PERMITTIVITY MEASUREMENT OF NANOCRYSTALS ZnO:Mn AT MICROWAVES WITH USING A BICONICAL CAVITY

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The measurement of the dielectric constant of nanocrystalline materials at microwave frequencies using a biconical resonator is under consideration. Obtaining ZnO and ZnO:Mn (2%) nanocrystals is carried out under non-equilibrium conditions by the method of ultrasonic aerosol pyrolysis. Estimates of the dielectric constant of these samples in the range of 8–12 GHz were obtained. Dielectric constant estimates are 8,3±0,2 and 12,4±0,2, respectively.

Keywords: ZnO, nanocrystal, dielectric constant, dielectric loss tangent, biconical resonator, microwave measurements.

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1. Introduction

Zinc oxide as a functional material has long been in the field of research in connection with various possibilities of practical application. This optically transparent wide-bandgap semiconductor, in which the bandgap is E_g ~3.4 eV, is used to create LEDs in the blue and ultraviolet regions of the spectrum, solar cells, sensor devices, optical filters, etc. [1]. Recently, studies of the physical properties of nanocrystals ZnO:Mn have caused a keen interest to this material. In the form of nanocrystals, this material showed ferromagnetic properties at room temperature [2]. This fact determines the prospects for its use in spintronics devices [3].

The technology for producing ZnO and ZnO:Mn (2 %) nanocrystals by ultrasonic aerosol pyrolysis is described in [4]. This method is based on the thermal decomposition of aerosol droplets of the initial solution as they pass through the thermal zone of the furnace. Zinc and manganese nitrates ($Zn(NO_3)_2{\cdot}6H_2O$ and $Mn(NO_3)_2{\cdot}6H_2O$) were used as precursors. An aqueous solution consisting of zinc nitrate with a concentration of 10% and the required amount of manganese nitrate was sprayed onto aerosol droplets of size d = 1–2 µm. These droplets, with the help of a carrier gas (air), were transported through the heated reaction zone of the furnace. In the oven for a limited time (6 – 8 s), the processes of drying drops and synthesizing ZnO:Mn nanocrystals took place. Nanocrystalline ZnO:Mn powder in the form of spherical granules was accumulated on the filter at a temperature of 250°C. The samples were synthesized at a temperature of T = 550°C. Dry granules, which are the final product of the synthesis, consist of ZnO:Mn nanocrystals agglomerates. These nanocrystals have a wurtzite-type crystal structure. A special feature of the method is that in it the formation of nanocrystals occurs within a short time, under nonequilibrium conditions. In this case, nanocrystals with a heterogeneous defect structure are formed. Such nanocrystals have a defect-free crystalline core and a defective shell. The shell contains a large amount of Mn impurities and intrinsic defects. In this regard, the question arises about studying the physical properties of such nanocrystals, for example, dielectric constant. It is important to compare the results obtained with the properties of bulk, polycrystalline ZnO and ZnO:Mn powders.

The purpose of this article is to compare the values of the dielectric constants of certain bulk and nanostructured materials in the frequency range of 8–12 GHz experimentally.

2. Circuit and measurement equipment

Resonator measurement methods ensure the high accuracy of measuring the value of dielectric constant [5, 6] if measurements in a spherical dielectric resonator are used in the millimeter range of wavelengths [7]. Then, in the range of 8–12 GHz, it is advisable to use biconical resonators, which have a high Q-factor due to the formation of reflections from caustic surfaces [6, 7]. This provides the possibility of using holes in the cone tops without distorting the field in the main part of the resonator. Since the caustic surfaces are inside the resonator, the radiation from its open ends is greatly reduced. This feature technologically ensures the placement of the sample in the middle of the resonator, and nanocrystalline ZnO:Mn was pressed into the dielectric tube. The measurement results are quite stable with respect to the errors of the shape and location of the sample [8].

The measuring equipment consists of a G4-83 generator with an operating frequency range of 7.5–10.5 GHz, a C4-27 spectrum analyzer and a biconical resonator with a maximum diameter of $2a_0$ = 50.50 mm and an angle at the top of the cone $\Theta = 30^\circ$ (Fig. 1). The coupling holes of the resonator with the vibration source and the detector are usually placed in the section of the maximum diameter of the resonator, that is, at the base of the cones. An increase in the size of the holes leads to an increase in the transmission coefficient and the degree of distortion of the electric field structure, as well as to a decrease in the resonant frequency and loaded Q- factor of biconical resonators. Such a combination of the diameters of the open ends of the biconical resonator and the diameter of the coupling holes is possible, in which its resonant frequency and loaded Q-factor will differ insignificantly from the same parameters for a resonator without holes [9]. When the diameter of the open end of the resonator reaches certain limit values, which can be characterized by the value of half the diameter of the base of the conical components of the resonator, the Q-factor of the resonator is significantly reduced, and its practical use loses its meaning.

The resonator structurally consists of two conical surfaces that are connected by means of screws. The conical walls of the resonator are made of copper by electroplating. The biconical resonator is connected to the measuring equipment using standard rectangular waveguides with a cross-section of 23×10 mm^2 according to the "through" scheme, the radii of the communication holes are r_1 = 4.00 mm and r_2 = 3.25 mm, which provides close to the maximum value of the coefficient transmission of this biconical resonator for oscillations of the H_{011} mode type. In such resonators, at this type of oscillation, it is possible to obtain the highest possible Q-factor due to small longitudinal currents in the metal walls.

The powder of the studied material was pressed into a dielectric tube made of polyethylene, which was placed along its axis through holes in the subcritical regions of the resonator so that the sample was in the middle of the resonator (Fig. 1).

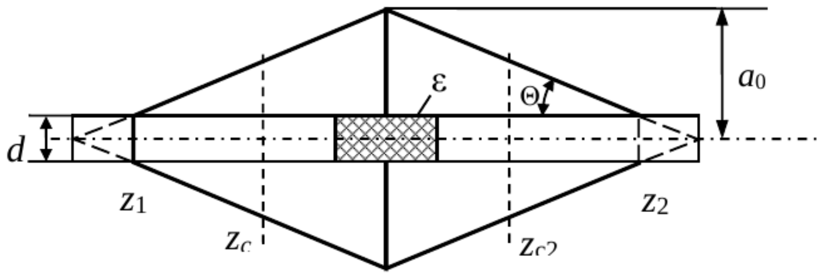

Fig. 1. Biconical resonator with the sample under study.

3. Experimental results and discussion

For the mode of H_{011} type, the resonance frequency of the resonator was 9552 MHz, the loaded Q-factor was 15600. In the case of placing a dielectric tube made of polyethylene with the outer diameter of 5 mm and the wall thickness of 0.5 mm, the frequency of the resonator decreased to 9523 MHz, and the Q-factor was 14500. The absolute measurement error of the frequency value was 0.5%, the measurement error of the frequency difference was estimated as 0.2 MHz.

The insert of the studied samples led to a decrease of the resonant frequency and Q-factor of the biconical resonator. The magnitude of these changes was used to estimate the dielectric constant and loss tangent of the sample under study. To determine the dielectric constant and tangent of the dielectric loss angle, the dependences of the resonant frequency and loaded Q-factor of the biconical resonator on sample parameters were calculated using numerical methods. The changes in the resonance frequency of oscillation H_{011} for the used resonator with the dielectric constant of the tested samples with the length of 3 and 6 mm are presented in Fig. 2. The asterisks mark the results of the experiment for samples of nanocrystalline ZnO with the length of 6 mm and ZnO:Mn (2 %) with the length of 3 mm.

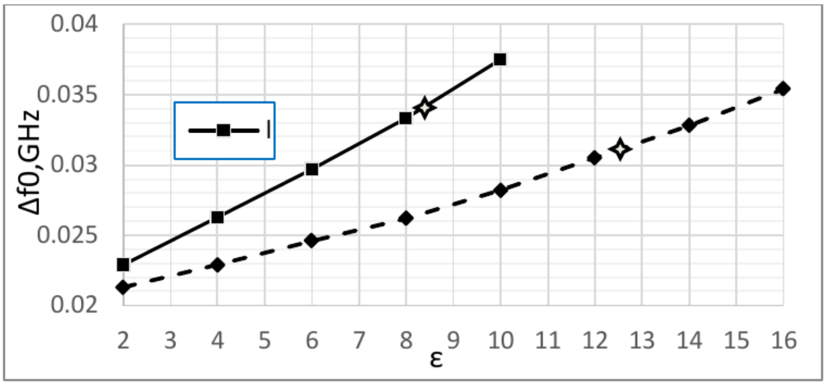

Fig. 2. The resonance frequency shift of the biconical resonator against the dielectric constant of the sample under study.

The dependences of the loaded Q-factor of the biconical resonator for H_{011} oscillation on the tangent of the dielectric loss angle of the tested samples with the lengths of 3 and 6 mm are shown in Fig. 2. The asterisks mark the results of the experiment for samples of nanocrystalline ZnO with the length of 6 mm and ZnO:Mn (2 %) with the length of 3 mm.

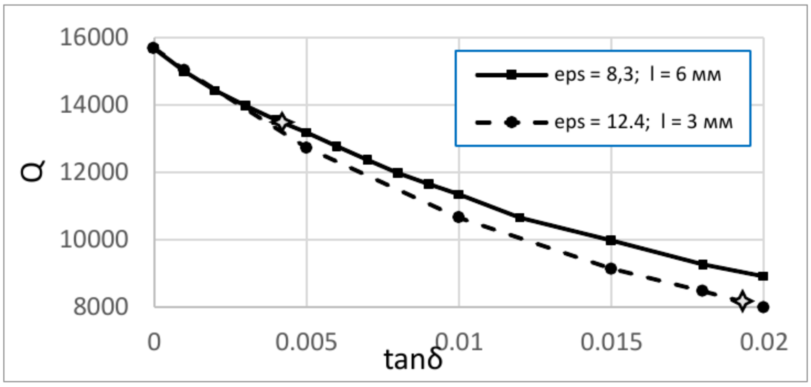

Fig. 3. The loaded Q-factor of the biconical resonator against the tanδ of the sample under study.

For a sample of pure nanocrystalline ZnO with the length of 6 mm, the estimate of dielectric constant was 8.3±0.2, which is close to the data given in the reference literature [10]. In the case of doping ZnO with manganese, the permeability of the material increases, for example, for a sample of ZnO:Mn (2%) synthesized by the method of ultrasonic aerosol pyrolysis at 550°C the permeability estimate was 12.4±0.2. The quality of the resonator with the considered samples decreased to 13500 for pure ZnO, which corresponds to the value tanδ ~ $2{\cdot}10^{-3}$, and to 8000 for the ZnO:Mn sample, which indicates a significant (to tanδ ~ $1.5{\cdot}10^{-2}$) increase in losses when ZnO nanocrystals are doped.

4. Conclusions

From the analysis of the results obtained because of numerical modeling, it is possible to determine the sensitivity of dimming, the addition of distortions in the dimming frequency, which can affect the generator, the transient attenuation of the signal, the number of points of dimming, and verify the value of the signal with theoretical models.

References

1. **Özgür, Ü.** Comprehensive Review of ZnO Materials and Devices / Ü. Özgür, Y. A. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S. J. Cho, H. A. Morkoç // J. Appl. Phys. – 2005. – Vol. 98. – P. 041301.

2. **Sharma, P.** Ferromagnetism above room temperature in bulk and transparent thin films of Mn-doped ZnO / P. Sharma, A. Gupta, K. Rao et al. // J. Nature Materials. – 2003. – Vol. 2. – P. 673 – 677.

3. **Mustaqima, M.** ZnO-based nanostructures for diluted magnetic semiconductor / M. Mustaqima, C. Liu // Turk J. Phys. – 2014. – Vol. 38. – P. 429 – 441.

4. **Kovalenko, O. V.** The effect of heat treatment on the magnetic properties of ZnO:Mn nanocrystals obtained by ultrasonic aerosol pyrolysis / O. V. Kovalenko, V. Yu. Vorovsky, O. V. Khmelenko // Functional Materials. – 2020. – Vol. 27, No. 4. – P. 687 – 694.

5. Microwave Electronic: Measurement and Materials Characterization / L. F. Chen, C. K. Ong, C. P. Neo, V. V. Varadan, and V. K. Varadan. – Chichester, WS, England: John Wiley & Sons, Ltd., 2004. – 537 p.

6. **Egorov, V. N.** Resonance methods for microwave studies of dielectrics (Review) / V. N. Egorov // Instruments and Experimental Techniques. – 2007. – Vol. 50, No. 2. – P. 143 – 175.

7. **Volovichev, I. N.** A Local Point Method Based on DFS Expansion of Boundary Conditions for Eigenfrequencies Calculation of BoR Cavities / I. N. Volovichev, G, P. Zouros, O. A. Breslavets, Z. E. Eremenko // IEEE Trans. Microwave Theory Tech. – 2023. – Vol. MTT-71, No. 11. – P. 4671 – 4681.

8. **Drobakhin, O. O.** Microwave Methods for Monitoring Parameters of Dielectrics Developed in Ukraine: Overview // Proc. 2019 24th Int. Seminar/Workshop on Direct and Inverse Problems of Electromagnetic and Acoustic Wave Theory, Lviv, Ukraine, Sept. 12-14, 2019. – P. 6 – 10.

9. **Andreev, M. V.** Measurement of Dielectric Material Properties Using Coupled Biconical Resonators / M. V. Andreev, O. O. Drobakhin, Ye. N. Privalov, D. Yu. Saltykov // Telecommunications and Radio Engineering. – 2014. – Vol. 73, No. 11. – P. 1017 – 1032.

10. **Andreev, M. V.** The Effect of Cylindricity and Coaxiality Deviations of Samples on Measurement Error of the Permittivity Using a Biconical Resonator / M. V. Andreev, O. O. Drobakhin, D. Yu. Saltykov // Proc. 2019 24th Int. Seminar/Workshop Direct and Inverse Problems of Electromagnetic and Acoustic Wave Theory, Lviv, Ukraine, Sept. 12-14, 2019. – P. 55 – 58.

11. **Drobakhin, O. O.** Taking into account the impact of coupling elements on the resonance phenomena in biconical resonators / O. O. Drobakhin, P. I. Zabolotnyy, Ye. N. Privalov // Radioelectronics and Communications Systems. – 2010. – Vol. 53, No. 7. – P. 389 – 394.

12. CRC Handbook of Chemistry and Physics: 95-ed. / Editor-in-Chief W. M. Haynes. – CRC Press, 2014. – 2664 p.