ISSN 1063-7834, Physics of the Solid State, 2019, Vol. 61, No. 8, pp. 1379–1382. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Fizika Tverdogo Tela, 2019, Vol. 61, No. 8, pp. 1433–1436.

SEMICONDUCTORS

Magnetoelectric Effect in a Paramagnetic Region in $Gd_{0.15}Mn_{0.85}Se$

S. S. Aplesnin[a, b], V. V. Kretinin[b], and O. B. Begisheva[b, *]

[a] *Kirensky Institute of Physics, Independent Subdivision of Federal Center KSC SB RAS, Krasnoyarsk, 660036 Russia*
[b] *Reshetnev Siberian State University of Science and Technologies, Krasnoyarsk, 660000 Russia*
**e-mail: fisenko_o@mail.ru*

Received March 19, 2019; revised March 19, 2019; accepted March 19, 2019

Abstract—The electric polarization in a zero magnetic field and in a magnetic field of 12 kOe is measured in a $Gd_xMn_{1-x}Se$ solid solution in the percolation concentration region in the temperature range 80–380 K. For composition $x = 0.15$, the polarization hysteresis and the dependence of the remanent polarization on magnetic field and temperature are determined. The hysteresis is explained in the model of migration polarization and the magnetoelectric effect is explained in the Maxwell–Wagner model.

Keywords: magnetoelectric effect, migration polarization, hysteresis, and polarization

DOI: 10.1134/S1063783419080067

1. INTRODUCTION

Materials in which correlations between magnetic and electrical properties are observed [1, 2], namely, magnetoelectrics and magnetoferroics [3, 4] are interesting from both fundamental and practical points of views. Of particular value are materials with magnetoelectric properties at room and higher temperatures, due to their application in microelectronics for data recording and storage. Among such studied materials is, for example, bismuth ferrite $BiFeO_3$ [5, 6]. In these compounds, the ferroelectric moment is caused by the ion displacement. The electric polarization appears also as electrons are redistributed between iron ion cations located in different crystallographic positions, for example, in $LuFe_2O_4$ [7].

In electrically inhomogeneous systems, the Maxwell–Wagner effect [8] and the contact effects can lead to giant values of the permittivity and to the dependence of the permittivity on magnetic field as a result of the tensor character of interaction and mixing longitudinal and transverse conductivity components [9]. An electrically inhomogeneous system can be prepared by synthesizing isostructural compounds with different values of the conductivity. For example, semiconductor MnSe with the gap 2 eV in the spectrum of electron excitations has an fcc lattice [10]. The initial gadolinium selenide belongs to degenerate semimetals [11]. The compound has the rock salt-type cubic crystal structure and the second-type ordering antiferromagnetic structure with the Néel temperature $T_N = 63$ K [11]. The substitution of gadolinium for manganese leads to the formation of a region with a higher conductivity and with a charge gap between manganese and gadolinium ions. The charge carriers, namely, lattice polarons, are pinned at the Mn–Gd ion boundary with the formation of a local lattice deformation and electric polarization. As a result, the dielectric properties can be controlled by electric and magnetic fields.

The aim of this work is to establish the contribution of the migration electron polarization and the Maxwell–Wagner effect to the magnetoelectric coupling in the spin-disordered region in the $Gd_xMn_{1-x}Se$ solid solution.

2. RESULTS AND DISCUSSION

We studied the substitution of gadolinium ions for manganese ions for two concentrations: $x = 0.15$ lower than the percolation concentration $x_c = 0.17$ for the fcc lattice and $x = 0.2$. In the second case, the covalent Gd–Gd bonds penetrate the entire lattice and the electric charge is transmitted the entire lattice by these bonds. The $Gd_xMn_{1-x}Se$ solid solution was synthesized by the solid-phase reaction method described in [12] from initial compound powders in evacuated quartz ampoules in a one-zone furnace.

The phase composition and the crystal structure of the sample were determined at 300 K on a DRON-3 X-ray diffractometer using CuK_α radiation. The X-ray diffraction data analysis [13] showed that the synthesized compound has the NaCl-type face-centered cubic (fcc) structure.

The electric polarization was measured in a quasistatic electric field at frequency $\nu = 3$ mHz in a zero magnetic field and in magnetic field $H = 12$ kOe (Fig. 1). Three cycles of measurements of $P(E)$ were carried out at the same temperature. As the number of

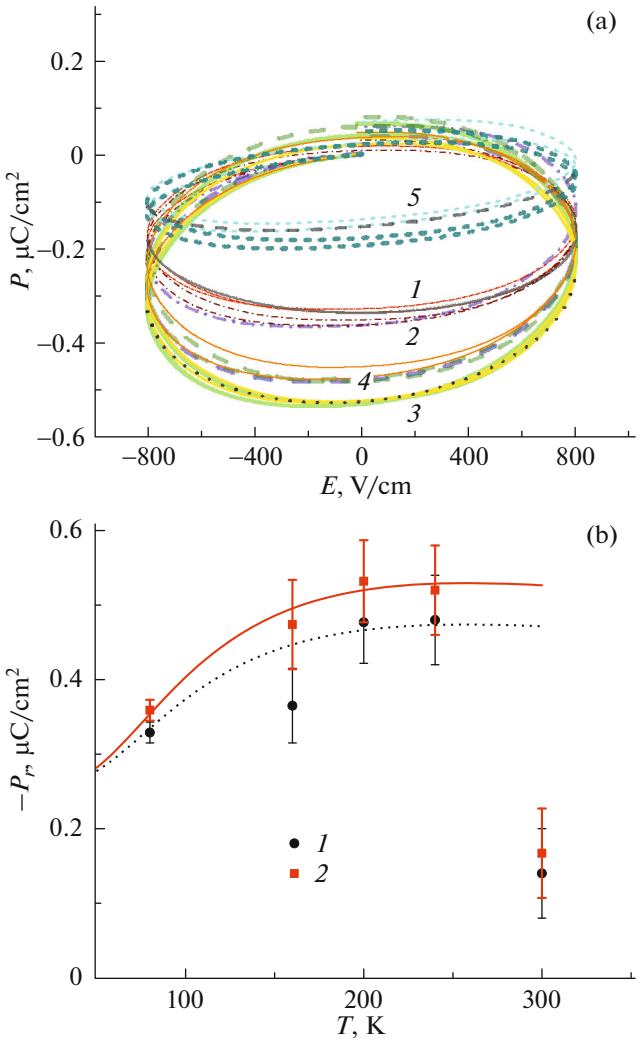

Fig. 1. (a) Electric polarization in $Gd_{0.15}Mn_{0.85}Se$ from the external electric field at a frequency of 3 mHz; the first and the third cycles measured in a zero magnetic field and in magnetic field $H = 12$ kOe at temperatures $T = (1)$ 80 K, (2) 160 K, (3) 200 K, (4) 240 K, and (5) 300 K and (solid lines) the theoretical calculations by Eq. (8). (b) The remanent polarization vs. temperature in fields $H = (1)$ 0, (2) 12 kOe, and (solid lines) in the polaron model $P_r = B/T\exp(-E_a/k_BT)$.

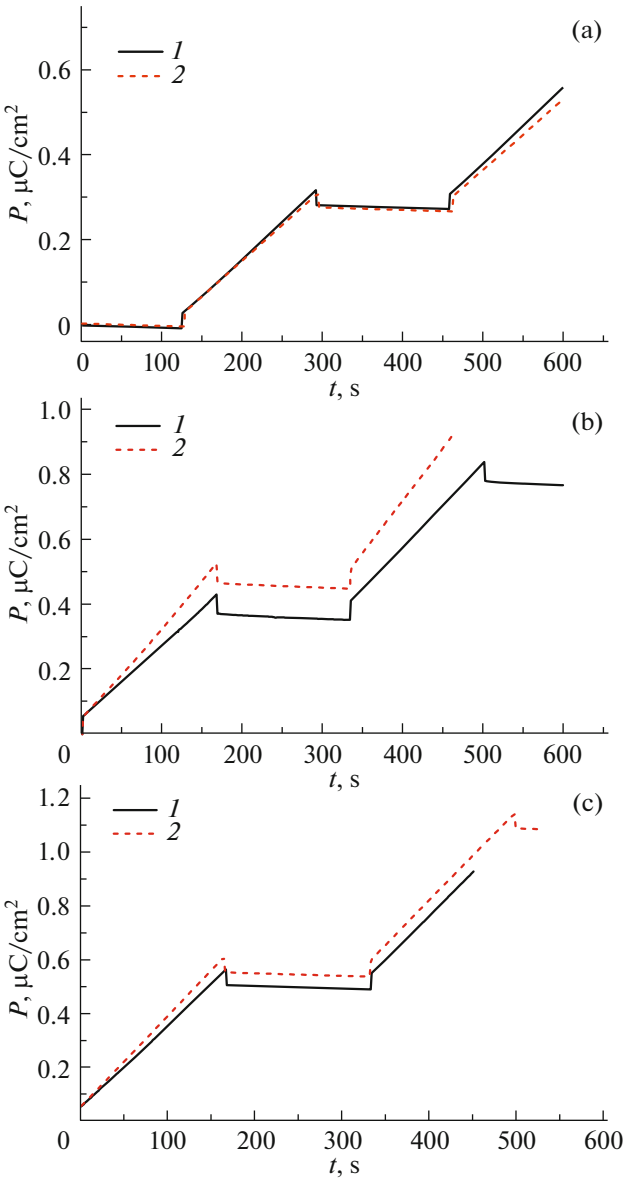

Fig. 2. Electric polarization in $Gd_{0.15}Mn_{0.85}Se$ during switching on and switching off of external electric field $E = 800$ V/cm vs. time measured in magnetic field $H = (1)$ 0 and (2) 12 kOe at temperatures $T =$ (a) 80 K, (b) 160 K, and (c) 250 K.

the cycles increases, the hysteresis loop shifts up by 5–7% along the polarization axis, and the hysteresis width increases in magnetic field by 10–30%. The remanent polarization (Fig. 1b) increases monotonically up to a maximum at $T = 200$ K and disappears at temperatures higher than 330 K.

In an external dc electric field, the polarization increases linearly with time (Fig. 2) and is described well by the electron migration polarizability $P = jt = \sigma Et$, where σ is the conductivity of a domain with resistivity $\rho = 2–6 \times 10^6$ Ω cm that decreases with increasing temperature. After the field is switched off, the polarization logarithmically decreases $P = P_0 - v \log t$, where v is the relaxation rate and P_0 is the induced polarization. This dependence is characteristic of spin and dipole glasses in which the magnetization (polarization) decreases by the logarithmic law after cooling in magnetic or electric fields [14]. In a magnetic field, the rate of increasing the electric polarization increases (Fig. 2).

The electric polarization of the composition with $x = 0.2$ (Fig. 3) increases linearly as the external electric field, and there is no hysteresis. The dielectric susceptibility in dc electric field $\chi = P/\varepsilon_0 E$ is independent of temperature up to 200 K, which is characteristic of

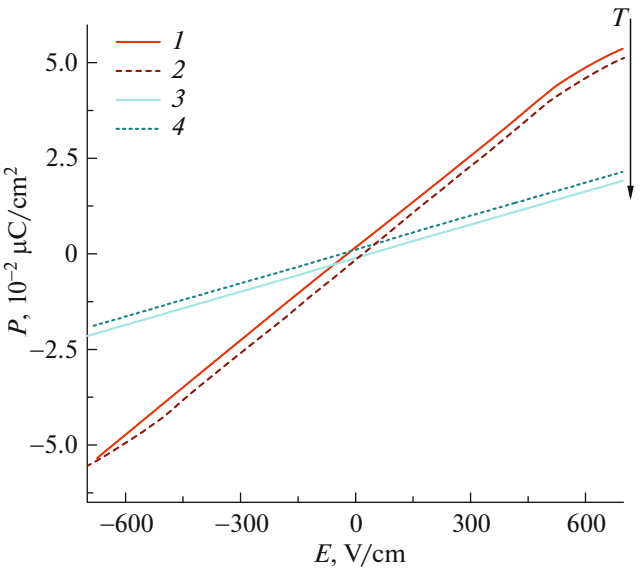

Fig. 3. Electric polarization in $Gd_{0.2}Mn_{0.8}Se$ from the external electric field at a frequency of 3 mHz measured in a zero magnetic field and in magnetic field $H = 12$ kOe at temperatures $T = 80$ K, 160 K, 200 K, 240 K, and 300 K.

materials with the electron type of the polarization. Below $T = 200$ K, the dielectric susceptibility decreases in magnetic field by 1–2%; above 240 K, the dielectric susceptibility increases by 3–5% in magnetic field.

3. MODEL

According to the theoretical LSDA + U calculations [5], trivalent gadolinium selenide is a metal, in which the conduction band is due to 5d electrons and the upper Hubbard subband of 4f electrons is 2 eV higher than the Fermi level. The conduction band width is 8 eV. Substitution of trivalent gadolinium ions for bivalent manganese ions leads to the electron doping and the degeneracy of t_{2g} electron states that is split by the electron–phonon and spin–orbit interactions. The charge carriers in MnSe are holes that interact with the optical vibration modes and form lattice polarons. Below $T = 330$ K, the conduction type is changed from the band to the hopping type [13]. As temperature decreases (below the Debye temperature $\theta = 250$ K), the polarons are pinned on a charge gap between Mn–Gd ions in the temperature range 200–250 K, and the resistance is only slightly changed with further decrease in the temperature. The polaron pinning causes the lattice deformation with a reduction of symmetry.

The hysteresis and the linear dependence of the polarization on time in a dc external electric field are caused by the accumulation of current carriers at the boundary of manganese ions surrounding gadolinium ions. The migration polarization from the field is expressed via the conductivity:

$$P(E) = \int j dt = \int \sigma E_0 \sin(\omega t) dt = \sigma^2 \sqrt{E_0^2 - E^2}/\omega, \quad (1)$$

where ω is the frequency of external electric field and E_0 is the field amplitude. The remanent polarization $P_r = 2\sigma E_0/\omega$ is determined by the charge accumulation at the interface for the time equal to the half-period $t = T/2$. The total polarization is determined as

$$P = P_r + \sigma^2 \sqrt{E_0^2 - E^2}/\omega + \int j_l dt, \quad (2)$$

where j_l is the leakage current. The experimental $P(E)$ data in Fig. 1a are well described by function (2) with two adjustable parameters: the conductivity of the CdSe region and the leakage current with the Gd–Mn interface. The temperature dependence of the conductivity is determined by a change in the lattice polaron mobility. The temperature changes in the current carrier concentration can be neglected up to 250 K, and the remanent polarization is adequately described by relationship

$$P_r = 2en\mu E_0/\omega = B/T \exp(-E_a/k_B T), \quad (3)$$

where n the current carrier concentration and E_a is the activation energy. The polarization in Fig. 3 is adequately described by Eq. (3) with $E_a = 0.022$ eV; this value agrees with the coupled optical and acoustic vibration modes $\omega = 192$ cm^{-1} [16]. At $T > 250$ K, the electron density in the vicinity of Mn–Gd ions decreases, which is possible with the disappearance of elastic stresses at the Mn–Gd interface. There is no charge gap in the channel of Gd–Gd ions in the compositions with $x = 0.2$.

4. CONCLUSIONS

In the $Gd_{0.15}Mn_{0.85}Se$ solid solution, we observed the hysteresis of the electric polarization and the remanent polarization, which increases on heating and disappears above the critical temperature. The hysteresis is absent at gadolinium concentrations higher than their percolation concentration in the fcc lattice. The remanent polarization is related to the accumulation of charge carriers at the boundary between manganese and gadolinium ions and is dependent on the mobility of polarons with the hopping conduction mechanism. The change in the polarization in magnetic field is related to the Maxwell–Wagner effect, and the delocalization of electrons leads to the disappearance of the remanent polarization.

FUNDING

This work was supported by the Russian foundation for Basic Research, the Government of the Krasnoyarsk

region, and Krasnoyarsk Regional Foundation for Science in the framework of the scientific project no. 18-42-240001 "Inversion of the sign of components of the magnetoelectric tensor in temperature in neodymium-substituted bismuth ferrite–garnet films," grant MK 591.2019.2, and state task no. 3.5743.2017/6.7.

CONFLICT OF INTEREST

The authors declare that they do not have conflicts of interest.

REFERENCES

1. W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London, U.K.) **442**, 759 (2006).
2. R. J. Zeches, M. D. Rossell, J. X. Zhang, A. J. Hatt, Q. He, and C. H. Yang, Science (Washington, DC, U.S.) **326**, 977 (2009).
3. A. N. Spaldin and S.-W. Cheong, Phys. Today **63**, 38 (2010).
4. A. P. Pyatakov and A. K. Zvezdin, Phys. Usp. **55**, 557 (2012).
5. J. C. Yang, Q. He, S. J. Suresha, C. Y. Kuo, C. Y. Peng, R. C. Haislmaier, and M. A. Motyka, Phys. Rev. Lett. **109**, 247606 (2012).
6. A. K. Zvezdin and A. P. Pyatakov, Phys. Usp. **52**, 845 (2009).
7. T. Kambe, Y. Fukada, J. Kano, T. Nagata, H. Okazaki, T. Yokoya, S. Wakimoto, K. Kakurai, and N. Ikeda, Phys. Rev. Lett. **110**, 117602 (2013).
8. J. C. Maxwell, *Treatise on Electricity and Magnetism*, 3rd ed. (Dover, New York, 1991).
9. G. Catalan, Appl. Phys. Lett. **88**, 102902 (2006).
10. M. Prasad, A. K. Pandit, T. H. Ansari, and R. A. Singh, Mater. Chem. Phys. **30**, 13 (1991).
11. M. M. R. Costa, M. J. M. de Almeida, W. J. Nuttall, W. G. Stirling, C. C. Tang, J. B. Forsyth, and M. J. Cooper, J. Phys.: Condens. Matter **8**, 2425 (1996).
12. S. Aplesnin, A. Galyas, O. Demidenko, G. Makovetskii, A. Panasevich, and K. Yanushkevich, Acta Phys. Polon. A **127**, 371 (2015).
13. O. B. Romanova, S. S. Aplesnin, A. M. Khar'kov, A. N. Masyugin, and K. I. Yanushkevich, Phys. Solid State **59**, 1314 (2017).
14. B. E. Vugmeister and M. D. Glinchuk, Sov. Phys. Usp. **28**, 589 (1985).
15. D. B. Ghosh, M. De, and S. K. De, J. Phys.: Condens. Matter **15**, 7095 (2003).
16. A. Milutinovic, Z. V. Popovic, N. Tomic, and S. Devic, Mater. Sci. Forum **229**, 453 (2004).

Translated by Yu. Ryzhkov