

STRUCTURAL PECULIARITIES AND DIELECTRIC PROPERTIES OF HIGH-DENSITY POLYETHYLENE FILMS CONTAINING InP AND Ge PARTICLES

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High density polyethylene (HDPE) films of various thickness (100,200 μm) and content (2-10 vol.%) of InP/Ge particles were obtained by hot pressing a homogeneous mixture of fillers with a polymer matrix under a pressure of 10 MPa and at a temperature $T=413\text{K}$. HDPE films with dispersed InP and Ge particles were characterized by a combination of X-ray fluorescence microscopy (XRFM), X-ray diffractometry (XRD) and infrared Fourier transform spectroscopy (FT-IR) methods. It is shown that the obtained samples are HDPE-based composites with nanostructured InP and Ge-particles with a size of coherent scattering regions (CSR) of 44.1 and 55.7 nm, respectively. By scanning the surface of the films with a spot of a beam with a diameter of 10 μm , local concentrations of InP and Ge particles in the samples were determined. The dependence of the characteristic frequencies of FT-IR for HDPE at 719 and 730 cm^{-1} on the concentration of the filler was established. The temperature (in the range of 290–440K) and frequency (range 25– 10^6 Hz) dependences of the dielectric constant and the angle of the tangent of dielectric losses were measured. The dependence of the values of dielectric characteristics on the content of the filler in the composite is established.

Keywords: InP, Ge, HDPE, X-ray fluorescence microscopy, X-ray diffractometry, infrared Fourier spectroscopy, dielectric properties.

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1. INTRODUCTION

Development of methods for synthesizing polymer composites containing nanostructured semiconductor particles, both simple (Si,Ge,etc.) and complex ($\text{A}_3\text{B}_5, \text{A}_2\text{B}_6$, etc.), determining their structure, optical, magnetic, dielectric, thermal properties is of fundamental and practical interest. These materials are used as LEDs, lasers, photovoltaic cells, gas sensors, etc. They have unique electrical, optical, magnetic properties, which, however, strongly depend on the composition and technology of these materials [1,2].

There is a huge amount of semiconductor compounds, and in practice we can always find semiconductors with well applicable properties. The most investigated binary semiconductors. As a rule, they are classified according to the crystal-chemical principle or according to the structure, the arrangement of the initial elements in the periodic system, the name of the anion-forming agent. For example, compounds like A_3B_5 , such as nitrides, phosphides, arsenide, antimonides, are compounds of elements of the V-group (N,P,Sb) with metals (Al,Ga,In,Tl) of group I and compounds A_2B such as chalcogenides, sulfides, selenides, tellurides-compounds of group VI elements (S,Se,Te) with metals (Zn,Cd,Hg). These compounds are isoelectronic analogs of diamond, silicon, germanium (the total number of valence electrons in these compounds is 8, the coordination number is 4) and have the same properties as these simple semiconductors [3,4].

This paper presents the results of studying the structural features and dielectric properties of thin HDPE films with different contents (2-10 vol. %) Of InP and Ge particles using X-ray fluorescence microscopy, X-ray diffractometry and IR spectroscopy,

and measuring the dielectric characteristics of these composite materials.

2. MATERIALS AND METHODS

Mechanical mixtures of InP/Ge powders and HDPE powders were hot pressed under a pressure of 10 MPa at $T = 413\text{K}$ for a period of 15 minutes and rapidly cooled to room temperature. Films with different content of InP/Ge particles and thicknesses of 100 and 200 microns were prepared by this method. XGT 7000 X-ray fluorescence microscope, Horiba and XRD D8 X-ray diffractometers, Bruker, Germany, XRD TD 3500, China were used to study the distribution of InP and Ge particles in polymer composites and the phase composition of the composites, respectively. The microscope used allows analyzing the elemental composition of solid samples by scanning the surface from 0.512x0.512 mm to 10 cm x 10 cm with a resolution of 100 μm and 10 μm . The performed x-ray microanalysis was used for the local concentration of InP and Ge particles in samples of the composite material, to investigate the influence of the preparation conditions on their distribution in the samples [5,6]. FT-IR infrared spectrometer Varian 3600 was used to monitor the effect of the filler on the structure of polymer films. FT-IR spectra were recorded at room temperature in the frequency range of 4000–400 cm^{-1} . Measurements of the dielectric constant $-\epsilon$ and the tangent of the angle of dielectric loss $-\text{tg}\delta$ were carried out in the temperature range of 290-520K with a linear temperature rise at a speed of 2.5 deg/min. The frequency dependence of the dielectric constant $-\epsilon$ and dielectric loss tangent $-\text{tg}\delta$ was carried out in the frequency range from 102 to 105 Hz, the amplitude of the measured voltage -1V. Measurements of ϵ and $\text{tg}\delta$

were carried out using an E8-7 bridge with an alternating current at a frequency of 1 kHz and an E7-20 meter. Samples for measuring the dependence of dielectric characteristics in an exemplary electric field were prepared in the form of disks with a diameter of 20 mm and a thickness of about 100 microns. Reliable electrical contact of stainless steel electrodes with a diameter of 20 mm was ensured by

using extruded electrodes of aluminum foil with a thickness of 9 μm [7, 8].

3. RESULTS AND DISCUSSION

XRFM data. Fig. 1 and Table 1 present the X-ray fluorescence spectrum and data for the InP-Ge/HDPE composite film, respectively.

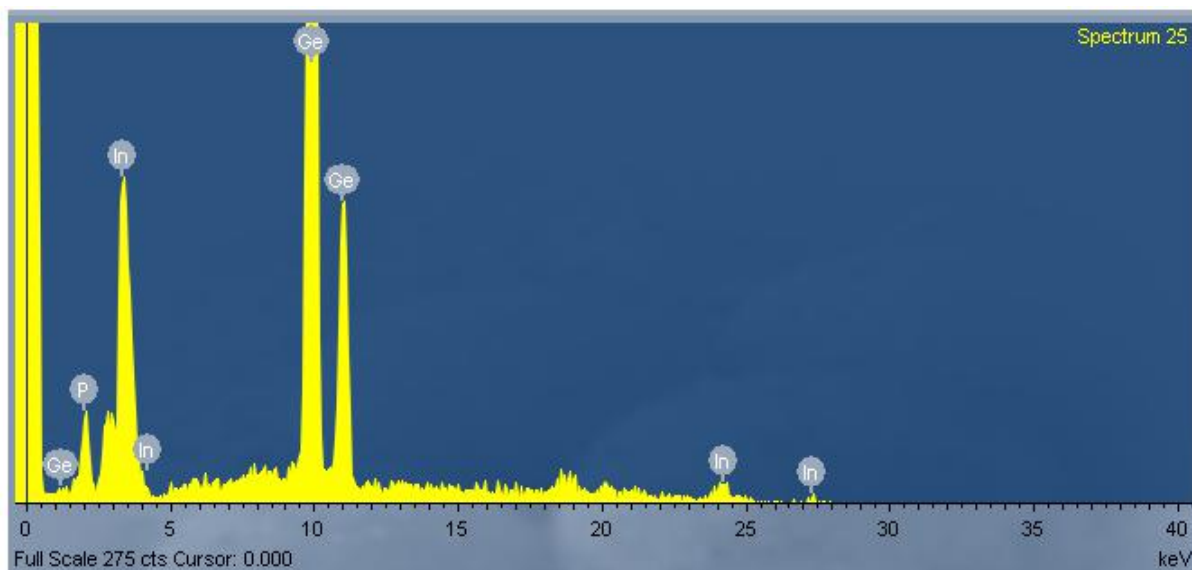


Fig. 1. X - ray fluorescence spectrum of the InP-Ge/HDPE composite film with a thickness of 100 microns.

Table 1.

The content of elements in the Ge-InP/HDPE film in five points randomly selected on the film surface according to X-ray fluorescence microscopy.

* Element	Line	Mas., [%]	3 - Sigma	* Element	Line	Mas., [%]	3 - Sigma
GeInP (1-5)				GeInP (3)			
¹⁵ P	K	4,51	0,79	¹⁵ P	K	5,13	0,81
³² Ge	K	49,45	1,87	³² Ge	K	52,52	2,47
⁴⁹ In	L	16,74	2,04	⁴⁹ In	L	19,03	2,68
GeInP (1)				GeInP (4)			
¹⁵ P	K	4,97	2,41	¹⁵ P	K	3,77	0,67
³² Ge	K	49,15	3,15	³² Ge	K	44,41	1,43
⁴⁹ In	L	18,43	3,03	⁴⁹ In	L	13,99	1,54
GeInP (2)				GeInP (5)			
¹⁵ P	K	4,67	1,62	¹⁵ P	K	4,43	3,72
³² Ge	K	51,85	2,56	³² Ge	K	54,31	4,37
⁴⁹ In	L	17,34	1,33	⁴⁹ In	L	16,44	2,98

* The results shown in the table refer to a sample whose surface is scanned with a spot of a beam with a diameter of 10 microns.

As can be seen from table 1, the values of local concentrations of InP and Ge particles in arbitrarily selected parts of a HDPE film are close and it can be stated that the particles are almost uniform in the HDPE film.

4. X - RAY PHASE ANALYSIS

In fig. 2, a, b shows radiographs of an InP/Ge mixture with a molar ratio of ~1:1 and a composite with a composition of 9% (InP+Ge)/91% HDPE, which is a

composite based on polyethylene HDPE, containing a total of 9% by volume of particles InP and Ge, respectively.

As can be seen from the diffractogram (fig. 2, b), the composite under study consists of well-crystallized HDPE with a very small amount of amorphous phase. Characteristic of HDPE according to JCPDS 00-040-1995 appear at 21.56°, 23.87°, 30.18° and 36.29°, which corresponds to the (110), (200), (210) and (020), respectively [7, 8]. Peaks of fillers embedded in HDPE

(fig. 2, b) refer to Ge and InP with a cubic structure. The average size of coherent scattering regions (44.1 and 55.74 nm) of indium and germanium phosphide particles was estimated.

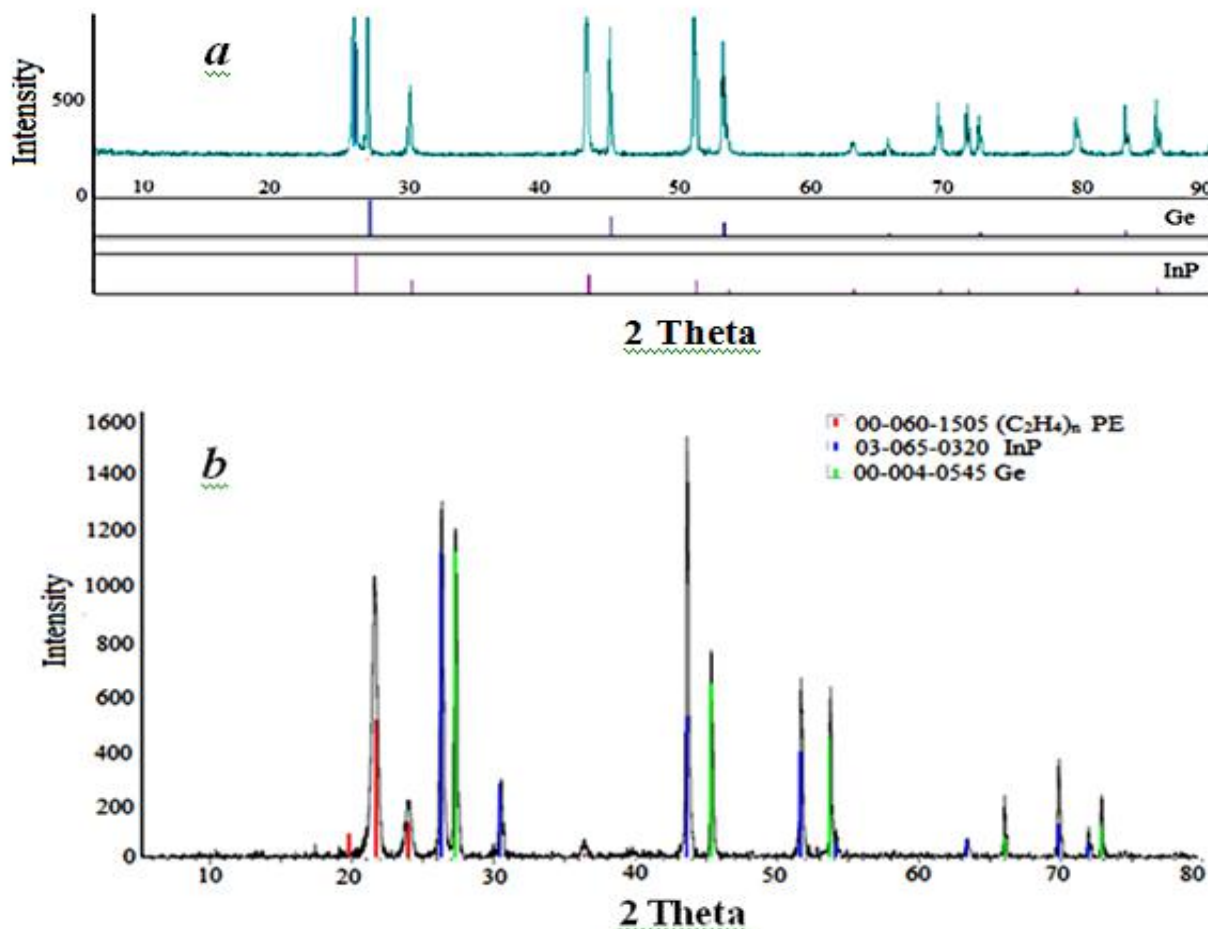


Fig. 2. XRD patterns of the: a) InP / Ge mixture with mol to mol ratio ~1:1 and b) 9% (InP+Ge)/91% HDPE mixture.

As can be seen from the diffractogram (fig. 2, b), the composite under study consists of well-crystallized HDPE with a very small amount of amorphous phase. Characteristic of HDPE according to JCPDS 00-040-1995 appear at 21.56 °, 23.87 °, 30.18 ° and 36.29 °, which corresponds to the (110), (200), (210) and (020), respectively [7, 8]. Peaks of fillers embedded in HDPE

(fig. 2, b) refer to Ge and InP with a cubic structure. The average size of coherent scattering regions (44.1 and 55.74 nm) of indium and germanium phosphide particles was estimated.

Table 2 shows the XRD parameters and crystallite size values determined on the basis of the values of these parameters.

Table 2.

XRD parameters and crystallite size values for InP, Ge and HDPE*.

	InP	Ge	HDPE
* FWHM, rad.	0,184	0,146	0,48
Lattice parameters, nm	Cubic: F-43m (216) a: 0.58687	Cubic: Fd-3m (227) a: 0.56576	Orthorhombic: Pnam (62) a: 0.74188; b: 0.49382; c: 0.25496
Crystallite Size D, nm	44.1	55.74	16.95

* Full width at half peak height.

** The calculation of the interplanar distances d was determined by the Wolf-Bragg equation: $2 \sin \theta = (\lambda / d)$; The average crystallite size, i.e. the areas of coherent scattering (OCD) was calculated using the Scherrer formula: $D = (\xi \lambda / \beta \cos \theta)$, where θ is the reflection angles in degrees; D is the average crystallite size, nm; ξ is a factor taking into account the shape of the particles and the indices of the reflecting plane, since the range of changes from 0.98 to 1.39 in practice is $\xi = 1$; β is the integral width; λ is the Cu - K α radiation wavelength ($\lambda = 0.15418$ nm).

Thus, based on the analysis of the obtained X-ray diffraction patterns, we can conclude that: a) the raw powder under investigation consists of a mechanical mixture of indium and germanium phosphide, b) the resulting composite consists of a well-crystallized polyethylene matrix containing the phases of indium

and germanium phosphide, spatially separated from each other in a polymeric matrix.

FT-IR data. Below are the FT-IR spectra of pure HDPE and HDPE, containing various concentrations of InP/Ge particles with a thickness of 100 and 200 microns.

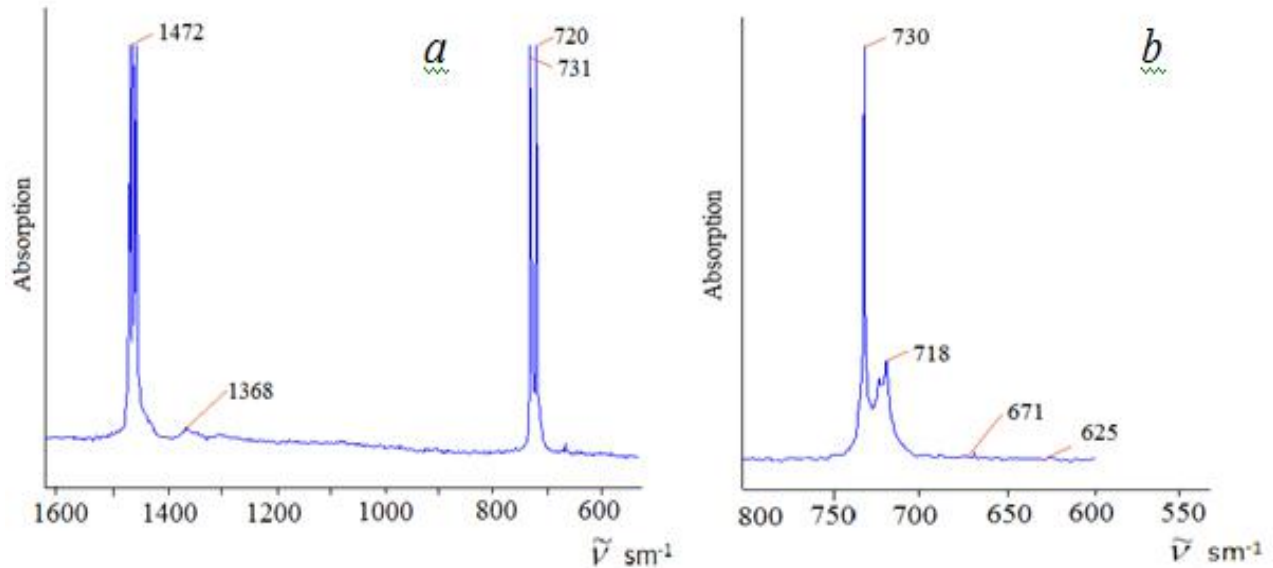


Fig. 3. FT-IR spectra of the: a) HDPE with 6 vol. % InP/Ge (100 μm) b) HDPE with 6 vol. % InP/Ge (200 μm).

From fig. 3 it can be seen that all the characteristic bands necessary for identifying the structure of the polymer, namely, doublets $720\text{--}730\text{ cm}^{-1}$ and $1462\text{--}1473\text{ cm}^{-1}$ for PE, are clearly visible on these spectra. The first (doublet $720\text{--}730\text{ cm}^{-1}$) are due to the pendulum oscillations of methylene groups in the crystalline parts of polyethylene with molecules in a flat trans-conformation and are sensitive to the intermolecular interaction and conformational state of macromolecules [14]. Changes in the characteristic frequencies of polyethylene, depending on the concentration of the filler, can be clearly traced by the spectra of FT-IR HDPE films with containing 6 % (100 μm and 200 μm) by volume of fillers, respectively in the regions: a) $1460\text{--}1480$ and b) $700\text{--}750\text{ cm}^{-1}$. The doublet observed in the IR spectrum is due to the splitting of the 1460 cm^{-1} band. The 1472 cm^{-1} band characterizes the crystalline region in HDPE samples, and the 1462 cm^{-1} band is characteristic of the amorphous component of HDPE. As can be seen, the introduction of InP/Ge microparticles into the polymer leads to a redistribution of the intensities of doublet bands.

5. DIELECTRIC PROPERTIES

The results of the study of the temperature-frequency dependence of the dielectric constant and dielectric loss of the compositions of HDPE + x vol. % InP/Ge ($0 \leq x \leq 9$) are shown in figures 4 and 5.

As follows from fig. 4a for all the above composites in the temperature range studied, the dielectric constant decreases linearly with increasing temperature. With an increase in the volume content of the InP filler, an increase in the dielectric constant occurs, in particular, for pure high-density polyethylene ϵ at room temperature is 2.07 (curve 3), for a composite with the addition of 3 vol. % InP 1.86 (curve 1), for the composite, 5 vol. % InP 1.95 (curve 2), for the composite, 7 vol. % InP 2.4 (curve 4), and 9 vol. % InP, 3.48 (curve 5).

In fig. 5 shows the frequency dependences of the dielectric constant and dielectric loss of HDPE composites with different InP/Ge filler contents in the frequency range 25-106 Hz. As follows from fig. 5a in the studied frequency range for all composites and pure HDPE ϵ practically does not change with increasing frequency.

Thus, the above experimental results allow us to state the following.

1. When modifying the polymer matrix with nanostructured InP/Ge micro-size particles, there are noticeable changes in the structural and dielectric properties for samples containing up to 4% by volume of filler, most pronounced in the FTIR spectra.

2. The mechanism of interaction of the matrix with the solid phase of the modifier is not obvious, since polyethylene, which in this case serves as a matrix and is a product of ethylene polymerization, does not contain groups that are active in the reaction with the filler.

3. The dependence of the intensity of the bands in the FTIR spectra on the content of the filler introduced into the polymer can be used to study the nature of the mechanism of influence of fillers on the structure of HDPE.

4. To control the technology of obtaining composite HDPE samples with nanostructured InP/Ge particles, X-ray fluorescence microscopy and IR spectroscopy are most suitable. The above studies have

shown that the distribution of indium and germanium phosphide particles, as well as the intensity ratio of the characteristic HDPE bands in the IR spectra, depend on the concentration of fillers. These methods allow you to control the concentration of filler particles in the manufacture of a composite material of the desired composition by measuring X-ray fluorescence and IR spectra.

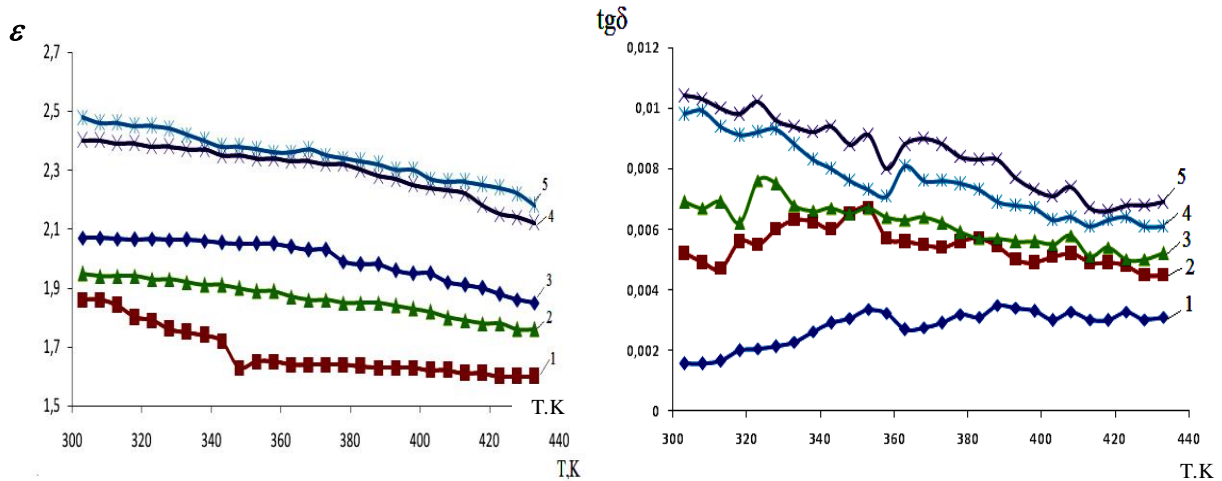


Fig. 4. Temperature dependences of the dielectric constant (a) of HDPE compositions with different filler contents of InP/Ge (in vol. %): 1-3; 2-5; thirty; 4-7; 5-9 and dielectric losses (b) of HDPE compositions with different filler contents of InP/Ge (in vol. %): 1-0; 2-3; 3-5; 4-9; 5-7 of the measurement temperature.

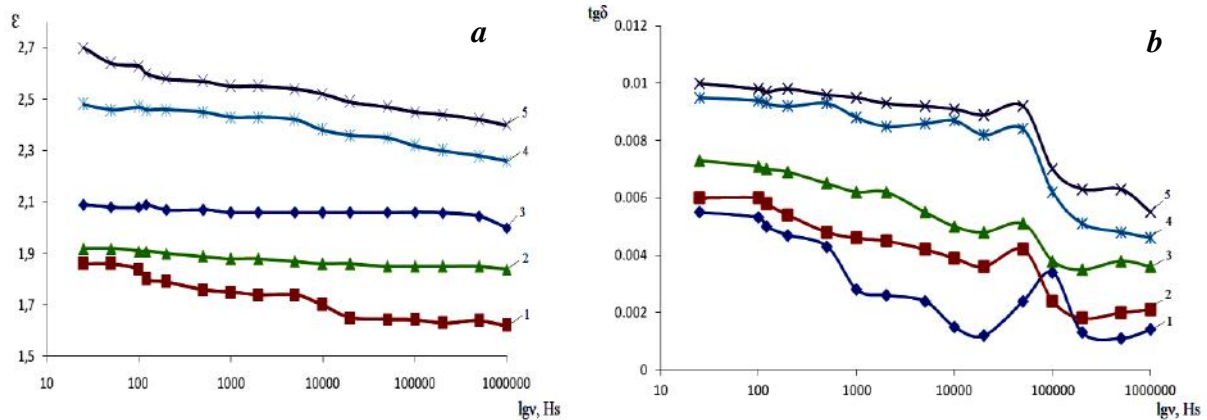


Fig. 5. Frequency dependences of the dielectric constant (a) of HDPE compositions with different content of InP/Ge filler (in vol. %): 1-3; 2-5; 3-0; 4-9; 5-7 and dielectric losses (b) of HDPE compositions with different filler contents of InP/Ge (in vol. %): 1-0; 2-3; 3-5; 4-9; 5-7 of the measurement temperature.

6. CONCLUSION

Structural features and dielectric properties of HDPE films of various thickness (100, 200 μm) modified by germanium and indium phosphide in a 1:1 ratio by weight and total content of 2-10% by volume were studied using a combination of X-ray fluorescence, X-ray diffraction and infrared spectroscopy. Changes in the structure and dielectric properties of the composite depending on the filler content are established. It is shown that the methods of X-ray fluorescence microscopy and IR spectroscopy are most suitable for optimizing the concentration of

the filler and controlling the distribution of its particles in the polymer.

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