

Твердотельная электроника

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Polarization Mechanisms in Thermal Stable Microwave BLT Ceramics Part 2: Paramagnetism suppress soft mode

The objects of study are vacant perovskite-like structures of $BaLn_2Ti_4O_{12}$ (BLTs). These polycrystalline dielectrics allocated among many other microwave dielectrics that their permittivity ε is several times higher than in other types of microwave ceramics. Electronic relaxation process with extremely low activation energy has no influence on microwave losses but defines BLTs dielectric thermal stability. Very low relaxation time is due to the nanoscale clusters, electronic by their nature and build-in the BLT structure. Dielectric losses of this type ceramics are associated with structural disordering, especially if the second polar phase is present. References 3, figures 4, tables 2.

Keywords: dielectric permittivity ε ; temperature coefficient of dielectric permittivity $TC\varepsilon$; thermal stability; paraelectric; rutile; barium-lanthanum tetratitanate; rare earth elements.

I. Introduction

In the first part of the paper considered the possibility of creating ceramic materials with high dielectric constant and relative thermal stability parameters. It was shown that the "hard" paraelectrics (such as rutile and perovskite) have sufficiently low losses at microwave frequencies ($\tan\delta \sim 10^{-3}$), however, they are very nonthermostable ($TC\varepsilon \sim 1000 \text{ ppm/K}$). Substantially reduce the critical dependence of $\varepsilon(T)$ in rutile can be achieved by the allocation between the oxygen octahedron TiO_6 various additives.

Monophasic polycrystalline mixed oxides BLT have a great ε at microwave frequencies (usually characteristic of para- and ferroelectrics) and relatively low microwave loss (indicating a low inertia of the basic mechanisms of polarization) and make it possible to control the magnitude and the sign of

$TK\varepsilon$. This last feature of BLT makes it possible to get based on them the ceramic solid solutions with $TK\varepsilon \rightarrow 0$: as a sign $TK\varepsilon$ varies between neodymium and samarium in the regular solid solution can be combined BLT with $TK\varepsilon < 0$ and $TK\varepsilon > 0$.

II. Paraelectrics doped by rare-earth ions

Among all of TiO_2 -based microwave dielectrics, the $nTiO_2$ -BaO system is the best studied [3]. Fig. 1, a demonstrates the change in the $TC\varepsilon$ and ε in the ceramic composition BaO- TiO_2 . Barium is characterized by the empty 4f electronic level (Table 1), consequently ion Ba^{+2} has a big radius (0,14 nm) that exceeds ion O^{-2} radius (0,13 nm) and, all the more, ion Ti^{+4} radius (0,70 nm). Located between TiO_6 octahedrons, ion Ba^{+2} strongly affects on the rutile electrical properties. Ion Ba^{+2} electronic shell $5s^25p^6$ is very remote from the Ba-core due to 4f level is empty, that is why ion Ba^{+2} has strong influence on the electronic shells of surrounding O^{-2} ions. This impact may neutralize the interaction of TiO_2 -shells that causes high ε and its thermal instability.

Turning back to Fig. 1, a, it is obvious that the case of 100% TiO_2 corresponds to the rutile with its $\varepsilon_{mic} = 100$, $\tan\delta = 10^{-3}$ and $TC\varepsilon = -900 \text{ ppm}\cdot\text{K}^{-1}$ while the occasion of $n = 1$ corresponds to the tetragonal $BaTiO_3 = TiO_2$ -BaO which is ferroelectric with $\varepsilon_{mic} = 500$, $\tan\delta = 0,3$, $TC\varepsilon = +200 \text{ ppm}\cdot\text{K}^{-1}$. It seems that "ideal" thermal stability (when $TC\varepsilon$ curve in the Fig. 1, a crosses a zero line) is observed at the TiO_2 concentration of about 65%, but at this combination of the TiO_2 and BaO components a multi-phase dielectric is formed. It holds ferroelectric (polar) phase; therefore this multi-phase dielectric is characterized by a big dielectric losses and unserviceable at microwaves.

Table 1. Location of the electron spins in the orbitals and parameters of REE

	4 <i>f</i>	5 <i>s</i>	5 <i>p</i>	5 <i>d</i>	6 <i>s</i>	Magnetic moment, μ_B	r_{ion} , nm
Ba	□ □ □ □ □ □ □ □	↑↓	↑↓ ↑↓ ↑↓	□ □ □ □ □ □	↑↓	0	0,149
La	□ □ □ □ □ □ □ □	↑↓	↑↓ ↑↓ ↑↓	↑ □ □ □ □ □ □ □	↑↓	0	0,117
Ce	↑ ↑ □ □ □ □ □ □	↑↓	↑↓ ↑↓ ↑↓	□ □ □ □ □ □ □ □	↑↓	2,56	0,115
Pr	↑ ↑ ↑ □ □ □ □ □	↑↓	↑↓ ↑↓ ↑↓	□ □ □ □ □ □ □ □	↑↓	3,62	0,113
Nd	↑ ↑ ↑ ↑ □ □ □ □	↑↓	↑↓ ↑↓ ↑↓	□ □ □ □ □ □ □ □	↑↓	3,68	0,112
Pm	↑ ↑ ↑ ↑ ↑ □ □ □	↑↓	↑↓ ↑↓ ↑↓	□ □ □ □ □ □ □ □	↑↓	2,83	0,111
Sm	↑ ↑ ↑ ↑ ↑ ↑ □ □	↑↓	↑↓ ↑↓ ↑↓	□ □ □ □ □ □ □ □	↑↓	1,60	0,110
Eu	↑ ↑ ↑ ↑ ↑ ↑ ↑ □	↑↓	↑↓ ↑↓ ↑↓	□ □ □ □ □ □ □ □	↑↓	3,45	0,109
Gd	↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑	↑↓	↑↓ ↑↓ ↑↓	↑ □ □ □ □ □ □ □	↑↓	7,94	0,108

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On the other hand, the $TC\epsilon$ -curve of $n\text{TiO}_2\text{-BaO}$ system shows a maximum that goes up very close to the zero- $TC\epsilon$ line. In the vicinity of this maximum two very important microwave dielectrics exist: $4\text{TiO}_2\text{BaO}$ and $4,5\text{TiO}_2\text{BaO}$. They have very low losses ($\tan\delta = 10^{-4}$) and very small negative $TC\epsilon$ but their dielectric permittivity is not very big: $\epsilon_{mic} \leq 40$. Nevertheless, this value of ϵ_{mic} is sufficient for applications in the centimetre wave range but in the decimetre and metre wave ranges the value of $\epsilon_{mic} \geq 100$ is desirable.

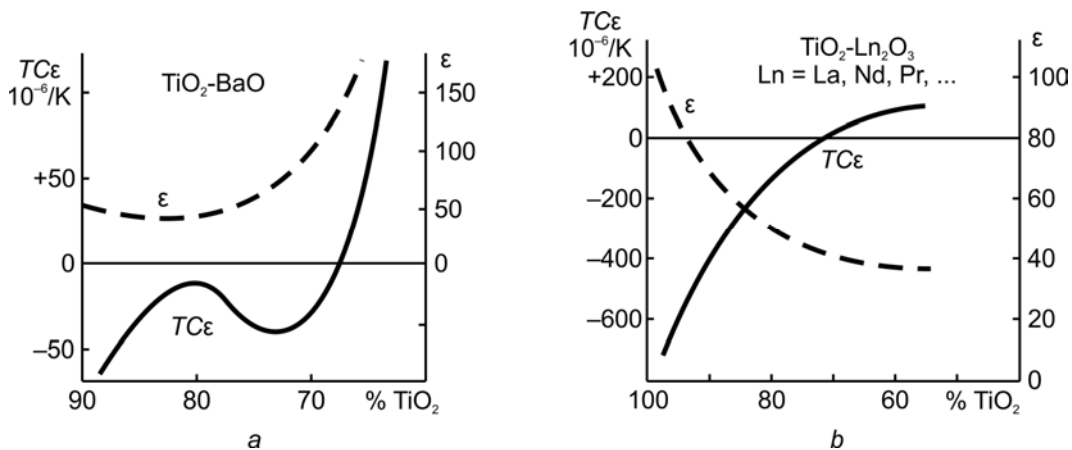


Fig. 1. Thermostable microwave dielectrics $TC\epsilon$ and ϵ dependences: a) – binary system of barium-titanium oxides, shown is $\text{TiO}_2\text{-BaO}$ concentration; b) – binary system of lanthanum-titanium oxides, shown is $\text{TiO}_2\text{-Ln}_2\text{O}_3$ concentration

Fig. 1, b shows another way of microwave high permittivity dielectrics elaboration (with $\epsilon_{mic} \approx 80$), using the rare-earth ions doping of TiO_2 : Ln_2TiO_5 ,

$\text{Ln}_2\text{Ti}_2\text{O}_7$ or $\text{Ln}_2\text{Ti}_3\text{O}_{11}$ ceramics where Ln means cerium row: Ce, Pr, Nd, Pm, Sm, Eu, Gd [2]. Lanthanum ion has electronic configuration $5s^2 5f^6$ (the

similar to Ba^{+2}) but La^{+3} is much smaller than barium ion ($\sim 0,1$ nm), Table 1. It is important also that ion La^{+3} has empty $4f$ shell and, therefore it is a diamagnetic (as the barium ion is). However, while barium more then 2 times reduces rutile ϵ_{mic} (for $n = 4$ or for $n = 4,5$), in $TiO_2-La_2O_3$ ceramics microwave properties remain practically similar to the TiO_2 ones, including $\epsilon_{mic} \approx 110$ and $TC\epsilon \approx -700$, Table 2. Small increase in ϵ_{mic} is explained later as relaxation process.

Noticeable effect on the microwave properties, especially on the thermal stability, shows system $TiO_2-Ln_2O_3$ with paramagnetic lanthanides [1]. Their electronic configuration is $4f^{1...7}5s^25p^6$, so all of them are paramagnetics with gradually increasing in the magnetic moment from one to seven of Bohr magnetons. Keeping a big dielectric permittiv-

ity ($\epsilon_{mic} \approx 80$, that two times exceeds the ϵ_{mic} in $nTiO_2-BaO$ system), the $TiO_2-Ln_2O_3$ compositions can change the $TC\epsilon$ coefficient from the negative value to the positive one, Table 2.

Described in the Table 2 compositions look like paraelectrics and paramagnetics simultaneously; at that, in the $\epsilon(T)$ characteristic the impact of paramagnetism predominates over paraelectricity. In the $TiO_2-Ln_2O_3$ compositions paraelectric Curie-Weiss law becomes gradually suppressed: from Ce to Gd (as paramagnetism becomes stronger) the $TC\epsilon$ changes greatly. Fig. 1, b characterizes the $TC\epsilon$ change in dependence on the % ratio of the TiO_2 . It is obvious that using solid solution, for example, $(Nd-Sm)La_2TiO_5$, it is possible to reach a zero thermal coefficient $TC\epsilon$.

Table 2. BLTs permittivity and $TC\epsilon$ at 300 K according microwave measurements at frequency of 9.4 GHz

Parameter	Ln								
	0La	1Ce	2Pr	3Nd	5Sm	6Eu	7Gd	TiO2	CaTiO3
ϵ_{mic}	110	90	85	83	80	75	65	100	150
$TC\epsilon$, 10 ⁻⁶ K ⁻¹	-700	-400	-250	-80	+60	+100	+160	-900	-1600

Note. Upper index before RE shows the filling of $4f$ -shell, for comparison the parameters of rutile and perovskite are given as well.

It is necessary to mark that relatively simple compositions of the $nTiO_2-Ln_2O_3$ type (as Ln_2TiO_5 or $Ln_2Ti_2O_7$ ceramics) which are available to reach $TC\epsilon \approx 0$ are non-stable in the processing, while the more stable in technology composition $Ln_2Ti_3O_{11}$ is characterized by the $TC\epsilon < 0$ (as the TiO_2 -rutile ceramics).

Efficient described decision is the perovskite-like structure of the barium-lanthanum tetratitanates ($BaLn_2Ti_4O_{12}$ that is usually titled as BLT). Monophase perovskite-like structures BLTs exist only for cerium group of lanthanide row: $Ln = La, Ce, Pr, Nd, Sm, Eu$. The valence of Ln^{+3} is different from Ba^{+2} so BLTs are vacant (non-usual) perovskites. For technical application, those dielectrics are usually realized in the complex monophase systems in which thermal stability could be controlled by the change of their composition, Fig. 2. It is seen that the case of $TC\epsilon = 0$ is located between neodymium and samarium. Some more recent elaborations using BLTs doping permits to achieve $\epsilon \geq 140$.

All paraelectrics are characterized by a large negative $TC\epsilon$, so it is important to clear up a physical reason why in the lanthanides a very important

parameter $TC\epsilon$ becomes positive. In this connection it should be noted that besides of ionic radius (in 1,5 times smaller than in barium) lanthanides are paramagnetic materials; moreover, they have so-called "lanthanide contraction" that is a smooth decrease of ionic size (from 0,115 nm in cerium down to 0,109 nm for europium, Table 1). It would be interesting to establish what of these two physical mechanisms looks as a dominant.

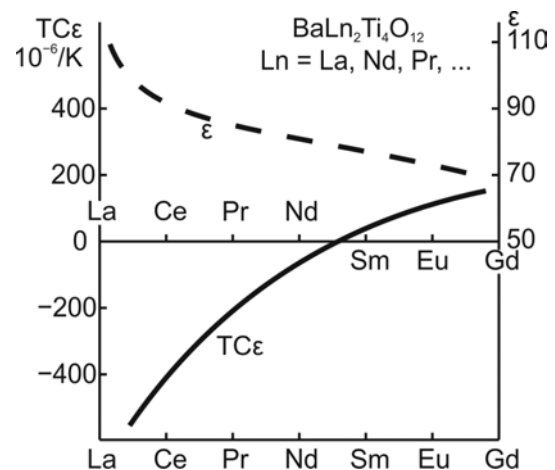


Fig 2. BLTs permittivity ϵ and temperature coefficient $TC\epsilon$ for rare-earth cerium row

With that end in view, in this work the frequency properties of lanthanides were studied in a wide frequency and temperature ranges.

The comparison of the inverse permittivity for some paraelectrics and some BLTs is shown in Fig. 3. Electrical properties of the "basic" composition La-BLT above 100 K is very close to the TiO_2 properties, and, at first glance, they are similar to the CaTiO_3 paraelectric by the equality in the sign of the TC_ε , Table 2. Diamagnetic lanthanum ion has radius $\sim 0,10$ nm that is smaller than ionic radii of paramagnetic praseodymium, neodymium and samarium. It is important to note that the additive of diamagnetic La^{+3} practically no changes paraelectric properties of TiO_2 (at least, above the temperature of ~ 50 K). At the same time, paramagnetic ions (Pr, Nd, Sm in Fig. 3) suppresses paraelectric-type temperature instability: as far as paramagnetism gains strength the temperature dependence of ε disappears, moreover, the TC_ε from negative in the La-BLT becomes positive in the Sm-BLT.

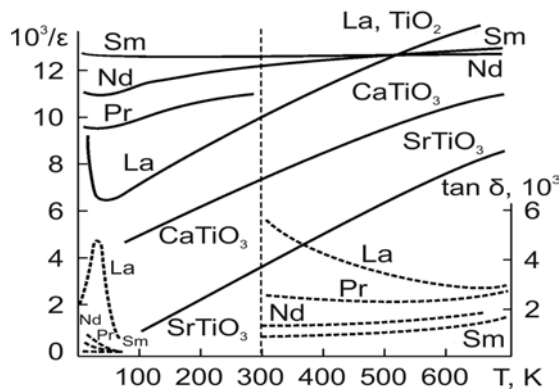


Fig. 3. Temperature dependence of $1/\varepsilon$ (solid curves) and $\tan\delta$ (dashed curves) for BLTs (La, Pr, Nd, Sm) and paraelectrics; below 300 K frequency is 1 MHz, above 300 K – 10 GHz

It is seen from Fig. 3, at low temperatures the $\varepsilon(T)$ -dependence even in La-BLT is different from $\varepsilon(T)$ for paraelectrics: the $1/\varepsilon(T)$ characteristic shows a minimum which points to the presence of relaxation polarization. While $\varepsilon(T)$ -dependence in the paraelectrics follows Curie-Weiss law

$\varepsilon = \varepsilon_1 + C/(T - \theta)$, in some of BLTs the $\varepsilon(T)$ -dependence is satisfied to the relaxation law $\varepsilon(T) = \varepsilon_1 + K/T$.

Temperature anomalies in the BLTs permittivity are accompanied by the dielectric losses maximums (Fig. 3), which are typical for relaxation polarization. At temperature decreases, the maximums of ε and $\tan\delta$, firstly, decrease along the line La-Pr-Nd (and disappear for Sm), and, secondly, they shift to lower temperatures.

With increasing frequency, Fig. 4, as it should be for the relaxation processes, the losses maximums shift to the higher frequencies. Very low activation energy results in the fact that above the temperature 100 K maximums of losses can be observed only in the millimetre wavelength range (at 100...200 GHz), Fig. 4.

It turned out, that in the BLTs about 80% of their dielectric constant is determined by the lattice polarization which is strongly coupled with electronic relaxation process. The last has very low activation energy ($U \sim 0,01$ eV) that seems to escape notice at microwave losses at the application temperatures (250...350 K) but have a pronounced effect on BLTs ε -thermal stability. Namely, electronic bonds for lanthanide $4f/5d$ -hybrid viscously suppresses the correlation between octahedrons, and conventional temperature dependence of paraelectric-like lattice vibration mode.

Permittivity and loss factor frequency characteristics for three typical barium-lanthanides are shown in Fig. 5. In the La-BLT the minimum of losses is located near the frequency of 0,1 GHz. More important for applications Sm- and Nd-BLTs (that are the components for solid solution with $TC_\varepsilon \approx 0$) have the minimum of losses just between meter and decimeter waves where these dielectrics with their $\varepsilon \geq 100$ are the most perspective.

Mechanisms of the BLTs dielectric losses are associated with structural disordering, especially with a presence of unwanted polar phase. Any boundaries (interfaces) between grains have disordered structure and their relaxation frequency may reach microwave range. It is polar ionic nanoscale regions that are the main reason of microwave absorption. That is why BLTs ceramic processing should avoid appearance of polar phase.

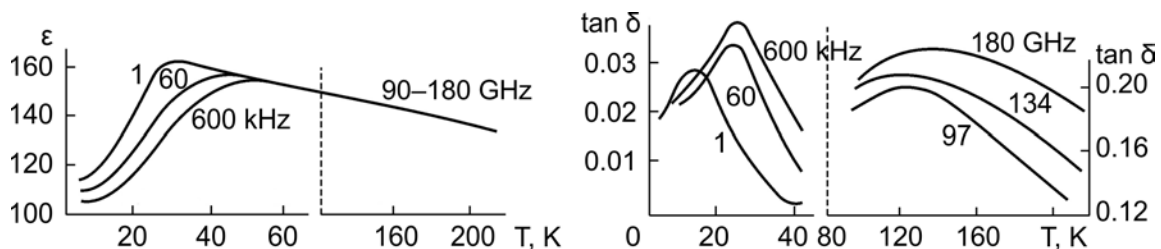


Fig. 4. Low-energy relaxation process in the La-BLT: at frequencies 1...600 kHz anomalies in ε and $\tan\delta$ are seen in temperature interval of 4...60 K and at frequencies of 90...180 GHz

When used in practice (in the temperature interval of 200...400 K) the internal relaxation frequency of these processes exceeds the microwave range, so that the "relaxation supplement" altogether with the lattice contribution provides the thermal stability of total dielectric permittivity.

Conclusions

Acceptable monophasic perovskite-like structure for BLT can be realized only for cerium group of the lanthanide row. The main special feature of this structure is linked in the corners TiO_6 -octahedrons. In this work it is supposed that in the well-known microwave dielectrics of the BLT-types the electronic bonds of $4f/5d$ -hybrid, caused by the rare-earth ions, viscously suppress the interplay of TiO_6 octahedrons and this neutralization is highly favourable to the ϵ thermal stability. Dielectric spectroscopy method, initiated from very low frequencies and extended up to far infrared range, was applied in the temperature interval of 10...600 K was used to check this assumption.

Mechanism of the anomalously high ϵ_{mic} and low $TC\epsilon$ in BLT is that "soft" lattice vibration mode (that usually give rise to high ϵ but thermal non-stability) is "suppressed" by the rare-earth ions, violating a long-range correlation peaks connected by oxygen octahedra TiO_6 . The main reason of this effect is the paramagnetism that is peculiar to the cerium row of lanthanides. Barium plays a supporting role for thermal stability and, moreover, supports to BLTs manufacturability.

The reason for a significant increase in dielectric losses in the BLTs in the range of microwaves and millimetric waves is a low-frequency lattice vibrations associated with the low-energy relaxation process. However, this feature of the BLTs is not a big disadvantage when they are used in the metric and decimetric waves.

Doping "hard paraelectric" by the paramagnetic REE ions leads to the fact that in the $\epsilon(T)$ characteristic the paramagnetism suppresses paraelectricity. Therefore, it can be assumed that the paramagnetism prevents the appearance the polar phase and thus lowers the microwave loss due to the polar phase.

References

1. *Belous A. G., Butko V. I., Novitskaia G. N., Poplavko Y. M., Ushatkin E. F.* (1985), "Dielectric spectra of perovskites $\text{La}_{2/3-x}\text{M}_{3x}\text{TiO}_3$ ". Solid State Physics. Vol. 27, no. 7, pp. 2013–2017. (Rus)
2. *Butko V. I., Belous A. G., Polianetskaia S. V. [et al.]* (1984), "Electrical parameters of the solid solutions titanates of rare earths". Ukrainian Chemistry Journal. Vol. 50, no. 11, pp. 1139–1142. (Rus)
3. *Poplavko Y., Borisov V., Molchanov V.* (1994), "Microwave dielectric relaxation in barium lanthanide tetratitanates (BLT)" Ferroelectrics. Vol. 156, no. 1, pp. 351–356.

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Механізми поляризації у термостабільній БЛТ кераміці на надвисоких частотах Частина 2: Придушення «м'якої» моди парамагнетизмом

Об'єктами дослідження є вакансійні перовскітоподібні структури $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ (БЛТ). Ці полікристалічні діелектрики виділяються серед багатьох інших СВЧ діелектриків тим, що їх проникність ϵ в кілька разів вища, ніж в інших типах СВЧ кераміки. Процес електронної релаксації із край низькою енергією активації не впливає на НВЧ втрати, але визначає термостабільність БЛТ. Час релаксації дуже малий за рахунок нанорозмірних кластерів, електронних за своєю природою і вбудованих в структуру БЛТ. Діелектричні втрати в кераміці цього типу пов'язані зі структурним розупорядкуванням, особливо якщо присутня друга полярна фаза. Бібл. 3, рис. 4, табл. 2.

Ключові слова: діелектрична проникність ϵ ; температурний коефіцієнт діелектричної проникності $Tk\epsilon$; термостабільність; параелектрик; рутил; барійлантаноїдний тетратитанат; рідкоземельний елемент.

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Механізми поляризації в термостабільній БЛТ кераміці на сверхвысоких частотах Часть 2: Подавление «мягкой» моды парамагнетизмом

Объектами исследования являются вакансионные перовскитоподобные структуры $BaLn_2Ti_4O_{12}$ (БЛТ). Эти поликристаллические диэлектрики выделяются среди многих других СВЧ диэлектриков тем, что их проницаемость ϵ в несколько раз выше, чем в других типах СВЧ керамики. Процесс электронной релаксации с крайне низкой энергией активации не влияет на СВЧ потери, но определяет термостабильность БЛТ. Время релаксации очень мало за счет наноразмерных кластеров, электронных по своей природе и встроены в структуру БЛТ. Диэлектрические потери в керамике этого типа связаны со структурным разупорядочением, особенно если присутствует вторая полярная фаза. Библ. 3, рис. 4, табл. 2.

Ключевые слова: диэлектрическая проницаемость ϵ ; температурный коэффициент диэлектрической проницаемости $Tk\epsilon$; термостабильность; параэлектрик; рутил; барійлантаноїдний тетратитанат; рідкоземельний елемент.

Список использованных источников

1. Белоус А. Г. Диэлектрические спектры перовскитов $La_{2/3-x}M_{3x}TiO_3$ / А. Г. Белоус, В. И. Бутко, Г. Н. Новицкая, Ю. М. Поплавко, Е. Ф. Ушаткин // ФТТ. – 1985. – Т. 27, № 7. – С. 2013–2017.
2. Бутко В. И. Электрические параметры твердых растворов титанатов редких земель / В. И. Бутко, А. Г. Белоус, С. В. Полянецкая [и др.] // Укр. хим. журнал. – 1984. – Т. 50, № 11. – С. 1139–1142.
3. Poplavko Y. Microwave dielectric relaxation in barium lanthanide tetratitanates (BLT) / Y. Poplavko, V. Borisov, V. Molchanov // Ferroelectrics (USA). – 1994. – Vol. 156, No. 1. – PP. 351–356