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**PECULIARITIES IN DIELECTRIC  
AND MAGNETIC-RESONANCE CHARACTERISTICS  
OF NANOCRYSTALLINE POTASSIUM TANTALATE****I.S. GOLOVINA,<sup>1</sup> I.N. GEIFMAN,<sup>2</sup> N.M. PROKOPIV<sup>3</sup>**<sup>1</sup>**V. Lashkaryov Institute of Semiconductor Physics, Nat. Acad. of Sci. of Ukraine**  
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A broad peak independent of the measurement frequency has been detected in the temperature dependence of the dielectric constant of nanocrystalline potassium tantalate in the temperature interval  $20\text{ K} < T < 40\text{ K}$ . The observed maximum was supposed to be associated with a ferroelectric phase transition at the Curie temperature  $T_c = 29 \pm 2\text{ K}$ . The dielectric constant was determined to obey the Curie–Weiss law, and the corresponding Curie–Weiss constant was obtained to equal  $C = (2.5 \pm 1) \times 10^3\text{ K}$ . An unknown impurity, which locally destroys the cubic symmetry of the lattice and gives rise to the formation of polar microregions, was supposed to be responsible for the phase transition. Two types of EPR spectra were revealed. A probable application of the new material has been discussed.

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**1. Introduction**

Potassium tantalate ( $\text{KTaO}_3$ ) proved itself well as a material for fabricating microwave dielectric resonators used at fixed temperatures, which considerably enhance the sensitivity of electron paramagnetic resonance (EPR) spectrometers [1–5]. The efficiency of this material is associated with its high dielectric permittivity ( $\epsilon = 261$  at  $300\text{ K}$ ) and low dielectric losses ( $\tan \delta = 0.001$  at  $300\text{ K}$ ).  $\text{KTaO}_3$  by its structure (the spatial group  $O_h^1$ ) belongs to the perovskite class. It is a virtual ferroelectric, and its symmetry remains cubic down to the zero temperature [6]. The dielectric permittivity of single-crystalline potassium tantalate monotonously grows as the temperature decreases and reaches a value of  $4 \times 10^3$  at  $T = 4.2\text{ K}$  [7]. Since the size of a dielectric resonator

is determined straightforwardly by the magnitude of dielectric permittivity of the substance – namely, the size is reciprocal to  $\epsilon^{1/2}$  – the abrupt dependence  $\epsilon(T)$  does not allow a resonator developed, e.g., for room temperature, to be used in EPR experiments carried out at liquid nitrogen temperature, for instance ( $\epsilon \approx 800$  at  $T = 77\text{ K}$ ).

Recently, a new technology of the potassium tantalate synthesis by oxidizing a metal tantalum powder with the use of melted potassium nitrate with potassium hydroxide additives has been developed [8]. This method was found to enable a nanodispersed powder with the average crystal dimension of  $80\text{ nm}$  to be fabricated. It is known that ceramic specimens have, in general, a lower dielectric permittivity in comparison with that for the corresponding single-crystal state. Therefore, our task was to find which dielectric properties are inherent to ceramics fabricated from a potassium tantalate nanocrystalline powder and whether this ceramics is promising for manufacturing dielectric resonators, which could be applied to enhance the sensitivity of the EPR method at low temperatures, in particular, at  $77\text{ K}$ . In addition, in this work, we registered and analyzed EPR spectra in order to determine the presence of impurities in both powder and ceramic specimens.

**2. Research Technique**

A detailed description of the procedure of synthesis of specimens was given in work [8].

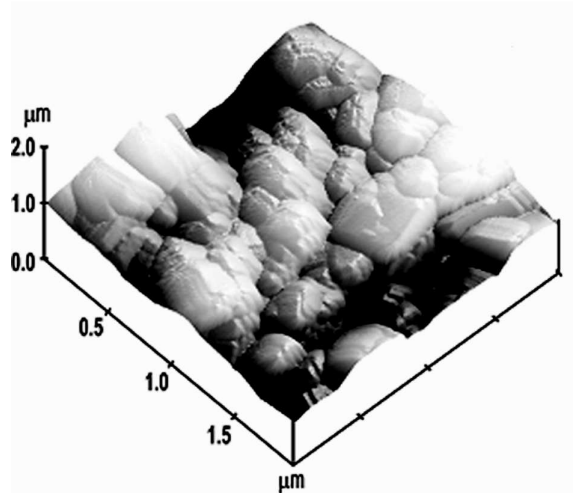


Fig. 1. AFM pattern of the unpolished surface of a ceramic specimen

The composition of synthesized products was studied using the X-ray phase analysis method on a DRON-3M diffractometer and applying  $\text{Cu}_{K\alpha}$  radiation. It was found that a pure cubic phase of  $\text{KTaO}_3$  with the lattice parameter  $a = 3.988 \text{ \AA}$  is formed. The crystallite dimensions were estimated by analyzing diffraction patterns according to the Debye-Scherrer formula

$$d = \frac{0,9\lambda}{B \cos \Theta}, \quad (1)$$

where  $\lambda = 0.1542 \text{ nm}$  is the wavelength of X-ray radiation,  $B$  is the halfwidth of the diffraction maximum measured in terms of radians, and  $\Theta$  is an angle that corresponds to the position of a diffraction line in the X-ray pattern.

Powders with various particle dispersion degrees were selected to study: 70 (powder 1), 80 (powder 2), and 90 nm (powder 3). Ceramic specimens were fabricated in the form of cylindrical pellets 5 mm in diameter and 1–2 mm in thickness by compressing each powder to pressures of 245, 345, and 490 MPa at room temperature. Each of three powders was divided into two parts: alcohol was added to one of them before compressing to form a pasty mixture, and the other was pressed without adding alcohol. The pressed pellets were sintered for 2 h at a temperature of 1250 °C.

The surface morphology of ceramic specimens (the dimensions and the shape of crystallites) was determined making use of a NanoScope IIIa Dimension 3000™ (Digital Instruments, USA) atomic force microscope (AFM).

For dielectric measurements, a silver paste was burning onto the parallel surfaces of pellets at a temperature of 500 °C.

The dielectric permittivity and the dielectric losses of specimens were measured with the help of an LCR E7-20 digital measuring instrument in a wide frequency range from 25 Hz to 1 MHz and in the temperature interval  $4.2 \text{ K} < T < 300 \text{ K}$ .

EPR spectra were registered on a Radiopan SE/X 2544 spectrometer in the 3-cm wavelength range and at a temperature of 300 K.

### 3. Experimental Results and Their Discussion

The results of porosity measurements for ceramic specimens fabricated from powders 1, 2, and 3, which were compressed to the pressures  $P = 245$  and 345 MPa, are presented in Table. Pellets prepared from powders 1 and 3 and compressed under the pressure  $P = 490$  MPa fell apart after being sintered. Pellets fabricated from powder 2 and compressed under the pressure  $P = 490$  MPa were stratified just after being pressed. Analyzing the data presented in Table, a conclusion can be drawn that a pressure of 245 MPa and an addition of a small amount of alcohol to the powder before their compressing are the best conditions to obtain ceramics with the lowest porosity. Since all pressed specimens were sintered at the same temperature and were kept at this temperature within the same time interval, the influence of the mentioned factors was not studied.

For further researches, we selected a specimen with the lowest porosity. It was a ceramic specimen fabricated from powder 3. The surface morphology of the selected ceramic specimen was analyzed making use of an AFM. The obtained results are exhibited in Fig. 1. Cubic-shaped agglomerates formed according to the crystal symmetry were observed on the unpolished surface of the specimen. The agglomerates consisted of crystallites 100–500 nm in dimension. The absence of a liquid phase during the sintering was confirmed by pronounced facets of crystallites.

The temperature dependences of the dielectric permittivity  $\epsilon$ , which were measured at frequencies of 25 Hz, 1 kHz, 100 kHz, and 1 MHz, are depicted in Fig. 2. Dielectric losses ( $\tan \delta$ ) were measured together with the

#### Porosity of ceramic specimens fabricated from powders 1, 2, and 3

Powder No.	$P = 245 \text{ MPa}$		$P = 345 \text{ MPa}$	
	With alcohol	Without alcohol	With alcohol	Without alcohol
1	55%	58%	62%	67%
2	32%	36%	46%	54%
3	22%	28%	48%	52%

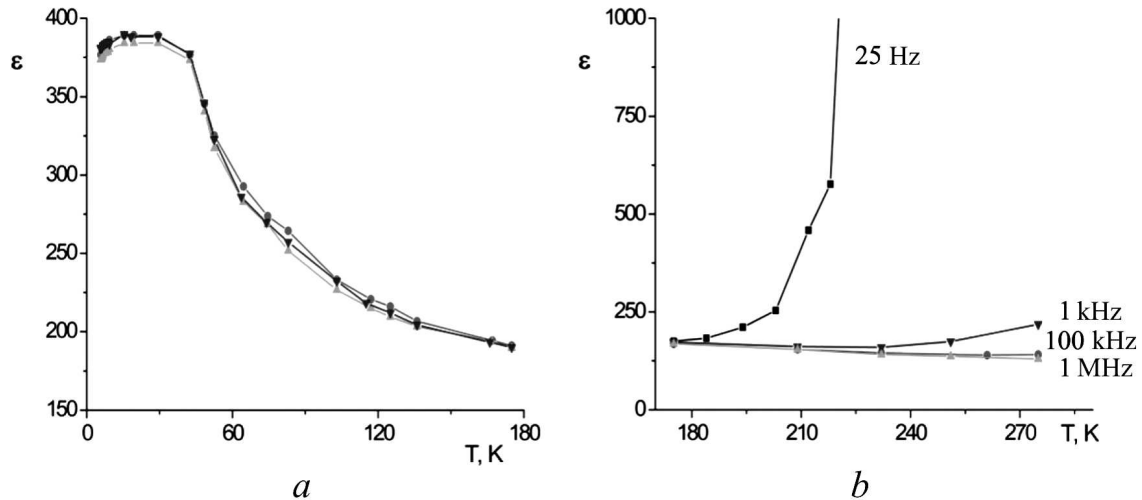


Fig. 2. Temperature dependences of the dielectric permittivity  $\varepsilon$  of a ceramic  $\text{KTaO}_3$  specimen obtained at frequencies of 25 Hz (squares), 1 kHz (nablas), 100 kHz (circles), and 1 MHz (deltas) in the temperature intervals 4.2–180 K (a) and 180–290 K (b)

dielectric permittivity  $\varepsilon$ . In the temperature interval  $20 \text{ K} < T < 180 \text{ K}$ , they practically did not change and amounted to  $\tan \delta = 0.025$  at frequencies 1 and 100 kHz and to  $\tan \delta = 0.02$  at a frequency of 1 MHz. In the interval  $10 \text{ K} < T < 20 \text{ K}$ , a small increase of losses to  $\tan \delta = 0.03$  was observed at frequencies of 1 and 100 kHz and to  $\tan \delta = 0.025$  at a frequency of 1 MHz.

As Fig. 2 demonstrates, there exists a strong frequency dependence of  $\varepsilon$  in the frequency interval 25 Hz–1 kHz and at  $T > 180 \text{ K}$ , whereas it is practically absent at  $T < 180 \text{ K}$ . This dependence may most probably be associated with a substantial increase of the conductivity in the high-temperature interval [8,9]. In the interval 20–30 K, the dielectric permittivity has a broad maximum with the peak value  $\varepsilon = 390 \div 400$ . This maximum drew our attention, because it is absent for single-crystalline potassium tantalate [7]. It is known that a maximum in the temperature dependence of the dielectric permittivity can evidence a phase transition (PT) or the presence of impurities (or intrinsic defects) that induce the polarization relaxation.

Let us examine the former probable reason of the maximum emergence. It is known that a ferroelectric PT can be induced by such external factors as an electric field, doping, or pressure. In the production of a ceramics, the initial powder was compressed by applying a considerable pressure, which may result in a PT. For instance, the authors of work [10] showed that a pressure of 525 MPa gives rise to the occurrence of a PT in a  $\text{KTaO}_3$  crystal at 2 K. In addition, the dimensional effects affect the temperature of the ferroelectric PT, which is referred to as the Curie temperature,  $T_c$ . In particular, calcula-

tions in work [11], which were made in the framework of the Landau–Ginzburg–Devonshire theory, testified that a long-range ferroelectric ordering can appear in potassium tantalate in the nano-range ( $< 100 \text{ nm}$ ). In this case, the Curie temperature elevates from  $T_c = 20 \text{ K}$  for particles 80–90 nm in dimension to  $T_c = 300 \text{ K}$  for 7-nm particles, provided that the coefficient of particle deformation  $\mu = 40 \text{ N/m}$ . In addition to the pure ferroelectric PT, a transition into the dipole glass state can also take place in potassium tantalate. The PT of such a type occurs, e.g., when this substance is doped with a small amount of lithium or niobium [12, 13]. Anyway, for the presence of a PT in our ceramic specimen and its type to be established experimentally, special researches of the polarization and the soft mode dynamics in the low-temperature interval (at  $4.2 \text{ K} < T < 30 \text{ K}$ ) are to be carried out, which may become the aim of our next work.

Concerning the latter reason for the appearance of a maximum, it is known that the relaxation polarization usually manifests itself in the frequency dependence of  $\varepsilon(T)$ , at which the  $\varepsilon$ -maximum decreases and shifts toward higher temperatures as the frequency grows. For instance, in work [14], the frequency dependence of the dielectric permittivity was observed for ceramic specimens of strontium titanate doped with lanthanum. Moreover, in work [15], the dielectric relaxation was detected in strontium titanate ceramics doped with vanadium. Since strontium titanate is also a virtual ferroelectric, which is similar to potassium tantalate by a good many of their properties, the authors of work [16] accepted on the basis of cited works that the ceramic

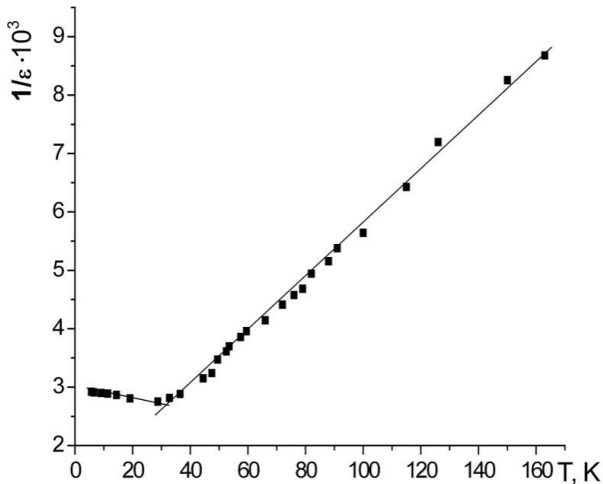


Fig. 3. Temperature dependence of the reciprocal dielectric permittivity,  $1/\varepsilon$

specimens of potassium tantalate also contain impurities (for example, vanadium ones) which are responsible for the appearance of a maximum in the dependence  $\varepsilon(T)$ , as well as characteristic features in the behavior of the polarization. As for our specimen, our measurements of the dielectric permittivity did not reveal any substantial dependence on the frequency at  $T < 180$  K (Fig. 2). Therefore, we may assert that this fact evidences the absence of the relaxation polarization, as well as the realization of the dipole glass state in the given substance.

When considering only the temperature interval  $T < 180$  K, where the conductivity is not a key factor, we obtained the dependence  $1/\varepsilon = f(T)$  (see Fig. 3). Figure 3 makes it evident that the dielectric permittivity obeys the Curie-Weiss law expressed in the form  $\varepsilon = \varepsilon_b + C(T - T_c)^{-1}$ , where  $\varepsilon_b = 125 \pm 10$  is the background permittivity of the lattice at  $T \rightarrow \infty$ , the Curie temperature  $T_c = (29 \pm 2)$  K, and the Curie-Weiss constant  $C = (2.5 \pm 1) \times 10^3$  K. Note that, in potassium tantalate single crystals, the background permittivity of the lattice  $\varepsilon_b = 48$ , and the Curie-Weiss constant  $C = 5 \times 10^4$  K [6].

It should be noticed that the data depicted in Fig. 2 correspond to a composite; namely,  $\text{KTaO}_3$  crystallites with a high dielectric permittivity are separated by pores with a low dielectric constant. This means that we measured the dielectric constant of a ceramic specimen changed by the contribution from the pores. To estimate the dielectric constant of the substance itself, without the pore contribution, we can use a technique expounded in work [17]. According to this technique, pores are considered as random inclusions with  $\varepsilon_2 = 1$  into a highly

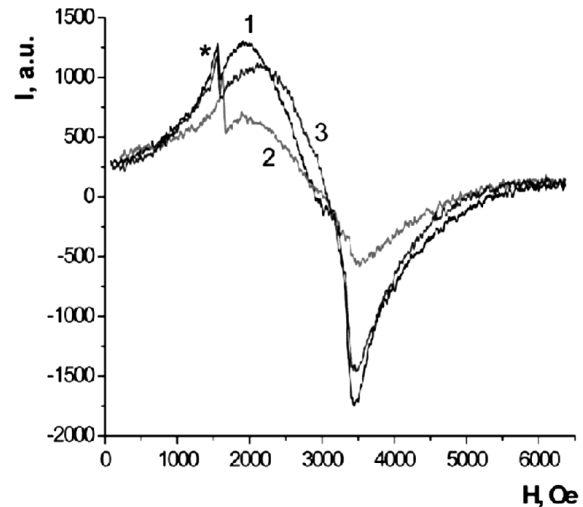


Fig. 4. EPR spectra registered for powders 1 (1), 2 (2), and 3 at the frequency  $\nu = 9386$  MHz

polarized matrix with  $\varepsilon_1$ , so that  $\varepsilon_1 \gg \varepsilon_2$ . In this case, the dielectric permittivity of the composite is determined as  $\varepsilon_m \approx \varepsilon_1(1 - 1.5V_2)$ , where  $V_2$  is the pore volume. For our ceramic specimen with the lowest porosity,  $V_2 \approx 0.2$ . Therefore, we obtain  $\varepsilon_1 \approx 557$  at  $T = 29$  K.

Figure 4 demonstrates the EPR spectra registered for all powders: 1, 2, and 3. All spectra were recorded under identical conditions: a power of incident MW radiation of 10 mW, a modulation of 2.5 Oe, and a gain factor of  $4 \times 10^4$ . However, the powder masses were different: 69.3 mg for powder 1, 46.2 mg for powder 2, and 50.5 mg for powder 3. As is seen from Fig. 4, the spectra are qualitatively identical for all powders and include a very broad asymmetric line. The asterisk (\*) in Fig. 4 marks the line produced by the material of a test tube, in which the experiment was made. The broad powder line has no angular dependence.

To verify the appearance of the registered EPR signal, we studied reactants used at the synthesis of powders, namely, tantalum powder (Ta), potassium nitrate ( $\text{KNO}_3$ ), and potassium hydroxide (KOH). No EPR signals were registered for KOH. Tantalum and potassium nitrate powders produce EPR signals depicted in Fig. 5. The recording conditions were identical: an MW power of 10 mW, a modulation of 3.2 Oe, and a gain factor of  $1 \times 10^5$ .

EPR spectra were also registered for a ceramic specimen fabricated from powder 3 (Fig. 6). The spectra were recorded at two orientations of a ceramic pellet with respect to a constant magnetic field,  $\mathbf{H}$ , and under identical recording conditions: an MW power of 10 mW, a modulation of 2.5 Oe, and a gain factor of  $4 \times 10^3$ . As is

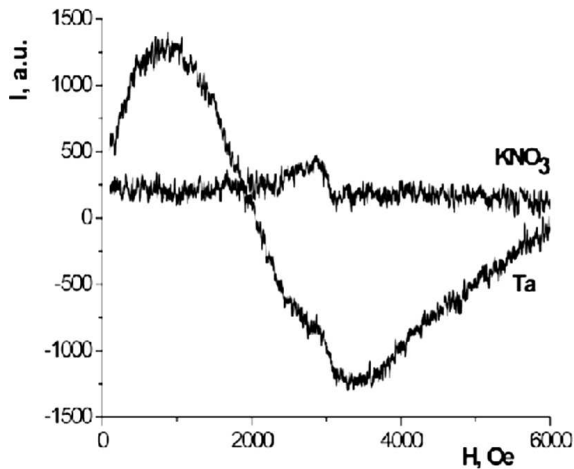


Fig. 5. EPR spectra of Ta and  $\text{KNO}_3$  powders recorded at the frequencies  $\nu = 9391$  MHz (Ta) and 9380 MHz ( $\text{KNO}_3$ )

seen from Fig. 6, the spectrum of the ceramic specimen is also a broad asymmetric line, but with a pronounced angular dependence. At the magnetic field orientation perpendicularly to the pressure,  $\mathbf{P}$ , direction at compressing, i.e. at  $\mathbf{H} \perp \mathbf{P}$ , the linewidth was 1660 Oe. If the field was oriented along the pressure direction, i.e. at  $\mathbf{H} \parallel \mathbf{P}$ , the linewidth was a little smaller and amounted to about 1350 Oe. In addition, the line shape changed at the rotation, and the maximum and the minimum became shifted by different magnitudes. In particular, the line maximum became shifted by 460 Oe, whereas the line minimum by only 190 Oe. This shift difference may testify to the presence of several signals of different nature in the spectrum.

In order to verify this assumption, we resolved the experimental spectrum obtained for powder specimen 3 making use of the Magic Plot computer software package. The result of calculations is shown in Fig. 7, from which it becomes evident that the spectrum consists of 6 signals. The unambiguity of resolution was checked by the achievement of a minimum error (resolutions using different numbers of signals and other signal shapes resulted in an error increment). The signals marked in Fig. 7 as I had the width  $\Delta H_{\text{pp}} = 1100$  Oe (at  $H_{\text{res}} = 2620$  Oe) and  $\Delta H_{\text{pp}} = 600$  Oe (at  $H_{\text{res}} = 3060$  Oe). The signal marked as II had the width  $\Delta H_{\text{pp}} = 260$  Oe (at  $H_{\text{res}} = 3300$  Oe). Three other signals with small intensities had the widths ranging from 60 to 90 Oe. All the lines have the Lorentzian shape. Notice that the widest signal with  $\Delta H_{\text{pp}} = 1100$  Oe, being observed in a substantially lower field (in comparison with  $g = 2.0023$ ), had the integrated intensity 5 times as large as that for the signal with  $\Delta H_{\text{pp}} = 600$  Oe and 10 times as large as

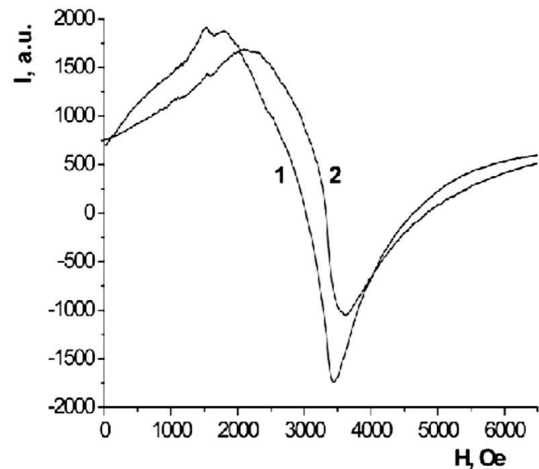


Fig. 6. EPR spectra of a ceramic specimen registered at a temperature of 300 K, the frequency  $\nu = 9385$  MHz, and two orientations of a ceramic pellet with respect to the direction of a constant magnetic field  $\mathbf{H}$ : (1)  $\mathbf{H} \perp \mathbf{P}$  and (2)  $\mathbf{H} \parallel \mathbf{P}$ , where  $\mathbf{P}$  is the pressure direction at compressing

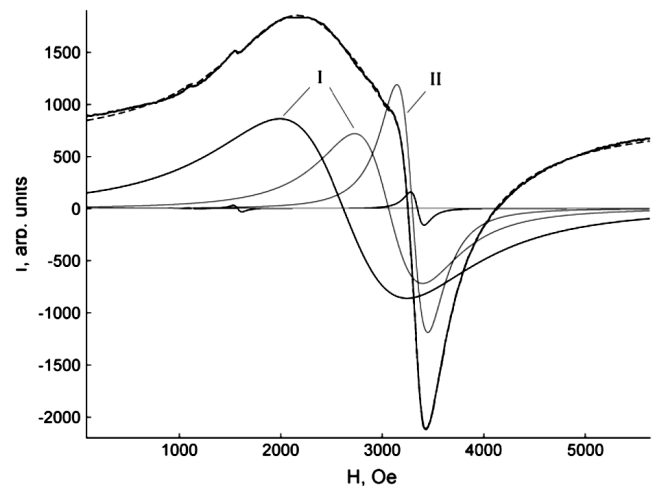


Fig. 7. Resolution of the experimental spectrum of powder 3 registered at a temperature of 300 K and the frequency  $\nu = 9367$  MHz

those for other signals. This combination of properties testifies that the given signal differs from the others by its nature. Usually, such properties are typical of signals associated with ferromagnetic absorption. The signal with  $\Delta H_{\text{pp}} = 600$  Oe also had a considerably larger integrated intensity than ordinary EPR signals and can represent a signal obtained from superparamagnetic nanoclusters. The other signals had no such features and represent ordinary EPR signals from individual paramagnetic centers.

The following experiment can be a confirmation of the fact that ferromagnetic inclusions are available in our

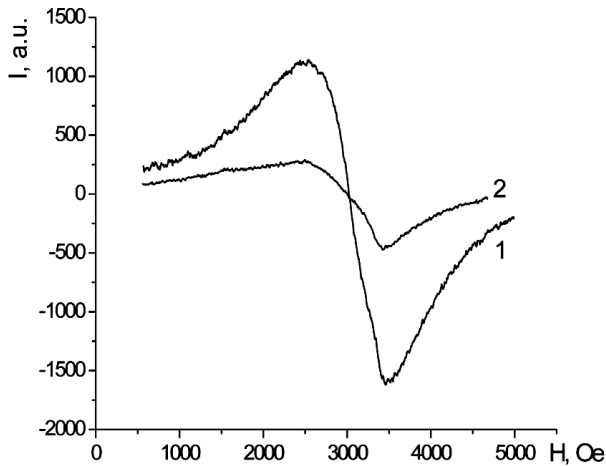


Fig. 8. EPR spectra of  $\text{KTaO}_3$  nanopowders synthesized using metallic Ta (spectrum 1) and  $\text{Ta}_2\text{O}_5$  oxide (spectrum 2) recorded under identical conditions and at the frequency  $\nu = 9354$  MHz

substance. A  $\text{KTaO}_3$  powder was mixed with paraffin and put into a quartz ampoule. First, a spectrum was registered at  $T = 300$  K, which had no angular dependence. Then the ampoule with the mixture was heated up to  $T = 380$  K and embedded into a constant magnetic field of about 0.65 T. Afterward, the ampoule was cooled down to  $T = 300$  K, and a spectrum was also registered; in this case, it turned out anisotropic. The magnetic anisotropy manifested itself with respect to the magnetization direction. The subsequent heating and the cooling of the ampoule together with a remagnetization of the specimen in the other direction gave rise to a corresponding change of the spectrum anisotropy direction.

A qualitative comparison between the spectra of a  $\text{KTaO}_3$  powder and a ceramic specimen, on the one hand, and the spectra of Ta and  $\text{KNO}_3$  reactants, on the other hand, allowed us to assume that the signals from the synthesized products include the signals from centers in reactants as well. A quantitative comparison of the integrated signal intensities in powder 3 (Fig. 4) and a Ta powder (Fig. 5) with a signal obtained from the reference specimen with a known number of spins, together with the account of powder masses, testifies that magnetic inclusions in a Ta powder can contribute to the spectrum of powder 3, with the corresponding contribution being about 60–70%. This means that the remaining 30–40% of magnetic inclusions are formed in a  $\text{KTaO}_3$  powder in the course of synthesis.

Iron is known to be an uncontrollable impurity, which is registered most frequently by the EPR method in nominally pure potassium tantalate single crystals. Usually,

these are individual  $\text{Fe}^{3+}$  or  $\text{Fe}^+$  ions, which substitute  $\text{Ta}^{5+}$  or  $\text{K}^+$  ions in the lattice. The EPR spectra of these centers include lines 50–90 Oe in width characterized by various symmetry types, from cubic to rhombic one. Therefore, our assumption consists in that iron is also present in nanocrystalline potassium tantalate. However, in contrast to a single crystal, iron ions interact with one another in a nano-sized powder. Hence, we may suppose that signals I reflect the presence of magnetic inclusions (clusters) of various dimensions, whereas three narrow signals with low intensities can be associated with the presence of individual (not aggregated into clusters) paramagnetic (probably, iron) ions in the substance. Concerning the nature of signal II, the authors have no hypothesis for this moment.

For nanocrystalline potassium tantalate to be used as a material to fabricate resonators, the requirement must be satisfied that there must be no intrinsic EPR signals. To meet this condition and to check that a part of the spectrum is formed by centers that appear during the synthesis, we synthesized a specimen with the use of  $\text{Ta}_2\text{O}_5$  oxide with a very-high-purity specification rather than metallic Ta. Note that no signals were detected in the EPR spectrum of  $\text{Ta}_2\text{O}_5$  oxide at 300 K. However, a wide asymmetric line was registered for the synthesized powder (Fig. 8, spectrum 2), whose integrated intensity, taking the powder mass into account, is almost one third as high as that for the powder synthesized with the use of metallic Ta (Fig. 8, spectrum 1). This fact confirms our estimate given above that 30–40% of paramagnetic centers are formed in the course of synthesis.

Our microanalysis by the procedure described in work [18] showed that an undoped  $\text{KTaO}_3$  powder includes iron and nickel as magnetic elements, the contents of which are about 0.04 and 0.008 mol.%, respectively. Hence, a conclusion can be drawn that the EPR spectrum for a nanocrystalline  $\text{KTaO}_3$  powder includes signals of two types. We supposed that they are generated by an uncontrollable magnetic impurity. For the nature of registered spectra to be established more exactly, we carried out additional researches concerning the influence that the temperature and various environments (oxygen, hydrogen, helium) exert on the EPR spectrum [18].

We used the values obtained in this work for the dielectric permittivity of and the dielectric losses in  $\text{KTaO}_3$  ceramics in computer-assisted calculations by the Ansoft High Frequency Structure Simulator software program (HFSS version 10.0, Ansoft Corporation, Pittsburgh, PA, USA). The preliminary results testify to a possibility of using the material concerned for manufac-

turing resonators in the 3-cm wavelength range. Every of those resonators can be applied at that or another fixed low temperature, e.g., a resonator for measurements at a temperature of either liquid nitrogen ( $T = 77$  K) or liquid helium ( $T = 4.2$  K). However, if such resonators are used to increase the EPR method sensitivity, the purest reactants must be used, and the cleanness of the equipment for synthesis – e.g., a crucible – must be checked to prevent the appearance of intrinsic signals.

#### 4. Conclusions

A broad maximum in the interval  $20 \text{ K} < T < 40 \text{ K}$  was detected in the temperature dependence of the dielectric permittivity measured for a ceramic specimen of nanocrystalline  $\text{KTaO}_3$ . This maximum was found to shift toward high temperatures, if the measurement frequency grew from 25 Hz to 1 MHz. An assumption was made that this fact testifies to the occurring of a ferroelectric phase transition with the Curie temperature  $T_c = 29 \pm 2$  K. The dielectric permittivity was found to follows the Curie–Weiss law, and the corresponding Curie–Weiss constant  $C = (2.5 \pm 1) \times 10^3$  K was determined. Since the results of AFM analysis showed that the dimensions of crystallites in a ceramic specimen (250–300 nm) exceeded 100 nm, the size effects are hardly to induce the phase transition. The latter should be considered as a result of the self-manifestation of uncontrollable impurities, which destroy the highly symmetric cubic lattice and lead to the appearance of polar microregions.

Signals of two types were revealed in the studied EPR spectra. We consider that the latter are formed by uncontrollable impurities – hypothetically, Fe ions – which are contained in the  $\text{KTaO}_3$  lattice as both individual (noninteracting) ions and, probably, ions that form clusters, in which they interact with one another.

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#### ОСОБЛИВОСТІ ДІЕЛЕКТРИЧНИХ І МАГНІТНО-РЕЗОНАНСНИХ ХАРАКТЕРИСТИК НАНОКРИСТАЛІЧНОГО ТАНТАЛАТУ КАЛІЮ

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#### Резюме

У температурній залежності діелектричної проникності нанокристалічного танталату калію виявлено широкий максимум у інтервалі  $20 < T < 40$  К, який не залежить від частоти вимірювань. Припускається, що даний максимум свідчить про наявність сегнетоелектричного фазового переходу із температурою Кюрі  $T_c = 29 \pm 2$  К. Встановлено, що діелектрична проникність підпорядковується закону Кюрі–Вейса, і визначено сталу Кюрі–Вейса  $C = (2,5 \pm 1) \cdot 10^3$  К. Причиною фазового переходу вважається наявність неідентифікованої домішки, яка локально порушує кубічну симетрію ґратки і приводить до появи полярних мікрообластей. У спектрах ЕПР виявлено два типи ліній. Обговорено можливе застосування нового матеріалу.