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Microwave Absorption of Electromagnetic Radiation by Ferroelectric Complex Nb Oxides.

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ABSTRACT

In the presented paper solid solutions of complex Nb oxide systems (1-x)$NaNbO_3$ – $xCa_2Nb_2O_7$ and (1-x) $NaNbO_3$ – $xSr_2Nb_2O_7$ were produced using two-stage solid-phase synthesis with the following sintering by means of the regular ceramics technology; their dissipative characteristics were studied in the frequency range of (1.0 ÷ 11.0) GHz. It was demonstrated that the maximum values of microwave power absorption in systems of solid solutions, which contain phase transitions of various nature, are observed, generally, at phase boundaries. The paper suggests that, presumably, that phenomenon is related to the development of defect situation in corresponding media due to opening of chemical bonds during rearrangement of structure, accumulation of vacations and impurity phases and increase of number of interphase boundaries. The study revealed the features of dielectric properties of the discussed solid solutions. It was concluded that it is possible to use the obtained results for the development of new functional materials, which can be applied in various branches of industry using microwave technologies, in particular, for solution of problems of electromagnetic compatibility of radioelectronic systems, as well as for development of components of electronic devices, including IC technology.

Keywords: Microwave Absorption, Dissipative Characteristics, Nb Oxides, Crystalline Structures.

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INTRODUCTION

Nowadays, development and operation of radio-technical microwave systems lead to appearance of problems related with electromagnetic compatibility. Long-term and regular influence of microwave radiation on human body negatively affects brain, blood vessels, blood, vision and provokes formation of tumors. Therefore it is important provide safe level of radiation and comply with requirements of sanitation safety codes, in order to prevent negative influence of that kind of devices on human health.

Effective way to meet requirements of electromagnetic ecology and compatibility of radioelectronic systems is application of screening and radiowave-absorbing materials (RAM) and coatings (RAC). RAC can be used for protection of computer information processing systems from unauthorized access, space engineering, for absorption of electromagnetic radiation (EMR) in screening devices, absorbing coverings and housings, as well as in anechoic measurement chambers [1].

Another important factor for effective operation of engineering devices is the problem of noise reduction. In many cases it is necessary to localize fields, which are generated by microwave energy emitters, in order to exclude or attenuate their influence on adjacent sensitive elements of radio equipment. Parasite reflections and interference of electromagnetic waves also can be source of serious noise [2].

The paper presents continuation and development of the previous studies of microwaves: absorption of electromagnetic radiation by complex oxides and their solid solutions (SS) of various composition with special electrical and magnetic properties [3-5]. The goal of the presented study is to identify mechanisms of formation of dissipation properties of several electrically active materials, in particular, character of change of frequency in the range (1.0-11.0) GHz, as well as to evaluate irregularity of frequency characteristics of loses, which can limit acceptability of the mentioned materials at high frequencies in wide band devices.

OBJECTS, METHODS OF PRODUCTION AND STUDY OF SPECIMENS

Objects of study are SS of binary systems (1-x)$NaNbO_3$ – x$Ca_2Nb_2O_7$ и (1-x) $NaNbO_3$ – x$Sr_2Nb_2O_7$, in which $NaNbO_3$ – antiferroelectric perovskite-type structures, element cell (at room temperature) is rhombic and space group is Pbma. $Ca_2Nb_2O_7$, $Sr_2Nb_2O_7$ is ferroelectrics with lamellar perovskite-type structure, which belong to homologous series with common chemical formula $A_nB_nO_{3n+2}$ (n-thickness of perovskite layer, which is equal to number of BO6 octahedrons), elemental cells are rhombic and space group is C_{mc21}. Interest to study of the mentioned systems is related to non-isostructurality of its boundary components, and, therefore, it is possible to form phases with unique electrical properties, as well as with high Curie temperature of boundary components of the systems (1580 °C).

SS are obtained by means of repeated synthesis with temperatures of T_1 = (850-980) °C (depending on composition), T_2 = (900-1200) °C (depending on composition) and duration of exposure $\tau_1 = \tau_2$ = 4 hours with the following sintering using regular ceramic technology with temperatures, which are gradually increasing from 1260 °C for $NaNbO_3$ and to 1400 °C for $Ca_2(Sr_2)Nb_2O_7$. In further all ceramic workpieces were cut and polished in order to obtain disc-shaped specimens of 10 mm diameter and thickness of 1 mm.

For study of dissipative properties of objects we used the device base on network analyzer PNA E8363B produced by AgilentTechnologies with range of measured frequencies f = 10 kHz – 40 GHz and microstrip line (MSL), on which the measured specimen was placed. MSL, which is a strip conductor of rectangular cross-section (width is much bigger than its thickness), which is placed on the thin dielectric substrate. The opposite side of the substrate is metallized and acts as grounded screen. As measured parameters for evaluation of microwave absorption of electromagnetic field by the study objects we used elements of normalized wavefront scattering matrix S_{11} и S_{21} [6], which are, respectively, complex coefficient of reflection and transmission of the quadripole demonstrated in Fig.1. If the quadripole is connected to two transmission lines (Fig.1) and from the side of input 1-1' it is excited by ideal power source E, then equations, which are defining linear connection between amplitudes of voltages incident ... and reflected ...waves at input and output of the quadripole, are as follows:

$$\dot{u}_{1incident} = \dot{S}_{11}\dot{u}_{1reflected} + \dot{S}_{12}\dot{u}_{2reflected},$$
$$\dot{u}_{2incident} = \dot{S}_{21}\dot{u}_{1reflected} + \dot{S}_{22}\dot{u}_{2reflected} \quad (1)$$

where $\dot{S}_{11}$ and $\dot{S}_{21}$, respectively, are the complex coefficients of reflection and transmission of the quadripole in the case it is excited by the voltage source *Eco* from the side of the input 1-1', $\dot{u}_{1reflected}$ and $\dot{u}_{2incident}$ – amplitudes of voltages of waves, which are reflected from the input 1-1' of the quadripole and which are incident on the input 2-2' of the quadripole, respectively. If the quadripole doesn't have energy losses and is harmonized from the side of inputs 1-1' and 2-2' with resistances Z_0, then energy conservation law is obeyed in that case $|S_{11}|^2 + |S_{21}|^2 = 1$. In a case there are losses in the quadripole $|S_{11}|^2 + |S_{21}|^2 < 1$ and the difference of the sum $|S_{11}|^2 + |S_{21}|^2$ from 1 can act as the measure of losses in the quadripole [7].

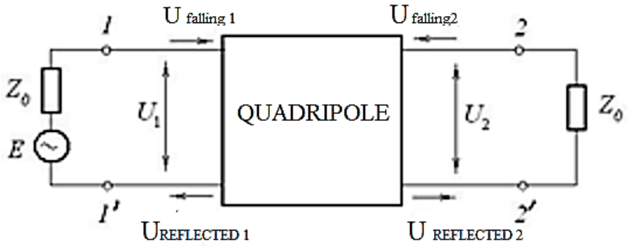


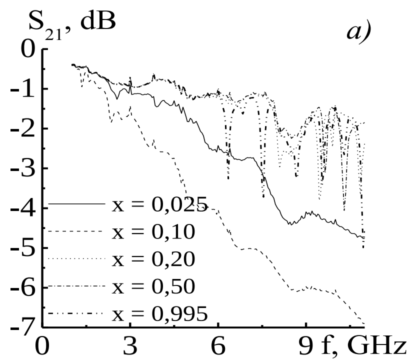
Figure 1: Scheme demonstrating connection of the quadripole in long transmission line.

At the first stage we measured frequency relationships of the modules $|S_{21}|$ and $|S_{11}|$ of MSL without the studied specimen. (MSL without a specimen has its own losses due to finite conductance of metal conductors of the line itself and the screen, losses in a dielectric material and losses on radiation in places, where MSL is connected to an instrument). After that frequency relationships of the modules $|S_{21}|$ and $|S_{11}|$ of MSL were measured in the same manner. Difference of values $|S_{11}|^2 + |S_{21}|^2$, which correspond to MSL with the specimen and without it can act as measure against losses (absorption) in the studied specimen with the condition of minor value of radiation at boundaries of the specimen itself. Minor value of that radiation was checked by putting a hand close to the specimen, at that, considerable changes in frequency characteristics took place only at direct contact with specimens.

Studies of relationships of relative dielectric permeability, $\varepsilon/\varepsilon_0$, and temperature with various frequencies *f* of alternating electric measuring fields were carried out using precision LCR – meter AgilentE4980A in range of temperatures of (25-600) °C and range of frequencies of 25 Hz – 1 MHz.

EXPERIMENTAL RESULTS DISCUSSION

Fig.2 demonstrates frequency relationships of coefficients of transfer $|S_{21}|$(*a, b*) and reflection $|S_{11}|$(*c, d*) in the range of frequencies (1.0-11.0) GHz. As it can be seen in Fig. 2, relationship of coefficients of transmission (*a, b*) and reflection (*c, d*) of the studied specimens are explicitly resonance, at that, periodicity and spectra depth is increasing with frequency.



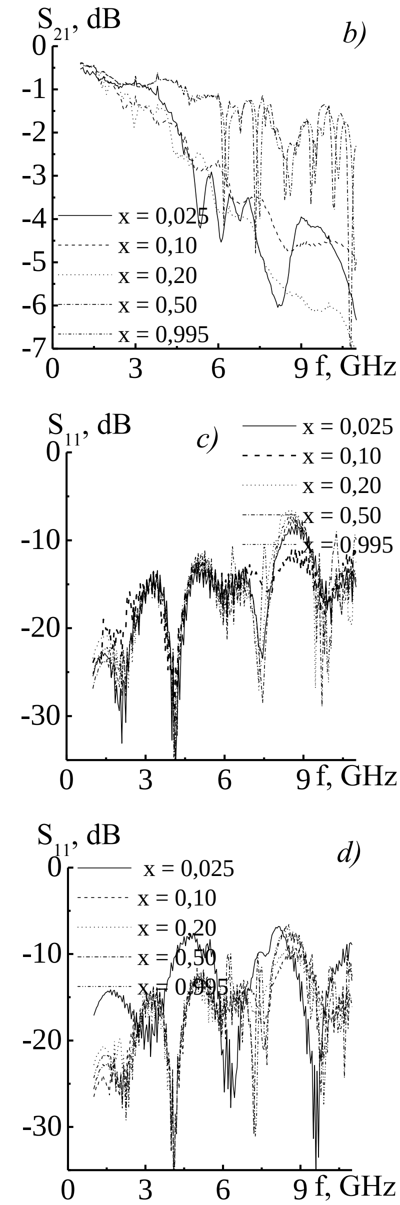
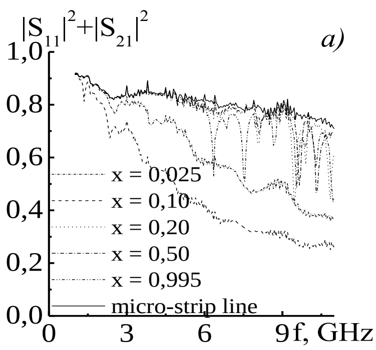


Figure 2: Frequency relationships of coefficients of transmission (*a, b*) and reflection (*c, d*) of the studied specimens of SS systems ((1-x)$NaNbO_3$ – x$Ca_2Nb_2O_7$ (*a,* c), (1-x)$NaNbO_3$ – x$Sr_2Nb_2O_7$ (*b, d*)) in the range (1.0-11.0) GHz.

Fig. 3 shows calculated frequency relationships of values α, which equal to $|S_{11}|^2 + |S_{21}|^2$ (in relative units) for the strip line (continuous line) without specimen and with the same specimens (dotted line и dash-dot line) (a – b) and difference of the sum $|S_{11}|^2 + |S_{21}|^2$ from 1, which is also the measure of losses in *(c)* of the radiating SS.



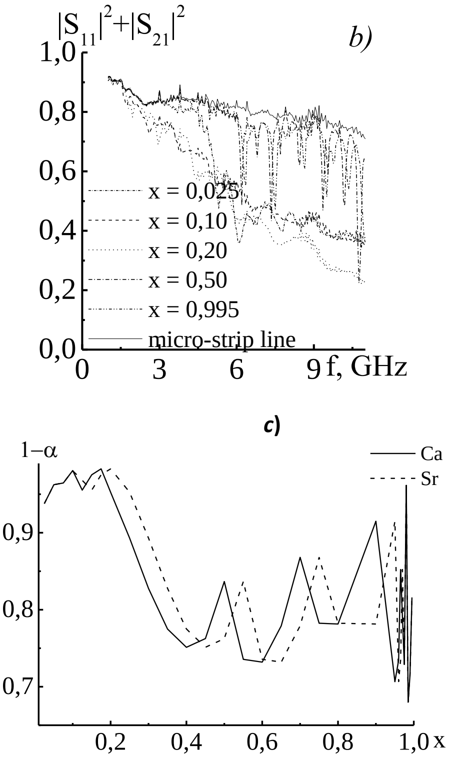


Figure 3: Relationship of losses (absorption) of microwave energy in the strip line without specimens (continuous lines) and with the specimens (dotted lines and dash-dot lines) of SS systems (1-x)$NaNbO_3$–x$Ca_2Nb_2O_7$) (*a*), (1-x)$NaNbO_3$ – x$Sr_2Nb_2O_7$ (*b*), Relationships of losses (absorption) of microwave energy of SS of the studied systems (c).

Fig. 3 demonstrates that those losses are increasing almost monotonously with increase of frequency, at that, rapid changes of losses are not detected, in spite of presence of intrinsic resonance frequencies (Fig. 2) of the specimens in the discussed frequency range.

Analysis of the obtained data was carried out using the results of study of structures of SS and their dielectric properties.

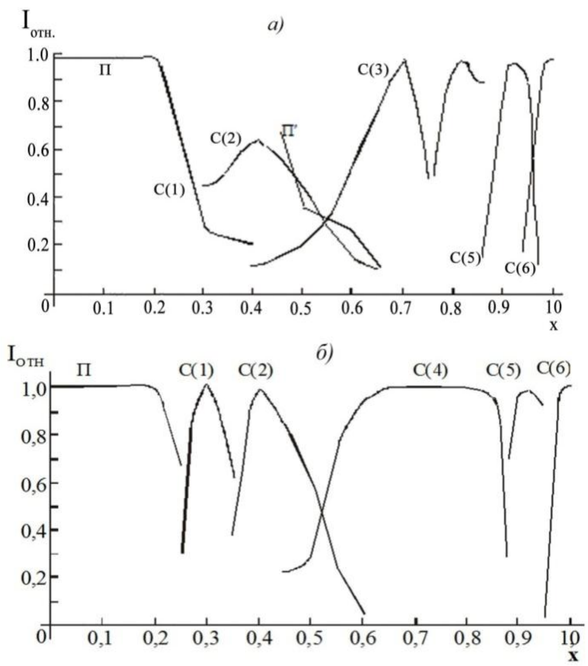
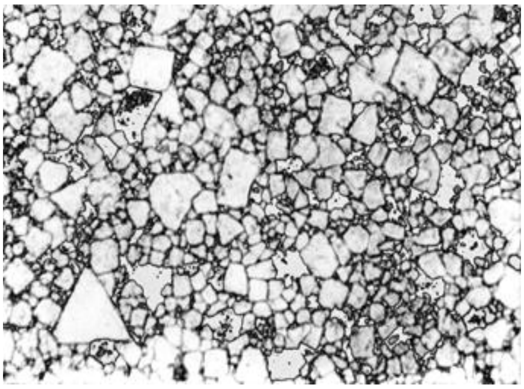


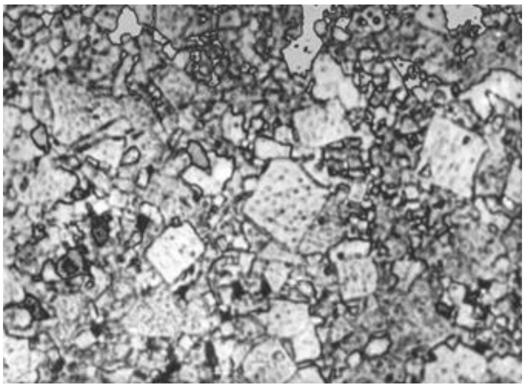
Figure 4: Phase diagrams of the systems (1-*x*)$NaNbO_3$ – *x*$Ca_2Nb_2O_7$ (*a*), (1-*x*)$NaNbO_3$ – *x*$Sr_2Nb_2O_7$ (*b*).

Fig. 4 shows phase diagrams of (1-x)$NaNbO_3$ – x$Ca_2Nb_2O_7$ (a), (1-x)$NaNbO_3$ – x$Sr_2Nb_2O_7$ (b). In those systems for 0 ≤ x ≤ 0.2 SS are formed with structure of perovskite type (P), which symmetry, along with increase of x, is changing from rhombic (R) which quadrupled monoclinic sub-cell (M4) to cubic with superstructure (C2), and then without it (C). Two areas can with mixed type of structures can be marked out, including those combining monoclinic cells of various levels of multiplicity. With moving "inside" of the systems perovskite structures change to laminar structure (*c*) with various levels of *n.* Alternation of laminar phases, which crystallize as independent forms with x = 0.33(C(1), $Na_4Ca(Sr)_2Nb_5O_{19}$, b = 60.14÷60.85 Å, *n*= 12), 0.40 (C(2), $Na_3Ca(Sr)_2Nb_5O_{11}$, *b* = 52.24÷53.3 Å, *n* = 10), 0.67 (C(3), $NaCa(Sr)_2Nb_5O_{10}$, *b* = 37.7 Å, *n* = 6), 0.80 (C(4), $NaCa(Sr)_4Nb_5O_{17}$, *b* = 32.1÷32.8 Å, *n* = 5), 0.89 (C(5), $NaCa(Sr)_8Nb_9O_{31}$, *b* = 58.8÷5.5 Å, *n* = 4.5), 1.0 (C(6), $NaCa(Sr)_2Nb_2O_7$, *b* = 26.0÷26.9, *n* = 4), is accompanied by the decrease of *n*. In a whole, phase conditions in both systems is almost the same, with the exception of that in system with $Ca_2Nb_2O_7$ structures C(1) and C(2) exist with others, forming multiple phase zones, and in system with $Sr_2Nb_2O_7$ in interval 0.6 < *x* < 0.85 phase of varied composition on the basis of compounds C(3) and C(4) is formed.

Fig. 5 and 6 show microphotographs of the systems (1-x)$NaNbO_3$ – x$Ca_2Nb_2O_7$, (1-x)$NaNbO_3$ – x$Sr_2Nb_2O_7$.



a



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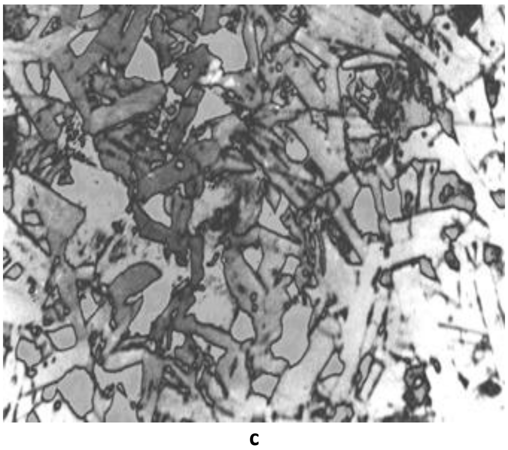

c

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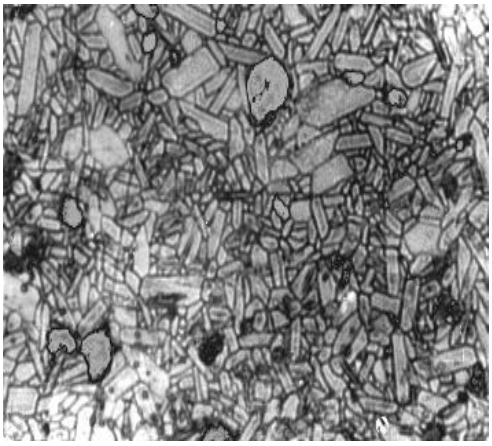
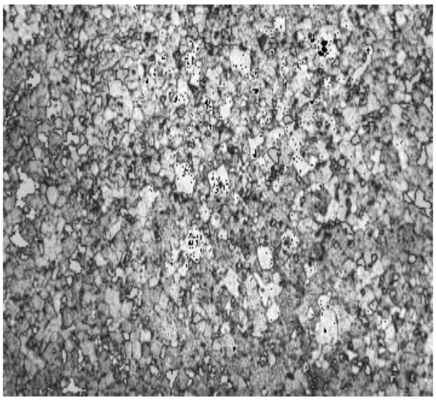


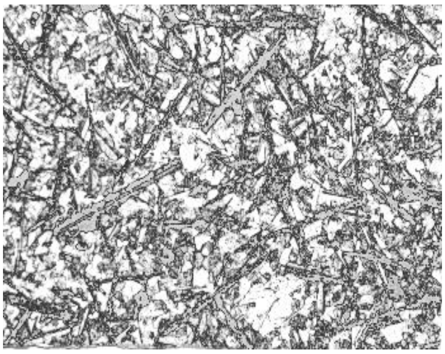
d

Figure 5: Transitions of microstructure of SS (1-x)$NaNbO_3$ – x$Ca_2Nb_2O_7$). In Figures x = 0 (a), x = 0.20 (b), x = 0.70 (c), x = 1.0 (d). Magnification x300.

It was established that in the range $0 \le x < 0.20$ for both systems isometric type of granular structure, which is characteristic to $NaNbO_3$, is dominant, but for $0.20 \le x \le 1.0$ needle-shaped type is dominant, which is characteristic to laminar structures [10].



a



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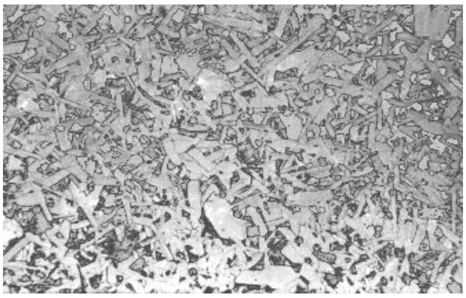

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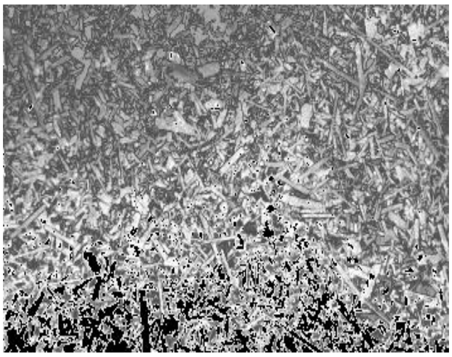


d

Figure 6: Transitions of microstructure of SS (1-x)$NaNbO_3$ – x$Sr_2Nb_2O_7$). In Figures x = 0.075 (a), x = 0.20 (b), x = 0.80 (c), x = 1.0 (d). Magnification x300.

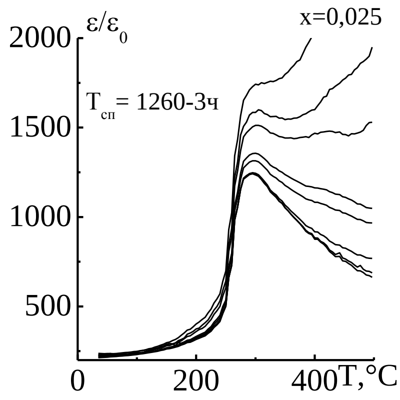
As it can be seen from the presented Figures, for both systems maximum absorption is observed near boundary components – pyroniobates of Ca and Sr, while "middle" (main) parts of systems have moderate values of losses; large values of losses are observed in the system with $Ca_2Nb_2O_7$.

That phenomenon can be related with features of crystal chemistry of compounds $Ca_2Nb_2O_7$ and $Sr_2Nb_2O_7$, which have laminar crystalline structure, producing specific (needle-shaped) from of ceramic grains. Local maximums of absorption (Fig. 2 (*a, b*)) are observed near phase boundaries, which is, presumably, is related with development of defect situation in corresponding medias due to opening of chemical bonds during rearrangement of structure, accumulation of vacations and impurity phases and increase of number of interphase boundaries.

Results of the studies of dielectric properties of SS of both systems of perovskite zone in wide range of temperatures and frequencies are presented in Fig. 7. The common feature for the curves, corresponding to the perovskite zone, is behavior of $\varepsilon/\varepsilon_0$ with maximum in Curie point (T_C), which is specific for antiferroelectrics.

For the both cases ferroelectirc-paraelectric transition is diffused (generally, by calcium compound), and its width in the range of perovskite area is changing nonmonotonously, which is followed by phase transformations in that fragment of the system's phase diagrams. (We identified the following relationship between the observed changes of structure $P(M_4) \rightarrow P(M_4 + M_2) \rightarrow P(M_2) \rightarrow P(M_2) + K \rightarrow K$). In zones, where phases coexist, there is maximum diffusion of the transition zone. Numerous anomalies of$\varepsilon/\varepsilon_0$ both higher and lower than T_C are also observed; formation of weak dispersion of $\varepsilon/\varepsilon_0$ lower T_C with various degrees of its occurrence in both systems with various x and at various temperature zones; appearance of considerable $\varepsilon/\varepsilon_0$ Curie point and considerably higher it, which is increasing with increase of temperature and decrease of frequency *f*, alternating electric field; small shift of maximum $\varepsilon/\varepsilon_0$ in the zone of lower temperatures in some cases (SS with $Sr_2Nb_2O_7$, x = 0.025); decrease of peak value $(\varepsilon/\varepsilon_0)_{max}$ with increase of *f*. Observed effects of low-temperature and high-temperature (higher than T_C) dispersion of $\varepsilon/\varepsilon_0$, shift of T_C in the area of low temperatures, rapid growth of $\varepsilon/\varepsilon_0$ higher than T_C at low frequencies, decrease of$(\varepsilon/\varepsilon_0)_{max}$ with increase of *f* are related with influence of electrical conductivity, which is caused by presence of even minor amount of defects [8]. At high temperatures in specimens with low content of the second component, it is possible to increase electrical conductivity due to appearance of oxygen vacancies during reduction $Nb^{5+} \rightarrow Nb^{4+}$ [9].

The results obtained in that study can be applied for development of new functional materials, which can be applied in various branches of industry using microwave technologies, in particular, for protection of radio-receiving equipment from external electromagnetic noises, as well as for development of components of electronic devices, including IC technology.


ε/ε0
x=0,025
Tсп = 1260-3ч
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1500
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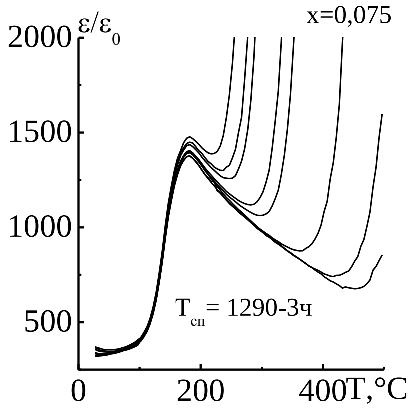
T,°C

a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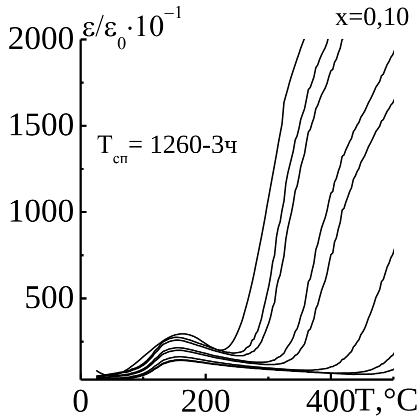
ε/ε0·10−1
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Tсп = 1260-3ч
2000
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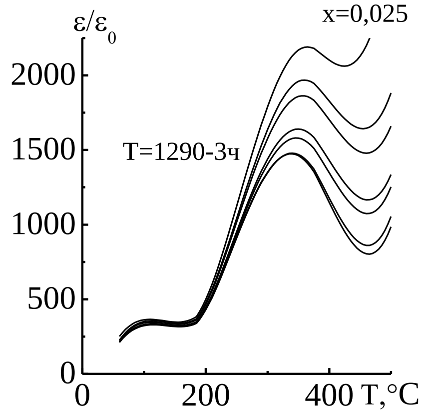
T,°C

c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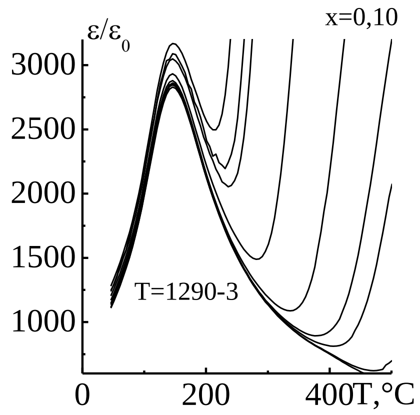
d



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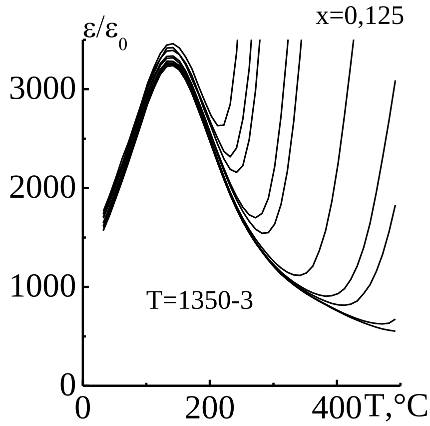

f

Figure 7: Temperature relationships of dielectric permeability ($\varepsilon/\varepsilon_0$) of the studied object for various contents of $Ca_2Nb_2O_7$ – (a, b, c) and $Sr_2Nb_2O_7$ – (d, e, f).

CONCLUSION

In the course of the study we investigated characteristics of SS of systems (1-x)$NaNbO_3$ – x$Ca_2Nb_2O_7$ и (1-x) $NaNbO_3$ – x$Sr_2Nb_2O_7$ in the range of frequencies of (1.0 ÷ 11.0) GHz. Phase of diagrams of the discussed systems are plotted. It was demonstrated that in the systems of SS, which contain phase transitions of various nature, maximum values of microwave power absorption are observed near phase boundaries. The study revealed features of dielectric properties of the discussed solid solutions. Opportunities of application of the obtained results for development of new functional materials, which are used in many branches of industry, using microwave technologies, are discussed.

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