https://doi.org/10.15407/ujpe66.6.497

S.V. LEMISHKO,[1] I.P. VORONA,[1] I.S. GOLOVINA,[1,2] V.O. YUKHYMCHUK,[1] S.M. OKULOV,[1] V.V. NOSENKO,[1] S.O. SOLOPAN,[3] A.G. BELOUS[3]

[1] V.E. Lashkaryov Institute of Semiconductor Physics, Nat. Acad. of Sci. of Ukraine
(41, Nauka Ave., Kyiv 03028, Ukraine)
[2] Drexel University
(Philadelphia, PA 19104, USA)
[3] V.I. Vernadsky Institute of General and Inorganic Chemistry, Nat. Acad. of Sci. of Ukraine
(32/34, Academician Palladin Ave., Kyiv 03142, Ukraine)

DEVELOPMENT AND CHARACTERIZATION OF CERAMIC INSERTS USED IN METALLIC RESONATORS OF EPR SPECTROMETERS TO INCREASE THEIR SENSITIVITY

Cylindrical dielectric inserts for a standard EPR spectrometer with a metallic resonator have been developed on the basis of doped barium tetratitanate ceramics ($BaTi_4O_9 + 8.5\%$ ZnO) with the dielectric constant $\varepsilon = 36$ and low dielectric losses ($\tan\delta \approx 1.887 \times 10^{-4}$) in a frequency interval of 9–10 GHz. It was found that the application of such dielectric inserts allows the EPR signal to be amplified owing to the redistribution of the microwave field in a standard rectangular TE_{102} resonator. The amplification is observed for both unsaturated samples and samples characterized by the saturation of the EPR signals. A gain factor of 9 was obtained for unsaturated test $MnCl_2$ samples, and 1.5 for saturated test $MgO:Mn$ ones.

Keywords: EPR spectroscopy, dielectric resonators, EPR sensitivity, barium tetratitanate.

1. Introduction

The further development of society inevitably depends on the functionality improvement of electronic devices in all spheres of human life. This fact dictates the necessity of studies of fundamental properties inherent to objects of various types the size of which becomes smaller and smaller. It is important to understand the physicochemical processes taking place in the structures for which not only the effects arising owing to a substantial reduction of geometric dimensions, but also the quantum-dimensional ones are significant. Such an understanding is important for both the creation of a general theory for such objects and the application of this theory in practice.

Today, much attention of scientists is focused on the research of nanoobjects the size of which varies from a few to several tens of nanometers. In a lot of cases, such objects cannot be principally obtained in quantities that would be enough to study them using conventional spectroscopic methods. This circumstance especially concerns biological materials applied in medicine and ecology. All those factors make the task of increasing the sensitivity of traditional methods used for diagnostics of micro- and nanoobjects extremely challenging.

The electron paramagnetic resonance (EPR) turned out to be a powerful method not only in solid-state physics and chemistry, but also in biology and medicine [1–3]. Today, the efforts of many scientists are aimed at increasing the sensitivity in order to register signals from extremely small amounts of materials. One of the approaches that allow this purpose to be achieved is the application of higher EPR frequencies for signal registration [4]. Really, the intensity of the EPR signal is proportional to $\omega^{3/2}$, where ω is microwave frequency [5, 6]. Therefore, the doubling of the latter almost triplicates ($2\sqrt{2} \approx 2.83$) the EPR sensitivity. At the same time, higher frequencies require the higher intensities of applied magnetic fields. The capabilities of classical magnets are limited to fields of about 1.5 T. Therefore, in order to create strong enough magnetic fields in high-

frequency EPR spectrometers, cryostats with superconducting solenoids are used. As a result, both the cost of the spectrometers themselves and the cost of a research grow considerably. Other ways to increase the sensitivity of the EPR method include the application of rapid-passage conditions [7] and the overmodulation of EPR signals [8]. However, those methods also have some limitations.

Another effective approach to increase the sensitivity of EPR spectrometers is the application of dielectric resonators (DRs) or dielectric inserts (DIs) in standard metallic resonators. Really, since DIs are made of materials with a high value of dielectric constant ε, the microwave field becomes concentrated in the sample region, which increases the resonator fill factor [9–13]. The advantages of DRs were considered in work [14] in detail. However, their application has some technical difficulties associated with the excitation of standing electromagnetic waves in them.

The DIs have no such shortcoming because they are arranged immediately in standard metallic resonators, for which this problem has already been solved. The first DIs made of crystalline sapphire were proposed by Bruker Co., which is now the world leader in the manufacture of EPR spectrometers [15]. Despite that those DIs have been successfully commercialized, the increase of the EPR signal intensity in them was insignificant because of the low dielectric constant of sapphire ($\varepsilon \approx 10$).

The most successful variant was the application of DIs made of monocrystalline potassium tantalate. Due to its high dielectric constant ($\varepsilon = 261$ at room temperature), its usage as a DI allowed the EPR signal from the studied samples to be increased by a factor from 50 to 100 depending on the DI geometry [9–14, 16]. Another advantage of DIs fabricated from potassium tantalate is the absence of the EPR signals of the latter, which became possible due to the development of a special technology for growing crystals [17]. However, the application of potassium-tantalate-based DIs is restricted to temperatures of 300 ± 50 K, because this material has a steep temperature dependence of ε below 250 K. Moreover, those DIs are very expensive, because they include expensive tantalum, and the process of growing the single crystals is also expensive. So, a task was formulated to find an optimal material for manufacturing DIs.

One of the known microwave dielectric materials is barium tetratitanate $BaTi_4O_9$ [18, 19]. It has the dielectric constant $\varepsilon = 36$ and low dielectric losses ($\tan\delta \approx 2 \times 10^{-4}$) in a frequency interval of 9–10 GHz. The temperature coefficient of the dielectric constant is positive, $\tau_f = +15$ ppm/°C. At the same time, by doping $BaTi_4O_9$ with zinc oxide to 5–10%, it is possible to achieve the zero value for the temperature coefficient of dielectric constant, $\tau_f = 0$ ppm/°C [20]. Such properties give us grounds to consider a $BaTi_4O_9$-based material as a promising candidate for fabricating DIs.

Hence, the aim of this work was to determine whether the ceramics based on doped barium tetratitanate ($BaTi_4O_9$ + 8.5% ZnO) can be used to amplify the EPR signal intensity in a standard metallic rectangular resonator of an X-band EPR spectrometer (9.5 GHz). For this purpose, a computer simulation of the optimal sizes of DIs was carried out, and both saturated and unsaturated test samples with and without DIs were experimentally tested.

2. Materials and Methods

Ceramics prepared on the basis of barium tetratitanate ($BaTi_4O_9$ + 8.5% ZnO) and synthesized using the solid-phase reaction method was used as a material for producing DIs. As initial reagents for synthesizing ceramics, $BaCO_3$, and TiO_2 of the A.C.S. chemical grade and ZnO of the reagent chemical grade were used. The research of both the initial components and the synthesized ceramics showed the absence of intrinsic paramagnetic centers, which allows these ceramics to be used as DIs to increase the intensity of EPR signals obtained from the examined samples.

The calculation of the DI sizes, the simulation of the distribution of electromagnetic standing waves in a metallic TE_{102} resonator, and the study of the DI influence on this distribution was carried out with the help of the Ansys HFSS simulation software.

Experimental verification of the enhancement of the EPR spectrometer's sensitivity owing to the application of DIs was performed on an X-band spectrometer Radiopan SE/X2544 using the test $MnCl_2$ and MgO : Mn samples.

3. Simulation of DI's Geometric Sizes

A rectangular metallic TE_{102} resonator $23 \times 10 \times 44$ mm^3 in dimensions with a DI arranged inside

was used as the main resonator. A resonance is attained in such a resonator provided that the electromagnetic wave frequency equals $\nu = c\sqrt{k/(2\pi\varepsilon)}$ [21], which corresponds to the wave vector magnitude $k = (k_x^2 + k_y^2 + k_z^2)^{1/2}$, where $k_x = m\pi/a$, $k_y = n\pi/b$, and $k_z = l\pi/d$; a, b, and d are the linear dimensions of the resonator; and m, n, and l are integers indicating the number of standing half-waves along the resonator axes and determining the resonance mode TE_{mnl}. In particular, at the excitation of the TE_{012} mode, the resonance frequency was equal to 9.428 GHz [microwave interval]. In this case, the sample was arranged at the resonator's geometric center, where the magnetic component the microwave field was large, and the electric component was small. For other modes (e.g., TE_{021} and TE_{014}), there also exists a region at the resonator's center, where the electric and magnetic field components have small and large, respectively, values. But those modes are excited at much higher frequencies. In order to amplify the magnetic component in the region, where the test sample is located (the geometric center of the TE_{102} resonator), inserts made of a dielectric material can be used, which change the distributions of the electric and magnetic components of the microwave field in the resonator.

Since a DI is used to amplify the signal in a standard EPR spectrometer, it has to satisfy some requirements. First, the insert geometry should allow both its free arrangement in the metallic resonator and the free arrangement of the test sample in the region with the enhanced magnetic component of the microwave field. Second, the resonance frequency shift must stay within the operating interval of an microwave generator.

At the simulation, a cylinder with a cylindrical through-hole was used as an insert (see Fig. 1). It was arranged inside the resonator as is also shown in Fig. 1.

By varying the geometric parameters of the DIs, their optimal values were determined: the outer radius $R = 2.85$ mm, the inner radius $r = 0.75$ mm, and the height $h = 1.85$ mm. It should be noted that the set of the parameters that can affect the field distribution in the DI includes the outer radius of the middle part of the cylinder: its reduction changes the homogeneity degree of the magnetic microwave field in the inner hole, which is intended for the sample arrangement [22]. However, such a modification gives

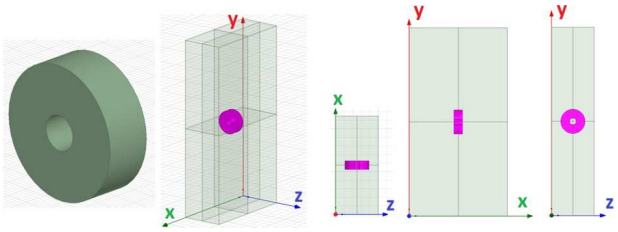


Fig. 1. Arrangement of a dielectric insert in the resonator

rise to a large cylinder height and, accordingly, to a substantial shift of the resonance frequency. Furthermore, at small height values, this modification has no significant effect.

The distribution of electromagnetic fields in an empty rectangular TE_{102} resonator is well known (see, e.g., work [5]). If an insert is present, a redistribution of standing microwave electromagnetic waves takes place with the concentration of the magnetic component at the resonator center, whereas the electric component remains rather small in this region (Fig. 2). The distributions of the electric, E, and magnetic, H, components point to the relative distribution of the fields in the TE_{102} resonator. At the same time, the magnitudes of E and H depend on the incident microwave power and the Q factor of the system.

4. Experimental Results and Their Discussion

In order to experimentally confirm the effect of the DI application, EPR studies of test samples were carried out. The role of the latter was played by a capillary 1.4 mm in diameter and 2 mm in height filled with the $MnCl_2$ or $MgO:Mn$ powder. Figure 3 demonstrates the EPR spectra of the $MnCl_2$ test sample registered at identical operating parameters of the EPR spectrometer in the cases of a rectangular resonator with and without an insert. One can see that the application of DI led to the growth in the intensity of the EPR signal by about a factor of 9.

The EPR signal from the sample is a result of the presence of Mn^{2+} ions. Due to a high concentration of those ions in $MnCl_2$, they are located close to one another, so that their wave functions overlap and there emerges the exchange interaction between them. It is well known [5] that the EPR signal from such ions is characterized by rapid relaxation times and is not saturated with the increase of the incident microwave

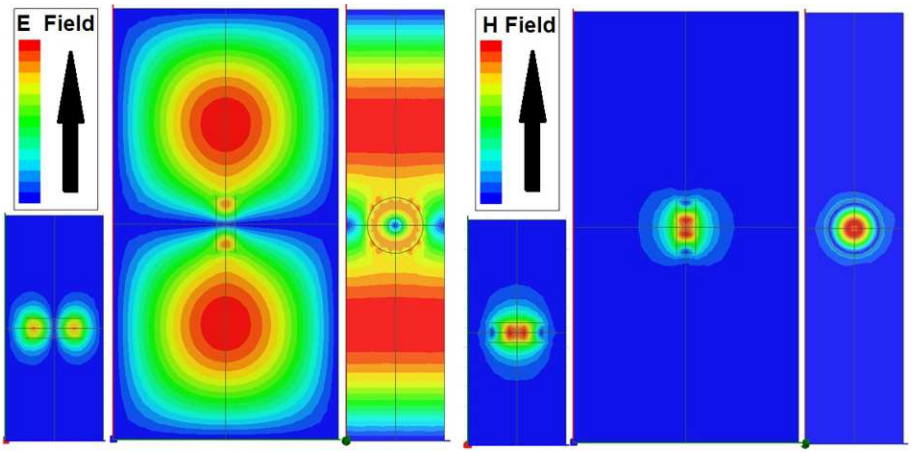


Fig. 2. Distributions of the electric and magnetic components of the standing electromagnetic waves in a $23 \times 10 \times 44$ mm^3 rectangular metallic resonator with a dielectric insert with optimum parameters ($R = 2.85$ mm, $r = 0.75$ mm, $h = 1.85$ mm, and $\varepsilon = 36$) in three mutually perpendicular planes that pass through the resonator center

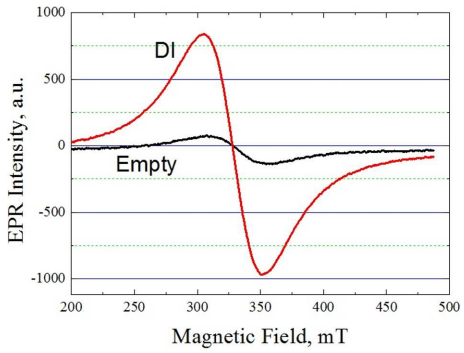


Fig. 3. EPR signal from the $MnCl_2$ sample in the rectangular resonator without and with the dielectric insert (DI). The operating parameters of the EPR spectrometer are the same

power, namely, it linearly grows with the increasing power. In other words, the application of DI in this case is equivalent to the application of a more powerful microwave field. To analyze this effect, let us use the expression that characterizes the intensity of the EPR signal I in the absence of saturation [5],

$$I \sim Q\eta P^{1/2}, \tag{1}$$

where Q is the resonator quality factor, η the resonator fill factor, and P the power of the incident microwave radiation.

The EPR spectra shown in Fig. 4 were registered, when the values of all operating parameters of the EPR spectrometer were the same, so the power of microwave radiation was also the same. If a DI is arranged in the resonator, the quality factor of the latter can only decrease because of additional dielectric losses at this DI:

$$Q_{C+I} = \frac{Q_C Q_I}{Q_C + Q_I} < Q_C,$$

where Q_C and Q_{C+I} are the quality factors of the empty resonator and the resonator with the DI, respectively, and the quantity Q_I^{-1} is proportional to dielectric losses at the DI. Therefore, the intensity growth of the EPR signal, when the DI is applied, can be associated only with the increase of the fill factor value [5]

$$\eta = \frac{\chi \int\limits_{\text{sample}} H^2 dV}{\int\limits_{\text{cavity}} H^2 dV}, \tag{2}$$

where χ is the magnetic susceptibility of the sample, and H is the strength of the magnetic component of the microwave electromagnetic field.

The DI concentrates the magnetic field at the center of a standard metallic resonator (see Fig. 2). Therefore, the magnitude of H in the sample arranged at the resonator center increases substantially, and the fill factor also increases [mainly owing to the growth of the numerator in expression (2)]. As a result, in accordance with expression (1), the intensity of the EPR signal increases.

The EPR signals obtained from the paramagnetic centers that arise owing to exchange interaction are separate lines, which are uninformative. More interesting in the EPR spectroscopy are signals from isolated paramagnetic centers. As a rule, they are characterized by longer relaxation times. Therefore, at certain microwave powers, they become saturated. Expression (1) is not suitable to describe the dependence of the intensity of such EPR signals on the power of the incident microwave radiation. The proper formula must take the signal saturation into account [5],

$$I = y_0 H_1 s^{3/2}, \tag{3}$$

where y_0 is the maximum signal intensity in the absence of saturation, and H_1 the strength of the microwave magnetic field at the sample (as a rule, it is put equal to $P^{1/2}$). The saturation factor s is determined by the expression

$$s = \frac{1}{1 + \frac{1}{4} H_1^2 \gamma^2 T_1 T_2}, \tag{4}$$

where γ is the gyromagnetic ratio, and T_1 and T_2 are the spin-lattice and spin-spin relaxation times, respectively.

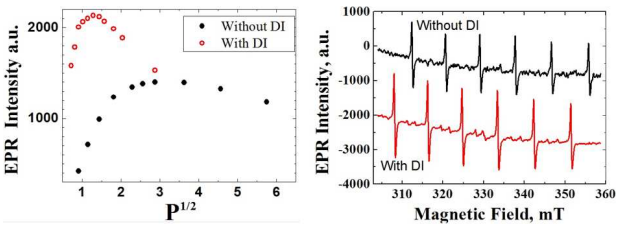
Figure 4 demonstrates the saturation curves obtained for a test sample of MgO : Mn powder in a capillary 1.4 mm in diameter and 2 mm in height, when the registration was carried out without and with the application of DI. Unlike the linear dependence (1) of the EPR signal intensity on the square root of microwave power, formula (3) for the dependence of the signal intensity on the incident power in the case of saturation is more complicated. In particular, it has the maximum value

$$I_{\max} = \frac{8}{5\sqrt{5}} \frac{y_0}{\gamma \sqrt{T_1 T_2}}$$

at

$$(H_1)_{\max} = \frac{1}{\gamma \sqrt{T_1 T_2}}.$$

It is evident that the value of $(H_1)_{\max}$ is determined only by the intrinsic parameters of the examined paramagnetic center (the relaxation times). Therefore, the horizontal shift of the saturation curves in Fig. 4, *a* toward smaller $\sqrt{P}$-values is associated with the DI-induced concentration of the magnetic component of the microwave field at the sample. In this case,



a *b*

Fig. 4. Dependences of the EPR signal intensity on the incident microwave power for the MgO : Mn sample (*a*). EPR spectra registered at the microwave powers corresponding to the EPR signal maximum in the saturation curves in panel *a* (*b*)

there is such a redistribution of the microwave field in the resonator that the value $(H_1)_{\max}$ at the sample is achieved at lower valuesof incident power. Then the value of the denominator in expression (2) becomes smaller and the fill factor increases, which gives rise to the growth of the EPR signal.

In Fig. 4, *b*, the EPR spectra of the researched MgO : Mn sample registered without and with the application of DI are depicted. The microwave powers correspond to the maxima of the EPR signal in the saturation curves shown in Fig. 4, *a*. It is evident that the use of DI resulted in an increase of the EPR signal intensity (approximately by a factor of 1.5) and the improvement of the signal-to-noise ratio, which allowed us to reliably register the EPR lines from forbidden transitions (doublets between the lines of basic allowed transitions).

5. Conclusions

It was found that the application of a DI made of ceramics on the basis of barium tetratitanate ($BaTi_4O_9$ + 8.5% ZnO) enhances the EPR signal. The enhancement occurs owing to the redistribution of the microwave field in a standard rectangular TE_{102} resonator in the case of both unsaturated samples and samples characterized by the saturation of EPR signals. A cylindrical ceramic DI with a through-hole along the cylinder axis (the outer radius R = 2.85 mm, the inner radius r = 0.75 mm, and the height h = 1.85 mm) made it possible to enhance the EPR signal for the $MnCl_2$ and MgO : Mn samples. The gain factor is about 9 for the unsaturated sample ($MnCl_2$) and about 1.5 for the saturated one(MgO : Mn).

The work was sponsored in the framework of the target program of basic research of the National

Academy of Sciences of Ukraine "Development of new dielectric microwave materials for resonators that will increase the sensitivity of EPR instruments and the creation on their basis of a mini-EPR analyzer for express analysis in medicine and environmental monitoring" (reg. No. 0120U102727 and No. 0118U002317).

1. G.R. Eaton, S.S. Eaton, D.P. Barr, R.T. Weber. *Quantitative EPR: A Practitioner's Guide* (Springer, 2010) [ISBN: 978-3-211-9294-76].
2. V.I. Chizhik, Y.S. Chernyshev, A.V. Donets, V. Frolov, A. Komolkin, M.G. Shelyapina. *Magnetic Resonance and Its Applications* (Springer, 2014) [ISBN: 978-3-319-05298-4].
3. I. Golovina, B. Shanina, S. Kolesnik, I. Geifman, A. Andriiko. Magnetic defects in $KTaO_3$ and $KTaO_3:Fe$ nanopowders. *Phys. Status Solidi B* **249**, 2263 (2012).
4. F. Muller, M.A. Hopkins, N. Coron, M. Grynberg, L.C. Brunel, G. Martinez. A high magnetic field EPR spectrometer. *Rev. Sci. Instrum.* **60**, 3681 (1989).
5. Ch.P. Poole Jr. *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques* (Dover, 1997) [ISBN: 978-5-94836-220-5].
6. G.A. Rinard, R.W. Quine, J.R. Harbridge, R. Song, G.R. Eaton, S.S. Eaton. Frequency dependence of EPR signal-to-noise. *J. Magn. Reson.* **140**, 218 (1999).
7. V.E. Galtsev, E.V. Galtseva, O.Y. Grinberg, Y.S. Lebedev. Human tooth EPR dosimetry with enhanced sensitivity. *J. Radioanal. Nucl. Chem.* **186**, 35 (1994).
8. Y. Deng, R.P. Pandian, R. Ahmad, P. Kuppusamy, J.L. Zweier. Application of magnetic field over-modulation for improved EPR linewidth measurements using probes with Lorentzian lineshape. *J. Magn. Reson.* **181**, 254 (2006).
9. I.N. Geifman, I.S. Golovina, V.I. Kofman, E.R. Zusmanov. The use of ferroelectric material for increasing the sensitivity of EPR spectrometers. *Ferroelectrics* **234**, 81 (1999).
10. I.N. Geifman, I.S. Golovina, E.R. Zusmanov, V.I. Kofman. Raising the sensitivity of the electron-paramagnetic-resonance spectrometer using a ferroelectric resonator. *Techn. Phys.* **45**, 263 (2000).
11. I. Geifman, I.S. Golovina. Electromagnetic characterization of rectangular ferroelectric resonators. *J. Magn. Reson.* **174**, 292 (2005).
12. R.R. Mett, J.W. Sidabras, I.S. Golovina, J.S. Hyde. Dielectric microwave resonators in TE_{011} cavities for electron paramagnetic resonance spectroscopy. *Rev. Sci. Instrum.* **79**, 094702 (2008).
13. J.S. Hyde, R.R. Mett. EPR uniform field signal enhancement by dielectric tubes in cavities. *Appl. Magn. Reson.* **48**, 1185 (2017).
14. I.S. Golovina, I.N. Geifman, V.E. Rodionov. *Dielectric Resonators for EPR Spectroscopy* (V.E. Lashkarev Institute of Semiconductor Physics, 2015) (in Russian) [ISBN: 978-966-02-7675-8].
15. R. Biehl. The dielectric ring TE_{011} cavity. *Bruker Report* No. 1, 45 (1986).
16. A. Blank, E. Stavitski, H. Levanon, F. Gubaydullin. Transparent miniature dielectric resonator for electron paramagnetic resonance experiments. *Rev. Sci. Instrum.* **74**, 2853 (2003).
17. I.N. Geifman, I.S. Golovina. Magnetic resonance spectrometer. US Patent No. 7,268,549 B2. Issued Sept. 11, 2007.
18. A. Munir, Z.M. Khan. Microstructure and microwave dielectric properties of $BaTi_4O_9$ ceramics derived from a sol-gel precursor. *Adv. Mater. Res.* **326**, 127 (2011).
19. X. Huang, Y. Song, F. Wang. Microwave dielectric properties of $BaTi_4O_9$–$BaSm_2Ti_4O_{12}$ composite ceramics. *J. Ceram. Soc. Japan* **121,** 880 (2013).
20. A. Belous, O. Ovchar, D. Durilin, M. Macek-Krzmanc, M. Valant. The homogeneity range and the microwave dielectric properties of the $BaZn_2Ti_4O_{11}$ ceramics. *J. Eur. Ceram. Soc.* **26**, 3733 (2006).
21. M.E. Ilchenko, V.F. Vzyatyshev, L.G. Gassanov *et al. Dielectric Resonators* (Radio i Svyaz', 1989) (in Russian) [ISBN: 5256002171, 9785256002176].
22. V.N. Syryamina, A.G. Matveeva, Y.V. Vasiliev, A. Savitsky, Y.A. Grishin. Improving B_1 field homogeneity in dielectric tube resonators for EPR spectroscopy via controlled shaping of the dielectric insert. *J. Magn. Reson.* **311**, 32 (2020).

Received 01.07.20.
Translated from Ukrainian by O.I. Voitenko

С.В. Лемішко, І.П. Ворона,
І.С. Головіна, В.О. Юхимчук, С.М. Окулов,
В.В. Носенко, С.О. Солопан, А.Г. Білоус

РОЗРОБКА ТА ХАРАКТЕРИЗАЦІЯ КЕРАМІЧНИХ ВСТАВОК В МЕТАЛЕВІ РЕЗОНАТОРИ ЕПР СПЕКТРОМЕТРІВ ДЛЯ ПІДВИЩЕННЯ ЇХ ЧУТЛИВОСТІ

На основі кераміки легованого тетратитанату барію ($BaTi_4O_9 + 8{,}5\%$ ZnO) з діелектричною сталою $\varepsilon = 36$ і низькими діелектричними втратами ($\operatorname{tg}\delta \approx 1{,}887 \cdot 10^{-4}$) у діапазоні частот 9–10 ГГц розроблено діелектричні вставки циліндричної форми та певних розмірів в стандартний металевий ЕПР спектрометр. Встановлено, що їх використання дозволяє підсилити сигнал ЕПР за рахунок перерозподілу НВЧ поля всередині стандартного прямокутного TE_{102} резонатора як у випадку зразків, що не насичуються, так і зразків, для яких характерне насичення сигналів ЕПР. Зокрема, для тестових зразків $MnCl_2$, що не насичуються, отримано підсилення в 9 разів, а для тестових зразків, що насичуються ($MgO:Mn$), приблизно в 1,5 рази.

Ключові слова: ЕПР спектроскопія, діелектричні резонатори, чутливість ЕПР, тетратитанат барію.