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Dielectric properties of photoanodes for dye-sensitized solar cells

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Abstract. Solar energy (SE) research is relevant today, especially as far as dye-sensitized solar cells (DSSC) are concerned, which are third-generation devices. The prospect of their future development lies in the creation of architectural and interior-integrated panels, flexible and portable devices for SE conversion. Examining the properties of their components and their mutual impact is crucial for improving the efficiency of DSSC and moving away from the standard cell design.

In this work, we investigated dielectric properties of photoanodes (PhA) for DSSC. The influence of a dye on dielectric properties of PhA is shown. By measuring dielectric properties in the samples, we obtained dielectric permittivity and dielectric loss tangent that ranged from −50 to 150 °C and from 10^{-1} to 10^{6} Hz. Our results make a significant contribution towards a better understanding of the influence that the dye has on dielectric properties of PhA and can serve to develop new efficient composite materials for new-generation photoelectronic devices.

Keywords: dielectric properties, mesoporous layer, titanium dioxide, dye-sensitized solar cells, composite materials, organic dyes

Introduction

A growing interest in DSSC witnessed since 1991 (O'Regan, Grätzel 1991) is a result of its low production cost, extended service life, ability to work under poor or artificial lighting, transparency and mechanical strength. The combination of properties and color solutions makes DSSC a viable alternative power source for architectural-integrated photovoltaic systems (Szindler et al. 2021) and portable electronics, which can help to support the concept of the 'internet of things' (Kim, Han 2020).

Standard device design includes a photoanode (PhA) and a photocathode with an electrolyte between them. The PhA is conductive-coated glass (FTO or ITO) with a semiconductor porous layer of metal oxide on it, which is sensitized by a dye.

The primary problem with DSSC is that it is not as efficient as silicon solar cells, but this issue can be solved by optimizing devices, expanding their applications and scaling them.

Scaling is economically profitable, but it can be even more profitable to replace an expensive metal-containing dye with an organic one, which has a much lower cost. Since titanium dioxide material is a semiconductor, which negatively affects the operation of the device, the impact of adding organic material on the conductivity of material is yet to be determined. We should thus examine the impact of the organic dye on the semiconductor layer and dielectric properties of the photoanode.

Given interaction between functional layers in DSSC devices, it is important to study their properties in both ways: independently and synthesized multiple components.

Dielectric properties are affected by microstructural features such as grain size, porosity, secondary phases, impurities and structural defects (point defects and cracks). However, most of the work on dielectric properties of titanium dioxide in its different modifications (rutile, brookite, anatase) refers to powders or compressed samples (Bonkerud et al. 2021; Wypych et al. 2014). Another question is how a metal-free dye affects dielectric properties of materials in devices.

Given all the above, it makes sense to research dielectric properties for DSSC, where TiO_2 is used as a mesoporous layer in PhA, and to conduct dielectric studies directly on PhA, both with and without dyes.

Thus, this work aims to study the dielectric properties of PhA and investigate the influence of dyes on these properties.

Methods and materials

The work was researched by PhA for DSSC. PhA has a multilayer structure: a glass substrate with a conductive coating, with a semiconductor mesoporous layer of metal oxide applied, which can be sensitized by various dyes. Ti-Nanoxide T/SP, particle size 15–20 nm (Solaronix), fluorine-doped tin oxide (FTO) coated glasses, 20 × 20 mm, (Solaronix) were used. To obtain samples of titanium dioxide films on glass with a conductive coating, we applied the 'doctor blade' paste technique (Berni et al. 2004), active area 6 × 6 mm. Step-by-step heating and extracting at 450 °C were used, which ensured gradual removal of the solvent both from the surface of the layer and from its volume, thus avoiding stresses and cracking. Chloroform dye solutions $c = 5 \times 10^{-4}$ mol/l were made for sensitization of the titanium dioxide layer. After that the glass with the pre-formed film was placed in this solution with an exposure of t = 24h. The photoanode was then extracted from the solution and dried at room temperature in the air. Organic D-π-A dyes IS5 and IS10, synthesized and investigated earlier (Steparuk et al. 2022), were chosen for the survey. These dyes have a thieno[3,2-*b*]indole nucleus, electrodonor part. The main distinction is the acceptor group: 2-cyanoacryl acid in IS5 and 5-(methylene) barbiturate acid in IS10.

Dielectric measurements were carried out by a Novocontrol Technologies 'Concept-81' spectrometer (Novocontrol Technologies GmbH & Co. KG, Montabaur, Germany; 'Modern physical and chemical methods of formation and study of materials for the needs of industry, science and education', Herzen University). In order to measure the dielectric properties of the mesoporous layer of titanium dioxide in the form used in DSSC, an attachment has been made to allow direct measurement of the PhA (Fig. 1). This attachment (holder) was needed to measure the porous film (thickness of the μm order) on the glass, precisely as the materials are used in DSSC devices.

We used parallel plate measurement. The measuring design is a capacitor with the measured material placed between the plates. When the formed samples are measured, the contact area and thickness of the measured layer is the same. Temperature measurement ranges from –50 to 150 °C, and frequencies vary from 10^{-1} to 10^{6} Hz.

Results and discussions

Dielectric permittivity describes the interaction of the material with the electric field and is a complex quantity:

$$\varepsilon^* = \varepsilon' + \varepsilon'' \quad (1)$$

where ε' and ε'' are the real part and the imaginary one, respectively. The ε' value shows how much of external electric field energy is stored in the material. The imaginary part of permittivity ε'' is called the loss factor and shows the level of dissipation or loss of the external electric field in the material. Figures 2a-c show the temperature-frequency dependencies of ε' measured for the non-sensitized PhA (2a) and PhA with a dye (2b, c).

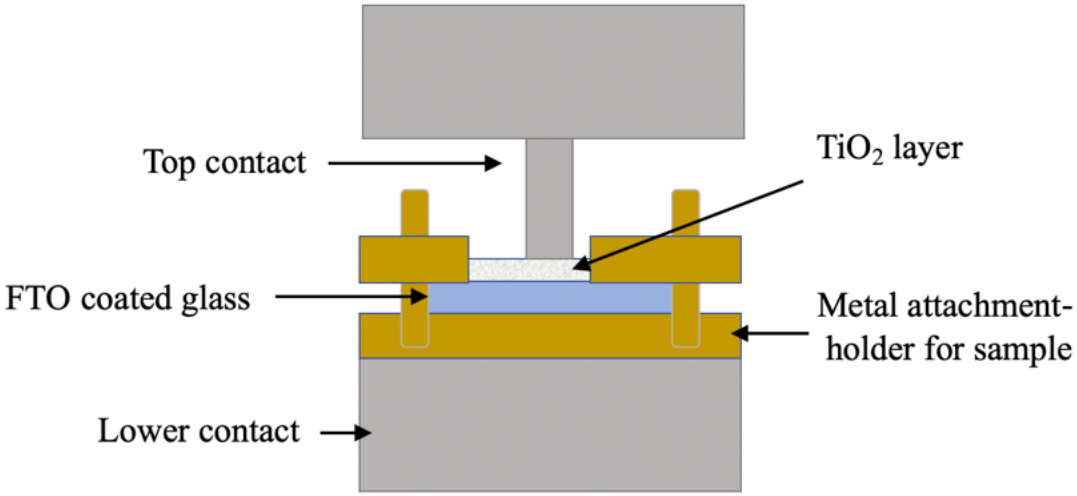

Fig. 1. Diagram of the cell for measuring the dielectric properties of the titanium dioxide film formed on FTO conductive glass

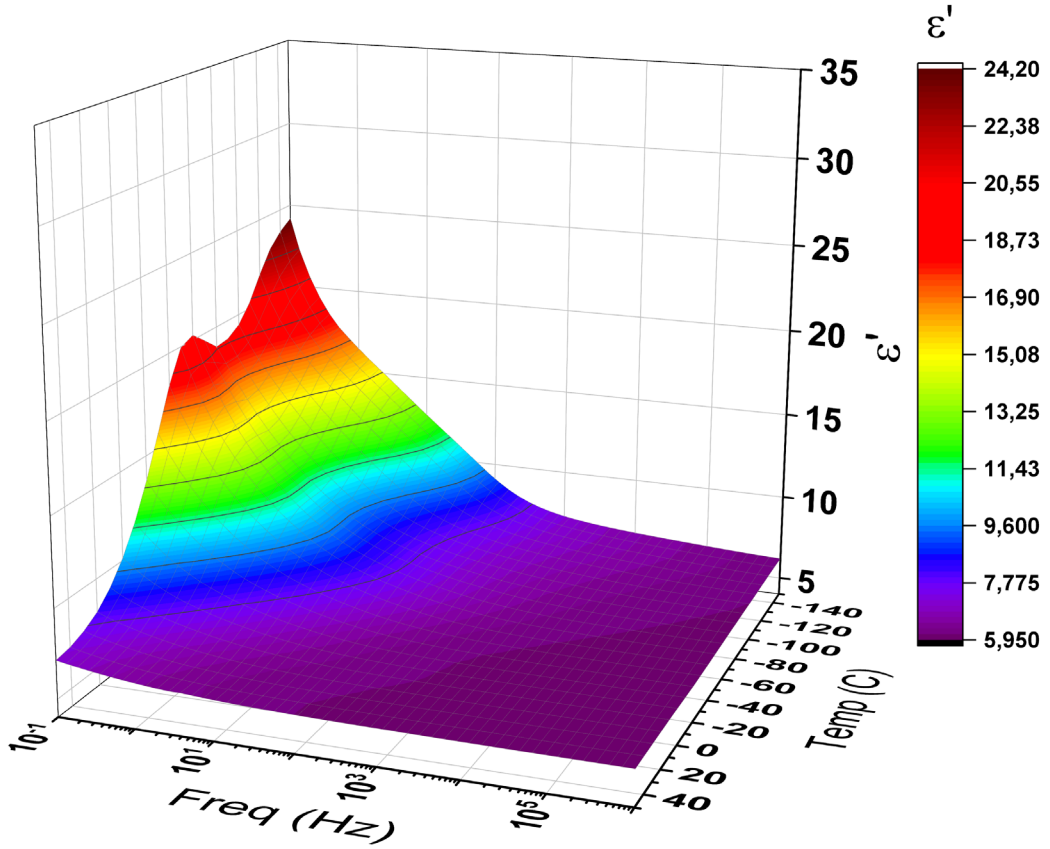

Fig. 2a. Temperature-frequency graphs of the real part of permittivity measured for the PhA without dyes

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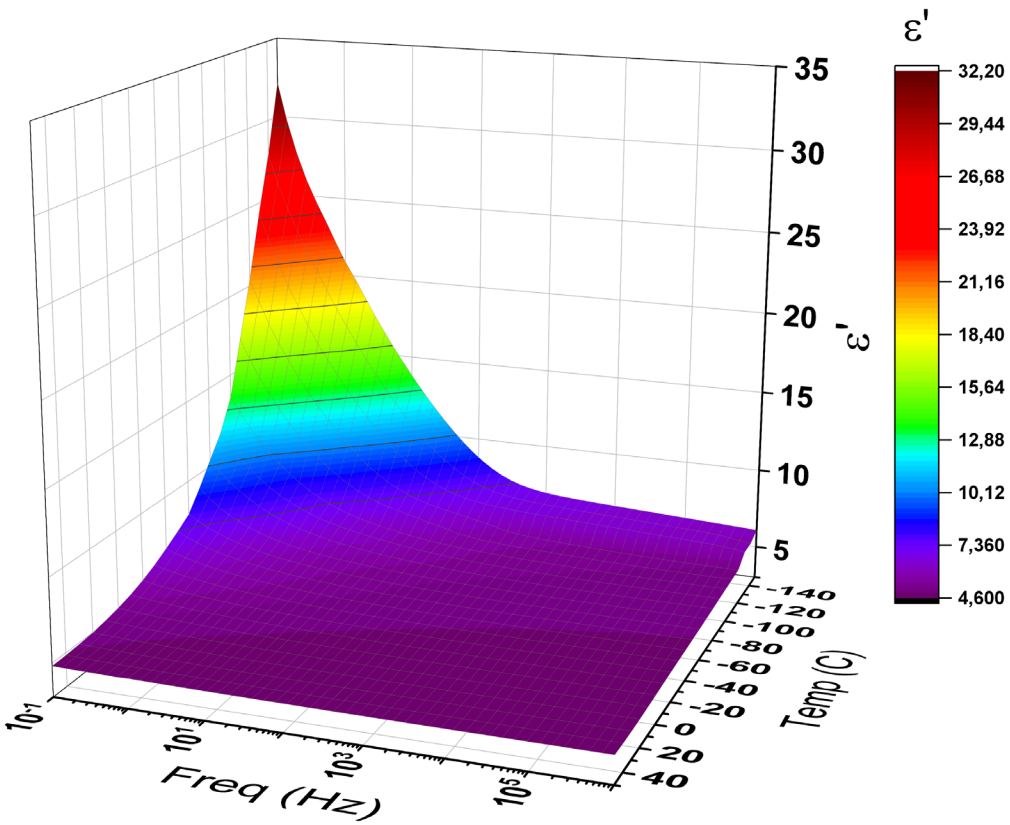

Fig. 2b Temperature-frequency graphs of the real part of permittivity measured for the PhA sensitized by the IS5 dye

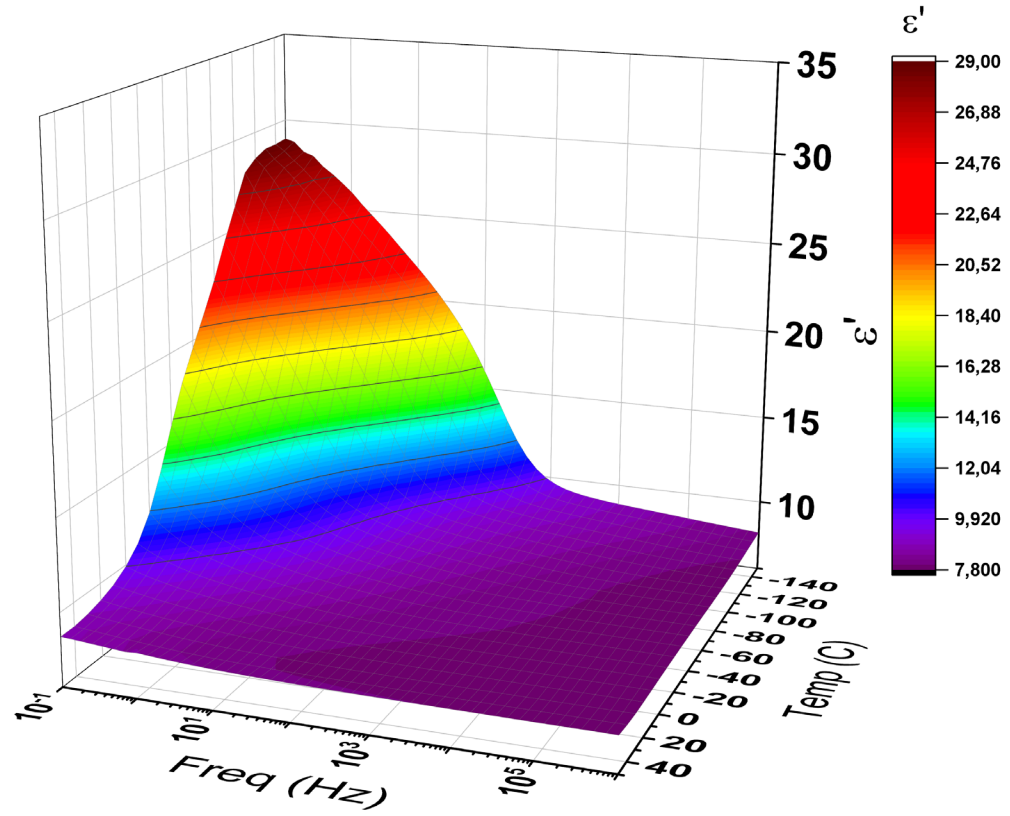

Fig. 2c Temperature-frequency graphs of the real part of permittivity measured for the PhA sensitized by the IS10 dye

The graphs show that frequency increases (to about 10^3 Hz), permittivity decreases while significant dispersion is observed only in the region of negative temperature. Meanwhile, changes are insignificant in the temperature range close to room temperature. Similar effect for metal oxides was discussed in another article (Wang et al. 2006). Reduced permittivity with increased frequency is observed here due to dielectric relaxation since the speed of rotation of the dipole at high frequency is not enough to match the displacement of the applied variable voltage. This may be due to the fact that in this material electrical response is complex and consists mainly of contributions of polarization from different molecular levels and polarization of the space charge. It should also be noted that the studied titanium dioxide consisting of nanocrystals is porous and really represents the system consisting of a mixture of a semiconductor and air. The values of the ε' titanium dioxide-dye system (Figure 2b, c) differ from the pure TiO_2 layer (Figure 2a) at all frequencies due to the dipole-dipole interaction when adding fillers as organic dyes. It also shows that dielectric properties of such composites can be regulated by varying the type and concentration of the filling agent (Huang et al. 2005). The combined Maxwell-Wagner-Sillars effect has its own dipole polarization, and polarization on the inner surfaces of the polarization section explains this difference (Ramesan 2015). It can also be seen that after the dye is added, polarization in the material decreases with an increase in frequency faster than in the dye-free material. This may indicate a cumulative increase in the rotation rate of dipoles in the material and a global deterioration in the ability of the system to store energy from the external electric field. However, it may also indicate an increase in the conductivity of the composite material. It is important to note that there is a difference in the influence of dyes with different anchor groups on the behavior of the system. For the IS5 dye there is only a faster decrease in the ε value with increasing frequency, and in the case of the IS10 dye, we see the preservation of the value of the actual polarization component at low frequencies and only after increasing frequency, that is, in this range, does the system better accumulate the energy of the external electric field. We can conclude that the dye carrying 5-(methylene) barbituric acid as an anchor group makes a greater change in the dielectric properties of the system which indirectly indicates its better ability to fit into pores of TiO_2 film.

The tangent of dielectric loss tan (δ) was determined by:

$$\tan(\delta) = \frac{\varepsilon''}{\varepsilon'} \quad (2)$$

Assuming that dielectric loss is caused by polarization, the graph will show a maximum, which is observed in all samples for high temperatures 130–150 °C for pure titanium dioxide (Fig. 3) and dye-sensitized one (IS5) (Fig. 3a), and 90–150 °C for titanium dioxide with the IS10 dye as a sensitizer (Fig. 3b,c). After sensitization, the value of the dielectric loss tangent increases slightly, which may be due to denser packaging because the semiconductor oxide matrix contains dye molecules and there is friction when the dipoles are rotated by an external electric field, which also effects the value. It should be noted that the contribution of this type of loss is small, and the increase in loss is small, accordingly. There is also a downward trend in losses as the frequency increases after the maximum loss as dipoles and ions do not have time to rotate or shift following the frequency of the electric field, and therefore losses are reduced. The maximum loss for the pure TiO_2 film and IS5-dye-sensitive TiO_2 film is at 10^2, and in the case of sensitization by the IS10 dye carrying 5-(methylene) barbituric acid as an anchor group, shifts to a value close to 10^3 Hz for temperatures 100–150 °C. The relaxation phenomenon indicated by the arrow in the tangent image of the loss angle tan (δ) for all cases (Fig. 3, 3a, 3b) may be related to energy dissipation at grain boundaries or/and electrode influence (Mohamed et al. 2011; Romeu et al. 2013). Higher tan(δ) values at higher frequencies may be associated with spatial charge polarization with the addition of a dye, macroscopic distortion and higher interphase polarization (Huang et al. 2005).

Conclusions

We studied nanocrystalline titanium dioxide layers used as photoanodes for DSSC, both with dye molecules in TiO_2 pores and without. Supplementation of a titanium dioxide matrix with an organic dye has been proven to affect dielectric properties. Specifically, organic dyes contribute to the dipole-dipole interaction, which reduces the values of permittivity at all frequencies, compared to the pure material, which may affect the capacity of the DSSC device itself. Changes in permittivity and the dielectric loss tangent also depend on the type of the dye incorporated into the system, which indicates the ability

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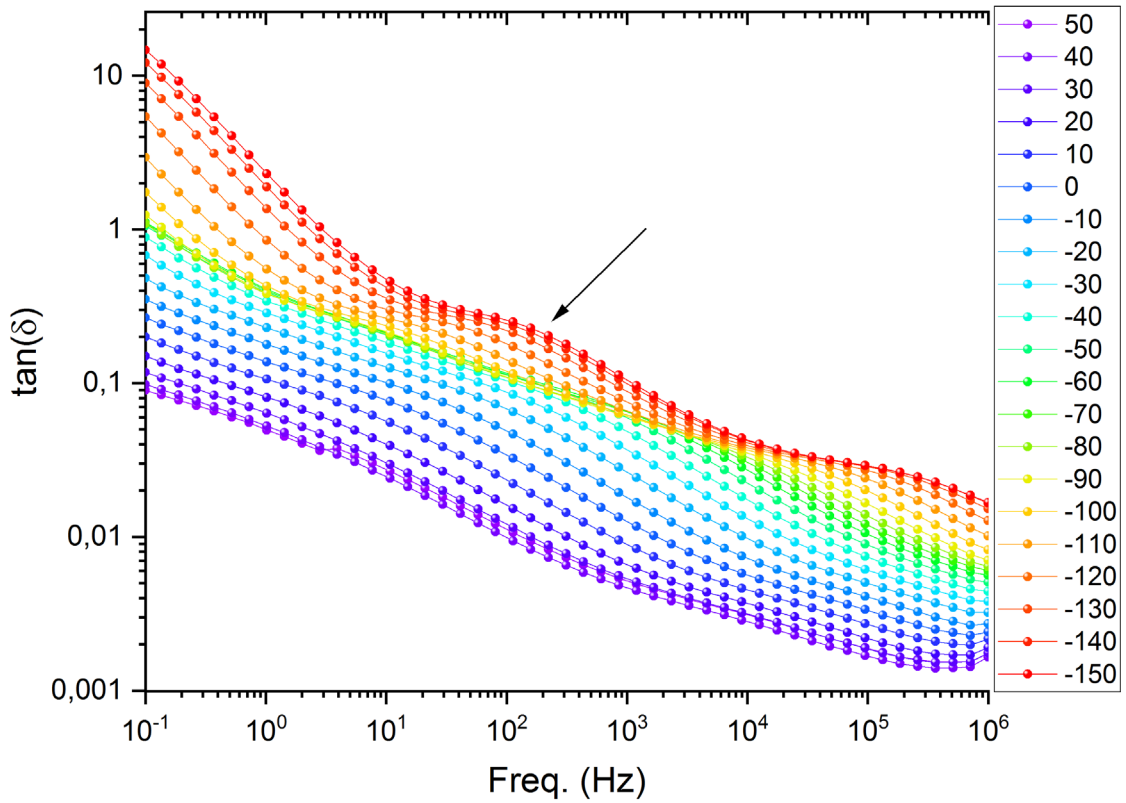

Fig. 3a. Frequency dependence of the tangent of dielectric loss tan (δ) measured at different temperatures for the PhA without dyes

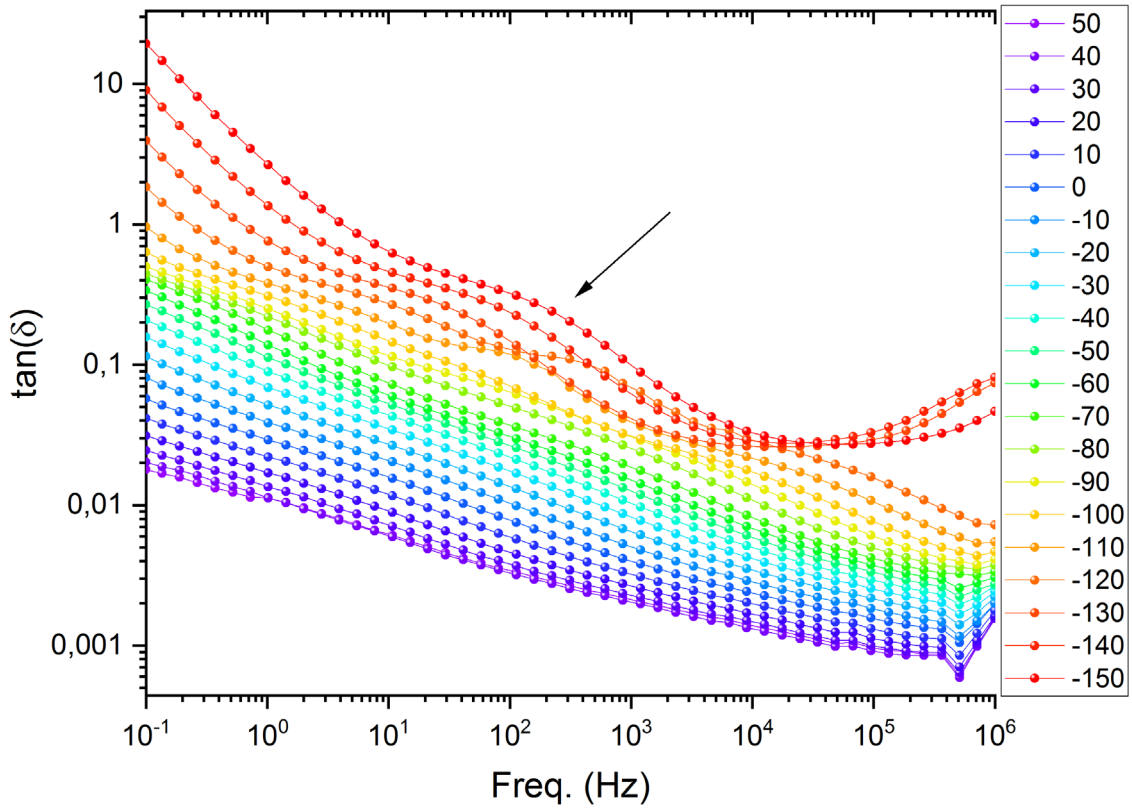

Fig. 3b. Frequency dependence of the tangent of dielectric loss tan (δ) measured at different temperatures for the PhA sensitized by the IS5 dye

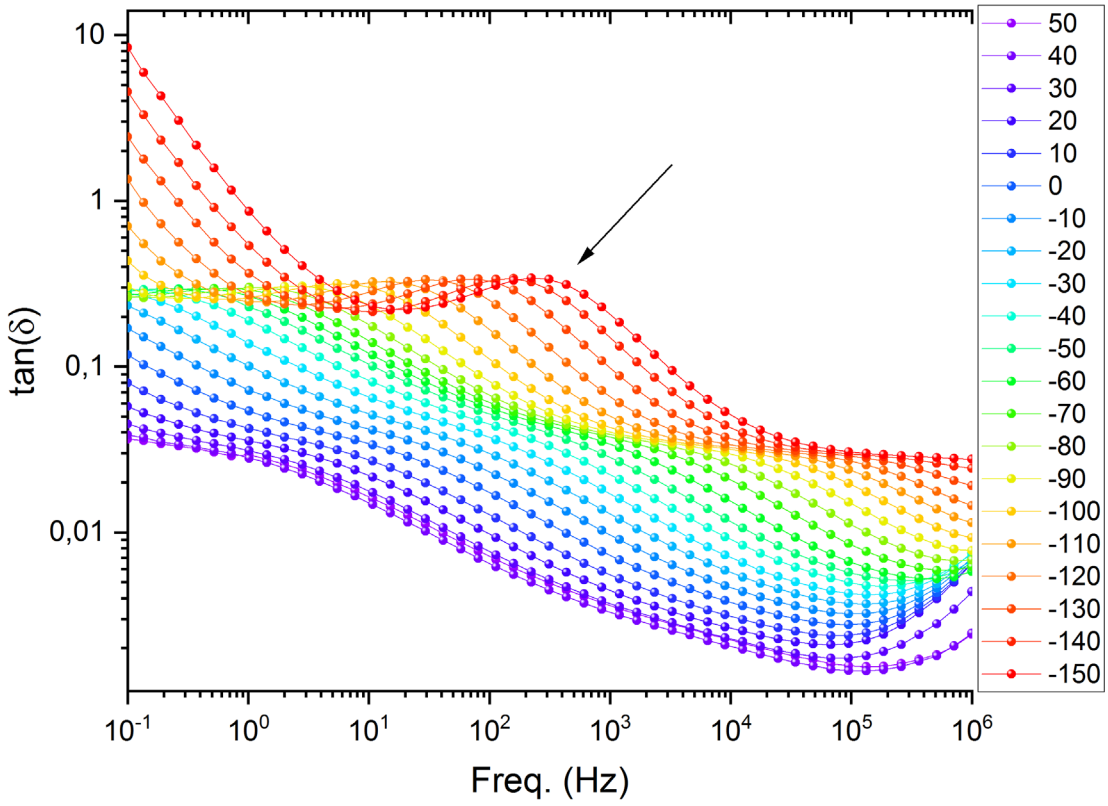

Fig. 3c. Frequency dependence of the tangent of dielectric loss tan (δ) measured at different temperatures for the PhA sensitized by the IS10 dye

to vary the properties of the composite material by adding dyes of different molecules and influence the efficiency and durability of the devices. Both dyes contribute to dielectric changes due to denser packaging of the material given the presence of dye molecules. According to the obtained data, we can conclude that the dye carrying 5-(methylene) barbituric acid in its molecule makes a greater change in the dielectric properties of the system than the dye with 2-cyanoacrylic acid as an anchor group, which indirectly implies better ability to fit into the porous titanium dioxide film, not only by physical penetration into the pores, but also chemically, more radically changing the characteristics of the composite.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

Conceptualization, methodology: S. A. Kozyukhin; device fabrication: E. V. Tekshina, A. S. Steparuk, D. A. Krupanova; validation: P. I. Lazarenko; writing-original draft preparation: E. V. Tekshina, P. I. Lazarenko; supervision: S. A. Kozyukhin.

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