

High dielectric constant microwave ceramics

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Abstract

The isomorphism regions and a behavior of the electric parameters in relation to the $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ (BLT) solid solution composition for the $(\text{A}_x\text{Ba}_{1-x})(\text{B}_y\text{Ln}_{2-y})(\text{C}_z\text{Ti}_{4-z})\text{O}_{12}$ system, where Ln = Nd, Sm and A stands for Sr or Pb; B stands for Bi; C stands for Zr are studied. The dielectric constant of solid solutions can lie in the range 80–125 with the temperature coefficient of dielectric constant near to zero. The advantage of the chemical precipitation technique over the solid-phase synthesis for obtaining of a ceramics with maximum ϵ and quality factor is shown. A study of the quality factor of materials on the base of the BLT solid solutions has shown rather weak temperature dependence within the range -80 – $+80$ °C. The dielectric constant of the obtained materials does not change up to the submillimeter band and the product of the quality factor and of the frequency is practically constant. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Creation of microwave ceramics with a high dielectric constant (ϵ) and good thermostability together with small dielectric losses in wide temperature and frequency ranges is an actual problem since the application of such materials in the microwave technology ensures reduction of mass and overall dimensions of microwave equipment.

A combined study of both the crystal structure and the electrophysical properties of new compounds and solid solutions is necessary for the development of new ceramic materials. A refinement of stoichiometric compositions and homogeneity regions new materials is desirable. Effective synthesis techniques providing reproducibility in commercial production of high electrophysical parameters of ceramic materials and of microwave elements based on them have to be developed.

In the present paper results of the study of ceramics based on the barium, titanium and rare-earth elements (REE) oxides are presented. This group of compositions are very interesting due to their unique properties: a combination of high dielectric constant ($\epsilon \geq 80$) and small temperature coefficient of ϵ ($\text{TC}\epsilon$) with rather

small dielectric losses in a wide range of temperatures and frequencies.

Ceramic materials of the $\text{BaO-Ln}_2\text{O}_3\text{-TiO}_2$ system (with Ln standing for Nd and Sm first of all) are applied for manufacturing high-frequency ceramic capacitors and microwave dielectric resonators, substrates and other microwave elements. However, the stoichiometry and structure of these materials are subjects of discussion up to last time. The solution of these problems is particularly actual because of very high requirements to electric parameters of elements for microwave devices. These parameters depend first of all on the chemical and phase composition optimality of the ceramic materials.

The first data on crystallography of compounds belonging to this system were published in Refs. 1 and 2. However, for a few years the composition of compounds based on barium, titanium and REE oxides that are most promising from the point of view of electrical properties was erroneously taken for one with the ratio of starting oxides 1:1:5 ($\text{Ba Ln}_2 \text{Ti}_5 \text{O}_{14}$). At the same time, in Refs. 3 and 4 the composition of this compound was taken for one with the ratio of starting oxides 1:1:4 ($\text{Ba Ln}_2 \text{Ti}_4 \text{O}_{12}$) (BLT), where Ln stands for La, Pr, Nd, Sm or Eu. A wide homogeneity region with regard to titanium ($4 \leq n \leq 5,5$) was assumed in Ref. 5, but this was ruled out in Ref. 6 and the absence of such a region for BLT was proved. Phases of rutile and barium polytitanate $\text{Ba Ti}_4\text{O}_9$ are observed at a titanium content greater than four moles, and beginning from the TiO_2 content of five

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moles a phase of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ appears apart from the rutile phase which continues extending. Similar results were obtained in Refs. 7 and 8

The structure of the compound was determined for the composition 15 BaO 19 Ln_2O_3 72 TiO_2 ($\text{Ln} \equiv \text{Pr}$) (15:19:72) on the monocrystal. A combination of the perovskite and tetragonal potassium tungsten bronze structure motives is characteristic of this structure. The composition refined by a structure study corresponds to the formula $\text{Ba}_{3.75}\text{Pr}_{9.5}\text{Ti}_{18}\text{O}_{54}$.⁹

In 1990, we have shown that the composition 15-19-72 is a aliovalent BLT solid solution where REE cations can substitute for barium ones. There is a succession of solid solutions with the elementary cell volume, ε and $\text{TC}\varepsilon$ smoothly depending on composition. The maximum ε was obtained for the compositions containing La, Pr, Nd or Sm with the maximum barium content of 18:18:72 or $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ which were described taking into consideration⁹ as $\text{Ba}_{3.5}[\text{Ba}_{1.0}\text{Ln}_{9.0}][\text{Ti}_9\text{O}_{27}]_2$.¹⁰

Therefore, BLT has a wide isomorphism region including the heterovalence substitution of barium by La, Pr, Nd or Sm. However, forming of the above solid solutions does not lead to further increase of ε . Our study has shown that the formation of the 1:1:4 optimal composition is sometimes followed by the emergence of the impurity phases BaTi_4O_9 , $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$, $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$, and $\text{Ln}_2\text{Ti}_2\text{O}_7$ which lowers the ε value and, sometimes, the quality factor of samples. Having in mind searching for a possibility to increase the dielectric constant and/or the quality factor keeping $\text{TC}\varepsilon$ close to zero, we studied the structure and dielectric properties of new BLT compositions belonging to the $(\text{A}_x\text{Ba}_{1-x})(\text{B}_y\text{Ln}_{2-y})(\text{C}_z\text{Ti}_{4-z})\text{O}_{12}$ systems with Ln standing for Nd when Ba was substituted by Sr or Pb, Ln was substituted by Bi, and Ti by Zr. We searched for optimum synthesis techniques ensuring stability of the phase composition at the minimum content of impurity phases and the maximum ε value, quality factor ($Q \sim 1/\text{tg}\delta$) and thermostability.

2. Samples preparation

Samples of different compositions were obtained both by the standard solid-phase synthesis from Ba and Sr carbonates and oxides of REE, TiO_2 and by chemical coprecipitation from salt solutions with subsequent burning of the residue. Both of the methods are described in Refs. 6, 11 and 12. BaCO_3 , SrCO_3 , chemically pure Bi_2O_3 , Nd_2O_3 and Sm_2O_3 of the NO-E and SmO-E classes and TiO_2 with 99.9 wt.% content of the basic matter were used as raw materials for the solid-phase synthesis. Samples of the composition under study were initially synthesized at 1200–1300 °C. Then the free Ba and REE oxide content of the powder was analyzed. The free oxide content did not exceed 0.5% after the synthesis. Insoluble impure phases were extracted in the form of insoluble

solid residues (ISR) by dissolving the main phase by concentrated hydrochloric acid. The amount of ISR was determined with an accuracy of ± 0.02 wt.%.⁶ In a similar way, the initial powders of the compositions under study obtained by the chemical coprecipitation technique were analyzed after the thermal treatment. Disk samples of the size necessary for electric measurements in the 10^3 – 10^6 , $(4-5)10^9$ and 10^{11} – 10^{12} Hz frequency bands were prepared by the hydraulic pressing technique. Samples were sintered at 1260–1500 °C in an electric chamber furnace in air atmosphere until the cessation of water absorption. X-ray study of the synthesized samples, extracted ISR and of the sintered samples was carried out with a DRON-3 X-ray diffractometer (CuK_α radiation, Ni filter).

3. Results and discussion

Monophase samples of BLT solid solutions are formed for the $(\text{A}_x\text{Ba}_{1-x})\text{Ln}_2\text{Ti}_4\text{O}_{12}$ system, where A stands for Sr and Ln for Nd up to $x=0.4$ (for A = Sr and Ln = Nd). The appearance of the second phase of the $\text{SrNd}_2\text{Ti}_4\text{O}_{12}$ type with perovskite structure and doubled lattice spacing (it is described in Ref. 13) is found beginning from $x=0.6$. A substitution of Ba^{2+} cations for Sr^{2+} reduces the elementary cell volume of BLT solid solutions (Fig. 1a). Two phases of solid solutions with BLT and $\text{SrNd}_2\text{Ti}_4\text{O}_{12}$ structures are found in the concentration range $x=0.5$ – 0.8 in the $(\text{Sr}_x\text{Ba}_{1-x})\text{Nd}_2\text{Ti}_4\text{O}_{12}$ system. One phase of the $\text{SrNd}_2\text{Ti}_4\text{O}_{12}$ structure is formed at $x=1$.

A reduction in elementary cell volume due to introduction of strontium is observed in materials of the $(\text{Sr}_x\text{Ba}_{1-x})\text{Sm}_2\text{Ti}_4\text{O}_{12}$ system too (Fig. 1a). A phase with the pyrochlore structure is formed at $x=0.2$, and a third phase of $\text{SrSm}_2\text{Ti}_4\text{O}_{12}$ ($a=7.722\text{Å}$) with perovskite structure (it is described in Ref 13 too) appears at $x=0.6$. As is evident from Fig. 1b, the dielectric constant depends weakly on the Sr content of the solid solution, slightly increasing for compositions approaching the isomorphism region boundary.

Substitution of Ln^{3+} and Ti^{4+} cations for ones with larger ionic radius, Nd for Bi^{3+} and Ti^{4+} for Zr^{4+} , leads to the formation of a solid solution with an enlarged elementary cell volume. Data for the BLT system with the Ti^{4+} ions substituted for Zr^{4+} in the $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ compound are depicted in Fig. 2. X-ray study shows that the formation of BLT solid solutions is observed in a wide range of substituting ions and is accompanied by elementary cell increase with increasing Zr concentration in the solid solution, which leads to a certain decrease of ε and of the $\text{TC}\varepsilon$ absolute value. The total content of impurity phases does not exceed 3%.

Only introduction of Bi^{3+} instead of Ln^{3+} into the solid solution is shown to increase $\text{BLT}\varepsilon$, but it is

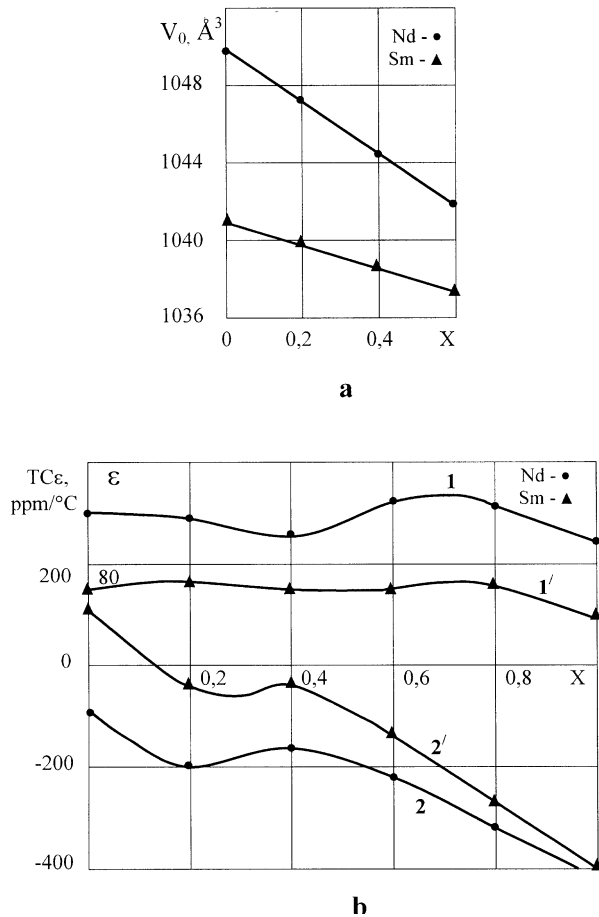


Fig. 1. Composition dependence of (a) the BLT solid-solution elementary cell volume V_0 , (b) dielectric constant ϵ (1, 1') and TC ϵ (2, 2') for the $(\text{Sr}_x\text{Ba}_{1-x})\text{Nd}_2\text{Ti}_4\text{O}_{12}$ (1,2) and $(\text{Sr}_x\text{Ba}_{1-x})\text{Sm}_2\text{Ti}_4\text{O}_{12}$ (1', 2') systems.

accompanied sometimes by an essential decrease of the sample quality factor. One of the reasons is formation of impurity phases of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ type.

In this regard, the results of the study of solid solutions with a simultaneous substitution of Ba^{2+} for Pb^{2+} and Nd^{3+} for Bi^{3+} are of particular interest. The results of the X-ray study of some compositions belonging to the system $(\text{Pb}, \text{Ba})(\text{Nd}, \text{Bi})_2\text{Ti}_4\text{O}_{12}$ synthesized by the solid-phase technique are presented in Table 1.

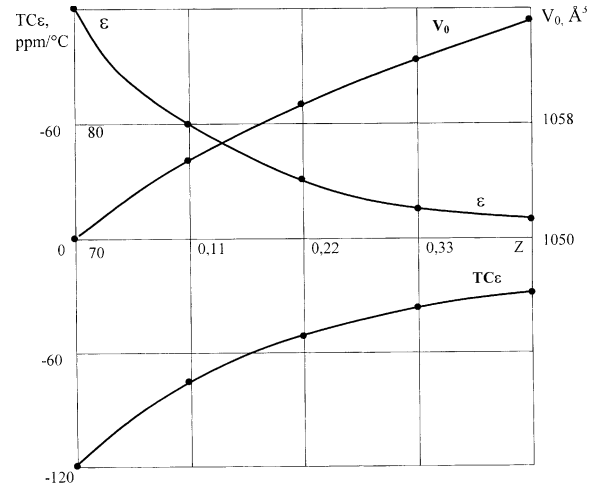


Fig. 2. Composition dependence of the BLT solid-solution elementary cell volume V_0 , dielectric constant ϵ and TC ϵ for the $\text{BaNd}_2(\text{Zr}_{1-x}\text{Ti}_{4-x})\text{O}_{12}$ system.

As is evident from these data, the BLT solid solution elementary cell volume rises with Bi^{3+} introduction and slightly decreases with increasing Pb concentration. Isomorphous solid solutions with close elementary cell parameters are formed on simultaneous introduction of these elements in a wide range of compositions. Our study has shown that the chemical precipitation technique¹¹ makes it possible to increase the reaction completeness during BLT solid solution formation and, simultaneously, to reduce by approximately 100° the preliminary synthesis and sintering temperatures for some compositions in comparison with the solid-phase synthesis technique. Comparative data on the impurity phase content of insoluble solid residues (ISR) of samples belonging to the $(\text{Pb}, \text{Ba})(\text{Nd}, \text{Bi})_2\text{Ti}_4\text{O}_{12}$ system obtained both by the solid-phase synthesis (1) and by chemical precipitation technique (2) are presented in Fig. 3. Phases of $(\text{Ba}, \text{Pb})\text{Bi}_4\text{Ti}_4\text{O}_{15}$, $\text{Nd}_2\text{Ti}_2\text{O}_7$, BaTi_4O_9 , and pyrochlore its (content increases with increasing $y > 0.5$) were found by X-ray phase analysis as main impurities in the given system of samples. The total amount of impurities in samples does not exceed 5% in the isomorphism region. The dielectric constant of such compositions reaches a value of $\epsilon = 105\text{--}125$ with small TC ϵ and $\text{tg}\delta$. A sharp fall of TC ϵ

Table 1
X-ray study results for BLT solid solutions of the $(\text{Pb}_x\text{Ba}_{1-x})(\text{Bi}_y\text{Nd}_{2-y})\text{Ti}_4\text{O}_{12}$ system obtained by the solid-phase synthesis technique

Composition		Elementary cell parameters			Elementary cell volume V_0 (\AA^3)
X	y	a , (\AA) ± 0.006	b , (\AA) ± 0.002	c , (\AA) ± 0.0005	
0	0	22.380	12.200	3.8470	1050.4
0.15	0	22.289	12.163	3.8343	1039.5
0.10	0.6	23.346	12.211	3.8534	1051.5
0.15	0.4	22.340	12.118	3.8470	1050.0
0.15	0.6	22.358	12.210	3.8512	1051.3
0.25	0.2	22.364	12.200	3.8424	1048.4

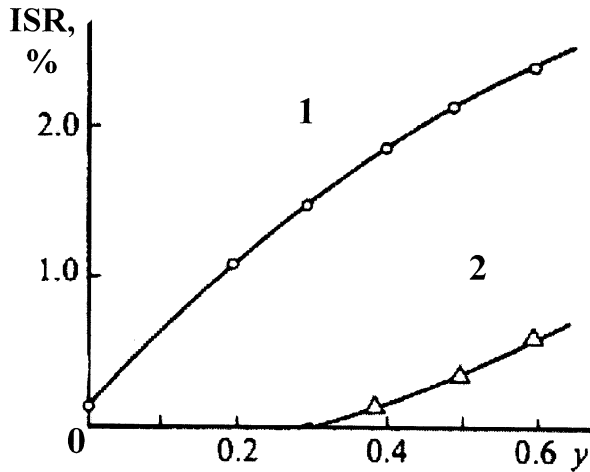


Fig. 3. Content of the insoluble solid residue (ISR) in samples of the $(\text{Pb}_{0.1}\text{Ba}_{0.9})(\text{Bi}_y\text{Nd}_{2-y})\text{Ti}_4\text{O}_{12}$ system obtained by (1) the solid-state synthesis and (2) by the chemical coprecipitation technique.

(Fig. 4) is observed with increasing $y > 0.5$ due to the appearance and growth of the phase with pyrochlore structure as we said above.

The chemical precipitation technique permits one to obtain homogeneous fine-grained (crystallite size $\sim 1 \mu\text{m}$) practically monophasic solid solutions in a wide range of substituting ion concentrations. Data on Q and ε for microwave ceramics based on BLT solid solutions obtained by the solid-phase synthesis and by the chemical precipitation technique are depicted in Fig. 5. The advantage of the latter is apparent from the figure.

The temperature dependence of the Q is shown in Fig. 6. The quality factor slightly increases with increasing temperature for the most of the materials obtained

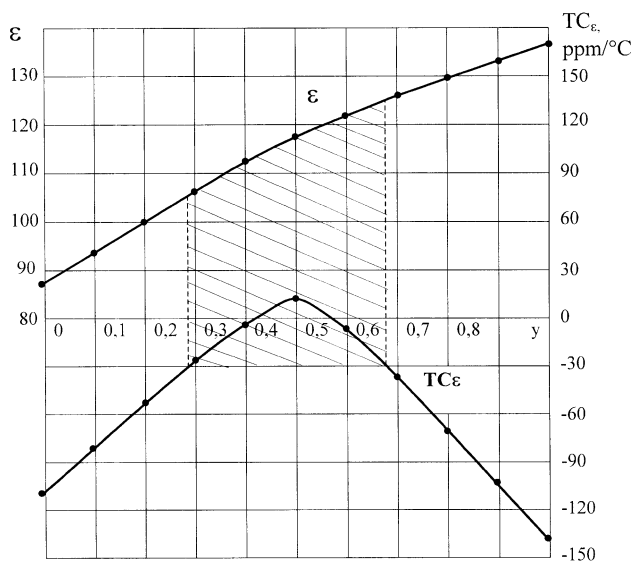


Fig. 4. Composition dependence of the dielectric constant ε and $\text{TC}\varepsilon$ for samples of the $(\text{Pb}_{0.1}\text{Ba}_{0.9})(\text{Bi}_y\text{Nd}_{2-y})\text{Ti}_4\text{O}_{12}$ system (chemical coprecipitation technique).

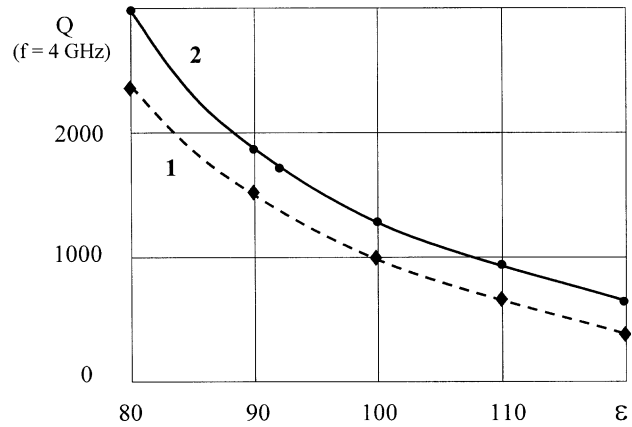


Fig. 5. Quality factor (Q) of ceramic samples prepared on the base of the BLT solid solutions with a use of: (1) solid-phase synthesis; (2) chemical coprecipitation technique.

with $\varepsilon > 90$ within the temperature range -80 – $+80^\circ\text{N}$. Q is practically constant at low temperatures for the material with $\varepsilon = 80$. The data agree with the results of a study of the temperature and frequency relations of complex dielectric constant for samples belonging to the BLT system.¹⁴ In this paper a relaxational nature of dielectric losses in the $\text{BaLa}_2\text{Ti}_4\text{O}_{12}$ compound at low temperatures was shown.

Fragments of experimental data on the dielectric spectra of isovalent BLT solid solutions within the frequency ranges 117–146 and 800–1000 GHz measured on “Epsilon” submillimeter spectrometer¹⁵ are presented in Table 2 and Fig. 7.

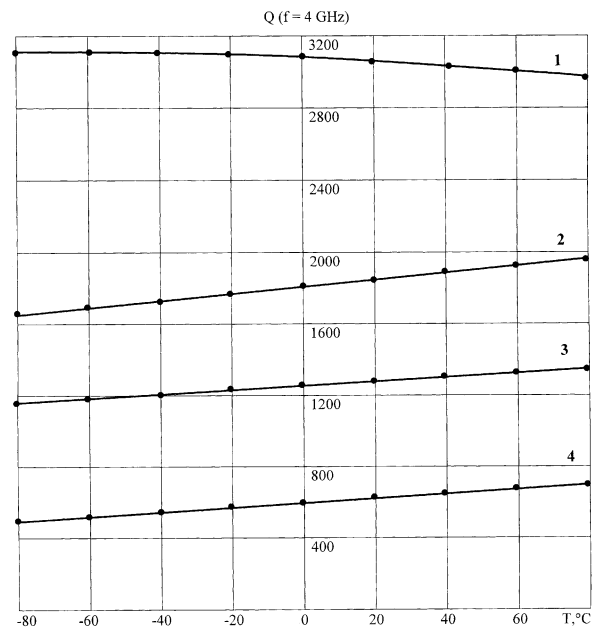


Fig. 6. Temperature dependence of ceramic samples prepared on the base of the BLT solid solutions. (1) $\varepsilon = 80$; (2) $\varepsilon = 90$; (3) $\varepsilon = 100$; (4) $\varepsilon = 125$.

Table 2

Fragment of BLT solid-solution dielectric spectrum measured with the submillimeter spectrometer “Epsilon”¹⁵

f , (GHz)	ϵ'	ϵ''	$\text{tg}\delta$	$Q \cdot f$, (GHz)
117.720	107.975	3.81866	0.03537	3329
132.398	108.034	4.28331	0.03965	3339
146.774	108.518	4.76101	0.04387	3345
161.602	108.308	5.13452	0.04741	3408
176.732	107.766	5.37053	0.04984	3546

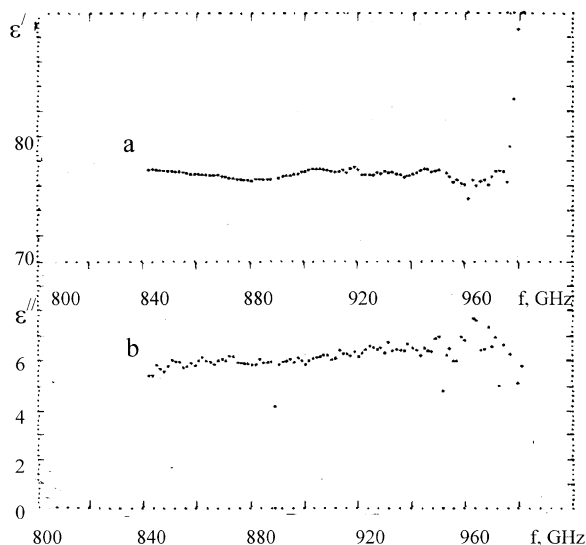


Fig. 7. The submillimeter band frequency dependence of ϵ' (a) and ϵ'' (b) of a sample prepared from the BLT solid solution.

As is evident from the data, the dielectric constant of BLT solid solutions does not practically depend on frequency up to ~ 1000 GHz, and the dielectric loss tangent increases proportionally to frequency so that the product $Q \cdot f$ is practically constant.

4. Conclusions

Regions of isovalent $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ solid solution formation on substitution of Ba for Sr or Pb, of a lanthanide (Ln = Nd, Sm) for Bi, and of Ti for Zr have been studied. Dependence of the dielectric constant and of its temperature coefficient on the composition and substituting cation concentration has been established. It is shown that the dielectric constant of thermostable ceramic materials based on solid solution can be increased from 80 to 125 by simultaneous substitution of Ba for Pb and of Nd for Bi. In this case, the quality factor of samples changes from 3000 to 600 at a frequency of 4 GHz for the starting powders prepared by the chemical precipitation technique. The dielectric constant (ϵ') of ceramic materials does not change with the frequency

increase up to 1000 GHz, while the product of quality and frequency is a constant.

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