4.2\,K$ — $P_x = 19\,\mu C/m^2$ $(x = 0)$; $P_x = 40\,C/m^2$ $(x = 0.5)$; $P_x = 18\,\mu C/m^2$ $(x = 0.75)$). It is commonly known that the non-zero electric polarization shall be induced by factors that reduce crystal symmetry. It is supposed that such factor may be a uniaxial anisotropy generated by induced mechanical stresses due to magnetoelastic interactions [14]. Thus, it appears that the highest stresses are observed when there are approximately equal proportions of samarium and lanthanum ions.

As the magnetic field increases, increase (decrease) in electric polarization was observed for the magnetic field direction parallel to the x axis (y axis). In high fields (higher than 20 kOe), magnetoelectric polarizations P_{xx} and P_{xy} are almost equal in absolute value for each of the compositions.

It is assumed that two competitive processes take place when Sm^{3+} are substituted with La^{3+}. On the one hand, a decrease in samarium ions shall lead to a decrease in the magnitude of magnetoelectric effect, because it is shown that primarily a rare-earth subsystem is responsible for the magnetoelectric effect in ferroborates [23].

On the other hand, La^{3+} have the largest ionic radius among rare earth elements, and this shall affect cation

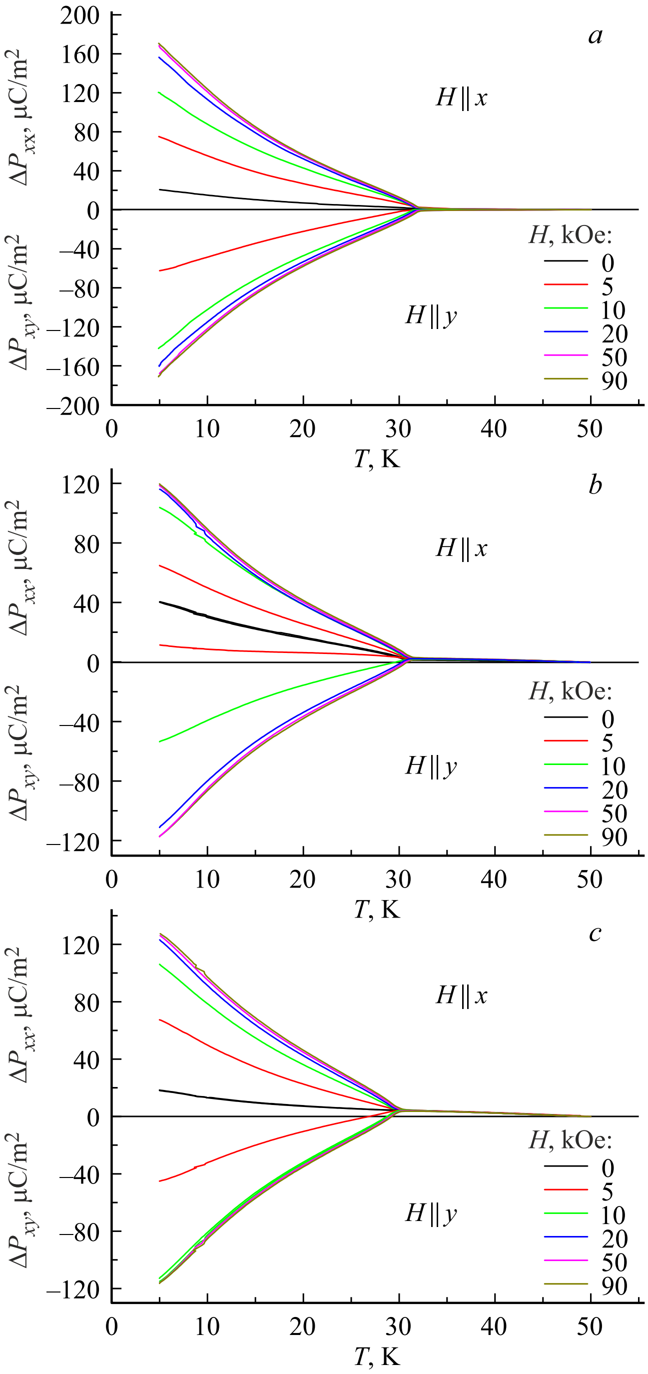

Figure 2. Temperature dependences of magnetoelectric polarization, $Sm_{1-x}La_xFe_3(BO_3)_4$, measured in different fields: *a* — $x = 0$, *b* — $x = 0.5$, *c* — $x = 0.75$.

mobility in a local anionic environment, as a result the magnetoelectric effect shall increase.

As shown from comparison in Figure 2, *a* and *b*, the first process prevails over the second. However, comparison of Figure 2, *b* and *c* suggests that both processes already balance each other, thus, the magnetoelectric polarizations in high fields (> 20 kOe) for compounds $x = 0.5$ and 0.75 are almost equal to each other.

Modification of magnetoelastic properties depending on the content of Sm^{3+} may be followed by means of magnetostriction study. Such study was performed on all compounds in magnetic field up to 14 T. Field dependences of magnetostriction along x and magnetic field orientations along x are shown in Figure 3. Figure shows that the shape of magnetostriction curves $\Delta x(H_x)/x(0)$ is close to the field dependences of magnetoelectric polarization P_{xx} shown in Figure 4. In relatively low fields (10–20 kOe), both quantities increase rapidly, which is associated with the

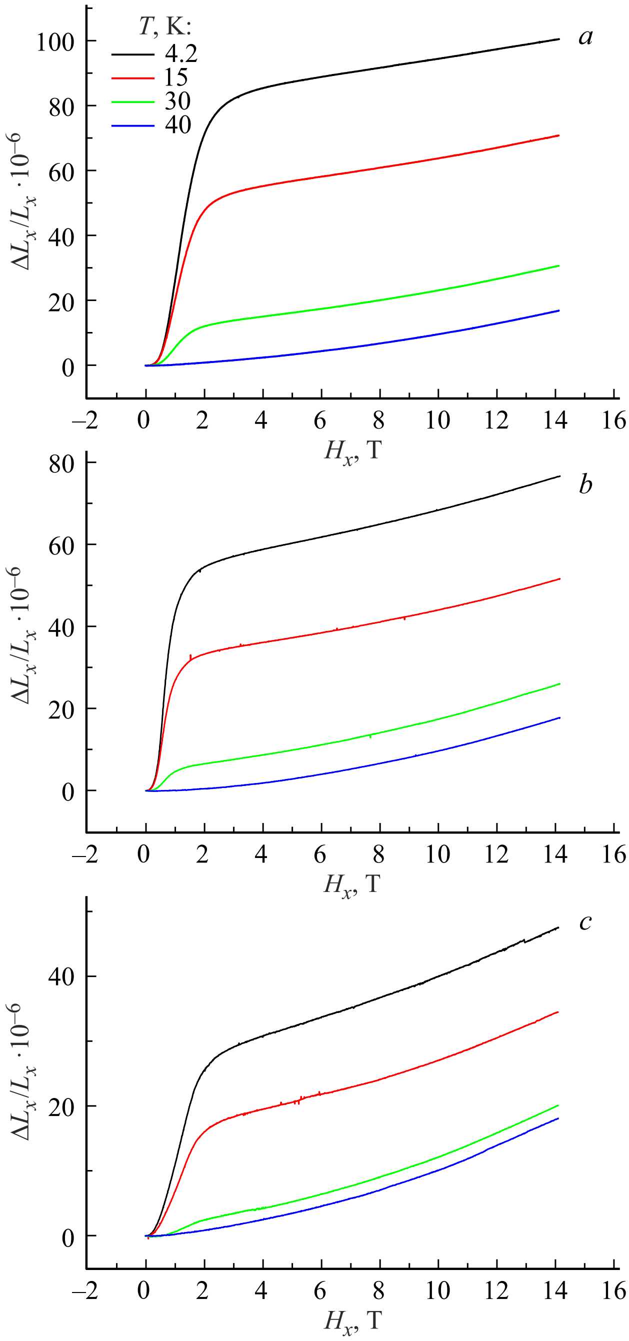

Figure 3. Field dependences of magnetostriction, $Sm_{1-x}La_xFe_3(BO_3)_4$, measured at different temperatures: *a* — $x = 0$, *b* — $x = 0.5$, *c* — $x = 0.75$.

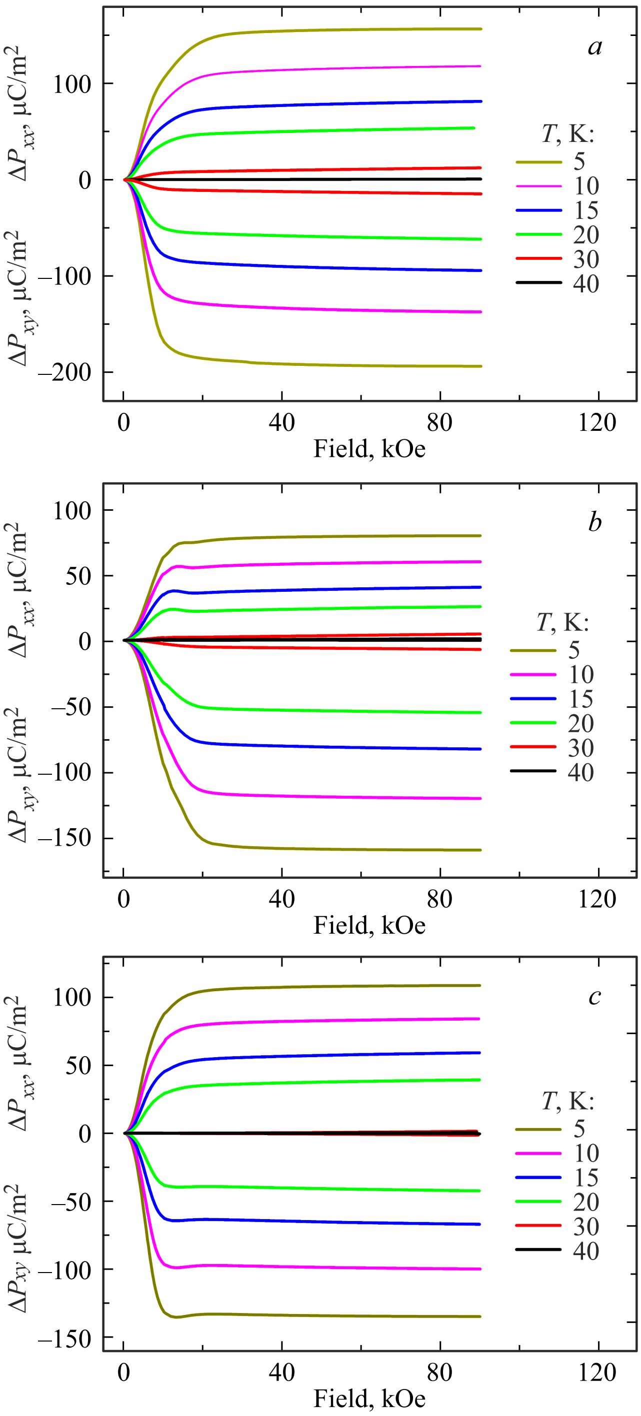

Figure 4. Field dependences of magnetoelectric polarization, $Sm_{1-x}La_xFe_3(BO_3)_4$: *a* — $x = 0$, *b* — $x = 0.5$, *c* — $x = 0.75$.

establishment of homogeneous antiferromagnetic ordering throughout the crystal volume.

In [24], a symmetric approach for rare-earth ferroborates was used to explain the behavior of magnetoelectric and magnetoelastic properties. It was shown that longitudinal polarizations and magnetostriction $(u_{xx} - u_{yy})$ are composed of contributions associated both with antiferromagnetic order parameter **L** and with magnetic moments m_i of rare-earth ions:

$$P_x = c_1 L_y L_z + c_2(L_x^2 - L_y^2) + \frac{1}{2}\sum_{i=1}^{2}\left\{c_3(m_{ix}^2 - m_{iy}^2) + c_4 m_{iz}^2 H_y + c_5 m_{iz} m_{iy}\right\}, \quad (1)$$

$$u_x x - u_{yy} = b_1 L_y L_z + b_2(L_x^2 - L_y^2) + \frac{1}{2}\sum_{i=1}^{2}\left\{b_3(m_{ix}^2 - m_{iy}^2) + b_5 m_{iz} m_{iy}\right\} \quad (2)$$

summation is performed on two rare-earth sublattices $i = 1, 2$. Due to the fact that all rare-earth ions occupy identical crystallographic positions and differ just in the exchange field acting on them, b_i, c_i are similar for both sublattices.

In case of the „easy-plane“ type anisotropy, when magnetic moments of iron and rare earth ions lie in plane, the notation is simplified:

$$P_x = c_2(L_x^2 - L_y^2) + \frac{1}{2}\sum_{i=1}^{2}\{c_3(m_{ix}^2 - m_{iy}^2)\}, \quad (3)$$

$$u_{xx} - u_{yy} = b_2(L_x^2 - L_y^2) + \frac{1}{2}\sum_{i=1}^{2}\{b_3(m_{ix}^2 - m_{iy}^2)\}. \quad (4)$$

As can be seen from equations (3), (4), transition to uniaxial antiferromagnetic state shall be followed by a polarization and magnetostriction jump in easy-plane ferroborates as shown in Figures 3 and 4. In our case, the initially inhomogeneous state is associated with the presence of antiferromagnetic domains. It can be also seen from these expressions that magnetoelectric polarization and magnetostriction shall decrease as the content of Sm^{3+} decreases as shown for magnetostriction (Figure 3). For magnetoelectric polarization, the situation is slightly different. A decrease in samarium ions, on the one hand, leads to a decrease in the effect (equation (3)), on the other hand, to an increase in mobility of ions responsible for magnetoelectric polarization.

4. Conclusion

Correlation between the magnetoelectric and magnetostriction properties was observed for the longitudinal effect. It is suggested that the magnetoelectric effect variation when Sm^{3+} are substituted with La^{3+} may be explained by the crystal field distortion induced by local distortions of anionic environment of the rare-earth ion. Thus, as x increases, the magnetoelectric polarization in $Sm_{1-x}La_xFe_3(BO_3)_4$ doesn't decrease monotonously as opposed to the magnetostriction variation. Magnetoelastic interaction apparently causes magnetoelectric interaction, but in this case, there is a competing mechanism in the form of an increase in ion mobility that affects magnetoelectric properties, but doesn't affect magnetoelastic properties.

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Conflict of interest

The authors declare that they have no conflict of interest.

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