
DIELECTRIC MATERIAL

Edited by **Marius Alexandru Silaghi**

Dielectric Material

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Contributors

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Preface

This book attempts to bring together the theory and practice of dielectric materials for different kind of industrial applications.

Fragmented information on dielectric theory and properties of materials, design of equipment and state of the art in applications relevant to the manufacturing industry should be collated and updated and presented as a single reference volume.

In this book relevant and useful information is presented in the quoted literature and covered by our key patent applications.

As an Editor and also Author in this field, I am honored to edit this book written by a selected group of researchers.

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Microwave Dielectrics Based on Complex Oxide Systems

A.G. Belous

Additional information is available at the end of the chapter

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1. Introduction

The development of modern telecommunication systems calls for the creation of novel materials with a high level of electrophysical parameters in the MW range. These materials must have in the MW range a high permittivity ($\epsilon \geq 20$), a low dielectric loss ($\text{tg } \delta \leq 10^{-3} - 10^{-4}$) and a high thermostability of electrophysical properties (temperature coefficient of permittivity ($\text{TC}\epsilon$) or resonant frequency (τ_f) $\sim 10^{-6}\text{K}^{-1}$). Such materials can be used in the development of resonant elements of radio-frequency filters, solid state oscillators, substrates for hybrid MW circuits, allow the size of communication systems to be greatly reduced and improve their parameters. Moreover, the use of them reduces the manufacturing and operating costs for modern communication systems.

The choice of the permittivity value of MW materials is largely determined by the frequency range of the operation of communication systems, the type of exciting wave and the requirement of the optimal size of dielectric element. The value of ϵ determines the size of radio components. The influence of microminiaturization is based on the fact that the electromagnetic wavelength in dielectric decreases in inverse proportion to $\sqrt{\epsilon}$. Therefore, in the decimeter wave band, high-Q thermostable materials with high permittivity value ($\epsilon \geq 80-600$) are required, whereas in the centimeter and millimeter wave bands, thermostable materials with $\epsilon \sim 15-30$ but with extremely high Q ($Q \times f \geq 80000$, where $Q = 1/\text{tg } \delta$ and f is frequency in GHz) are needed.

It should be noted that low dielectric loss in the MW range $10^9 - 10^{11}$ Hz is characteristic only of optical and infrared polarization mechanisms. Other polarization mechanisms give rise, as a rule, to considerable dielectric loss [1].

In the case of optical polarization, dielectrics are characterized by a low negative temperature coefficient of permittivity ($\text{TC}\epsilon \sim 10^{-5}\text{K}^{-1}$). However, the dielectric contribution of optical

polarization is usually small. Therefore, large permittivity values together with high temperature stability of dielectric parameters and low dielectric loss can be observed only in the dielectrics where the main contribution to polarization is made by infrared polarization mechanism [1, 2]. This mechanism is bound up with cation and anion sublattice displacement in electric field, which is only possible in ionic crystals. The contribution of infrared polarization mechanism to permittivity may be $\Delta \varepsilon_{ir} = 1 - 10^4$ in the MW range. The temperature instability of ε increases, as a rule, with increasing ε . The large magnitude of infrared polarization is usually due to the presence of a soft mode in crystal, whose frequency varies by the critical law $\omega_T = A\sqrt{T - Q}$; this leads in accordance with the Liddéin–Sax–Teller (LST) relation:

$$\frac{\varepsilon_{MW}}{\varepsilon_{Opt}} = \prod_i \frac{\omega_L^2}{\omega_T^2} \quad (1)$$

to the Curie – Weiss law for permittivity:

$$\varepsilon_{MW} = \varepsilon_L + \frac{C}{T - Q} \quad (2)$$

where ω_L and ω_T are the frequencies of longitudinal and transverse optical phonons in the center of Brillouin zone (one of the transverse phonons is soft), C is a constant, Q is Curie – Weiss temperature, ε_L is dielectric contribution, which depends only slightly on temperature [1].

The frequency of transverse and longitudinal optical phonons can be calculated from the equations:

$$\omega_T^2 = \frac{c}{m} - \frac{nq^2}{3\varepsilon_0 m} \cdot \frac{\varepsilon_\infty + 2}{3} \quad \text{and} \quad \omega_L^2 = \frac{c}{m} + \frac{2nq^2}{3\varepsilon_0 m} \cdot \frac{\varepsilon_\infty + 2}{3} \quad (3)$$

where c is the elastic coupling parameter of phonons; m is reduced mass; q, n are ion charge and concentration; ε_0 is an electric constant [1].

The parameters c, n, ε_{opt} are temperature-dependent; they decrease with rising temperature due to thermal expansion (lattice anharmonicity). It is evident from system (3) that ω_L is a weak function of temperature because it is determined by the sum of two terms, whereas the dependence $\omega_T(T)$ may be strong since ω_T depends on the difference of two terms (see Eqs (3)). The variation of this difference as a function of temperature depends on which effect predominates: the variation of c/m (minuend) or the variation of the subtrahend, which depends on n, ε_{opt} . Depending on ω_T , the dielectric contribution $\Delta \varepsilon_{ir}$ also varies with temperature [1]:

$$\Delta \varepsilon_{IR} = \varepsilon_{MW} - \varepsilon_{Opt} = \frac{nq^2}{m\omega_T^2 \varepsilon_0} \cdot \left(\frac{\varepsilon_{Opt} + 2}{3} \right).$$

The above analysis shows that the chemical composition can influence, in principle, the contribution of different polarization mechanisms and hence the value of permittivity and loss, as well as their variation in the MW range as a function of temperature.

The present paper considers the structure peculiarities, electrophysical properties and possible applications of inorganic microwave (MW) dielectrics based on oxide systems.

2. MW dielectrics based on (La, Ca)(Ti, Al)O₃ solid solutions

MW dielectrics are often synthesized on the basis of solid solutions, e.g. Ba(Zn, Mg)_{1/3}(Nb, Ta)_{2/3}O₃ [3, , 5], (La, Ca)(Ti, Al)O₃ [6, 7], etc. The substance of this approach is that solid solutions are formed by the interaction of phases belonging to the same crystal structure, which have in the MW range a different trend of the plot of permittivity against temperature and a low dielectric loss. Paraelectric is characterized by a low dielectric loss; for example, CaTiO₃, which crystallizes in perovskite structure, can be used in the CaTiO₃ – LaAlO₃ system as a phase with negative temperature coefficient of permittivity ($TC\epsilon < 0$) [6]. At the same time, LaAlO₃ can be used as a phase with perovskite structure having $TC\epsilon > 0$ [7]. By varying the ratio CaTiO₃ /LaAlO₃, one can control the value of $TC\epsilon$. Positive $TC\epsilon$ in dielectrics in the MW range usually indicates the presence of a high-temperature phase transition, which is connected with the existence of spontaneously polarized state (ferroelectrics, antiferroelectrics). However, the materials in which spontaneous polarization exists have, as a rule, a considerable dielectric loss in the MW range, which is inadmissible for the creation of high-Q dielectrics. In LaAlO₃, there is no spontaneous polarization. It should be noted that there are very few materials having $TC\epsilon > 0$ in the MW range and a low dielectric loss. Therefore, the development of high-Q MW dielectrics with high ϵ and positive temperature coefficient of permittivity ($TC\epsilon > 0$) is of independent scientific and practical interest.

3. Control of the $TC\epsilon$ value by influencing the phonon spectrum

As follows from the analysis of expressions (3), the trend of the plot of ϵ against temperature in the MW range can be controlled by influencing the phonon spectrum. One of the ways of influencing the phonon spectrum in some types of structures can be iso- and heterovalent substitutions in cation sublattices. As an example, we chose La_{2/3-x}(Na, K)_{3x}TiO₃ materials, which crystallize in defect-perovskite structure in a wide x range (Fig 1).

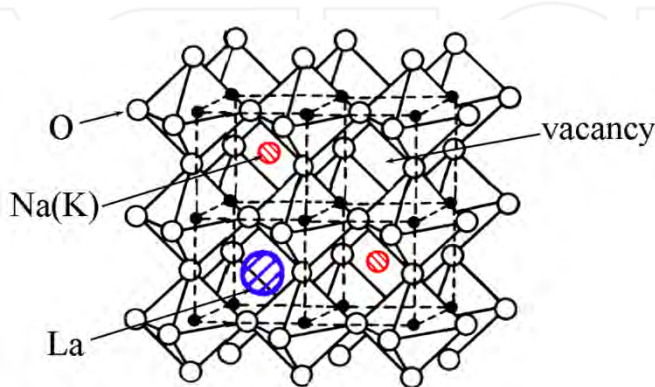


Figure 1. Crystal structure of La_{2/3-x}(Na, K)_{3x}TiO₃ perovskite

In this system, lanthanum ions in the oxidation state +3 are partially substituted by alkali (sodium or potassium) ions in the oxidation state +1. Substitution is performed so that the electroneutrality condition is satisfied. The value of x was varied from $1/24$ to $1/6$. In this case, lanthanum ions, alkali metal (sodium or potassium) ions and a structural vacancy (vacant crystal site) could be in one crystal sublattice at the same time. We hoped that in the case of such heterovalent substitution, the phonon spectrum, and hence the trend of the plot of ϵ against temperature in the MW range, had to change.

$\text{La}_{2/3-x}(\text{Na}, \text{K})_{3x}\text{TiO}_3$ materials are not characterized by high temperature stability of dielectric parameters. The dielectric properties of these materials had been studied in a wide frequency range [8, 9].

It had been found that by decreasing the number of structural vacancies, using heterovalent substitution in sublattices and locating different ions in vacant crystal sites, one can influence greatly the dielectric loss level (Fig 2) [10].

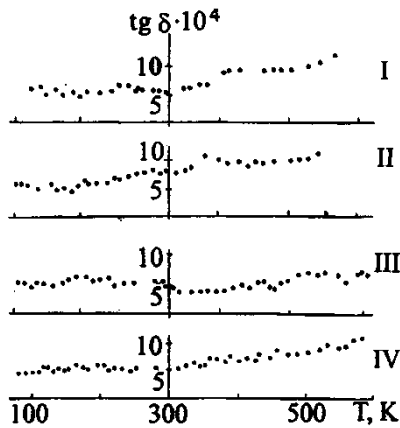


Figure 2. Plots of dielectric loss ($\text{tg } \delta$) in the $\text{La}_{2/3-x}(\text{Na}, \text{K})_{3x}\text{TiO}_3$ system at 1.2×10^{10} Hz against temperature: (I) $\text{La}_{1/2}\text{Na}_{1/2}\text{TiO}_3$, (II) $\text{Nd}_{1/2}\text{Na}_{1/2}\text{TiO}_3$, (III) $\text{La}_{1/2}\text{Na}_{1/4}\text{K}_{1/4}\text{TiO}_3$, (IV) $\text{La}_{7/12}\text{Na}_{1/4}\bullet_{1/6}\text{TiO}_3$, where \bullet is the structural vacancy

Investigations showed that heterovalent substitutions in cation sublattices affect greatly the value of $\text{TC}\epsilon$ too. To explain this effect, IR reflection spectra of $\text{La}_{2/3-x}\text{M}_{3x}\text{TiO}_3$ materials have been analyzed [11]. The analysis of IR reflection spectra made it possible to calculate the parameters of dispersion oscillators (Table 1). It is known that in the materials that crystallize in perovskite structure, a low-frequency lattice vibration exists which is responsible for the high ϵ value in the MW range [12].

The partial heterovalent substitution of ions in crystal sublattice gives rise to a low-frequency vibration, which affects noticeably the value of permittivity. In this case, the temperature stability of dielectric parameters increases greatly. Thus, the proposed method of influencing the phonon spectrum can be employed in the development of novel MW dielectrics with high temperature stability of dielectric properties.

La _{1/2} Na _{1/4} K _{1/4} TiO ₃ ($\epsilon = 106$)				La _{7/12} Na _{1/4} • _{1/6} TiO ₃ ($\epsilon = 87$)			
ω_{TO}	ω_{LO}	ΔE	g	ω_{TO}	ω_{LO}	ΔE	g
cm ⁻¹				cm ⁻¹			
116	163	74.0	0.75	133	178	55.0	0.64
198	258	22.0	0.44	201	224	19.5	0.31
237	334	3.0	0.21	230	265	4.1	0.30
336	375	0.2	0.33	270	343	1.8	0.26
381	489	0.4	0.16	345	460	0.2	0.10
554	747	1.2	0.10	563	694	1.0	0.11
785	816	0.1	0.12	789	860	0.3	0.30

* $\epsilon_{\infty} = 5.1$.

Table 1. Parameters of (La_{2/3-x}M_{3x} • _{1/3-2x})TiO₃ dispersion oscillators*

4. MW dielectrics based on Ba_{6-x}Ln_{8+2x/3}Ti₁₈O₅₄ (Ln = La-Gd)

The Ba_{6-x}Ln_{8+2x/3}Ti₁₈O₅₄ materials (Ln = La - Gd) (BLTss) have promise in the development on their basis of thermostable high-Q MW dielectrics with high permittivity ($\epsilon \approx 80 - 100$) [14]. They crystallize in KW bronze structure (Fig 3), which includes elements of perovskite structure [15, , 17]. In this structure, the octahedra are linked, as in perovskite, by their apices into parallel rectilinear chains. Unlike perovskite structure, however, the oxygen octahedra are linked so that they form pentangular, quadrangular and triangular channels, in which A ions can be, having in this case the coordination numbers 15, 12 and 9 respectively. This structure allows one to perform iso- and heterovalent substitutions in cation sublattices in a wide range, to control the number of vacant crystal sites in the A sublattice, to influence the partial redistribution of A ions among the pentangular, quadrangular and triangular channels and hence to control the electrophysical properties in the MW range, including the temperature dependence of ϵ .

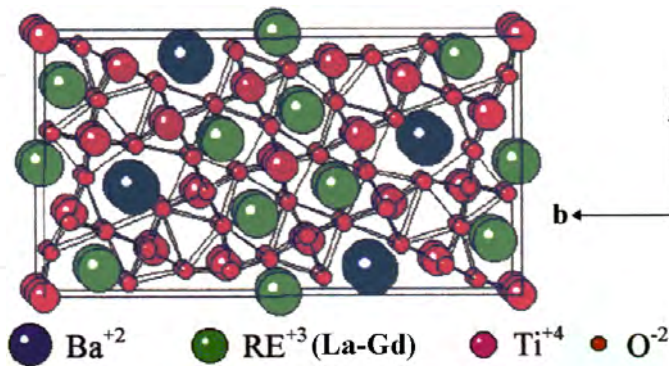


Figure 3. Unit cell of Ba_{6-x}Ln_{8+2x/3}Ti₁₈O₅₄ [17]

When investigating Ba_{6-x}Ln_{8+2x/3}Ti₁₈O₅₄ materials (Ln = La - Gd), which crystallize in KW bronze structure, a special attention was given to the study of formation reaction and the

anomalous behavior of the temperature characteristics of dielectric parameters. It should be noted that the knowledge of the reactions proceeding during the synthesis of compounds can allow dielectric loss to be reduced. The formation of $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ materials ($\text{Ln} = \text{Nd}, \text{Sm}$) when using the solid-state reaction method was studied on compositions with $x = 0.75, 1.5, 2.0$. BaCO_3 , Sm_2O_3 and TiO_2 were used as starting reagents. It was shown that it is a multistage process, which is accompanied by the formation of intermediate phases, e.g. $\text{Ln}_2\text{Ti}_2\text{O}_8$, BaTi_4O_9 , BaTiO_3 [18]. It has been found that independent of x value, the phase $\text{Ba}_{3.9}\text{Ln}_{9.4}\text{Ti}_{18}\text{O}_{54}$ is formed at first, which belongs to $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ solid solutions and corresponds to the maximum x value. The formation of the other phases, which belong to the region of $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ – type solid solutions, takes place as a result of interaction between intermediate $\text{Ba}_{3.9}\text{Ln}_{9.4}\text{Ti}_{18}\text{O}_{54}$ phases and barium metatitanate (BaTiO_3). The phase $\text{Ba}_{3.9}\text{Ln}_{9.4}\text{Ti}_{18}\text{O}_{54}$ crystallizes, as $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ materials, in KW bronze structure, which makes the identification of the phase $\text{Ba}_{3.9}\text{Ln}_{9.4}\text{Ti}_{18}\text{O}_{54}$ only by the data of X-ray phase analysis impossible. Therefore, EDS and TEM analyses were used additionally [18]. The latter analysis showed that even when all BaTiO_3 had reacted, the homogeneity of materials was not reached yet (Fig 4(a)). If the ceramic sintering time was relatively short, a phase, e.g. $\text{Ba}_{3.9}\text{Ln}_{9.4}\text{Ti}_{18}\text{O}_{54}$, was present (Fig 4(a)), which had low and high x values within the limits of formation of $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ solid solutions. The structural-defect concentration decreased, and the homogeneity of $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ materials increased only in the case of long ceramic sintering time ($t \geq 3\text{h}$) (Fig 4(b)).

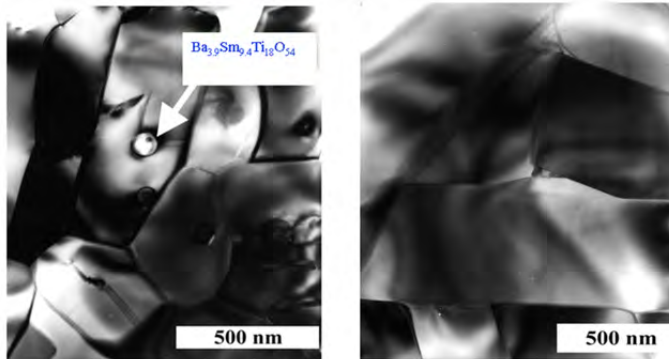


Figure 4. Results of a TEM analysis of $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ceramic; sintering time: 1 h (a), over 3 h (b)

The electrophysical characteristics of $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ depend largely upon ions in the A sublattice (Γ_A) [14, 19, 20]. When the rare-earth ion in the A sublattice is changed from La to Gd, the permittivity (ϵ) value and loss-angle tangent in BLTss decrease. At the same time, the temperature coefficient of permittivity, $\text{TC}\epsilon$, increases and changes its sign in the series of rare-earth ions, which are in the A sublattice, in going from Nd to Sm [20, 21]. When investigating $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ materials (where $x = 1.5$), we had found for the first time an anomaly on the plot of permittivity against temperature [21]. Later, anomalies on the plots of dielectric parameters (ϵ , $\text{tg } \delta$) against temperature were detected in the other $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ materials too [22]. The nature of these anomalies remained uncertain.

Moreover, there was no information about the existence of temperature dependence anomalies of dielectric parameters in other barium-lanthanide analogs, including La-, Nd-, Gd-containing $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$. Therefore, we tried to find out the cause of the temperature dependence anomalies of permittivity and dielectric loss since this makes it possible to establish the nature of the thermostability of electrophysical properties in these systems.

It has been found that temperature dependence anomalies of dielectric parameters in La- and Nd-containing BLTss are observed at low temperatures in a wide frequency range, including the submillimeter-wave region (Fig 5) [23], the position of these anomalies on the temperature scale depending not on measurement frequency, but on chemical composition.

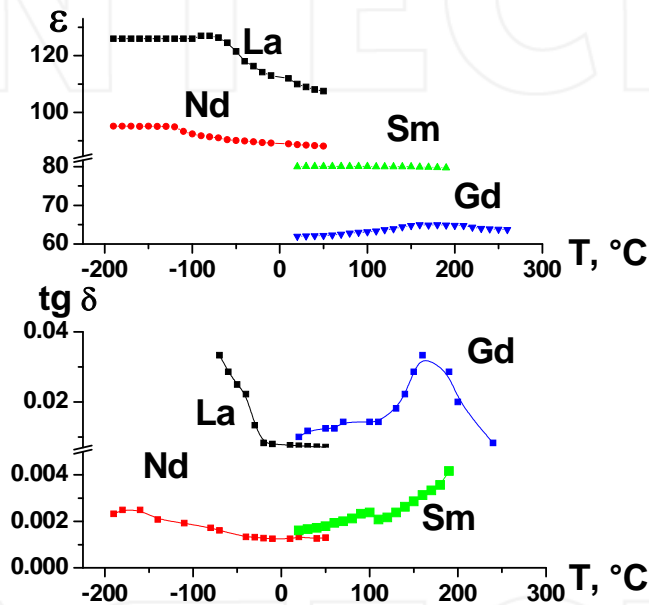


Figure 5. Plots of the dielectric parameters of $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ solid solutions ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}$) at 10 GHz against temperature

In Sm- and Gd-containing systems, anomalies of dielectric parameters appear at temperatures above room temperatures (Fig 5). The plots of dielectric parameters against temperature have a similar trend when ferroelectric or antiferroelectric ordering occurs. In the case of BLTss, however, no hysteresis loops were observed, and the temperature dependence of ϵ did not obey the Curie-Weiss law, which indicated the absence of spontaneously polarized state in these materials. It may be supposed that the appearance of dielectric anomalies is due to the presence of unknown phase transitions. Therefore, $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ systems ($x = 1.0$), in which dielectric anomalies of ϵ and $\text{tg } \delta$ were observed at 100-120 °C, have been studied by low-temperature differential scanning calorimetry (LT-DSC) and high-temperature X-ray structural analysis of samples. We did not find any phase

transitions [22], which was confirmed by the authors of [24], who carried out synchrotron X-ray diffraction studies of $\text{Ba}_{4.5}\text{Sm}_9\text{Ti}_{18}\text{O}_{54}$ samples in the temperature range 10-295 K. These data indicate the absence of structural transitions in the temperature ranges where anomalies of dielectric parameters were observed. It can be concluded that the temperature dependence anomalies of dielectric parameters are not coupled with the peculiarities of sample preparation and the presence of structural transitions.

On the basis of an analysis it was assumed that the nature of the anomaly of dielectric parameters is coupled with harmonic and anharmonic BLTs lattice vibration, which is different in the character of influence on the temperature behavior of dielectric parameters [23].

Investigations showed that the plots of ϵ and $\text{tg } \delta$ against temperature depend largely upon harmonic and anharmonic lattice vibration modes. Therefore, using different hetero- and isovalent substitutions in cation sublattices, one can influence the lattice phonon spectrum and hence obtain materials with high temperature stability of dielectric parameters, which are used in modern decimeter and centimeter wave band communication systems [25, , , 28].

5. MW dielectrics with “mobile sublattice”

The authors of [29] reported the development of novel MW dielectrics with high temperature stability of dielectric parameters based on solid solutions, where one of the phases (lithium-containing $\text{La}_{1/2}\text{Li}_{1/2}\text{TiO}_3$) had a positive temperature coefficient of permittivity ($\text{TC}\epsilon > 0$). However, there was no explanation of the nature of this fact in literature.

The phase $\text{La}_{1/2}\text{Li}_{1/2}\text{TiO}_3$, which crystallizes in perovskite structure, belongs to $\text{Ln}_{2.3-x}\text{M}_{3-x}\text{TiO}_3$ solid solutions (Ln = rare-earth elements, M = alkali metal ion) (Fig 6). In this system, the M ions partially substitute for rare-earth ions. In this case, the electroneutrality condition is satisfied [30, 31]. If $M = \text{Na}, \text{K}$, materials crystallize in perovskite structure and are characterized by low dielectric loss ($\text{tg } \delta \leq 10^{-3}$) and high permittivity in the MW range (about 100) and $\text{TC}\epsilon < 0$ [32].

At the same time, when $M = \text{Li}$, a system of solid solutions is formed, in which rare-earth ions, lithium ions, structural vacancies, which are characterized by $\text{TC}\epsilon > 0$, are in one sublattice at the same time. Lithium ions can move along structural channels, ensuring a high lithium-ion conductivity [33, 34], positive temperature coefficient of permittivity ($\text{TC}\epsilon > 0$) and causing considerable dielectric loss in the MW range. The latter is inadmissible in the creation of high-Q dielectrics. Investigations showed, however, that the dielectric loss in the MW range can be greatly reduced by decreasing lithium ion conductivity. The latter is achieved by substituting rare-earth ions with smaller radius for lanthanum ions. This leads to a decrease in the size of structural channels, in which lithium ions are; this reduces dielectric loss in the MW range through a decrease in lithium ion mobility in the structure. In this case, $\text{TC}\epsilon > 0$ is retained. As a result, solid solutions have been obtained, in which rare-earth ions are simultaneously substituted by alkali metal ions with large (Na, K) and small (Li) radius and which have a high temperature stability of dielectric parameters in the MW range (Table 2) [35].

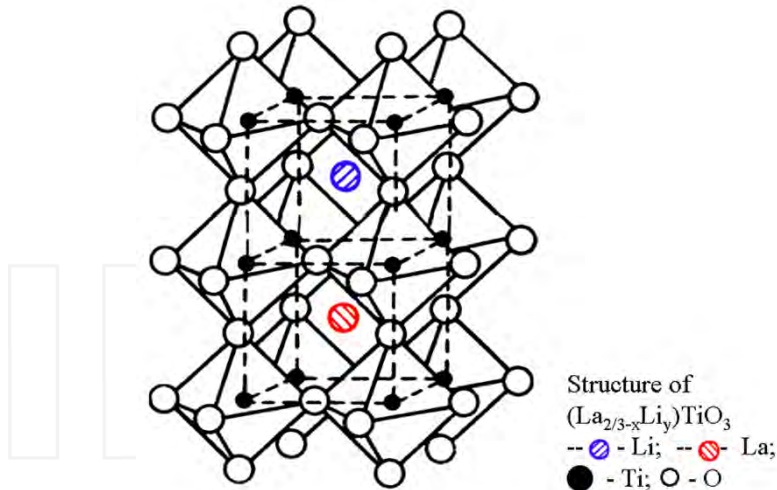


Figure 6. Perovskite structure of $La_{2/3-x}Li_{x/3}TiO_3$

x	ϵ	$TC\epsilon$, ppm/ $^{\circ}C$ (20–100 $^{\circ}C$)	Q (10 GHz)
0	80	-520	1300
0.30	95	-240	100
0.50	90	-140	150
0.55	85	-50	200
0.58	80	-5	200
0.60	75	+60	200
0.1	52	+580	100

Table 2. Dielectric parameters of the $Sm_{1/2}Li_{1/2}TiO_3 - (1-x)Sm_{1/2}Na_{1/2}TiO_3$ system at 10 GHz

6. MW dielectrics based on antiferroelectrics-paraelectrics

The permittivity value of the above-mentioned thermostable MW dielectrics is not over 80 – 100. To achieve higher permittivity values, use must be made of other polarization mechanisms connected with spontaneously polarized state. One of the possible ways of developing thermostable MW resonant elements is the creation of two-layer systems. Each of the layers must have a high Q ($Q = 1/ \text{tg } \delta$), a high permittivity and $TC\epsilon$ of different sign. A large number of high-Q dielectrics which have $TC\epsilon < 0$ in the MW range is known (mainly paraelectrics), whereas there are few of them with $TC\epsilon > 0$ ($LiNbO_3$, $LiTaO_3$, $LiAlO_3$ single crystals).

Besides, they are characterized by relatively low ϵ values ($\epsilon < 50$) in the MW range, and the use of them in this range makes it possible to obtain two-layer resonant dielectric elements with an effective permittivity (ϵ_{eff}) of not over 50. Therefore, we examined the possibility to use as high-Q materials with $TC\epsilon > 0$ antiferroelectrics based on tellurium-containing

Pb₂BTeO₆-type perovskites (B = bivalent metal ions) [36, 37]. It has been found that the plot of ϵ against temperature for lead-cobalt tellurate (Pb₂CoTeO₆) in the MW range passes through a maximum (phase transition from the antiferroelectric to the paraelectric state) at 380 K (Fig 7). At room temperature, the materials of this group have high permittivity values ($\epsilon > 110$). In the temperature range 220-350 K, the dependence ϵ (T) is close to linear one and has $TC\epsilon \sim 700 \times 10^{-6} \text{ K}^{-1}$. Two-layer resonant elements: Pb₂CoTeO₆ – TiO₂, Pb₂CoTeO₆ – CaTiO₃, Pb₂CoTeO₆ – SrTiO₃ have been prepared on the basis of paraelectrics (TiO₂, CaTiO₃, SrTiO₃) and the antiferroelectric Pb₂CoTeO₆. Known two-layer resonant dielectric LiNbO₃ – TiO₂ elements have been investigated for comparison. It can be seen from Table 3 and Fig 8 that Pb₂CoTeO₆ - SrTiO₃ based two-layer resonant elements have in the MW range a high effective permittivity ($\epsilon_{\text{eff}} \approx 135$), a high Q ($Q_{10\text{GHz}} \sim 900$) and a high temperature stability of dielectric parameters ($TC\epsilon$ tends to zero) [37]. Of course, two-layer systems have a number of demerits since they require mechanical bonding of different layers.

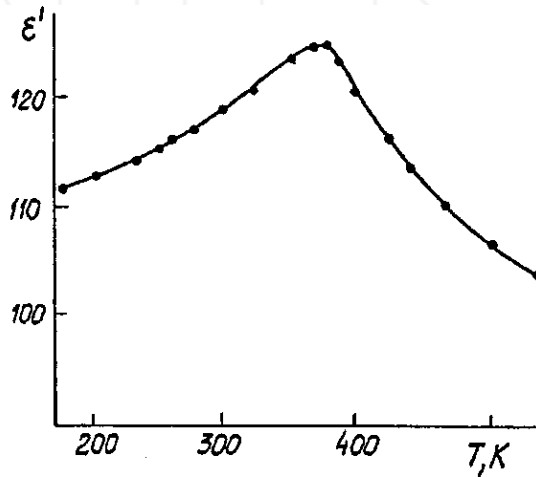


Figure 7. Plot of permittivity against temperature for Pb₂CoTe₆ at 10GHz

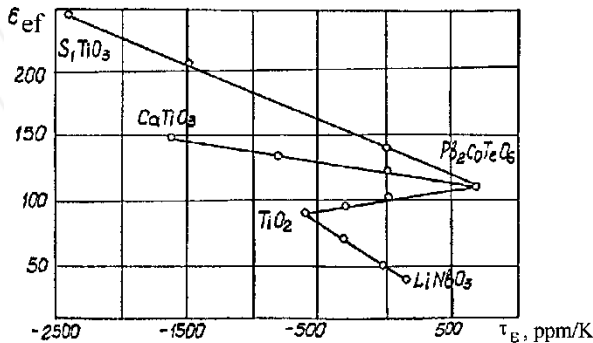


Figure 8. Dependence of the effective permittivity (ε_{eff}) of two layer resonant elements on the temperature coefficient of frequency (τ_E) at 10 GHz

Materials	Q _{ef.}	Q _{ef.}
Pb ₂ CoTe ₆ -TiO ₂	1000	110
Pb ₂ CoTe ₆ -CaTiO ₃	900	125
Pb ₂ CoTe ₆ -SrTiO ₃	900	135
LiNbO ₃ -TiO ₂	3000	49

Table 3. Properties of two-layer resonant elements at 10GHz

Thermostable MW dielectrics with high permittivity ($\epsilon \sim 430$) and Q ($Q_{1\text{GHz}} \sim 700$) have been obtained by the authors of [38] on the basis of the Ag (Nb, Ta) O₃ system, which is characterized by the spontaneously polarized state. However, in the materials in which the spontaneously polarized state is present, increase in permittivity is always accompanied by an increase in dielectric loss, which impairs the technical characteristics of MW elements made on their basis.

7. MW dielectrics based on spontaneously polarized phases

The materials in which there is a phase transition from the spontaneously polarized to the unpolarized state at high temperatures are characterized by positive TC ϵ . In the phase transition region, the tg δ values in the MW range are, as a rule, large, which is due to the presence of mobile domain walls (ferroelectrics). A salient feature of antiferroelectrics is the immobility of domain walls. This results in the fact that antiferroelectric (e.g. Pb₂CoTeO₆) is characterized by a relatively low tg δ value at room temperatures in the MW range [37]. In some cases, ferroelectrics, too, have low tg δ values, e.g. single-domain LiNbO₃ single crystal, in which phase transition is observed at high temperature (> 1200 °C).

It was interesting to find out whether it is possible to create thermostable MW dielectrics on the basis of solid solutions formed by ferroelectrics and/or antiferroelectrics, which are characterized by high phase transition temperature, and materials having a defect crystal structure (with vacancies). To this end, we investigated Ln_{2/3-x}Na_{3x}Nb₂O₆ materials (Ln = La, Nd), which were formed by interaction between the La_{2/3} • 4/3Nb₂O₆ phase with defect-perovskite structure (Fig 9) and the NaNbO₃ phase with perovskite structure (Fig 10), in which transition from the spontaneously polarized to the unpolarized state is observed at high temperature (> 520 °C).

An analysis of X-ray data for polycrystalline La_{2/3-x}Na_{3x} • 4/3-2xNb₂O₆ samples (Ln = La, Nd) showed that depending on x, solid solutions having three different space groups are formed. The space group changes in the order Pmmm \rightarrow Pmmn Pbcn with increasing x. In the interval $0 \leq x \leq 0.24$, the solid solutions have, independent of Ln, a defect-perovskite structure (La_{2/3} • 4/3Nb₂O₆), where is a vacancy in the cation sublattice with the space group Pmmm [39].

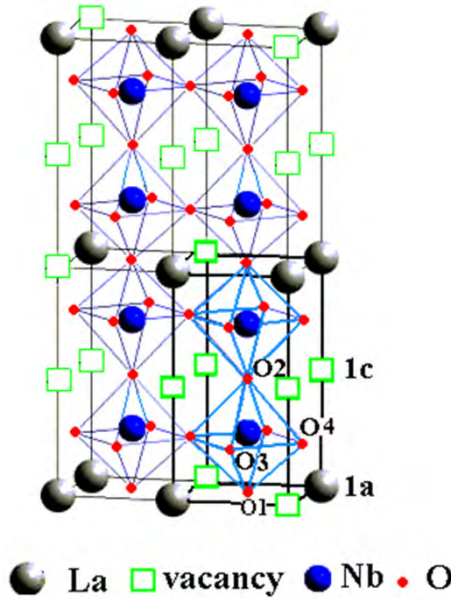


Figure 9. Defect-perovskite structure $\text{Ln}_{2/3} \bullet \frac{4}{3}\text{Nb}_2\text{O}_6$ (space group Pmmm). Atomic positions: La (1a) 000; Nb (2t) $\frac{1}{2} \frac{1}{2} z$; 0 (1) (1f) $\frac{1}{2} \frac{1}{2} 0$; 0 (2)

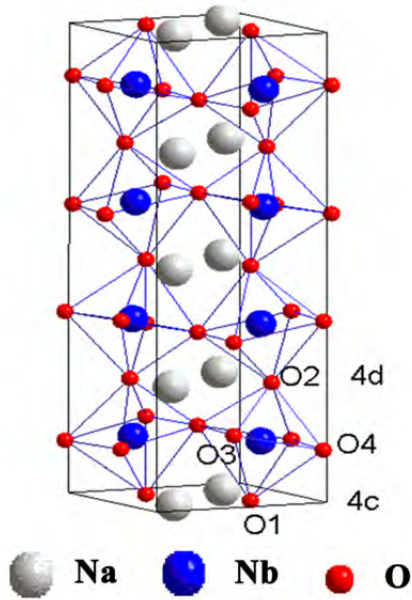


Figure 10. Perovskite structure of NaNbO_3 at room temperature (space group Pbcm). Atomic positions: Na (1) (4c) $x \frac{1}{4} 0$; Na (2) (4d) $x y \frac{1}{4}$; Nb (8c) $x y z$; O (1) (4c) $x \frac{1}{4} 0$; O (2) (4d) $x y \frac{1}{4}$; O (3) (8c) $x y z$; O (4) (8c) $x y z$

When x is increased, the space group changes, independent of the kind of Ln, from Pmmm to Pmnm. In neodymium-containing solid solutions, the change of space group does practically lead to change in normalized unit cell volume V/Z ; in lanthanum-containing solid solutions, monotonic variation of V/Z as a function of x is accompanied by a slight inflection in the sodium concentration range corresponding to the change from Pmmm to Pmnm. The observed differences in the trend of plots of $V/Z(x)$ are probably due to the fact that the ionic radius of Na^+ is smaller than that of the substituted La^{3+} ion, whereas the difference in the ionic radii of Na^+ and Nd^{3+} is small. The closeness of the ionic radius values of Na^+ and Nd^{3+} leads to the existence of a wider concentration range ($0.24 \leq x \leq 0.54$), which corresponds to the space group Pmmm, for neodymium-containing solid solutions as compared with lanthanum-containing ones ($0.24 \leq x \leq 0.45$).

In the intervals $0.54 \leq x \leq 0.66$, (for neodymium) and $0.45 \leq x \leq 0.66$ (for lanthanum), the crystal structure of $\text{La}_{2/3-x}\text{Na}_{3x} \cdot 4/3-2x\text{Nb}_2\text{O}_6$ solid solutions has the space group Pbcn, which is typical of NaNbO_3 at room temperature [40]. In fact, when the sodium content of the system is increased, a decrease in the symmetry of solid solutions from Pmmm to Pmnm and to Pbcn is observed.

$\text{La}_{2/3}\text{Nb}_2\text{O}_6$ and $\text{Nd}_{2/3}\text{Nb}_2\text{O}_6$ materials ($x = 0$) are characterized by a high permittivity value (130 and 160 respectively) and a relatively low dielectric loss (in both cases, $\text{tg } \delta$ is of the order of $2 - 5 \times 10^{-3}$ at a frequency of 10 GHz). There is no permittivity dispersion. The plot of $\epsilon(T)$ for $\text{La}_{2/3}\text{Nb}_2\text{O}_6$ and $\text{Nd}_{2/3}\text{Nb}_2\text{O}_6$ materials exhibits deflections in the MW range. In the low-temperature range, the ϵ value varies only slightly with rising temperature. As the x values in $\text{La}_{2/3-x}\text{Na}_{3x} \cdot 4/3-2x\text{Nb}_2\text{O}_6$ materials (Ln = La, Nd) increases, $\text{TC}\epsilon$ changes its sign from negative to positive. Plots of dielectric parameters against concentration in the MW range are shown in Fig 11. In the interval $0 \leq x \leq 0.24$ (space group) Pmmm, increasing the sodium concentration leads to a slight increase in permittivity independent of the kind of rare-earth element (La or Nd), which is accounted for by increase in cation vacancy concentration.

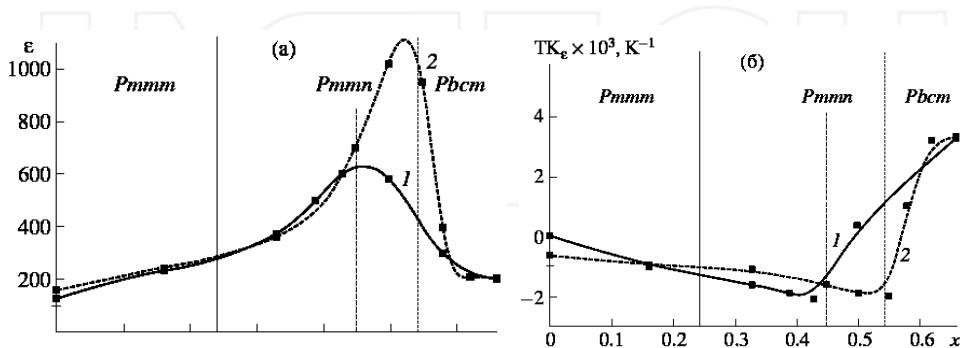


Figure 11. Plots of permittivity (a) and the temperature coefficient of permittivity (b) against the sodium content of the solid solutions $\text{La}_{2/3-x}\text{Na}_{3x} \cdot 4/3-2x\text{Nb}_2\text{O}_6$ (1) and $\text{Nd}_{2/3-x}\text{Na}_{3x} \cdot 4/3-2x\text{Nb}_2\text{O}_6$ (2)

Within the limits of the space group Pmmn, the permittivity value decreases greatly with increasing x , passing through a maximum, when the space group changes from Pmmn to Pbcn. Investigations showed that it is possible to create thermostable dielectrics based on the system in $\text{Ln}_{2/3}\text{Na}_{3x} \bullet_{4/3-2x}\text{Nb}_2\text{O}_6$ (Ln = La, Nd), which have a high permittivity ($\epsilon \sim 300-600$) and a relatively low dielectric loss ($\text{tg } \delta \sim 2-7 \times 10^{-3}$) in the MW range [41, , , 44].

The systems considered above have a relatively high thermostability of electrophysical properties ($\text{TC}\epsilon \sim 10^{-5} - 10^{-6}\text{K}^{-1}$), $Q \times f \leq 12000$ and relatively high permittivity values ($\epsilon \geq 80-600$) in the MW range. This makes it possible to develop on their basis elements for decimeter wave band communication systems, where the problems of microminiaturization, for the solution of which high ϵ values are required, are especially important.

In the centimeter wave band and especially in the millimeter wave band, however, materials with relatively low permittivity (10-30) are required, which must possess very high Q values ($Q \times f \geq 80000 - 100000$). Let us consider some systems, which have promise in gaining these purposes.

8. $\text{M}_{1+x}\text{Nb}_2\text{O}_6$ – Based MW dielectrics (M = Mg, Co, Zn) with columbite structure

Among the MW dielectrics known to date, $\text{M}^{2+}\text{Nb}_2\text{O}_6$ niobates (M = Mg, Co, Zn) are of considerable interest. The crystal structure of $\text{A}^{2+}\text{Nb}_2\text{O}_6$ columbite is infinite zigzag chains of oxygen linked by shared edges (Fig 12) [45]. For this structure, redistribution of crystal sites, which are in the oxygen octahedral, among A^{2+} ion size and the cation ratio $\text{Nb}^{5+} : \text{A}^{2+}$ in the unit cell will affect the crystallographic distortions of the columbite structure and hence the phase composition and electrophysical properties of synthesized materials.

The ZnNb_2O_6 and MgNb_2O_6 materials have a high Q (3000 and 9400 respectively) and permittivity (23 and 20 respectively) [46, 47, 48]. In contrast to magnesium- and zinc-containing niobates, the literature data on the dielectric properties of cobalt niobate (CoNb_2O_6) are very contradictory. For instance, Ref [46] reported low Q values for CoNb_2O_6 ($Q \times f = 40000$). Earlier it was shown [49, 50, 51, 52, 53] that the making of single-phase $\text{M}^{2+}\text{Nb}_2\text{O}_6$ materials depends largely upon their synthesis conditions. For instance, the difficulty of making single-phase magnesium niobate with columbite structure is accounted for, in particular, by the simultaneous formation of two phases: MgNb_2O_6 columbite and $\text{Mg}_4\text{Nb}_2\text{O}_9$ corundum [51]. It should be noted that in the Mg-Nb-O system, a number of compounds: MgNb_2O_6 , $\text{Mg}_4\text{Nb}_2\text{O}_9$, $\text{Mg}_5\text{Nb}_4\text{O}_{15}$, $\text{Mg}_{1/3}\text{Nb}_{11(1/3)}$ are formed [52, 53]; however, only the phases MgNb_2O_6 (columbite structure) and $\text{Mg}_4\text{Nb}_2\text{O}_9$ (corundum structure) are stable at room temperature [54]. Therefore, even after long heat treatment at high temperature ($T > 1100^\circ\text{C}$) [50], there were intermediate phases in the end product (generally a corundum phase). In such cases, the phase composition and electrophysical properties can be greatly affected even by a small deviation from stoichiometry. In view of this, we have studied the effect of small deviations from stoichiometry in $\text{A}^{2+}\text{Nb}_2\text{O}_6$ materials (A = Co, Mg, Zn) with columbite structure on phase composition, microstructure and MW properties [55, 56, 57].

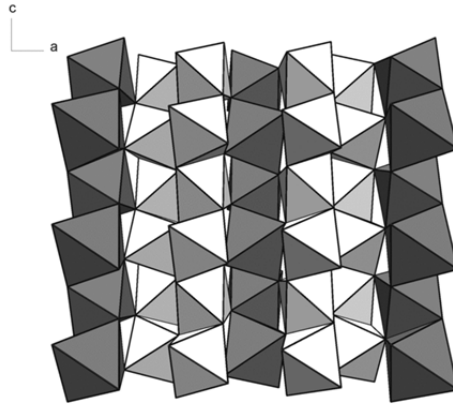
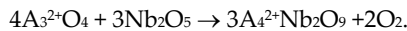
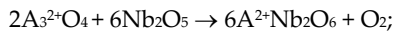
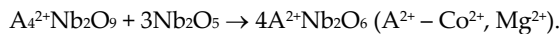


Figure 12. Columbite structure of $A^{2+}Nb_2O_6$

We have shown that when the solid-state reaction method is used, the formation of cobalt- and magnesium-containing niobates with columbite structure is a multistage process. In this case, two concurrent processes of formation of niobates with columbite structure ($A^{2+}Nb_2O_6$) and corundum structure ($A_4^{2+}Nb_2O_9$) ($A^{2+} = Co^{2+}, Mg^{2+}$) take place:



At higher temperatures (> 1000 °C), the formation of columbite structure took place by interaction between the $A_4^{2+}Nb_2O_9$ phase and unreacted Nb_2O_5 :



At the same time, the synthesis of $ZnNb_2O_6$ with columbite structure takes place in the temperature range 500-800 °C without formation of intermediate products.

In the case of deviation from stoichiometry in the $A_{1+x}Nb_2O_6$ system ($A^{2+} = Mg^{2+}, Co^{2+}, Zn^{2+}$), when $x < 0$, samples contained two phases: the main phase $A^{2+}Nb_2O_6$ with columbite structure and the Nb_2O_5 phase, whose concentration increased with x (Fig 13). At $x > 0$, a narrow concentration range, in which samples are single-phase ones, exists in all three systems. On further deviation from stoichiometry in the direction of increasing excess of cobalt, magnesium or zinc, extra phases are formed.

The results of investigating electrophysical properties in the MW range turned out unlooked-for. At $x < 0$, when there were traces of the minor phase Nb_2O_5 , the samples had a low Q . At the same time, extremely high Q values ($Q \times f$) were observed at $x > 0$ (Fig 14). For example, in $Mg_{1+x}Nb_2O_6$, $Q \times f$ reached a value of 128000 at $x \geq 0.03 - 0.05$ in multiphase samples, in which the phase $Mg_4Nb_2O_9$ (corundum structure) was present together with the main phase $MgNb_2O_6$ (columbite structure).

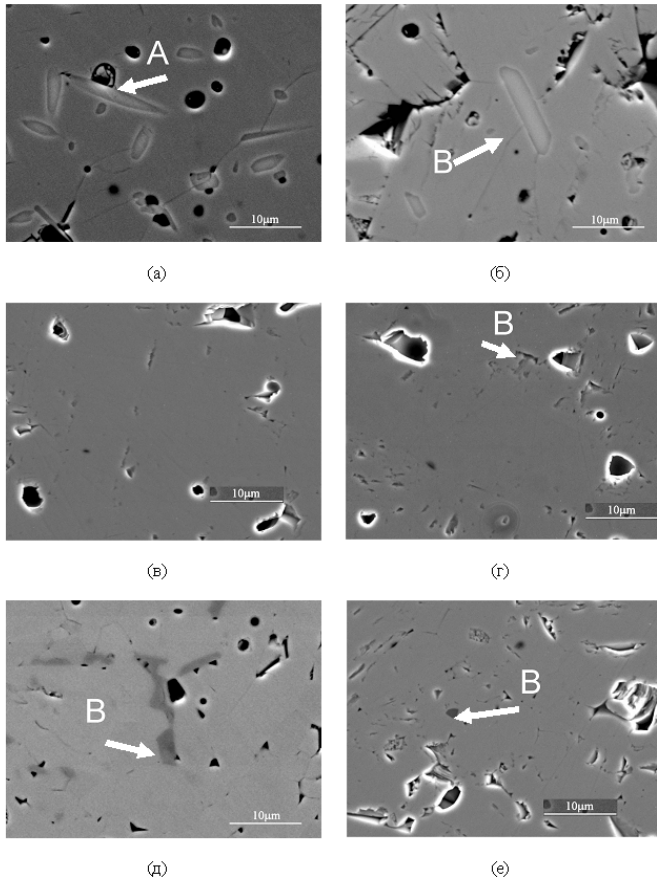


Figure 13. Micrographs of microsections of polycrystalline $\text{Co}_{1-x}\text{Nb}_2\text{O}_{6-x}$ samples with $x = 0.05$ (a), $x = 0.03$ (b), $x = 0$ (c), $x = -0.03$ (d), $x = -0.05$ (e, f), sintered at $1500\text{ }^\circ\text{C}$ for 1h (a - f), 6 h (e): A = Nb_2O_5 , B = $\text{Co}_4\text{Nb}_2\text{O}_9$

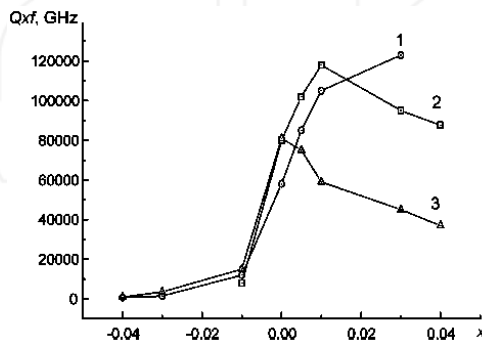


Figure 14. Plots of the product $Q \times f$ of $\text{A}_{1-x}\text{Nb}_2\text{O}_6$ samples (where A = Mg (1), Zn (2), Co(3)) against concentration. The samples were sintered in air for 8 h at $1400\text{ }^\circ\text{C}$ (1 and 3) and $1300\text{ }^\circ\text{C}$ (2).

This is accounted for by the high Q values ($Q \times f \sim 230000$) of the extra phase $\text{Mg}_2\text{Nb}_4\text{O}_9$. However, further deviation from stoichiometry leads to a considerable decrease in permittivity, which is due to the fact that ϵ of the corundum phase was 11.

This instance is interesting in that each of the phases MgNb_2O_6 and $\text{Mg}_2\text{Nb}_4\text{O}_9$ characterized by certain merits and demerits. Only multiphase materials based on them have both a relatively high permittivity ($\epsilon \sim 20$) and a high Q ($Q \times f \sim 128000$) in the MW range.

9. ZrO_2 - TiO_2 - SnO_2 – Based Mw dielectrics

The first information about ZrTiO_4 as a promising high- Q dielectric was presented in Ref [58]. Later, in the 1950s, investigations of solid solutions in the ZrO_2 - TiO_2 - SnO_2 system were carried out [59]. It was shown that the composition $\text{Zr}_{0.8}\text{Sn}_{0.2}\text{TiO}_4$ has the highest Q values [60, 61].

ZrTiO_4 crystallizes in orthorhombic structure (space group Pbcn) [62, 63, 64] with the space lattice parameters: $a = 4.806\text{\AA}$, $b = 5.447\text{\AA}$, $c = 5.032\text{\AA}$. The unit cell contains two formula units, theoretical density 5.15 g/cm^3 . It should be noted that in ZrTiO_4 there is an order-disorder phase transition in the temperature range 1100 - 1200°C [65, , , , 69]. When the temperature is decreased, this transition is from an α - PbO_2 – type high-temperature phase of which disordered arrangement of Zr and Ti ions is typical, to a low-temperature phase with ordered arrangement of Zr and Ti ions [70, 71]. Addition of Sn to ZrTiO_4 results in the stabilization of the disordered distribution of cations. The variation of the lattice parameters in the $\text{Zr}_{1-x}\text{Sn}_x\text{TiO}_4$ system with increasing x is shown in Fig15. As is seen from Fig 15, there are no noticeable changes in the behavior of the parameters a and b in the phase transition region (1100 - 1200°C) with increasing Sn content. At the same time, as Sn ions are added, a noticeable change in the dependence of the parameter c in the phase transition region is observed [69].

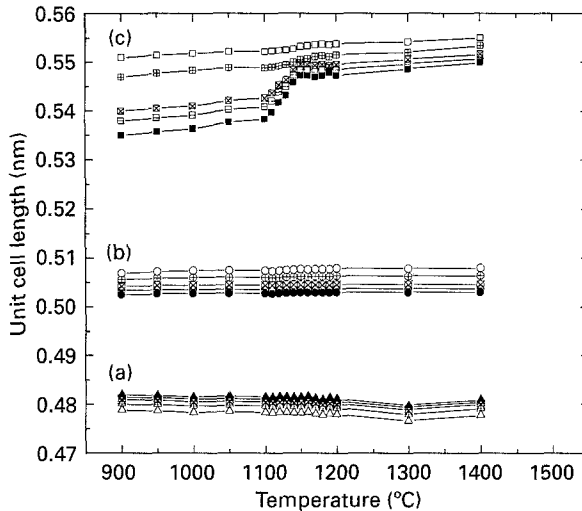


Figure 15. Variation of the lattice parameters of $\text{Zr}_{1-x}\text{Sn}_x\text{TiO}_4$ materials as a function of temperature: (■) - ZrTiO_4 ; (◻) $\text{Zr}_{0.95}\text{Sn}_{0.05}\text{TiO}_4$; (⊠) $\text{Zr}_{0.9}\text{Sn}_{0.1}\text{TiO}_4$; (◼) $\text{Zr}_{0.8}\text{Sn}_{0.2}\text{TiO}_4$; (□) $\text{Zr}_{0.7}\text{Sn}_{0.3}\text{TiO}_4$ [69].

The phase transition is greatly affected by the cooling rate of $Zr_{1-x}Sn_xTiO_4$ samples (Fig. 16.). At high cooling rates, the high-temperature disordered phase is frozen in the sample. As the cooling rate is decreased, a noticeable change in the behavior of the parameter c is observed, which is connected with increase in the degree of cation ordering [69].

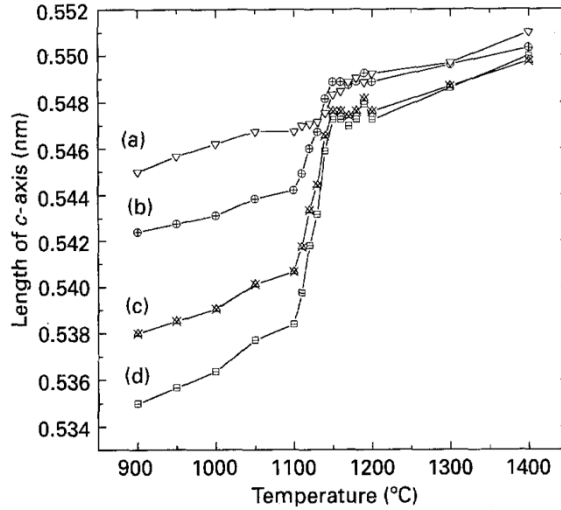


Figure 16. Variation of the parameter c of $Zr_{1-x}Sn_xTiO_4$ ceramic as a function of temperature at different cooling rates: (a) 100°C/h, (b) 15°C/h, (c) 5°C/h, (d) 1°C/h [69].

In the system $Zr_xSn_yTi_zO_4$, where $x+y+z = 2$, single-phase materials are formed in a limited region [62]. The partial substitution of Sn ions for Zr ions stabilized the high-temperature phase with disordered distribution of cations [72] and extends the temperature range of phase transition in $ZrTiO_4$ [73, 74].

Many authors studied the dielectric properties of $ZrTiO_4$ in the MW range and showed it to have the following parameters: $\epsilon = 42$, $Q \times f = 28\,000$ GHz, $\tau_f = 58$ ppm/°C [62, 63, 75, 76]. The partial substitution of Sn ions for Zr ions affects greatly the dielectric properties of $Zr_{1-x}Sn_xTiO_4$ materials.

The substitution of Sn ions for Zr ions results in the formation of $Zr_{0.8}Sn_{0.2}TiO_4$, which has good dielectric properties in the MW region: $\epsilon = 38$, $Q \times f = 49\,000$ GHz, $\tau_f = 0$ ppm/°C [77]. This made it possible to use widely this composition in engineering. The use of anatase as a starting reagent instead of rutile made it possible to increase the value of $Q \times f$ [78]. It should be noted that cation ordering in the $ZrTiO_4$ structure leads to an increase in $Q \times f$. It was shown that addition of tin leads to a decrease in cation ordering [62, 72, 79, 81], but in spite of this, the value of $Q \times f$ increases greatly. Cation ordering is also observed in tin-containing samples, but the ordering domain size decreases with increasing tin content [82]. These data indicate that the increase in $Q \times f$ on the partial substitution of tin ions for zirconium ions cannot be attributed to cation ordering. The authors of [80] suggested that segregation of tin

ions takes place at domain boundaries, which decrease their contribution to dielectric loss in ceramic.

Zr_{0.8}Sn_{0.2}TiO₄- based dielectric materials are widely used in the manufacture of various MW equipment elements [63, 83, , 85]. However, the manufacture of high-density Zr_{0.8}Sn_{0.2}TiO₄ ceramic is a big technological problem even at high temperatures (above 1600°C). Therefore, many authors studied the effect of small additions on the sintering temperature and density of Zr_{0.8}Sn_{0.2}TiO₄ [85,88]. The dopants ZnO, CuO, Y₂O₃ are generally used. Addition of small amounts, e.g. of ZnO, results in the formation of a liquid phase at grain boundaries, which increases greatly the ceramic density thanks to fast mass transport through the liquid phase and considerable decrease in sintering temperature.

10. Ba(M²⁺_{1/3} M⁵⁺_{2/3})O₃ – Based MW dielectrics (M²⁺ = Mg, Zn, Co, Ni; M⁵⁺ = Ta, Nb) with extremely high Q

Ba(B²⁺_{1/3} B⁵⁺_{2/3}) O₃ compounds where B²⁺ = Mg, Zn, Co, Ni; B⁵⁺ = Ta, Nb (perovskite crystal structure) had been synthesized for the first time by the authors of [89,, , 92]. In these compounds, a 2:1- type ion ordering in the B sublattice is observed, in which two layers filled with B⁵⁺ ions alternate with a layer filled with B²⁺ ions. The authors [93, 94] showed that tantalum-containing materials possess a high Q value in the MW range. It should be noted that the synthesis of these materials involves many problems. Ceramics sinter at a high temperature, which may result in considerable evaporation of constituents (cobalt, zinc) and hence in the impairment of electrical properties. In the case of synthesis by the solid-state reaction method, extra phases Ba₅Ta₄O₁₅, Ba₄Ta₂O₉ are often present in ceramics [95], which affect adversely the Q value. To prevent this, the authors of [96] carried out synthesis from solutions, where solutions containing Mg²⁺, Ta⁵⁺ were used as starting substances, to which a solution of ammonia with oxyquinoline was added.

It had been found that in this case, the single-phase product Ba(Mg_{1/3}Ta_{2/3})O₃ is formed above 1300 °C without intermediate phases. Single-phase Ba(Mg_{1/3}Ta_{2/3})O₃ had been obtained by the solid-state reaction method too, using highly active reagents as starting substances [95-97].

When synthesizing tantalum-containing materials, the preparation of high-density ceramics was a difficult problem. Therefore, Nomura with coauthors [98] proposed to prepare dense ceramics ($\rho \approx 7520 \text{ kg/m}^3$) by using additionally manganese impurities. Matsumoto and Hinga [99] used fast heating (330 °C/min) for the same purposes, which made it possible to achieve 96% of the theoretical density. To increase the rate of sintering and to order ions in the B sublattice, the authors of [100, 101] proposed preliminarily synthesized MTa₂O₆ (M = Mg, Zn) as starting reagents. Renoult with coworkers [102] had synthesized fine-grained Ba(MgTa)O₃ by the sol-gel method. In that case, dense ceramics could be obtained without additives.

The Q value in Ba(B²⁺_{1/3} B⁵⁺_{2/3})O₃ perovskites is greatly affected by the type and degree of ion ordering in the B sublattice [103]. It had been found that by the partial substitution of Zr⁴⁺,

Ti^{4+} , W^{6+} ions for ions in the B sublattice, one can increase the degree of 1:2 - type ion ordering and hence increase the Q value [104, 105].

Ion ordering in the B sublattice is also affected by slight substitutions of ions in the A sublattice. For instance, Ref [104] showed that partial substitution of La^{2+} ions for Ba^{2+} ions in magnesium-barium tantalate results in the change of ion ordering in the B sublattice from the 2:1 type (space group Pm3I) to the 1:1 type (space group Fm3m). Similar changes of the type of ion ordering in the B sublattice were found in the case of partial substitution of lanthanum ions for barium ions in zinc-barium niobate with perovskite structure [105]. This result shows that the type of ion ordering in the B sublattice is very sensitive to chemical composition and preparation technique. The 1:1-type ion ordering in the B sublattice in $\text{Ba}(\text{B}^{2+}_{1/3} \text{B}^{5+}_{2/3})\text{O}_3$ compounds was explained in terms of a "space-charge" model [106, 107], according to which only B^{2+} and B^{5+} ions can occupy the sites in the ordered $\text{Ba}(\beta'_{1/2} \beta'_{1/2})\text{O}_3$ structure (1:1 type). Since in this case the electroneutrality condition is not satisfied in the crystalline phase, it may be assumed that the domains of the ordered crystalline phase (ordering type 1:1), which has an uncompensated charge, are in a disordered matrix rich in B^{5+} ions, as a result of which the electroneutrality condition is satisfied throughout the sample volume.

However, when investigating the system of solid solutions $(1-x)\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{La}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ($0 \leq x \leq 0.6$), it was shown that 1:2 -type ordering persists in the interval $0 \leq x \leq 0.5$ [105], whereas in the interval $0.05 \leq x \leq 0.6$, 1:1 ion ordering in the B sublattice is observed. In this case, there is no aggregation. The investigation of the microstructure did not reveal the existence of disordered perovskite phase region, which was assumed in the "space-charge" model. Therefore, to describe the 1:1 ion ordering in the B sublattice, a "random-site" model was proposed [105, 108, , 110]. According to this model, 1:1 ordering in the above systems is described as follows. There are two alternating crystal planes, in which the B sublattice ions reside. One of them is occupied with B^{5+} cations and the other with B^{2+} cations and the remaining B^{5+} cations, which are disordered in this crystal plane.

Thus, in $\text{Ba}(\text{M}^{2+}_{1/3} \text{M}^{5+}_{2/3})\text{O}_3$ compounds with perovskite structure, the B sublattice ions may be fully disordered as well as have 1:2 or 1:1 ordering. A calculation of the lattice energy of ordered and disordered structures showed [111] that ordered structure is characterized by lower Madelung energy, indicating this structure to be stable. Investigations of the electrophysical properties of $\text{Ba}(\text{B}^{2+}_{1/3} \text{B}^{5+}_{2/3})\text{O}_3$ compounds showed that ion ordering in the B sublattice affects greatly the Q value [112].

It should be noted that $\text{Ba}(\text{B}^{2+}_{1/3} \text{B}^{5+}_{2/3})\text{O}_3$ compounds with perovskite structure and 1:1 cation ordering in the B sublattice have, as a rule, a relatively low Q [113]. The largest Q value is observed in the $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ and $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ compounds. In these compounds, the B cations are stoichiometrically ordered in the hexagonal unit cell Pm3I (2:1ordering), in which the layers of Ta^{5+} and $\text{Zn}(\text{Mg})^{2+}$ cations are sequentially arranged along the (111) crystal plane (Fig 17). The layers of cations are separated by oxygen layers, which are displaced in the direction of small pentavalent tantalum cations [112]. The Q value is very sensitive to ordering in the B sublattice [93, 114]. It can be greatly increased by using

additional annealing. For instance, the $Q \times f$ value increased from 60000 to 168000 after additional annealing at 1350 °C for 120 h [93].

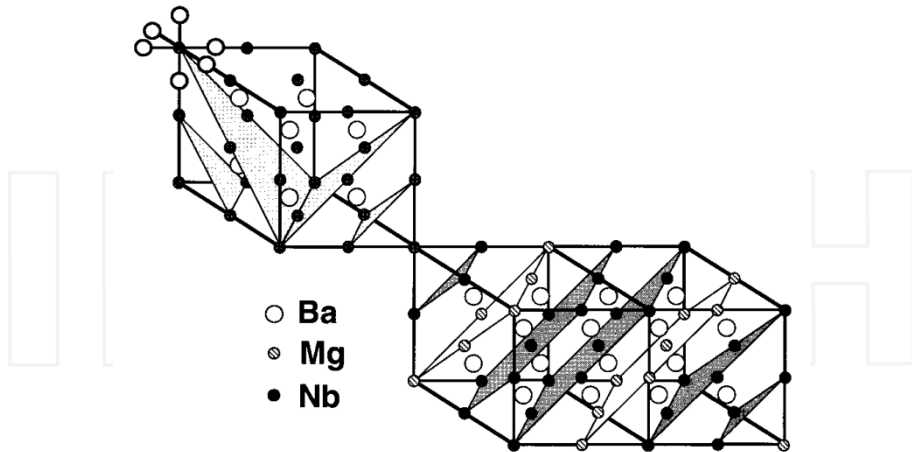


Figure 17. Schematic representation of 1:2 cation ordering in Ba(Zn_{1/3}Ta_{1/3})O₃. On the top left are shown two possible (111) directions for Zn and Ta orientation in the perovskite structure; on the right below is shown one of the possible variants of 1:2 ordering. The oxygen ions were omitted for clarity [108].

Tamura et al [115] showed that Q in Ba(Zn_{1/3}Ta_{2/3})O₃ can be improved by adding BaZrO₃(BZ) of low concentration (< 4 mol %). In this case, the ceramic sintering time is greatly reduced, which is required for the attainment of high Q values ($Q \times f = 105000$ had been attained by adding 4 mol % BZ).

This was accounted for by the formation of defects in the B sublattice, the presence of which increased the rate of cation ordering in this sublattice. As the BZ concentration was increased, the type of ordering changed (when substitution reached 4 mol %), the system came to have 1:1 ordering and a double cell. Similar regularities were observed when small amounts of BaWO₄ [116] and BaSnO₃ [117] were added to Ba(Mg_{1/3}Ta_{2/3})O₃. The individual compounds Ba(Mg_{1/3}Ta_{2/3})O₃ and Ba(Zn_{1/3}Ta_{2/3})O₃ allow one to achieve high Q values, but their electrophysical properties have a low thermostability. Therefore, to increase the thermostability of electrical properties, materials are synthesized on the basis of solid solutions, where the end members have temperature dependences of permittivity of different sign. The materials based on solid solutions possess a higher thermostability, but the Q value is lower as compared with individual compounds, which may be attributed, in particular, to decrease in cation ordering in the B sublattice. On the basis of a solid solution, e.g. Ba(Zn_{1/3}Ta_{2/3})O₃, materials have been obtained which have a high level of electrophysical properties: $\epsilon = 30-40$, $TC\epsilon = (0-28) \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, $Q_{8\text{GHz}} = 15000$.

The materials based on tantalum-containing perovskites possess today the highest Q values in the MW range among dielectrics with increased ϵ value. However, the difficulty of their synthesis: high sintering temperatures ($T_{\text{sint}} > 1600 \text{ } ^\circ\text{C}$), the necessity of long additional

annealing ($T_{\text{ann}} \approx 1500$ °C, 20-120 h), low reproducibility of properties, as well as the high price of tantalum (in 2000, the price of reagents containing tantalum increased by 500%) calls for search for new promising systems. Therefore, in recent years, attention has been given just to niobium-containing $\text{Ba}(\text{Nb}_{2/3}\text{B}^{2+}_{1/3})\text{O}_3$ compounds (where $\text{B}^{2+} = \text{Mg}, \text{Zn}, \text{Co}$), which crystallize in perovskite structure [118, 119, 120].

These materials sinter at lower temperature, and cheaper reagents are needed for them. However, their main disadvantage is a lower Q value as compared with tantalum-containing perovskites [121, 122]. We have shown for the first time that $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – based materials can have in some cases an extremely high Q ($Q \times f \approx 150000$) [123]. New papers appeared [5, 124, 125], which show the creation of high- Q MW dielectrics based on niobium-containing perovskites to be worth-while.

$\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BCN) offers a particularly attractive combination of properties. Polycrystalline $\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ has high dielectric permittivity ($\epsilon = 32$) and $Qf = 40000\text{--}60000$ GHz [126, 127]. At the same time, centimeter and millimeter wave applications require higher Q values. The properties of BCN are very weak functions of temperature. In particular, the temperature coefficient of its resonant frequency (τ_f) lies in the range -10 to -7 ppm/K, suggesting that it can be used in the production of high- Q /low- τ_f microwave materials [128, , 130]. The electrical properties of BCN, especially its Q (or its Qf product, where f is frequency), strongly depend on preparation conditions, in particular on the sintering temperature, heat-treatment time, and heating/cooling rate.

It is reasonable to assume that the observed variations in the properties of BCN are related to the ceramic microstructure evolution during the fabrication process, cation ordering, and lattice distortions. Such distortions can be produced in BCN via slight changes in its cation composition.

Therefore, we have studied the effect of partial nonstoichiometry in cation sublattices on the phase composition, microstructure and electrophysical properties of BCN.

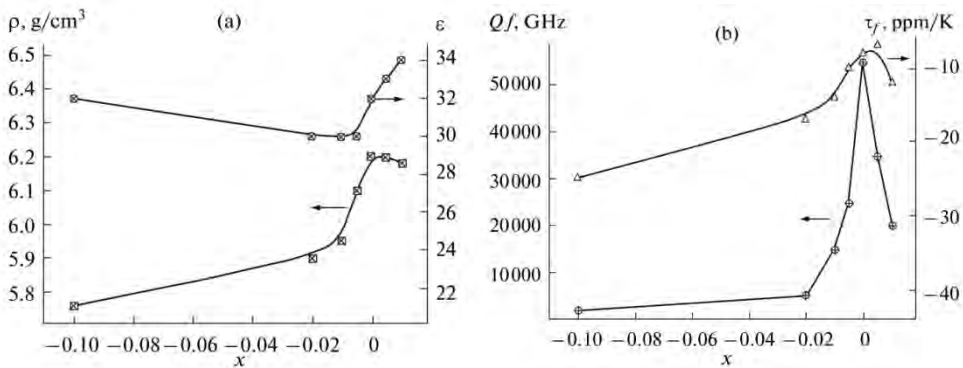


Figure 18. Composition dependences of the (a) apparent density (ρ), permittivity (ϵ), (b) Qf product, and temperature coefficient of resonant frequency (τ_f) for $\text{Ba}_{3+3x}\text{CoNb}_2\text{O}_{9+3x}$ materials; measurements at 10 GHz.

When studying nonstoichiometry in barium sublattice ($\text{Ba}_{1-x}\text{Co}_{1/3}\text{Nb}_{2/3}\text{O}_{3+x}$ at $-0.03 < x < 0.03$), an extra phase $\text{Ba}_9\text{CoNb}_{14}\text{O}_{45}$ appears, which makes a noticeable decreases greatly (Fig. 18(a)). Therefore, the highest Q values are observed for stoichiometric composition ($\text{BaCo}_{1/3}\text{Nb}_{2/3}\text{O}_3$) (Fig. 18(b)).

Interesting properties are observed in the case of nonstoichiometry in the cobalt sublattice ($\text{BaCo}_{1/3+y}\text{Nb}_{2/3}\text{O}_{3+y}$, where $-0.05 < y < 0.01$).

Increasing the cobalt content of this system with reference to stoichiometry leads to a monotonic increase in relative density and corresponding slight increase in permittivity ϵ in the range 32 to 34 (Fig. 19a). At higher cobalt deficiencies ($y < -0.02$), the samples contained an additional phase $\text{Ba}_8\text{CoNb}_6\text{O}_{24}$. In the range $-0.03 \leq y \leq 0.01$, the quality factor varies nonlinearly, with a maximum at $-0.03 \leq y \leq -0.02$. The Qf product exceeds that of stoichiometric BCN by 30–50%, reaching 80000–85000 GHz (Fig. 19b).

Electron diffraction data for the $\text{BaCo}_{1/3+y}\text{Nb}_{2/3}\text{O}_{3+y}$ samples indicates that cobalt deficiencies in the range $-0.03 \leq y \leq -0.02$ are favourable for 1 : 2 B-site cation ordering in the cobalt-containing perovskite (Fig. 20). As mentioned above, cation ordering is accompanied by an increase in quality factor, as observed in this system (Fig. 18b). The reduction in quality factor at large deviations from stoichiometry ($y < -0.1$) is due to the presence of a significant amount of $\text{Ba}_8\text{CoNb}_6\text{O}_{24}$.

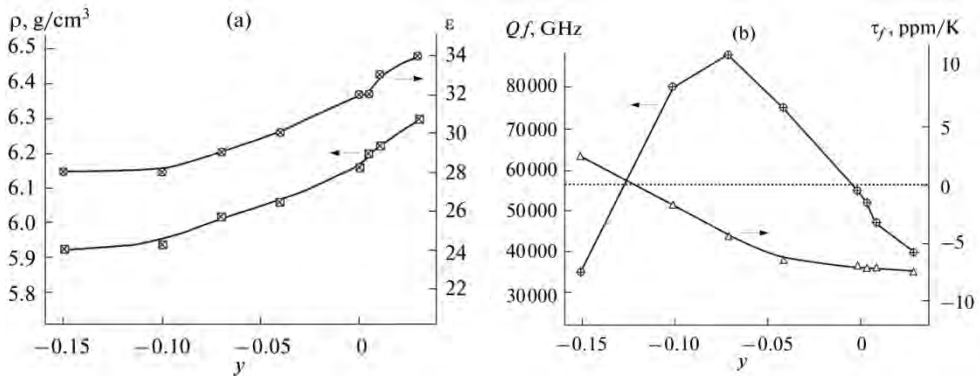


Figure 19. Composition dependences of the (a) apparent density (ρ), permittivity (ϵ), (b) Qf product, and temperature coefficient of resonant frequency (τ_f) for $\text{Ba}_3\text{Co}_{1+y}\text{Nb}_{2/3}\text{O}_{3+y}$ materials; measurements at 10 GHz.

The increase in $\text{Ba}_8\text{CoNb}_6\text{O}_{24}$ content with increasing cobalt deficiency ($y < 0$) leads to a result of practical interest: the temperature coefficient of resonant frequency switches sign (Fig. 18 b). The reason for this is that $\text{BaCo}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{Ba}_8\text{CoNb}_6\text{O}_{24}$ differ in the sign of τ_f : -7 and $+16$ ppm/K, respectively [129, 131]. Because of this, the $\text{BaCo}_{1/3+y}\text{Nb}_{2/3}\text{O}_{3+y}$ materials exhibit a temperature compensation effect, whose magnitude can be tuned by varying the cobalt content. The present results, therefore, suggest that cobalt-deficient $\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ is

an attractive host for engineering advanced temperature-stable microwave dielectric materials with Q_f on the order of 80000–90000 GHz and $\tau_f = -2$ to $+3$ ppm/K.

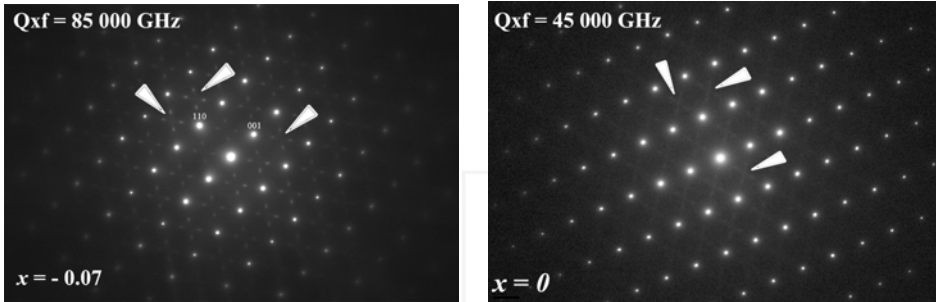


Figure 20. [110] electron diffraction patterns of the $\text{Ba}_3\text{Co}_{1+y}\text{Nb}_2\text{O}_{9+y}$ samples with $y =$ (a) -0.07 and (b) 0 . The arrows mark superlattice reflections.

11. Multiphase MW dielectrics

High Q value is usually observed in single-phase systems. In the case of complex cation sublattices, it is necessary that the ions should be ordered by a definite type [105, 106]. In multiphase systems, which are chemically inhomogeneous, considerable dielectric loss (relatively low Q) is generally observed. When investigating barium polytitanates, however, we showed that multiphase systems having a high Q and thermostability of electrophysical properties can be formed. When zinc oxide is added to barium polytitanates, an extra $\text{BaZn}_2\text{Ti}_4\text{O}_{11}$ phase is formed [132] which does not interact chemically with the main phase. A multiphase system is formed, in which the main and extra phases have the dependence $\varepsilon(T)$ of different sign, which ensures the realization of the volume temperature compensation effect and hence a high thermostability of electrophysical properties ($\text{TC}\varepsilon = \pm 2 \times 10^{-6}\text{K}^{-1}$) in the MW range. The multiphase dielectrics obtained have a high Q ($Q_{10\text{GHz}} \sim 6500\text{--}7000$).

One more example of multiphase MW dielectrics is TiO_2 materials, viz the compounds MgTiO_3 and Mg_2TiO_4 , which have a high Q ($Q_{10\text{GHz}} \sim 5000\text{--}10000$) and permittivity (14 and 16 respectively) [133]. A demerit of these materials is the temperature instability of electrophysical parameters ($\text{TC}\varepsilon = (40\text{--}50) \times 10^{-6}\text{K}^{-1}$). To increase the Q value, cobalt ions were partially substituted for magnesium ions, and to increase the temperature stability of electrophysical properties, small amounts of the paraelectric phase CaTiO_3 , which has a high negative value of $\text{TC}\varepsilon$, were added. Investigations showed that in this case multiphase systems of chemically noninteracting phases are formed (Fig 21) [134, , 136].

This made it possible to obtain MW dielectrics with a permittivity of 18–20, high Q values ($Q \times f \geq 5000\text{--}10000$) and thermostable electrical properties. It may be supposed that high Q values are due to the fact that the size of chemical inhomogeneity is much smaller than the electromagnetic wavelength in dielectric and does not cause, therefore, noticeable electromagnetic scattering.

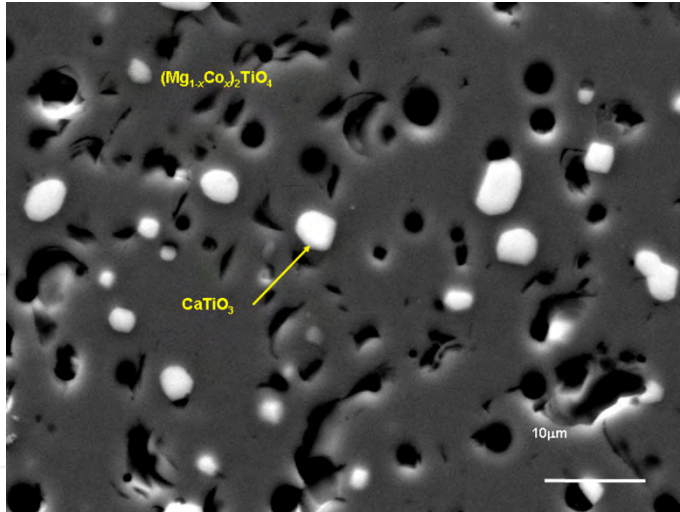


Figure 21. Micrograph of the microsection of 0.93 [0.98Mg₂TiO₄ - 0.02 Co₂TiO₄] - 0.07CaTiO₃ ceramic

12. Analysis of the physical properties of MW dielectrics

The main attention in the analysis of the physical properties of MW dielectrics is given to the temperature coefficient of permittivity (TC ϵ) and to dielectric loss (tg δ). The expression for TC ϵ can be derived directly from the Clausius-Mossotti equation [137]:

$$TC\epsilon = \frac{(\epsilon - 1)(\epsilon + 2)}{\epsilon} \left[\frac{v}{\alpha} \left(\frac{\partial \alpha}{\partial v} \right)_T a_l + \frac{1}{3\alpha} \left(\frac{\partial \alpha}{\partial T} \right)_v - a_l \right] \quad (4)$$

where a_l is linear thermal expansion coefficient.

It should be noted that polarization a in Eq (4) is equal to the sum of polarizations of all atoms of cell, whose volume is v , only if all atoms of the structure have a cubic environment. This is the case, e.g. for alkali halide crystals. In more complex structures, effective polarization a_{eff} is used [138]. For example, for perovskite structure, effective polarization a_{eff} is obtained by introducing an ionic component of polarization, Δa^i , in addition to the electronic and ionic polarization of all atoms in the unit cell. In this case, the last term a_l in expression (4) must be written as $a_l \Delta a^i$ [137]. An analysis of the TC ϵ value of different materials as a function of chemical composition showed [139] that the large positive value of TC ϵ in alkali halide crystals probably arises from high ionic polarizability a^i and great thermal expansion a_l . There are compounds, e.g. LaAlO₃, SrZrO₃, the behavior of whose $\epsilon(T)$ differs from that of paraelectrics. This is attributed to the presence of nonferroelectric phase transitions [137], which are coupled with the rotation of oxygen octahedra. Similar nonferroelectric phase transitions were found, e.g. in the system (Ba_xSr_{1-x})(Zn_{1/3} - Nb_{2/3})O₃ [140]. It was shown that structural transitions are accompanied by the reversal of the TC ϵ sign, though the ϵ quantity does not undergo noticeable changes, which are typical of

spontaneously polarized state. Similar dependences were also found in the system $(\text{Ba}_x\text{Sr}_{1-x})(\text{Mg}_{1/3}\text{-Nb}_{2/3})\text{O}_3$ [141]. When x is changed, a correlation between the value of tolerance factor (t) and the inclination of oxygen octahedra is observed, which results in the reversal of the $\text{TC}\varepsilon$ sign.

When MW dielectric loss is studied, three sources of loss are considered: 1) loss in perfect crystal, which is coupled with anharmonicity, which is due to interaction between crystal phonons, resulting in optical-phonon attenuation; such loss is usually called intrinsic loss; 2) loss in real homogeneous material, which is caused by deviation from lattice or defect periodicity (point defects, dopant atoms, vacancies or twin defects, which give rise to quasi-bound states); such defects give rise to phonon scattering; 3) loss in real inhomogeneous crystalline materials, which is caused by the existence of dislocations, grain boundaries, including minor phases; this loss is usually called extrinsic loss.

ε Dispersion for infrared polarization is usually described by the Drude-Lorentz equation:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 - \left(\frac{\omega}{\omega_T}\right)^2 + i\Gamma\frac{\omega}{\omega_T}} \quad (5)$$

where ε_∞ is permittivity at optical frequencies, ω_T is transverse optical mode frequency, $(\varepsilon_0 - \varepsilon_\infty)$ is dielectric oscillator strength, Γ is relative attenuation.

Using Eq (5), we can estimate dielectric loss ($\text{tg } \delta$) pertaining to phonon attenuation in the MW range (intrinsic loss) ($\omega \gg \omega_T$):

$$\text{tg } \delta \approx \Gamma \frac{\omega}{\omega_T^4} \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0} \quad (6)$$

Even in perfect crystal, loss may arise from the anharmonicity of vibration. In this case, three-phonon and four-phonon interactions may predominate, in which $\Gamma \sim T$ and $\Gamma \sim T^2$ respectively [142]. Equation (6) shows that if intrinsic loss predominates, the product of Q ($Q = 1/\text{tg } \delta$) and frequency f ($\omega = 2\pi f$) is a constant, which is employed for the analysis of MW dielectrics.

To determine intrinsic loss, IR spectroscopy is usually used [143, 144] since the value of intrinsic loss at IR frequencies is much larger than that of extrinsic loss. Having determined intrinsic loss at IR frequencies, one can approximate the quantity $Q \times f = \text{const}$ to MW frequencies and calculate thereby extrinsic loss, which is due to ceramic imperfection; this loss can be reduced by improving the technology.

One of the important questions concerning the determination of dielectric loss in MW ceramics is the possibility of determining intrinsic loss solely from IR spectroscopic data. To this end, the authors of [145, 146] investigated several $\text{Ba}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$ compounds in a wide frequency ($10^2 - 10^{14}$ Hz) and temperature (20-600 K) range. On the basis of the data obtained, they came to the following conclusions:

- MW loss calculated from IR spectra and Eq (6) can be interpreted as a lower limit of intrinsic loss.
- MW loss extrapolated from IR data is systematically lower than that determined in accordance with the microscopic theory [147].
- The value of intrinsic loss correlates with tolerance factor (t); increase in intrinsic loss with decreasing t indicates that the main contribution to it is made by low-frequency vibration mode.
- The value of intrinsic loss varies with the ϵ value as $\text{tg } \delta \sim \epsilon^a$, where $a = 4$.

It is not less important to elucidate the effect of cation ordering on MW loss. It was shown earlier [58] that cation ordering in $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ and $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ allows MW loss to be reduced. When investigating $(\text{Zr}_{1-x}\text{Sn}_x)\text{-TiO}_4$ materials, however, it was found that the substitution of Sn^{4+} ions for Zr^{4+} ions results in the suppression of cation ordering [148], and that the Q value increases in this case [140]. It is likely that in the system $(\text{Zr}_{1-x}\text{Sn}_x)\text{TiO}_4$, the increase in Q on the substitution of Sn^{4+} ions with smaller radius for Zr^{4+} ions with larger radius is due to a decrease in intrinsic loss.

13. Applications of MW dielectrics

MW dielectrics are used in modern communication systems, for the manufacture of dielectric resonators (DR) of various types, substrates for MW hybrid integrated circuits. On the basis of DRs, radio-frequency filters are developed; they are also used in the manufacture of solid state oscillators. In the frequency range 150 MHz – 3 GHz, coaxial resonators are often used, whose surface is metallized (Fig 22). The height of quarter-wave coaxial resonator is determined from the formula:

$$l = \frac{\lambda_0}{4} \frac{1}{\sqrt{\epsilon}} \quad (7)$$

where λ_0 is free-space electromagnetic wavelength, ϵ is permittivity in the operating frequency range.

At higher frequencies, open resonators are generally used (Fig 23), whose diameter is determined from the formula:

$$D = \frac{\lambda_0}{\sqrt{\epsilon}} \quad (8)$$

The characteristic modes for coaxial and open dielectric resonators are usually the modes TE_{01s} and H_{01s} .

The Q value of coaxial resonator is determined both by dielectric loss and by loss in the resonator metal coating, which may be high; therefore, the Q value of coaxial resonators is, as a rule, under 1000, which is their demerit. At the same time, Q of open resonators is determined only by dielectric loss (intrinsic and extrinsic). Therefore, Q of open resonators is

over 1000. Since open resonators have a high Q value, they can be used in the decimeter wave band (about 1 GHz), though in this case their size becomes large.



Figure 22. Coaxial dielectric resonators



Figure 23. Open dielectric resonators

The size of open dielectric resonators operating on the characteristic modes TE_{01s} and H_{01s} becomes very small at frequencies above 30 GHz, which makes their use in this band impossible. Therefore, at frequencies above 30 GHz, it is expedient to use extraordinary vibration modes such as whispering gallery modes.

The modern communication systems in which dielectric resonators are used operate in a temperature range of -40 – 80 °C. Therefore, high thermostability of dielectric resonator resonance frequency is required. It is necessary that the temperature coefficient of frequency should tend to zero; it is defined as:

$$TK\varepsilon = \frac{1}{f_p} \frac{\Delta f_p}{\Delta T} \quad (9)$$

where f_r is the resonance frequency of dielectric resonator, Δf_r is change in the resonance frequency of dielectric resonator in the temperature range ΔT .

Dielectric resonators are used for the frequency stabilization of oscillators, which are used, in turn, in radars, various communication systems. At frequencies below 200 MHz, quartz resonators are often used; in the frequency range 1000-3000 MHz, coaxial resonators and above 3000 MHz open resonators are used.

On the basis of dielectric resonators, miniature bandpass filters, frequency separators are developed (Fig 24) [149].

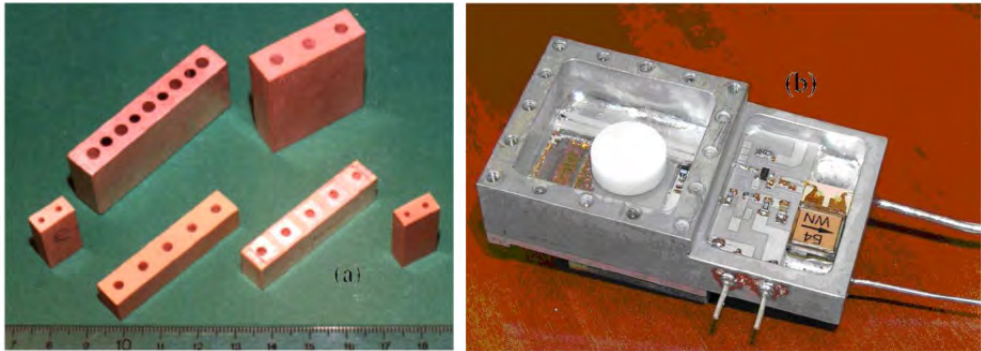


Figure 24. Monolithic ceramic blocks for the utilization in radiofilters operating in the decimetre wavelength band (a), and low-noise microwave oscillator for the frequency of around 9 GHz (b)..

Dielectric resonators are also used in the creation of antennas of the new generation. The advantages of such antennas are: small size, simplicity, relatively broad emission band, simple scheme of coupling with all commonly used transmission lines; possibility to obtain different radiative characteristics using different resonator modes.

As was mentioned above, the use of dielectric resonators operating on the TE_{01s} and H_{01s} modes is limited in the millimeter wave band since the size of resonators becomes too small. Therefore, it is expedient to use in the millimeter wave band dielectric resonators operating on whispering gallery modes [150]. Besides, it is relatively easy to suppress spurious modes in such resonators. It should be noted that the Q value in the resonators using whispering gallery modes is limited only by intrinsic loss in the material in contrast to coaxial and open resonators.

14. Conclusion

High- Q MW dielectrics with high thermostability of electrophysical properties can be developed on the basis of single-phase and multiphase systems. Single-phase MW dielectrics are produced on the basis of solid solutions [6, 15, 98] using heterovalent substitutions in one of the crystal sublattices and influencing thereby the phonon spectrum [10] and by making one of the sublattices “mobile” [151]. At the same time, high- Q thermostable MW dielectrics based on multiphase systems are developed using the volume temperature compensation effect [55-57, 124, 132, 135].

During the last decade, MW dielectrics with increased permittivity ($\epsilon \geq 10$) contribute, to a larger measure than other factors, to considerable miniaturization and reduction in the price of modern communication systems. It should be noted that there is still a great potential for further microminiaturization and reduction of prices of modern communication systems thanks to the use of components made on the basis of MW dielectrics.

Depending on the frequency range of modern communication systems, MW dielectrics with different properties are needed. In the decimeter wave band, high permittivity values ($\epsilon \geq 100$) are required along with the high thermostability of electrophysical properties and high Q , which enables effective solution of microminiaturization problems. At the present time, solid solutions based on barium-lanthanum titanates ($\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ ($\text{Ln} = \text{La-Gd}$)), which have a potassium-tungsten bronze structure and $\epsilon \approx 80-100$, meet best these requirements. However, the nature of the thermostability of the electrophysical properties of these solid solutions has not been elucidated definitively; there are only qualitative explanations, which greatly restrains the search for new promising MW dielectrics with high permittivity ($\epsilon \geq 100$). The presence of spontaneous polarization in dielectrics causes, along with increase in ϵ , a considerable increase in dielectric loss (the Q value decreases), which impairs greatly the technical characteristics of communication system elements based on them. Therefore, the acquirement of fundamental knowledge, which is required for obtaining thermostable high- Q materials with $\epsilon \geq 150-200$, is the most important problem in developing modern decimeter wave band communication systems.

In the centimeter and millimeter wave bands, where the electromagnetic wavelength is much smaller as compared with the decimeter wave band, thermostable MW dielectrics with extremely high Q values are required. In this case, permittivity values may be relatively low ($\epsilon = 15-30$). To date, tantalum-containing perovskites possess the highest Q values. However, the difficulty of their preparation and the high price call for search for new promising compounds, and it is going on in several directions. In particular, research is now under way to develop niobium-containing perovskites and to create multiphase systems, in which volume temperature compensation effect is realized. It is these directions that will probably be major directions in the next few years in developing high- Q centimeter and millimeter wave band MW dielectrics, though the search for new promising compounds will always be vital. Quite a number of problems pertaining to solid-state physics and chemistry will have to be solved. For instance, it is necessary to investigate the nature of extrinsic loss, which is coupled with various structural defects, as well as with the presence of grain boundaries, ordering of crystal sublattices and domain nanostructure. Research aimed at developing thermostable dielectrics, which will be used as millimeter wave band dielectric resonators using whispering gallery modes, will be of special scientific and practical interest. This requires considerable increase of the chemical and structural homogeneity of dielectrics.

An important problem is the creation of retunable resonant elements. To this end, multilayer bulk and film materials, which will contain a thermostable dielectric phase and a nonlinear magnetic or electrical phase at the same time, will probably have to be developed.

Thus, the synthesis of novel high-Q MW dielectrics and the investigation of their structure and properties are an important scientific-technical trend in solid-state chemistry.

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