DIELECTRIC AND CONDUCTIVITY PROPERTIES OF POLYETHYLENE DOPED WITH CaGa₂S₄:Eu⁺²

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The frequency and temperature dependences of dielectric permittivity and electric conductivity of high-density polyethylene with the addition of $CaGa_2S_4:Eu^{+2}$ are studied. It was shown that dielectric permitivity and electric conductance increase with increasing of filler concentration at all temperatures. In this case, conductivity has hopping mechanizm described by the Josher theory. The corresponding exponent parameter and activation energy slightly decreases with increasing of filler concentration. The experimental data of dielectric permitivity are compared with the Maxwell-Garnett theory.

Keywords: phosphor, high density polyethylene, dielectric permittivity; electric conductivity, composite material.
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INTRODUCTION

Production of high-performance devices for imaging and lighting, which are capable of competing with conventional systems, requires the obtaining of phosphors with specific properties. This necessity promoted the development of new materials and the optimization of existing phosphors. One of such promising materials is $CaGa_2S_4:Eu^{2+}$. Its monocrystal and polycrystal emits a broad yellow luminescence band is centered at 562 and 565 nm, respectively, under both 420 nm and 337.1 nm excitation wavelengths [1-2].

The spectroscopic properties of the phosphor $CaGa_2S_4:Eu^{2+}$ provide high performance. However, it is not only requirement for the respective devices. Active luminescent elements must be resistant to water, solar radiation and temperature. The phosphor cannot meet these requirements by itself. Its encapsulation is required. Typically, a polymer is used as the matrix. To predict the most optimal conditions for encapsulation, it is necessary to determine the interaction between the filler particles and the matrix. One of the methods is dielectric spectroscopy.

The aim of present work is the study of the effect of $CaGa_2S_4:Eu^{+2}$ on dielectric and conductivity properties of high density polyethylene.

EXPERIMENTAL

$CaGa_2S_4:Eu^{2+}$ (5 mol %) polycrystals were prepared from stoichiometric amounts of CaS and Ga_2S_3 powders. EuF_3 was used for the activation by europium. The synthesis of this material was done by a solid-state reaction in a graphite crucible covered with graphite powder at temperature of 1000°C and vacuum of 10^{-4} Torr for 4 hours. After the synthesis, a 4-hour annealing was carried out at 700°C in an argon atmosphere with hydrogen sulfide.

Powder was obtained by grinding in the planetary micro mill (the model Pulverisette 7, firm Fritsch, Germany).

The powder obtained was separated according to sedimentation time τ in a column with hexane according to the relation:

$$\tau = \frac{18h\eta}{(\rho_1 - \rho_2)gd^2}$$

(1)

where h is the height of the column; η is the viscosity coefficient of the liquid; ρ_1 and ρ_2 are the densities of this material and hexane; g is the acceleration of gravity; d is the transverse dimension of the particles. The fractions obtained were dried under a vacuum of 10^{-2} torr at $T = 50$°C for a week. This method produced a powder with an average particle size of 500 nm

We used high density polyethylene (HDPE) as a matrix. Melting and softening points of polymer are 130-135˚C and 80-90˚C, correspondingly. Then obtained mixture was shaken in a vortex mixer for 1 hour at room temperature, followed by sonication with dispergator Ultrasonic Cleaner NATO CD-4800 (China) for 4 hours. Disc-shaped samples of composites were obtained by hot pressing at temperature of 165˚C and pressure of 15 MPa. Pressing time after reaching the selected temperature is 15-20 minutes. The diameter and thickness of the obtained films were 4 cm and 80 - 90 μm, respectively. Aluminum electrodes with diameter of 3 cm and thickness of 10 μm are pressed on both sides of the films.

Dielectric measurements were carried out by the Precision LCR Meter 1920 (IET Labs. Inc., USA) over the frequency range of 20 Hz – 1 MHz and at temperatures between 18°C – 70°C. In such a case, applied voltage was 0.5 V. Electric capacity C and dissipation factor (the loss tangent) D were recorded by means of this device at different frequencies f. The magnitudes of dielectric permittivity ε were defined as:

$$\varepsilon = \frac{Cd}{\varepsilon_0 S}, \qquad (2)$$

where ε_0 is the permittivity of free space, d and S are the thickness and the square of the sample, respectively. The real ε' and image ε'' parts of dielectric permittivity and electric conductance σ were calculated by the expressions:

$$\varepsilon' = \frac{\varepsilon}{\sqrt{1+D^2}}, \qquad (3)$$

$$\varepsilon'' = \frac{\varepsilon D}{\sqrt{1+D^2}}, \qquad (4)$$

$$\sigma = 2\pi f \varepsilon_o \varepsilon'', \qquad (5)$$

RESULTS AND DISCUSSION

Figure 1 and figure 2 show the frequency dependences of the real and image parts of the dielectric permittivity for the composite with different concentrations of filler.
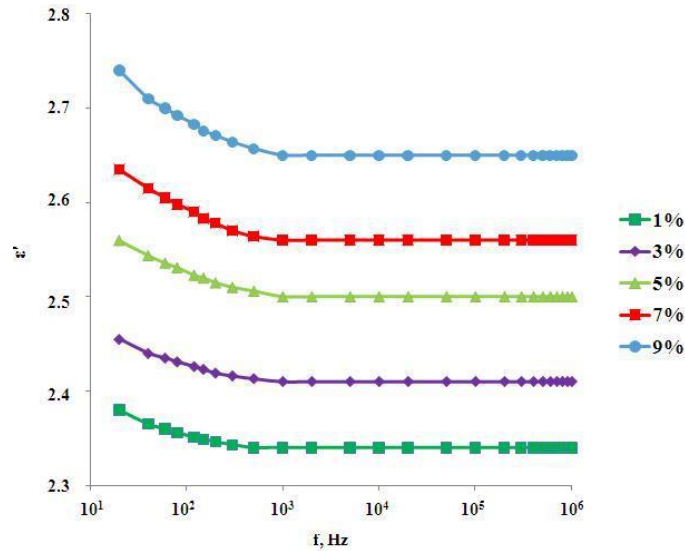

Fig. 1. Frequency dependences of real part of dielectric permittivity of the composite at different volume concentrations of filler and 20˚C.
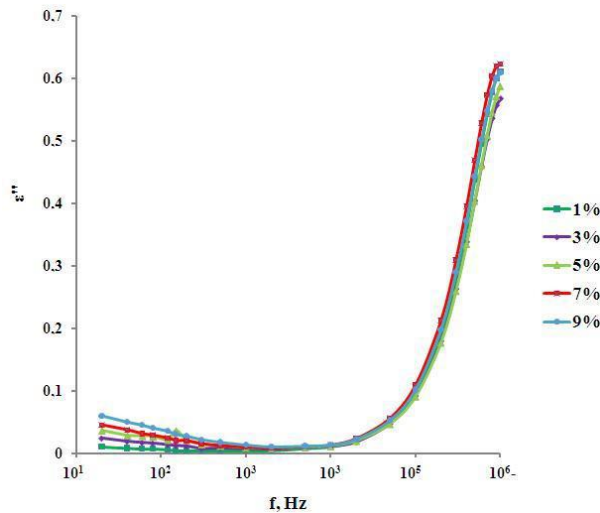

Fig. 2. Frequency dependences of image part of dielectric permittivity of the composite at different volume concentrations of filler and 20˚C.

As can be seen, with an increase in the filler concentration, both real and image parts of the dielectric permittivity increases at all frequencies. In this case, there is a slight decrease in the real ε' component of the permittivity with increasing frequency, which is explained by the delay of dipoles and a decrease in the number of particles involved in polarization. The presence of a significant electrical conductivity of composites at high filler concentrations also leads to the appearance of near-electrode polarization at low frequencies, which occurs in the layer adjacent to the electrode [3]. In this case, an increase in the permittivity at low frequencies is observed.

According to the Maxwell–Garnett theory [4], scalar dielectric permittivity ε_{eff} of a medium

consisted of particles with dielectric permittivity ε_p and the matrix with dielectric permittivity ε_m is

$$\varepsilon_{eff} = \frac{(1-f_v)\varepsilon_m + f_v\beta\varepsilon_p}{1-f_v+f_v\beta} \qquad (6)$$

where f_v is a volume fraction of the inclusions; β depends on the shape of the inclusions. In order to simplify the calculations, we will consider the particles to be spherical, then

$$\beta = \frac{3\varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \qquad (7)$$

and (6) reduces to

$$\varepsilon_{eff} = \varepsilon_m\left[1 + \frac{3f_v\left(\dfrac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m}\right)}{1-f_v\left(\dfrac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m}\right)}\right] \qquad (8)$$

Note that the Maxwell-Garnett approximation describes well isolated particles that are completely isolated from each other by the material of the medium.

In order to compare the experimental concentration dependences of the permittivity with the Maxwell-Garnett theory, we present them at the frequency of 1 kHz as well as theoretical curves on the same figure 3.
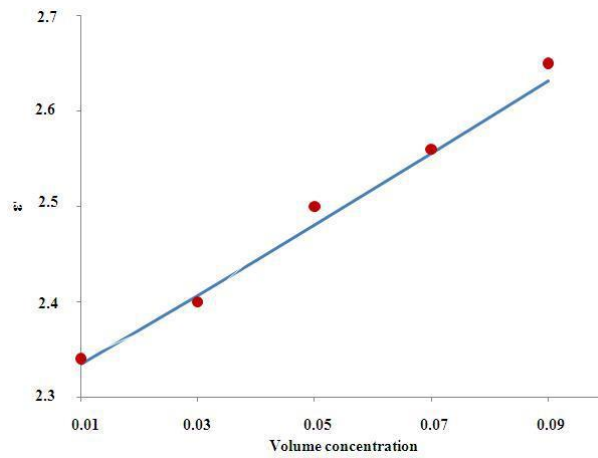

Fig. 3. Comparison of experimental data at frequency of 1 kHz with the Maxwell-Garnett theory: circles - experimental data, solid curve corresponds to the Maxwell-Garnett approximation.
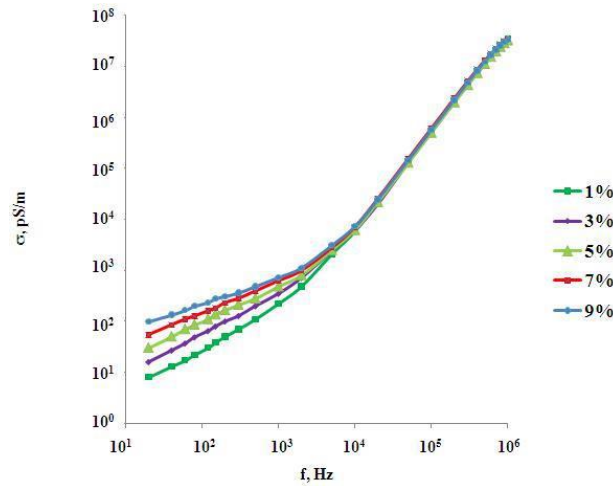

0Fig. 4. Frequency dependences of electric conductance of samples at 20˚C.

As can be seen, the experimental values are good agreed with theoretical curve. Frequency dependences of electric conductivity at different concentrations of filler are presented in figure 4. One can see from this figure, conductivity increases with increasing of frequency. In this case, conductivity is more for the composites with more concentration of filler.

The frequency dependence of the conductivity of composite materials has a hopping mechanism and can be described by the equation obtained in [5]

$$\sigma = \sigma_{dc} + Af^n, \qquad (9)$$

where σ_{dc} is the direct current conductivity, A is a

constant at given temperature, n is a parameter that varies from 0 to 1 and characterizes the degree of interaction of charge carriers with the matrix material. Conductivity occurs by hops between particles and along defects in the polymer matrix. Since the particles are randomly arranged, isolated conducting paths have a wide size distribution leading to conductance dispersion [6].

An analysis of the frequency dependences of the conductivity of composites showed that the coefficient n, which characterizes the degree of interaction of carriers with the matrix material, equals to 0.51 and does not change with an increase in the filler.

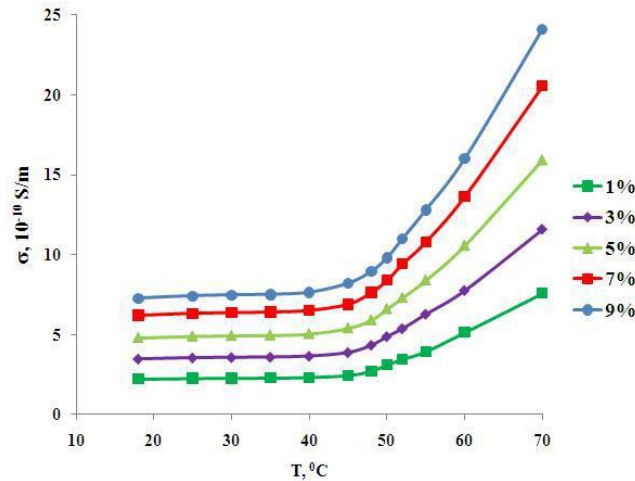Figure 5 shows the temperature dependences of conductivity for the composites.

Fig. 5. Temperature dependences of electric conductance of the composites at frequency of 1 kHz.

As can be seen, the conductivity increases with increasing temperature. Moreover, with an increase in the concentration of filler, the conductivity increases at all temperatures. At the same time, these dependencies obey the Arrhenius law:

$$\sigma = \sigma_0 e^{-\frac{E}{k_B N_A T}} , \qquad (10)$$

where σ_o is the pre-exponential factor, E is the activation energy of electrical conductivity. k_B is Boltzmann constant, N_A is the Avogadro number, T is Kelvin temperature.

From the last expression, it is possible to find the activation energy E of the composites. It equals to 121 kJ/ mol for the sample with 1% filler concentration and slightly decreases with increasing of concentration. The value of E consists of the activation energy of the motion of the carriers and the

energy necessary for the nucleation of new charges. It is an energy barrier which an ion must overcome to move inside the polymer medium. The larger the E, the harder the ions move within the composite and, accordingly, the lower the conductivity.

CONCLUSIONS

İt is shown that dielectric permittivity and electric conductivity of high-density polyethylene with the addition of $CaGa_2S_4:Eu^{+2}$ increase with increasing of filler concentration at all temperatures and frequences. In this case, conductivity has hopping mechanizm described by the Josher theory. The corresponding exponent parameter and activation energy slightly decreases with increasing of filler concentration. The experimental data of dielectric permitivity are compared with the Maxwell-Garnett theory.

[1] *C. Ronda, T. Justel, H. Nikol.* Rare earth phosphors: fundamentals and applications. J. of Alloys and Compounds. 1998, 669,275–277.

[2] *P. Benalloul, C. Barthou, C. Fouassier, A.N.Georgobiani, L.S. Lepnev, Yu.N. Emirov, A.N. Gruzintsev, B.G. Tagiev, O.B. Tagiev, R.B. Jabbarov.* Luminescence of Eu2¿ in Calcium Thiogallate. Journal of The Electrochemical Society, 2003,150, G62-G65.

[3] *H.Y. Chen, W. Lee.* Suppression of Field Screening in Nematic Liquid Crystals by Carbon

Nanotubes. Appl. Phys. Lett. 2006, 88, 222105-1-3.

[4] *C.F. Bohren, & D.R. Huffman.* 1983. Absorption and Scattering of Light by Small Particles, John wiley & Sons. New York 530 p.

[5] A.K. Josher. The 'Universal' Dielectric Response. Nature. 267 (1977) 673 – 679.

[6] Charge Transport in Disordered Solids with Applications in Electronics/ Ed. S. Baranovski. Chichester: John Wiley & Sons, 2006. 479 p.

DIELECTRIC AND CONDUCTIVITY PROPERTIES OF POLYETHYLENE DOPED WITH CaGa$_2$S$_4$:Eu^{+2}

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ДИЭЛЕКТРИЧЕСКИЕ И ПРОВОДЯЩИЕ СВОЙСТВА ПОЛИЭТИЛЕНА ЛЕГИРОВАННОГО CaGa$_2$S$_4$:Eu^{+2}

Исследованы частотные и температурные зависимости диэлектрической проницаемости и электропроводности полиэтилена высокой плотности с добавкой CaGa$_2$S$_4$:Eu^{+2}. Показано, что диэлектрическая проницаемость и электрическая проводимость увеличиваются с увеличением концентрации наполнителя при всех температурах. В этом случае проводимость имеет прыжковый механизм, описываемый теорией Джошера. Соответствующий показатель степени и энергия активации несколько уменьшаются с увеличением концентрации титаната бария. Экспериментальные данные диэлектрической проницаемости сопоставлены с теорией Максвелла-Гарнетта.

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CaGa$_2$S$_4$:Eu^{+2} İLƏ LEGİRLƏNƏN POLİETİLENİN DİELEKTRİK VƏ KEÇİRİCİ XASSƏLƏRİ

CaGa$_2$S$_4$:Eu^{+2} əlavəsi ilə legirlənən yüksək sıxlıqlı polietilenin dielektrik nüfuzluğunun və elektrik keçiriciliyinin tezlik və temperatur asılılıqları öyrənilmişdir. Göstərilmişdir ki, bütün temperaturlarda əlavənin konsentrasiyasının artması ilə dielektrik nüfuzluğunun və elektrik keçiriciliyinin qiyməti artır. Bu halda keçiricilik Josher nəzəriyyəsi ilə təsvir edilən sıçrayış mexanizminə malikdir. Müvafiq qüvvət üstü və aktivləşmə enerjisi barium titanatın konsentrasiyasının artması ilə bir qədər azalır. Dielektrik keçiriciliyin eksperimental qiymətləri Maksvell-Qarnet nəzəriyyəsi ilə müqayisə edilir.