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Microwave dielectrics with enhanced permittivity

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Abstract

Depending on the operating frequency range of modern communication systems various microwave elements are required for effective micro-miniaturization of radio equipment. In this work potential ways of developing microwave dielectrics with high permittivity are discussed. In particular, it has been shown that temperature stable microwave dielectrics with a permittivity of about 100 can be developed by either influencing the phonon spectrum by means of aliovalent substitution in the cation sublattices or by the formation of a mobile cation sublattice. However, microwave dielectrics with permittivity above 100 require the employment of polarization mechanisms related with the spontaneously polarized state. In this case an increase in permittivity is generally accompanied by an increase in dielectric loss. Chemical systems demonstrating temperature stable properties are discussed, and include those in which an increase in permittivity is accompanied by relatively low dielectric loss.

Keywords: Powders-solid state reaction; Defects; Dielectric properties; Perovskites; Functional applications

1. Introduction

The development of modern radio communication systems requires the use of new functional materials with a combination of good electro-physical parameters in the microwave (MW) frequency range. These materials must combine high permittivity (ε), low dielectric loss (tg δ), and good temperature stability of properties (τ_ε). The use of these materials in the development of components for filtering and oscillating devices means that their size can be reduced and their reliability improved. In addition to this, their use also leads to a reduction in manufacturing and maintenance costs.

The choice of the required permittivity of microwave materials is related to the operating frequency of radio component, excited wave mode, and the requirements to the optimum geometric dimensions. The ε value determines the overall dimensions of the radio components. The effect of micro-miniaturization is based on the fact that the electromagnetic wave length in dielectric media shortens by a factor of $\varepsilon^{1/2}$. Therefore, in the decimeter-wave band, high-quality temperature stable materials with $\varepsilon \sim 100$–600 are needed, whereas in the millimeter-wave band it is better to use materials with $\varepsilon \sim 15$–30.

This paper discusses ways of developing MW dielectrics with high permittivity only, which are based on both the literature data and the author's experimental results.

2. Results and discussion

2.1. $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (Ln = La–Gd) solid solutions

When investigating this class of materials, we paid particular attention to studying the solid-state reaction mechanism for the formation, and abnormal behavior of dielectric parameters, of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ solid solutions (Ln = Nd, Sm). In spite of the fact that understanding reaction mechanisms and kinetics is the crucial point for the suppression of extrinsic dielectric loss, only a few studies related to the formation of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ solid solutions (BLTss) can be found in the literature.[1,2] Extrinsic loss appear in well-processed single-phase $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ ceramics as a result of compositional inhomogeniety and a high concentration of structural defects. The published studies performed for co-precipitated starting powder[1] or starting powder with an excess of TiO_2,[2] disclosed some major reaction sequences; however, details on the formation of final $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ composition, which can determine the dielectric loss, were not revealed.

The solid-state reaction mechanisms of the formation of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (Ln = Nd, Sm) were examined for the compositions at $x = 0.75$, 1.5, and 2.0. Reagent-grade powders

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of $BaCO_3$, Sm_2O_3 and TiO_2 were used as starting reagents. The formation of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (Ln = Sm, Nd) solid solutions has been shown to begin with reactions between starting reagents yielding the intermediate products $Ln_2Ti_2O_7$, $BaTi_4O_9$, and $BaTiO_3$. According to the changes in the relative intensities of XRD peaks, it has been found that during the interaction of intermediate products, the high-x end members of the $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ solid solutions ($Ba_{3.9}Nd_{9.4}Ti_{18}O_{54}$ and $Ba_{3.9}Sm_{9.4}Ti_{18}O_{54}$) are formed during the first stage. Subsequently, these react with the residual $BaTiO_3$ to produce the intended $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ composition.

The $Ba_{3.9}Ln_{9.4}Ti_{18}O_{54}$ phase, as well as other members of the $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ family, has the structure of tetragonal tungsten bronze. Therefore, it was difficult to unambiguously identify the phase $Ba_{3.9}Ln_{9.4}Ti_{18}O_{54}$ from the results of X-ray phase analysis. We therefore, identified this phase by means of both EDX and TEM analyses.[3]

TEM investigations revealed that even when all of the $BaTiO_3$ reacted, compositional homogeneity was still not necessarily achieved. The ceramics sintered for a short time consisted of both low- and high-x $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ phases, and were characterized by a significant concentration of crystal-structure defects. The concentration of crystal-structure defects was suppressed and the compositional homogeneity of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ was improved after an extended period of sintering ($\geq$3 h).

In the BLTss the electrophysical characteristics strongly depend on the size of the A-site ions (r_A).[4–6] Whereas a change in the lanthanide ion from La to Gd results in a decrease in both the permittivity (ε) and the dielectric loss tangent (tg δ) of the BLTss at a fixed value of x, the temperature coefficient of the permittivity (τ_ε) increases and changes its sign when passing from Nd to Sm.[4,5] When investigating $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ ($x = 1.5$) using the dielectric resonator method in the frequency range of about 10^{10} Hz, we revealed, for the first time, anomalies in the temperature dependence of permittivity[7]. More recently, we observed anomalies in the temperature dependencies of the dielectric parameters (ε, tg δ) in the entire range of Sm-containing BLTss.[8]

The nature of these anomalies remained unknown. Moreover, there was no information about the existence of temperature anomalies in other barium-lanthanide analogues, including La-, Nd- and Gd-containing BLTss. Therefore, we tried to clear up the nature of the temperature anomalies of both the permittivity and dielectric loss in BLTss.

We found that in the La- and Nd-containing BLTss, the temperature anomalies of dielectric parameters occur at low temperature over a wide frequency range, including the submillimeter-wave (SMM) band.[9] The position of the anomalies on the plots of ε and tg δ against temperature depended on chemical composition (Fig. 1).

In the BLTss containing Sm- and Gd-, the anomalies of dielectric parameters occur at temperatures higher than room temperature (Fig. 2). The position of the anomalies on the T-axis is affected by the chemical composition of the BLTss, and it shifts toward lower temperatures with increasing x within the temperature region of +120 °C to +70 °C. Similar behavior is observed in the case of solid solutions with ferroelectric and antiferroelectric properties. However, in the case of BLTss the hysteresis loop is not detected, and Curie–Weiss behavior is not observed in the vicinity of the anomalies. Measurements in the SMM wavelength range revealed diffuse maximums on the temperature dependencies of both the absorption coefficient (α) and the imaginary component of the dielectric constant (ε'') at exactly those temperatures where the maximums of $\varepsilon(T)$ are observed at 10 GHz.[9] These results denote the non-relaxation nature of the anomalies of the dielectric parameters, and confirm the fact that these anomalies are not related to the processing effect.

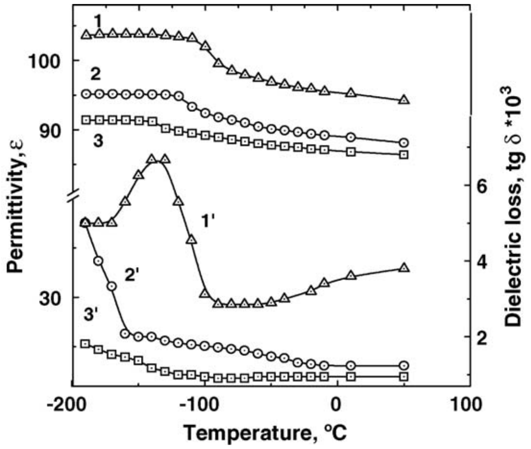

Fig. 1. Temperature dependencies of the permittivity (1)–(3) of and dielectric loss (1′)–(3′) in materials with the composition $Ba_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$. $x = 0.75$ (1), (1′); 1.5 (2), (2′); 2.0 (3), (3′); measurement frequency 10 GHz.

These experimental results suggested that the dielectric anomalies may be ascribed to unknown phase transitions. Therefore, samples with the composition $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ ($x = 1.0$), which are characterized by the strongest anomalies of dielectric parameters at about 120 °C amongst the Sm-containing BLTss, were investigated by both low-temperature

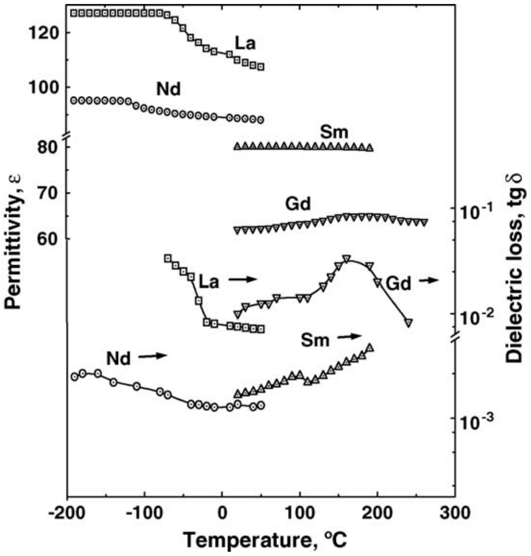

Fig. 2. Temperature dependencies of dielectric parameters of materials with the composition $Ba_{4.5}Ln_9Ti_{18}O_{54}$ ($x = 1.5$) at 10 GHz.

DSC and high-temperature XRD. The analysis was carried out over a wide temperature range including temperatures below and above the temperatures of the anomalies of $\varepsilon(T)$ and tg $\delta(T)$.

XRD patterns were collected in the range $5^\circ < 2\Theta < 55^\circ$ at room temperature, at 120 °C, and at 250 °C. No significant changes in the intensity or the position of the peaks (apart from those induced by the increased temperature) or any kind of peak splitting were observed in the patterns. In addition, a detailed XRD analysis was performed for the 2Θ range, where diffraction lines from superstructure phenomena were expected to appear ($10^\circ < 2\Theta < 25^\circ$). These patterns also did not indicate any structural changes.

LT-DSC was performed in the temperature range of −30 °C to 250 °C. In agreement with the XRD analysis the LT-DSC revealed no thermal effects that could be associated with structural changes. We concluded that within the sensitivity limits of both analytical methods there was no evidence for a structural transition that could be responsible for the anomaly in the temperature dependence of the dielectric properties. Our structural investigations are fully supported by the work of Tang et al.[10] The authors of Ref.[10] performed synchrotron XRD studies on the $Ba_{4.5}Nd_9Ti_{18}O_{54}$ analogue in the temperature range of 10–295 K. Their data revealed no evidence for the structural changes in this temperature range; the volume expansion was relatively smooth.

In consequence we can state that the observed anomalies of the dielectric parameters are associated neither with any processing peculiarities nor with the presence of structural transitions.

According to the analysis carried out, we suggested that the observed anomalies originate in the competing influence of both harmonic and inharmonic contributions to the phonons of the BLTss crystal lattice, which exhibit an opposite effect on the temperature behavior of permittivity and tg δ.[9]

2.2. $La_{2/3-x}(Na,K)_{3x}TiO_3$

The materials of this system are not characterized by a high temperature stability of properties but they are good model objects for studying the effect of aliovalent substitution in cation sublattices on the phonon spectrum.

Two characteristic regions can be distinguished in the dielectric spectra of these materials: below 10^8 Hz and within 10^8 to 2×10^{11} Hz, respectively. In the frequency range of 10^8 to 2×10^{11} Hz there is no dispersion of ε', and tg δ is determined by high-frequency polarization mechanisms.[11,12] At the frequency of 1.2×10^{10} Hz, the minimum tg δ value, which varies slightly with rising temperature, is observed in $La_{1/2}Na_{1/4}K_{1/4}TiO_3$, and its magnitude is $5\text{–}6 \times 10^{-4}$. The dynamic properties of lanthanum titanates $La_{2/3-x}M_{3x}TiO_3$ in the MW range are mainly determined by the $La_{2/3}TiO_3$ matrix, as evidenced by a small difference in tg δ values of different compounds. In the submillimeter-wave band, a similar trend of the frequency dependencies of both ε and tg δ is retained, but dielectric loss increases by more than an order of magnitude as compared with those measured in the centimeter-wave band.

In the submillimeter-wave band, the main source of dielectric loss is one-phonon absorption, which is associated with structural disorder. In the frequency range 10^{10}–10^{11} Hz, phonon processes of a higher order make an additional contribution to tg δ. Since the relaxation in lanthanum titanates is caused by the motion of alkali metal ions in the lanthanum sublattice, a reduction of MW dielectric loss can be achieved by decreasing the relaxation contribution to tg δ, this can be attained by stabilizing the structure of $La_{2/3}TiO_3$ with the alkaline elements with large ionic radii (Na, K, Cs).

It has been shown that additional sources of dielectric loss are unoccupied sites in the cation sublattice. Therefore, by reducing their number by means of aliovalent substitutions and by placing different ions in the vacant sites, one can significantly affect the dielectric loss in the MW range.[13]

Aliovalent substitutions in the cation sublattice greatly affect the temperature stability of the electrophysical properties of materials. To explain this effect, IR reflection spectra of $La_{2/3-x}M_{3x}TiO_3$ compounds were examined.[14]

As a result of processing experimental reflection spectra by dispersion analysis,[15] the dispersion oscillator parameters have been determined to describe the experimental reflection spectra. It is known that one low-frequency oscillation is responsible for the high permittivity values in the MW range in the compounds with the perovskite structure.[16] As is evident from the results obtained, aliovalent substitution gives rise to a second oscillation, which makes a noticeable contribution to permittivity.

The appearance of the second oscillation was accompanied by a substantial improvement of the temperature stability of electrophysiscal properties. This fact can be utilized to develop new MW dielectrics, in which a high permittivity, good temperature stability, and low dielectric loss are combined.

2.3. $Ln_{2/3-x}(Na,K,Li)_{3x}TiO_3$, Ln–La, Nd, Sm

The authors of Ref.[17] developed new temperature stable MW dielectrics based on solid solutions which involve lithium-containing phase ($Ln_{1/2}Li_{1/2}TiO_3$) as the end member with the positive temperature coefficient of dielectric constant ($\tau_\varepsilon > 0$). However, the data on the dielectric properties of lithium-containing phases are not yet sufficient to explain the nature of the positive sign of τ_ε.

It should be noted that the phases $Ln_{1/2}Li_{1/2}TiO_3$ belong to the wider family of complex oxides $Ln_{2/3-x}M_{3x}TiO_3$ (Ln is rare-earth element, and M is alkali metal), which are of a great scientific and engineering interest. The speciality of these oxides consists in the fact that atoms M partially substitute Ln.[18,19] In the case when M = Na, K compounds with the perovskite structure are formed. They are characterized by high MW permittivity (about 100) and $\tau_\varepsilon < 0$.[20] When cation sublattice contains both small lithium ions, which can move easily down the structural channels, and large lanthanum ions, which meet all geometric requirements for the perovskite structure, the perovskite structure can be formed. In this case the resulting products may display high cation conductivity of lithium ions. This approach was for the first time utilized by us in the materials $La_{2/3-x}Li_{3x}TiO_3$[21,22] and $La_{2/3-x}Li_{3x}Nb_2O_6$,[23] which are the cationic conductors and for this reason are characterized by high dielectric loss in the MW range. However, it is possible to assume that the dielectric loss in the compounds $Ln_{2/3-x}Li_{3x}TiO_3$ could be decreased by decreasing cation conductivity. This can be attained by decreasing the ionic radii of rare-earth elements substituted for larger-size La ions in the compounds $Ln_{2/3-x}Li_{3x}TiO_3$. In this case the positive temperature coefficient of permittivity is accompanied by relatively low dielectric loss. This makes it possible to obtain solid solutions exhibiting both high permittivity and temperature stability in the microwave range together with acceptable MW dielectric loss. These ceramics can be based, for instance, on both lithium- and sodium-containing rare-earth titanates with the perovskite structure, which differ because of contrary temperature behaviour of the dielectric constant.[24]

The above-mentioned systems enable the development of temperature stable dielectric materials with the permittivity of 80–100. To obtain higher permittivity values, there must be other polarization mechanisms, associated with spontaneously polarized state, along with the optical and infrared polarization mechanisms. For instance, the use of antiferroelectric Pb_2CoTeO_6 as a material with a positive temperature coefficient of permittivity allows temperature stabilization of composite microwave resonators with an effective permittivity of over 100.[25] MW dielectrics with good properties have been obtained by the authors of[26] using spontaneously polarized state in the system $Ag(Nb,Ta)O_3$. The permittivity of $Ag(Nb,Ta)O_3$ materials was very high ($\varepsilon \sim 430$), and dielectric loss was low ($Q = 700$ at 1 GHz). However, when using spontaneously polarized state, an increase in the permittivity is generally accompanied by an increase in dielectric loss.

2.4. $Ln_{2/3-x}Na_{3x}Nb_2O_6$ (Ln = La, Nd)

Investigations showed that in the system $Ln_{2/3-x}Na_{3x}Nb_2O_6$ (Ln = La, Nd), solid solutions with the perovskite structure are formed over the entire range of x values; they are characterized by three different space groups, which vary in the order *Pmmm* → *Pmmn* → *Pbcn* with increasing x. In the structure $Ln_{2/3}\square_{4/3}Nb_2O_6$ where $\square$ is cation vacancy ($x = 0$) the Ln atoms reside in the cuboctahedrons and the Nb atoms reside in octahedrons formed by oxygen atoms.[27] It should be noted that solid solutions with the defect-perovskite structure (space group *Pmmm*) are characterized by the additional ordering, which is associated with the presence of a large number of vacancies in the sublattice of rare-earth ions, and which is accompanied by the appearance of additional reflections at $2\Theta \sim 13°$ and $29.5°$. Regardless of the type of rare-earth element the space group changes from *Pmmm* to *Pmmn* with an increasing content of sodium atoms substituting for rare-earth elements (the increase in x), this is accompanied by a statistical distribution of vacancies in the sublattice of rare-earth ions. When the sodium content in the systems examined is further increased to the values corresponding to $0.54 \leq x \leq 0.66$ in the case of Nd and $0.45 \leq x \leq 0.66$ in the case of La, the crystal structure of solid solutions belongs to the space group *Pbcm*, which is typical for $NaNbO_3$ at room temperature.[28]

The materials $La_{2/3}Nb_2O_6$ and $Nd_{2/3}Nb_2O_6$ ($x = 0$) are characterized by high permittivity of 130 and 160, respectively and relatively low dielectric loss in the MW range (in both cases tg δ is of the order of $2\text{–}5 \times 10^{-3}$). In both cases the dispersion of permittivity was not observed. The results of the measurements of electrophysical properties of complex niobates $Ln_{2/3}Nb_2O_6$ (Ln = La, Nd) over the wide frequency (10^6–10^{10} Hz) and temperature (−100 °C to +100 °C) ranges indicate a change in the trends in the temperature dependencies of permittivity $\varepsilon(T)$ with increasing measurement frequency (Fig. 3).

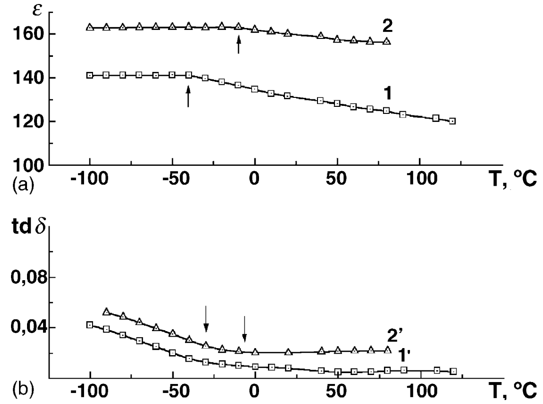

Fig. 3. Temperature dependencies of the permittivity (1, 2) and dielectric loss tangent (1′, 2′) of materials $Ln_{2/3}Nb_2O_6$ (1, 1′—Ln = La; 2, 2′—Ln = Nd) measured at 10^{10} Hz.

All examined polycrystalline materials based on the solid solutions $Ln_{2/3-x}Na_{3x}\square_{4/3-2x}Nb_2O_6$ (Ln = La, Nd) are characterized by low dielectric loss in the radio-frequency range (tg $\delta \approx 1\text{–}3 \times 10^{-6}$) (Fig. 4).

Concentration dependences of dielectric parameters of the materials investigated are shown in Fig. 5. As can be seen in Fig. 5, the variation of permittivity is of a nonmonotonic character. Within the limits of the space group *Pmmm* ($0 \leq x \leq 0.24$), increasing sodium content in the systems examined leads to a slight increase in the permittivity regardless of rare-earth element. The increase in ε value is due to the decrease in the cation

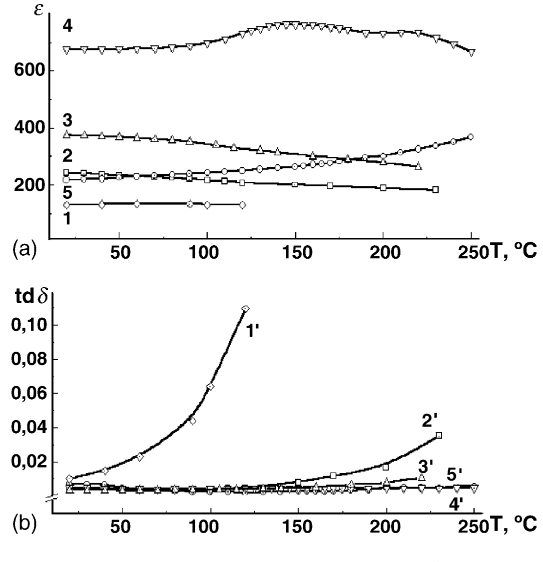

Fig. 4. Temperature dependencies of the permittivity (1–5) and dielectric loss tangent (1′–5′) of materials $(1 - 3x/2)Ln_{2/3}Nb_2O_6 - 3xNaNbO_3$; $x = 0$ (1, 1′); 1/6 (2, 2′); 1/3 (3, 3′); 1/2 (4, 4′); 2/3 (5, 5′)—measured at 10^6 Hz.

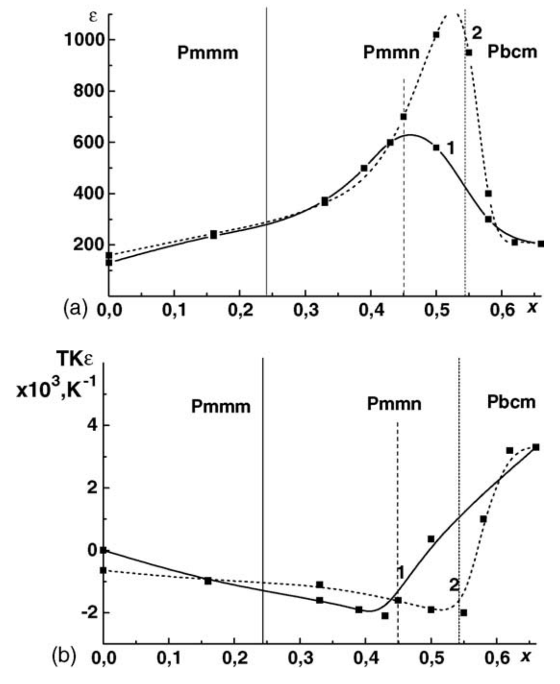

Fig. 5. (a and b) Dielectric characteristics of $Ln_{2/3-x}Na_{3x}\square_{4/3-2x}Nb_2O_6$ samples (where Ln = La (1), Nd (2)) as a function of sodium content.

vacancy concentration in the systems examined. For the space group *Pmmn*, a stronger dependence of permittivity on sodium content is observed (Fig. 5a). When changing from *Pmmn* to *Pbcm*, the ε magnitude passes through a maximum at room temperature. Due to the fact that in neodymium-containing solid solutions the change of the space group from *Pmmn* to *Pbcm* takes place at higher sodium concentrations, which corresponds to a lower vacancy content, $\varepsilon_{\max}$ reaches higher values comparing to those attained in lanthanum-containing solid solutions (Fig. 5a). Studies of temperature dependences of the permittivity of $Ln_{2/3-x}Na_{3x}\square_{4/3-2x}Nb_2O_6$-based materials (Ln = La, Nd) at different degrees of substitution show that the change of the space group from Pmmn to Pbcm is accompanied by a change in the sign of the temperature coefficient of permittivity (Fig. 5b). Investigations showed that materials with high, temperature-stable permittivity ($\varepsilon \approx 300/600$) and relatively low dielectric loss ($\mathrm{tg}\,\delta \approx 2\text{–}7 \times 10^{-3}$) can be obtained in $Ln_{2/3-x}Na_{3x}\square_{4/3-2x}Nb_2O_6$ systems (Ln = La, Nd).

3. Conclusions

When using only optical and infrared polarization mechanisms one can obtain MW dielectrics with the permittivity of about 80–100, for instance in the solid solutions $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (BLTss). It has been assumed that the temperature stabilization of permittivity in BLTss is due to the competing effect of both harmonic and inharmonic contributions to the phonons of the BLT crystal lattice, which exhibit an opposite influence on the temperature behavior of permittivity and $\mathrm{tg}\,\delta$.

Temperature stable MW dielectrics with the permittivity of around 100 could be synthesized by using solid solutions containing cation conductors as the phase with the positive temperature coefficient of permittivity to allow the effect of the volume temperature compensation.

Unoccupied sites in cation sublattices could be an additional source of dielectric loss, for instance in the system $La_{2/3-x}(Na,K)_{3x}TiO_3$. By reducing their concentration one can affect the dielectric loss in the MW range.

Temperature stable MW dielectrics with the permittivity above 100 could be produced by using polarization mechanisms related with the spontaneous polarization. However, in this case an increase in permittivity is generally accompanied by an increase in the dielectric loss. The possibility of synthesizing MW dielectrics with high permittivity based on complex niobium oxides with the defect-perovskite structure has been shown.

References

1. Takahashi, J., Ikegami, T. and Kageyama, K., Occurrence of dielectric 1:1:4 compound in the ternary system $BaO\text{-}Ln_2O_3\text{-}TiO_2$ (Ln = La, Nd, and Sm): I, an improved coprecipitation method for preparing a single-phase powder of ternary compound in the $BaO\text{-}La_2O_3\text{-}TiO_2$ system. *J. Am. Ceram. Soc.*, 1991, **74**(8), 1868–1872.
2. Wu, J. M., Chang, M. C. and Yao, P. C., Reaction sequence and effects of calcination and sintering on microwave properties of $(Ba,Sr)O\text{-}Sm_2O_3\text{-}TiO_2$ ceramics. *J. Am. Ceram. Soc.*, 1990, **73**(6), 1599–1605.
3. Belous, A., Ovchar, O., Valant, M. and Suvorov, D., Solid-state reaction mechanism for the formation of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (Ln = Nd, Sm) solid solutions. *J. Mater. Res.*, 2001, **16**(8), 2350–2356.
4. Negas, T. and Davies, P. K., Influence of chemistry and processing on the electrical properties of $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ solid solutions (materials and processes for wireless communications). *Ceram. Trans.*, 1995, **53**, 179–196.
5. Ohsato, H., Imaeda, M., Takagi, Y., Komura, A. and Okuda, T., Microwave quality factor improved by ordering of Ba and rare-earth on the tungsten bronze-type $Ba_{6-3x}Nd_{8+2x/}Ti_{18}O_{54}$ (R = La, Nd, and Sm) solid solutions. In *Proceedings of the Eleventh IEEE International Symposium on Applications of Ferroelectrics "ISAF XI", Vol. 129*, 1998, pp. 509–512.
6. Valant, M., Suvorov, D. and Rawn, C. J., Intrinsic reasons for variations in dielectric properties of $Ba_{6-3x}Nd_{8+2x/}Ti_{18}O_{54}$ (R = La-Gd) solid solutions. *Jpn. J. Appl. Phys.*, 1995, **38**, 2820–2826.
7. Butko, V. I., Belous, A. G., Nanasheva, Y. A., Poplavko, Y. M. and Ushatkin, E. F., MW dielectric properties of barium-lanthanide tetratitanates, *Fiz. Soviet Physics—Solid State*, 1984, **26**, 1783 translated from *Fiz. Tverd. Tela (Leningrad)*, 1984, **26**, 2951–2956.
8. Belous, A., Ovchar, O., Valant, M. and Suvorov, D., Anomalies in the temperature dependence of the microwave dielectric properties of $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$. *Appl. Phys. Lett.*, 2000, **11**, 1707–1709.
9. Belous, A., Ovchar, O., Valant, M. and Suvorov, D., Abnormal behavior of the dielectric parameters of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (Ln = La–Gd) solid solutions. *J. Appl. Phys.*, 2002, **92**(7), 3917–3922.
10. Tang, C. C., Roberts, M. A., Azough, F., Leach, C. and Freer, R., Synchrotron X-ray diffraction study of $Ba_{4.5}Nd_9Ti_{18}O_{54}$ microwave dielectric ceramics at 10–295 K. *J. Mater. Res.*, 2002, **17**, 675–682.
11. Belous, A. G., Butko, V. I., Novitskaya, G. N., Poplavko, Y. M. and Ushatkin, E. F., Dielectric spectra of the perovskites $La_{2/3-x}M_{3x}TiO_3$, in Russian. *Fiz. Tverd. Tela.*, 1985, **27**(7), 2013–2017.
12. Butko, V. I., Belous, A. G. and Polianetskaya, S. V., Electric parameters of solid solutions of the titanates of rare-earth elements. *Ukr. Khim. Zhurn. (Sov. Prog. Chem.)*, 1984, **50**(11), 1139–1142.
13. Belous, A. G., Physicochemical aspects of the development of new functional materials based on heterosubstituted titanates of rare-earth elements with the perovskite structure. *Theor. Exp. Chem.*, 1998, **34**(6), 301–318.

14. Butko, V. I., Belous, A. G. and Evtushenko, N. P., Oscillation spectra of the perovskites $La_{2/3-x}M_{3x}TiO_3$, in Russian. *Fiz. Tverd. Tela.*, 1986, **28**(4), 1181–1183.
15. Belousov, V. M. and Pogarev, D. E., Variance analysis of complex reflection spectra, in Russian. *Opt. Spectrosc.*, 1975, **38**(5), 1018–1020.
16. Knyazev, A. S., Poplavko, Y. M., Zaharov, V. P. and Alekseev, V. V., Soft mode in the oscillation spectrum of $CaTiO_3$, in Russian. *Fiz. Tverd. Tela.*, 1973, **15**(10), 3006–3010.
17. Takahashi, H., Baba, Y., Ezaki, K., Okamoto, Y., Shibato, K., Kuroki, K. and Nakano, S., Dielectric characteristics of $(A^{1+}_{1/2}A^{3+}_{1/2})TiO_3$ ceramics at microwave frequencies. *Jpn. J. Appl. Phys.*, 1991, **30**(9B), 2339–2342.
18. Belous, A. G., Novitskaya, G. N. and Polianetskaya, S. V., The investigation of the oxides $Ln_{2/3-x}M_{3x}TiO_3$ (Ln-Gd-Lu; M-Li, Na, K), in Russian. *Izv. Akad. Nauk. SSSR, ser. Neorgan. Mater.*, 1987, **8**(23), 1330–1332.
19. Belous, A. G., Novitskaya, G. N., Polianetskaya, S. V. and Gornikov, Y. I., Crystal-chemical and electro-physical characteristics of complex oxides $Ln_{2/3-x}M_{3x}TiO_3$, in Russian. *Zhurn. Neorg. Khimii.*, 1987, **2**(32), 283–286.
20. Belous, A. G., Novitskaya, G. N., Polianetskaya, S. V. and Gornikov, Y. I., Investigation of complex oxides of the composition $La_{2/3-x}Li_{3x}TiO_3$, in Russian. *Izv. Akad. Nauk SSSR, ser. Neorgan. Mater.*, 1987, **3**(23), 470–472.
21. Belous, A. G., Butko, V. I., Novitskaya, Polianetskaya, S. V., Homenko, B. S. and Poplavko, Y. M., Electrical conductivity of the perovskites, in Russian. *Ukr. Phys. J.*, 1986, **31**(4), 576–581.
22. Belous, A. G., Gavrilova, L. G., Polianetskaya, S. V., Makarova, Z. Y. and Chalyi, V. P., Stabilisation of perovskite structure in lanthanum titanate, in Russian. *Ukr. Khim. Zh.*, 1984, **50**(5), 460–461.
23. Belous, A. G., Novosadova, E. B., Diduh, I. R., Pashkova, E. V. and Homenko, B. S., Process of the formation of cation conductivity in complex perovskite-like niobates, in Russian. *Ionic Melts Solid Electrolytes*, 1989, **4**, 68–73.
24. Belous, A. G. and Ovchar, O. V., Temperature compensated microwave dielectrics based on lithium containing titanates. *J. Eur. Ceram. Soc.*, 2003, **23**, 2525–2528.
25. Belous, A. G., Politova, E. D., Venevtsev, Y. N., Tsykalov, V. G. and Poplavko, Y. M., Lead cobalt-tellurate—the material for MW dielectric resonators, in Russian. *Elektronnaya Technika, ser. Electroica SVCh*, 1981, **7**(331), 45–46.
26. Valant, M., Suvorov, D., Hoffman, C. and Sommariva, H., $Ag(Nb,Ta)O_3$-based ceramics with suppresses temperature dependence of permittivity. *J. Eur. Ceram. Soc.*, 2001, **21**, 2647–2651.
27. Latie, L., Villeneuve, G., Conte, D. and Le Flem, G., Ionic conductivity of oxides with general formula $Li_xLn_{1/3}Nb_{1-x}Ti_xO_3$ (Ln = Nd, Nd). *J. Sol. State Chem.*, 1984, **51**, 293–299.
28. Sakowski-Cowley, A. C., Lukasszewich, K. and Megaw, H. D., The structure of sodium niobate at room temperature, and the problem of reliability in pseudosymmetric structure. *Acta Cryst.*, 1969, **B25**, 851–865.