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## ELECTROPHYSICAL PROPERTIES OF HETEROSTRUCTURES CuS/ZnS AND PCTFE–CuS/ZnS SYSTEM

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*In order to synthesize the polymer composite system of the PCTFE–CuS/ZnS, the nanodispersed ZnS was synthesized by hydrothermal method afterwards heterostructures of CuS/ZnS were obtained using ion-substitution mechanism. The concentration dependence of the real and the imaginary components of the complex dielectric permeability and electrical conductivity of synthesized samples were investigated. Obtained composites have high values of the dielectric permeability at high frequencies and conductivity at low frequencies. At 50 % (molar) substitution of Zn ions by Cu the percolation threshold was determined at the volumetric content of CuS about 0.06.*

**Keywords:** composite materials, disperse filler, polychlorotrifluoroethylene, zinc sulfide, electrical conductivity

### INTRODUCTION

Zinc sulfide (ZnS) is wide-bandgap semiconductor material which has two polymorphs, namely cubic sphalerite and hexagonal wurtzite. The sphalerite with a bandgap energy of 3.72 eV is stable at room temperature while the wurtzite with a bandgap energy of 3.77 eV [1] is a metastable phase, meanwhile the bulk cubic ZnS can transform to the hexagonal structure over 1020 °C. ZnS is widely used in photocatalytic processes [2], sensors, ultraviolet light-emitting diodes, in infrared optical windows [3] and in LCD monitors technology [4].

In order to create materials that effectively interact with electromagnetic radiation, semiconductor nanoparticles of ZnS and CuS/ZnS heterogeneous system were synthesized.

### MATERIALS AND METHODS

Samples of nanodimensional ZnS were synthesised by hydrothermal method as follows: 2 mmol of  $Zn(CH_3COO)_2 \cdot 2H_2O$  and 4 mmol of  $CS(NH_2)_2$  were dissolved in 40 ml of ethylenediamine, ethanolamine and deionised water (1:1:18) at ambient temperature under continuous stirring. Then the mixture was placed in the Teflon-lined autoclave of 50 ml volume and was heated at 433 K for 6 h. Heterostructures of CuS/ZnS were obtained by substitution of Zn ions

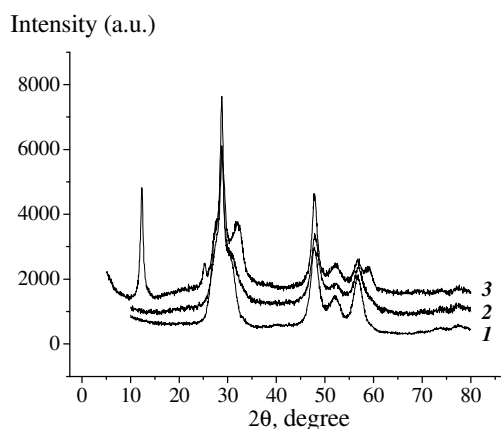
by Cu ions at 353 K for 1 h. Precipitate of nanoparticles was washed with distilled water and dried at 333 K in oven. The PCTFE–CuS/ZnS system was prepared by mixing of polychlorotrifluoroethylene (PCTFE) with the semiconductor powder of CuS/ZnS by grinding in the mechanical mill to form a homogeneous mixture which thereafter was compressed at the polymer melt temperature.

Crystal structure was determined using X-ray analysis (DRON-4-07, Lomo, USSR) in the emission of copper cathode with nickel filter in Bragg–Brentano geometry. The real ( $\sigma'$ ) and imaginary ( $\sigma''$ ) components of the complex electrical conductivity ( $\sigma^* = \sigma' + i\sigma''$ ) at low frequencies (0.1, 1 and 10 kHz) were measured using the immittance meter E7-14 by two-contacts method in the temperature range from 298 to 425 K. The real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) components of the complex permittivity in microwave (MW) range were measured using an interferometer at a frequency of 9 GHz [5]. The frequency dependence of the electrical conductivity was measured by an impedance spectrometer Solortron SI 1260 (Solortron analytical, UK) in the frequency range  $10^{-2}$ – $10^6$  Hz.

### RESULTS AND DISCUSSIONS

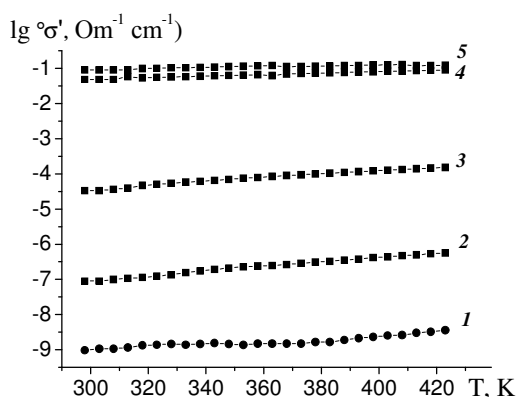
Identification of the structural characteristics was performed using diffraction patterns. XRD

graphs show diffraction peaks which indicate the formation of cubic ZnS (JCPDS 80–0020). The crystallite size was 8.2 nm (Fig. 1 curve 1).



**Fig. 1.** X-ray diffraction patterns: 1 – ZnS, 2 – 0.3 CuS/ZnS, 3 – 0.5 CuS/ZnS

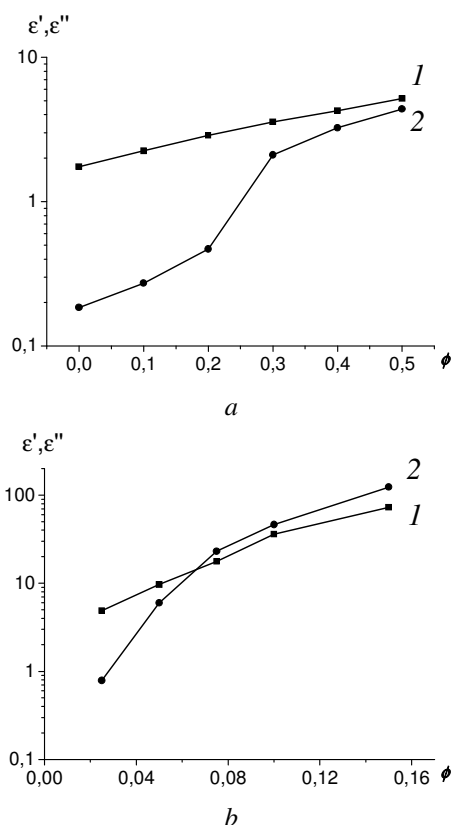
XRD patterns of 0.5 CuS/ZnS show diffraction peaks which corresponding hexagonal CuS (Fig. 1, curve 3). Heterostructure 0.5 CuS/ZnS exhibits additional reflection peaks at low angle (12.4°) corresponding to the orthorhombic structure ZnS in plates form [6, 7].



**Fig. 2.** Temperature dependence of the logarithm of electrical conductivity of synthesized samples: 1 – ZnS, 2 – 0.15 CuS/ZnS, 3 – 0.25 CuS/ZnS, 4 – 0.3 CuS/ZnS, 5 – 0.5 CuS/ZnS

In the presence of the crystal structure of CuS with posistor type conductivity on the surface of ZnS along the entire length of the sample, the temperature dependence of the electrical conductivity of the heterostructure CuS/ZnS should also have a metallic character [8]. For the test samples CuS/ZnS in the temperature dependence of electrical conductivity with increasing amounts of CuS decrease in the angle of inclination of the curves was observed (Fig. 2). XRD analysis of

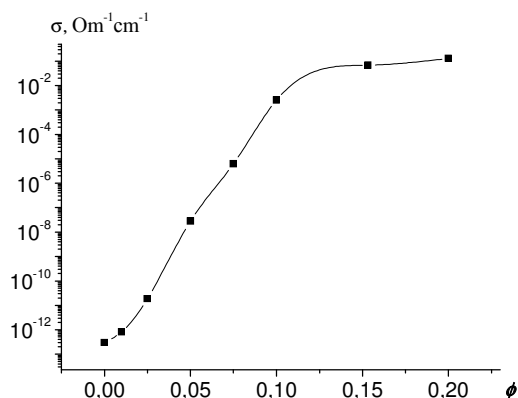
0.3 CuS/ZnS shows that reflections corresponding CuS is not observed (Fig. 1) and the copper sulfide on the surface ZnS is in the amorphous state and its amount is not sufficient for the formation of the crystalline structure. The electrical conductivity of the heterostructure 0.3 CuS/ZnS has a semiconductor character. With further increase amount of CuS on the surface of ZnS the crystal structure of CuS was formed and the temperature dependence of the electrical conductivity changes from semiconductor to metal (Fig. 2).



**Fig. 3.** The dependence of  $\varepsilon'$  (1) and  $\varepsilon''$  (2) on the content of nanocrystalline CuS in heterostructure CuS/ZnS (a) and in the system PCTFE–0.5 CuS/ZnS (b) at a frequency of 9 GHz

As shown in Fig. 3 a, for the real part of the dielectric permittivity at microwave frequencies in almost linear increase in values in a semi-logarithmic scale was observed. Its low value can be explained by a low bulk density of the measured samples which during the measurement does not exceed  $0.5 \text{ g/cm}^3$ . Slope of the curve of the concentration dependence of the imaginary component of the dielectric permittivity at the appropriate content of 0.2 may indicate the beginning of the formation of branched cluster.

With the introduction of highly dispersed heterostructure 0.5 CuS/ZnS in polymer, values of the real and imaginary components of the complex permittivity increase that may be associated with the manifestation of interfacial interaction of polymer and filler.



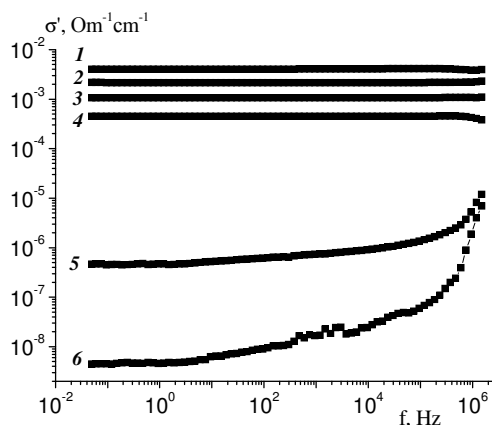
**Fig. 4.** Dependence of electric conductivity for the system PCTFE-0.5 CuS/ZnS on volume content CuS

Fig. 4 shows the dependence of electrical conductivity at 1 kHz for the system PCTFE-0.5 CuS/ZnS on the content of CuS. For these systems a percolation threshold is described by the equation:  $\sigma(\Theta) = \sigma_0(\Theta - \Theta_c)^t$ , where  $\Theta_c$  – the content of filler in the composite, which corresponds to a percolation threshold,  $t$  – is exponential quantity and  $\sigma_0$  – the electrical conductivity of the conductive component. The value of percolation threshold for the system PCTFE-0.5 CuS/ZnS was determined at the volumetric content of CuS about 0.06.

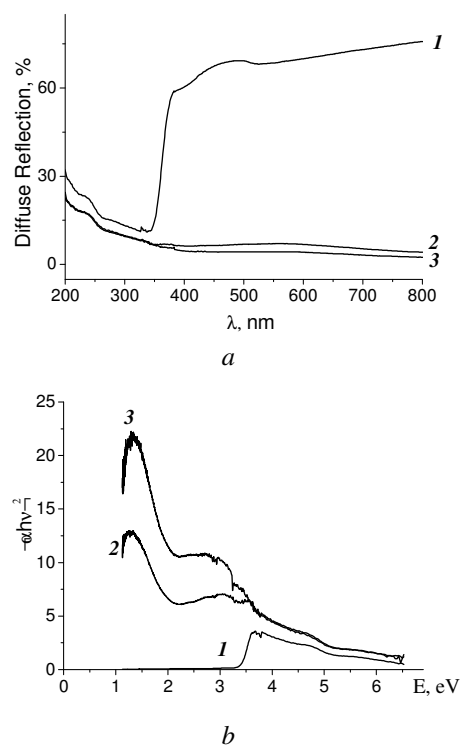
The frequency dependence of the real components of the electrical conductivity of semiconductor system PCTFE-0.5 CuS/ZnS (Fig. 5) show reduced of dependence conductivity values on frequency with increasing content of nanocrystalline CuS. After achieving percolation threshold the values of conductivity are independent of frequency in the range studied (Fig. 5 curves 1-4). When the volume content of CuS is less than the percolation threshold (Fig. 5 curves 5, 6) the real part of the complex conductivity  $\sigma'$  increases monotonically with increasing frequency and after  $5 \cdot 10^5$  Hz there is a sharp increase in the value of  $\sigma'$  due to the resonant process that corresponds to the change between capacitive and inductive nature of impedance of the composite.

The real component of the conductivity can be described by the degree dependence which

corresponds to the jumping mechanism of charge transfer between particles (Fig. 5 curve 5, 6) and given as an equation  $\sigma' = \sigma'_{DC} (1 + (\omega / \omega_H)^n)$ , where  $\sigma'_{DC}$  – the DC conductivity,  $\omega_H$  – the frequency of jump of the charge and  $n$  – the dimensionless parameter [9].



**Fig. 5.** The frequency dependence of the real components of the electrical conductivity ( $\sigma'$ ) of heterostructures 0.3 CuS/ZnS (4), 0.5 CuS/ZnS (3) and system PCTFE-0.5 CuS/ZnS with volume content of nanocrystalline CuS: 6 – 0.05, 5 – 0.075, 1 – 0.1, 2 – 0.15



**Fig. 6.** Diffuse reflection spectra (a) and transformation reflectance spectra using the Kubelka-Munk functions (b) (1 – ZnS, 2 – 0.15 CuS/ZnS, 3 – 0.3 CuS/ZnS)

Diffuse reflection spectra of the synthesized samples ZnS and CuS/ZnS are shown in Fig. 6 a. Converting spectra in coordinates  $(\alpha h\nu)^2$  and  $h\nu$  (Fig. 6 b) allows to determine the energy bandgap by extrapolating the linear region on the energy axis  $h\nu$ . For synthesized semiconductor ZnS bandgap is 3.4 eV. Position of the valence and conduction bands of the CuS and the ZnS in the heterostructure promotes absorption in the visible region of the optical spectrum [10].

#### CONCLUSION

In order to synthesize the polymer composite system of the PCTFE–CuS/ZnS, the nanodispersed ZnS was synthesized by hydrothermal method afterwards heterostructures of CuS/ZnS were obtained using ion-substitution mechanism. The concentration dependence of the real and the

imaginary components of the complex dielectric permeability and electrical conductivity of synthesized heterostructures CuS/ZnS were investigated. Exploration dependence  $\epsilon'$  and  $\epsilon''$  on content CuS on the surface of nanodispersed ZnS showed that content of 0.5 CuS, obtained by ion substitution, is sufficient for further introducing heterostructure in polymer.

For polymer system PCTFE–0.5 CuS/ZnS percolation threshold was determined at the volumetric content of CuS about 0.06. Of high values of  $\epsilon'=70$  and  $\epsilon''=125$  was achieved when the volume content of CuS is 0.15 due to the optimal distribution of the conducting phase in the composite and the effective use of the skin effect for the absorption of electromagnetic radiation.

### Електрофізичні властивості гетероструктури CuS/ZnS і системи CuS/ZnS-ПТФХЕ

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*Гідротермальним методом синтезовано нанорозмірний ZnS, гетероструктури CuS/ZnS шляхом йонного обміну та виготовлено полімерні композити на їх основі. Досліджено концентраційну залежність дійсної та уявної складових комплексної діелектричної проникності та електропровідності синтезованих зразків. Синтезовані композити мають високі значення діелектричної проникності у високочастотному діапазоні та провідності на низьких частотах. При 50 % заміщенні йонів Zn на йони Cu досягнення порогу перколяції в системі ПТФХЕ–CuS/ZnS відбувається при об'ємному вмісті CuS 0.06.*

**Ключові слова:** композитні матеріали, дисперсний наповнювач, політрифторхлоретилен, сульфід цинку, електропровідність

### Электрофизические свойства гетероструктуры CuS/ZnS и системы CuS/ZnS–ПТФХЭ

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*Гідротермальним методом синтезовані нанорозмірний ZnS, гетероструктури CuS/ZnS путем ионного обмена и изготовлены полимерные композиты на их основе. Исследована концентрационная зависимость действительной и мнимой составляющих комплексной диэлектрической проницаемости и электропроводности синтезированных образцов. Синтезированные композиты имеют высокие значения диэлектрической проницаемости в*

высокочастотном диапазоне и проводимости на низких частотах. При 50 % замещении ионов Zn на ионы Cu достижение порога перколяции в системе ПТФХЕ–CuS/ZnS происходит при объемном содержании CuS 0.06.

**Ключевые слова:** композитные материалы, дисперсный наполнитель, политрифторхлорэтилен, сульфид цинка, электропроводность

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