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Elastic magnetoresistive materials based on polyethylene

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Composite materials can often exhibit properties that are not typical for their individual components. New properties of such materials are of both physical and practical interest. In this article, the improper magnetoresistive and piezoresistive properties of new composite materials of the composition polyethylene/graphite/manganite $La_{0.7}Sr_{0.3}MnO_3$ have been experimentally studied. The components of these materials are low density polyethylene, natural large-size graphite crystal, and manganite $La_{0.7}Sr_{0.3}MnO_3$. The samples were examined by X-ray diffraction and electron microscopy. We also determined the magnitude of the magnetoresistive effect of the synthesized samples in a magnetic field up to 15 kOe in the geometry of the current along the field and perpendicular to the magnetic field strength. Investigations of extrinsic piezoresistive properties were carried out under the influence of uniaxial pressure up to 275 kPa, applied parallel to the direction of the current, in the region of elastic deformation. X-ray structural analysis showed an increase in the degree of crystallinity of the polyethylene matrix from 55% before synthesis to 90% after synthesis. Depending on the ratio of the components, these composites exhibit either positive or negative magnetoresistive effect. Thus, in the composite 15% polyethylene/55% graphite/30% $La_{0.7}Sr_{0.3}MnO_3$, the most significant positive magnetoresistive response of about 7.5% due to the diamagnetism of graphite, in a constant magnetic field H=15 kOe is achieved. The largest values of extrinsic negative piezoresistivity, reaching 45% at a uniaxial pressure of 275 kPa, are observed in the samples containing polyethylene and one of the conductive phases, namely graphite or manganite. Polyethylene/$La_{0.7}Sr_{0.3}MnO_3$ composites synthesized near the percolation threshold exhibit a small negative magnetoresistive effect (2%) in a field of 15 kOe, associated with spin-dependent electron tunneling of $La_{0.7}Sr_{0.3}MnO_3$.

Keywords: composite, polyethylene, piezoresistance, magnetoresistance.

УДК: 537.9

Эластичные магниторезистивные материалы на основе полиэтилена

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Композиционные материалы часто могут проявлять свойства, нетипичные для их отдельных компонентов. Новые свойства таких материалов представляют как физический, так и практический интерес. В данной статье экспериментально исследованы несобственные магниторезистивные и пьезорезистивные свойства новых композиционных материалов состава полиэтилен/графит/манганит $La_{0.7}Sr_{0.3}MnO_3$. Компонентами этих материалов являются: полиэтилен низкой плотности, природный крупнокристаллический графит и манганит $La_{0.7}Sr_{0.3}MnO_3$. Образцы исследовали методами рентгеновской дифракции и электронной микроскопии. Также были определены величины магниторезистивного эффекта синтезированных образцов в магнитном поле до 15 кЭ в геометрии ток вдоль поля и перпендикулярно напряженности магнитного поля. Проведены исследования несобственных пьезорезистивных свойств при воздействии одноосного давления до 275 кПа, приложенного параллельно направлению тока, в области упругой деформации. Рентгеноструктурный анализ показал увеличение степени кристалличности полиэтиленовой матрицы с 55% перед синтезом до 90% после синтеза. В зависимости от соотношения компонентов эти композиты проявляют либо положительную, либо отрицательную магниторезистивность. Так, в композите 15% полиэтилена/55% графита/30% $La_{0.7}Sr_{0.3}MnO_3$ достигается наиболее значительный положительный магниторезистивный отклик порядка 7.5% из-за диамагнетизма графита в постоянном магнитном поле H=15 кЭ. Наибольшие значения несобственной отрицательной пьезорезистивности, достигающие 45% при одноосном давлении 275 кПа, наблюдаются у образцов, содержащих полиэтилен и одну из проводящих фаз, а именно графит или манганит. Композиты полиэтилен/$La_{0.7}Sr_{0.3}MnO_3$, синтезированные вблизи порога перколяции, демонстрируют небольшую отрицательную магниторезистивность (2%) в поле 15 кОе, связанную со спин-зависимым туннелированием электронов $La_{0.7}Sr_{0.3}MnO_3$.

Ключевые слова: композит, полиэтилен, пьезорезистивность, магниторезистивность.

1. Introduction

Manufacturing of novel functional composites with a few responsesin external fields is of interest from physical and application points of view. It is known [1–8] that such composites can often exhibit properties that are not typical for their individual components. In [1,2], polyethylene/graphite composites with extrinsic piezoresistivity were synthesized. In these composites, the elastic properties and conductivity of the components, graphite (C) and polymer, differ [9,10] to a large extent. Researchers actively synthesize so-called magnetic elastomers, i.e., organic materials filled with magnetic particles, and these composites are sensitive to a magnetic field [3]. Such composites exhibit magnetoresistive properties due to the ordering of dispersed ferromagnetic particles in a magnetic field [3]. In [4,5], due to the presence of elastic organic additives in the composites, the desired property is enhanced — this is sensitivity to external pressure and fields. In [6], composites consisting of low-density polyethylene (LDPE) and manganite $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) are synthesized near the percolation threshold and exhibit both extrinsic piezoresistivity (ca. 17% at a pressure of 270 kPa) and negative magnetoresistivity of the tunnel type of ca. 2–3% in an external constant magnetic field H=15 kOe. In the LDPE/LSMO composite, the ferromagnet $La_{0.7}Sr_{0.3}MnO_3$ is used, and this component exhibits a high spin polarization of electrons, but at a ferromagnet — paramagnet phase transition at the temperature $T \approx 363$ K [7]. It is important to note that the sign of the two aforementioned effects is negative: when a magnetic field or pressure is acting, the electrical resistance of the composite decreases. It should be added that the LSMO/C samples described in [8] have a considerable positive magnetoresistive effect (up to 15%) in the external constant magnetic field $H \approx 15$ kOe. However, such composites do not exhibit remarkable elastic properties thereto.

The purpose of this work was to experimentally study the magnetoresistive and piezoresistive properties of polyethylene/manganite LSMO composites. In this regard, one of the tasks of this work was the synthesis of composites with both types of magnetoresistive effect (positive or negative) depending on the proportion of components: LDPE, C, and LSMO. The second task of the present work was the synthesis of composites that combine improper negative piezoresistivity and positive magnetorestivity, at specific fractions of two or three of aforementioned components, and the study on the physical properties of these composites.

2. Results and discussion

For this, a number of polyethylene-graphite-manganite composite samples have been synthesized using the technology described in our work [6]. In this case, the polyethylene content remained at the level of 15 mass %, near the percolation threshold [6]. Hereby, the fraction ratio of the conducting phases (C+LSMO) undergoes changes.

Table 1 shows the composition of the synthesized samples and their corresponding numbers in our work.

In Fig. 1 we show the microstructure of one of the 15% LDPE/55% C/30% LSMO composite samples. The present microstructure contains amorphous polyethylene agglomerates (marked by arrows in places) and graphite particles and LSMO particles (3–5 μm). The average size of graphite particles is 30–40 μm, and these particles (LSMO and C) are observed as dark areas along with bright areas (LDPE).

A fragment of the X-ray diffraction pattern of the 15% LDPE/55% C/30% LSMO sample is shown in Fig. 2, and our results on the X-ray structural study on the synthesized samples are shown in Table S1 (Supplementary material).

The accuracy of measurement of the cell parameters was ±0.0005 Å. Dimensions of coherent scattering regions (D) are estimated according to the Scherrer's formula [11]:

$$D = \lambda / \beta \cos\theta, \qquad (1)$$

where λ is the wavelength of incident radiation, β — half width at height of reflection X-ray diffraction, θ is the diffraction angle, in our case using the Bregg-Brentano

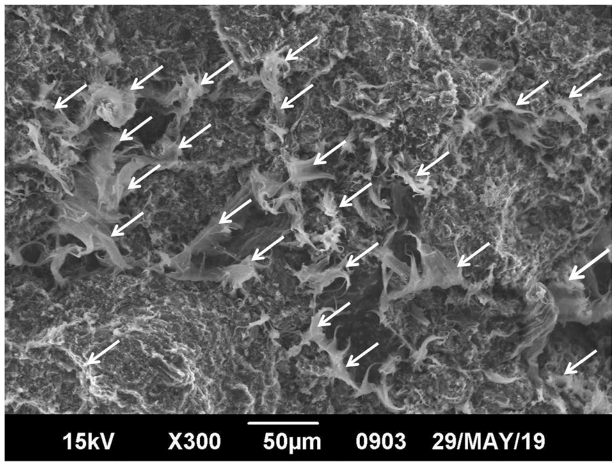

Fig. 1. Microstructure of a 15% LDPE/55% C/30% LSMO sample.

Table 1. Composition and numbers of samples.

Sample number	Sample composition	Mass fraction of LDPE, %	Mass fraction of C, %	Mass fraction of LSMO, %
1	15% LDPE/85% C	15	85	0
2	15% LDPE/80% C/5% LSMO	15	80	5
3	15% LDPE/78% C/7% LSMO	15	78	7
4	15% LDPE/75% C/10% LSMO	15	75	10
5	15% LDPE/70% C/15% LSMO	15	70	15
6	15% LDPE/65% C/20% LSMO	15	65	20
7	15% LDPE/60% C/25% LSMO	15	60	25
8	15% LDPE/55% C/30% LSMO	15	55	30
9	15% LDPE/45% C/40% LSMO	15	45	40
10	15% LDPE/35% C/50% LSMO	15	35	50
11	15% LDPE/25% C/60% LSMO	15	25	60
12	15% LDPE/15% C/70% LSMO	15	15	70
13	15% LDPE/5% C/80% LSMO	15	5	80
14	15% LDPE/2% C/83% LSMO	15	2	83
15	15% LDPE/85% LSMO	15	0	85
16	LSMO	0	0	100

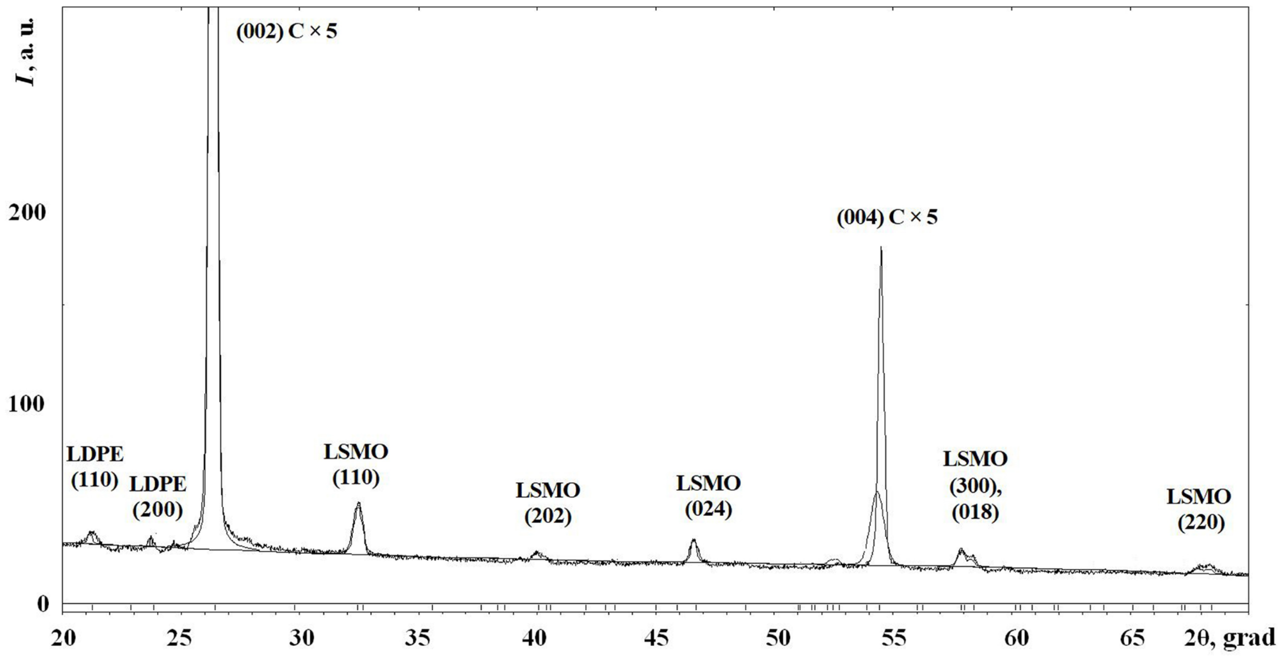

Fig. 2. Fragment of the X-ray diffraction pattern of a 15% LDPE/55% C/30% LSMO sample.

method, θ corresponds to the angle of rotation of the sample, or half of the angle of rotation of the counter. The method of Hermans-Weidinger [12] is used to estimate degree of crystallinity of polyethylene. Manganite and graphite are in the polycrystalline phase and therefore, for them, the degree of crystallinity can be taken as 100%.

The X-ray diffraction data of the prepared composite samples indicate the existence of a graphite texture in them, the flat particles of which are located mainly along the surface of the samples. This fact is consistent with the data of the work [9] wherein the authors synthesized polypropylene/graphite composites. In our experiments, after the synthesis of samples at $T = 433$ K, recrystallization of polyethylene was revealed. In this case, the values of the coherent scattering regions (D) of polyethylene increase, and crystallization effect of polyethylene increases.

Our measurements of the electrical resistance of the obtained composite samples under an uniaxial mechanical pressure are carried out by the two-electrode method at a constant current on a calibrated setup with an accuracy of 0.5 kPa. The measurement geometry means that the current flows along the pressure direction. For one of the 85% C/15% LDPE samples, the measurement results are shown in Fig. 3. Electrical resistance to pressure dependencies for other compositions are given in Fig. S1 (Supplementary material).

Piezoresistivity PR of the sample is calculated by the following formula:

$$\mathrm{PR} = \{(R(0) - R(P)) / R(0)\} \cdot 100\%, \qquad (2)$$

where $R(0)$ is the electrical resistance of the sample to direct current in the absence of external pressure (in addition

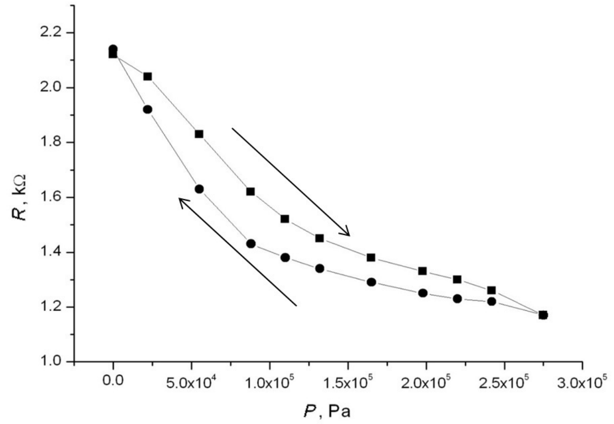

Fig. 3. Pressure dependence of the electrical resistance of the 85% C/15% LDPE sample, PR ≈ 45%.

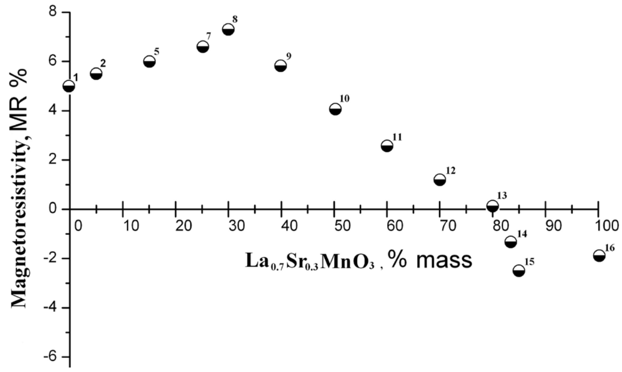

Fig. 4. Extrinsic magnetoresistivity depending on the fraction of components in 15% LDPE/*X*% C/*Y*% LSMO at $H = 15$ kOe.

to atmospheric), $R(P)$ is the resistance when the uniaxial pressure P is applied.

A slight hysteresis is observed in the $R(P)$ dependences (see Fig. 3), despite the fact [2] that the resistance measurements were performed one minute after each pressure change on the sample. After the termination of the pressure action, the sample returned to its original state.

Magnetoresistivity MR of the sample is calculated using the formula

$$\mathrm{MR} = \{(R(H) - R(0)) / R(0)\} \cdot 100\%, \tag{3}$$

where $R(0)$ is the resistance of the sample at $H = 0$, $R(H)$ is the resistance of this sample in the external magnetic field H.

The most interesting dependence of the magnitudes and sign of MR from Eq. 3 at $H = 15$ kOe on the fraction of LSMO is shown in Fig. 4.

At the same time, for all samples, except for pure ceramic LSMO, which is specially noted in Fig. 4, the mass fraction of LDPE was 15%. The ratio of the content of C and manganite changed. The highest values of MR with the positive sign are observed in the 15% LDPE/55% C/30% LSMO samples, and this is accounted for by the influence of diamagnetism of large-size graphite particles in these samples. According to the results in [7,8], diamagnetism of graphite plays an important role in the scattering of spin-polarized electrons in a magnetic field with significant crystallite sizes (1–50 μm), and with a large number of graphite-manganite contacts. In LSMO manganite crystals at room temperature, there is a high spin polarization of electrons, that is, those charge carriers that have the direction of the spin along the field, "up", prevail [7]. Other directions of the carrier spin are suppressed. Therefore, LSMO/C contacts, which are abundant at certain ratios of components (polyethylene, manganite, and graphite) apparently near concentrations of 15% LDPE/55% C/30% LSMO play the role of a spin filter [8]. In this case, the local diamagnetic fields of graphite atoms, which are directed against the external magnetic field, scatter polarized electrons with spin "up", emerging from the ferromagnetic LSMO particles, which leads to a spin flip. Further transport of charge carriers (through LSMO crystallites) is largely suppressed. A similar effect is observed in the $Fe_3O_4/SrTiO_3$/LSMO heterostructure [13].

Composite samples with a graphite content of less than 5% had a negative sign of MR, as follows from our studies. Fig. 4 shows some compositions with negative tunnel-type MR: e.g. the 15% LDPE/85% LSMO composite exhibits MR = 2.5%, and pure LSMO manganite is characterized by MR ≈ 2%. Additionally, magnetoresistivity of a number of samples is given in Fig. S2 (Supplementary material).

A significant anisotropy of the magnetoresistivity of the synthesized composites is also emphasized. Values of the sample resistances measured in the magnetic field H perpendicular to the current and in the H field oriented parallel to the current direction differ significantly. For instance, this difference for the 15% LDPE/55% C/30% LSMO composite reaches 60%. This fact is associated with the above-noted texture of graphite particles, and such a texture was also observed in work [9].

The manifestation of extrinsic piezoresistivity in the studied three-component composites with different fractions of components is illustrated by Fig. 5. We note that samples with a high content of one of the conductive components are characterized by significant PR from Eq. 2.

As can be seen (Fig. 5), the piezoresistive response in composites is minimal for samples with practically equal fractions of different-sized particles of C and LSMO of different densities.

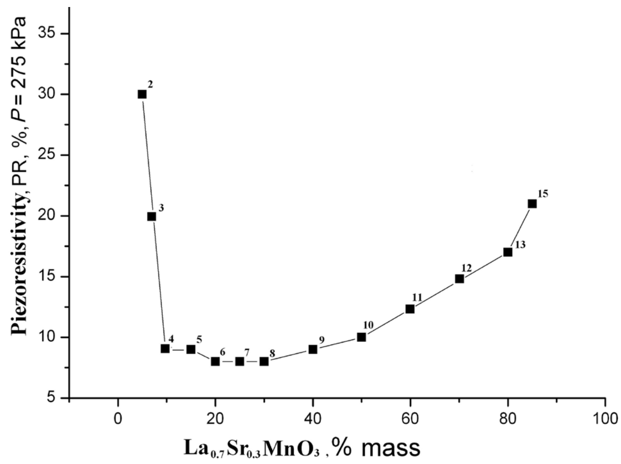

Fig. 5. Extrinsic piezoresistivity depending on the fraction of components in 15% LDPE/*X*% C/*Y*% LSMO composites at pressure of 275 kPa and at $X \div 0\ldots80\%$ and $Y \div 0\ldots85\%$. 15% LDPE/85% C not shown in figure, PR = 45%.

3. Conclusions

Thus, in the present study, we have synthesized and investigated novel functional composites of the polyethylene-graphite-manganite composition, which change their electrical resistance when exposed to both uniaxial pressure and magnetic fields.

The study of the behavior of the spin-dependent current of charge carriers in these composites in a constant magnetic field H=15 kOe, depending on the mass fractions of three components near the percolation threshold, have shown that the 15% LDPE/55% C/30% LSMO composite exhibits the highest positive magnetoresistive response by 7.5%. Samples with a graphite content near 5% mass fraction have magnetoresistivity values close to zero. This is due to the compensation of the tunnel effect and diamagnetic scattering of charge carriers in a magnetic field.

Samples with a C content of less than 5 mass % are characterized by negative MR due to spin-dependent tunneling of LSMO electrons through the finest layers of the insulator. The maximum value of negative isotropic tunneling MR (about 2%) in a magnetic field H=15 kOe is related to the 15% LDPE/85% LSMO sample. The 15% LDPE/85% C, 15% LDPE/80% C/5% LSMO and 15% LDPE/85% LSMO samples exhibit extrinsic piezoresistivity, and its value is, respectively, ca. 45%, 30% and 22% at a pressure of 275 kPa. It should be noted that the composites of the polyethylene/graphite/manganite composition studied in this work are mechanically more stable, in contrast to the pressed graphite-manganite composites [8].

Due to the unique combination of the studied characteristics, novel composites manufactured by us can be successfully applied as multifunctional sensors to be exploited in external magnetic and pressure fields.

Supplementary material. *The online version of this paper contains supplementary material available free of charge at the journal's Web site (lettersonmaterials.com).*

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