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Physicochemical aspects of the development of MW dielectrics and their use

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Abstract

Various methods for developing MW dielectrics based on multiphase and monophase systems have been considered. It has been shown that multiphase MW dielectrics can be developed in several ways: (a) by using paraelectrics together with antiferroelectrics in gradient MW dielectrics; (b) by using volume temperature compensation; (c) by developing composite materials containing an organic matrix and a fine inorganic multiphase filler. Monophase MW dielectrics can be developed on the basis of solid solutions, in which: (a) positive temperature dependence of permittivity (τ_ε) in compounds forming solid solution is attained by the existence of phase transitions or by the presence of a mobile sublattice; (b) aliovalent substitution in cation sublattices affects the phonon spectrum, resulting in a high temperature stability of electrophysical properties. Examples of the use of MW dielectrics developed in engineering are given.

Keywords: $BaTiO_3$ and titanates; Composites; Dielectric properties; Functional applications; Perovskites; Powders: solid state reaction

1. Introduction

The microwave technology uses widely various dielectric materials. Dielectrics, the use of which reduces substantially the overall dimensions of microwave circuits, i.e. dielectrics with high permittivity ($\varepsilon > 20$), are of special interest. The miniaturization effect is based on the $\varepsilon^{1/2}$-fold reduction of electromagnetic wave length in dielectric; the planar dimensions of microwave microcircuits decrease by a factor of ε. Dielectrics with high permittivity are used as dielectric resonators, microcircuit substrates, filter capacitors, etc. in microwave technology.

The main requirements to microwave dielectrics are high permittivity (ε), low dielectric loss (tg δ) and temperature coefficient of frequency (τ_f) tending to zero. It should be noted that high polarizability without strong energy absorption at 10^9–10^{11} Hz can be only achieved through optical and infrared polarization. Other electric polarization mechanisms make no microwave dielectric contribution or undergo microwave ε dispersion, which leads to high dielectric loss.[1]

Optical polarization is characterized by a low temperature coefficient ($\tau_\varepsilon = 10^{-5}$ K^{-1}) which is due to dielectric density change as a function of temperature. However, the dielectric contribution of optical polarization is usually small in most crystals. It follows that high temperature stability and low dielectric loss in the microwave range can be only observed in dielectrics with large infrared contribution to permittivity.[1,2] This polarization mechanism is due to a cation and anion sublattice displacement induced by an electric field, i.e. it is possible only in ionic crystals.

However, the change as a function of temperature is usually the larger, the higher ε. The high value of infrared polarization is generally due to the presence in crystal of a soft phonon mode, which varies with temperature by the critical law: $\omega_T = A(T-\Theta)^{1/2}$, leading in accordance with the Liddein–Sax–Teller relation:

$$\varepsilon_{MW}/\varepsilon_{opt} = \prod_i (\omega_{L_i}^2/\omega_{\tau_i}^2) \quad (1)$$

to the Curie–Weiss law for permittivity:

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

where ω_{L_i} and ω_{τ_i} are the frequencies of longitudinal and transverse optical phonons in the centre of Brillouin zone (one of the transverse phonons is soft), C is a constant, Θ the Curie–Weiss temperature and ε_L the dielectric contribution slightly dependent on temperature.

If the Curie–Weiss law holds, dielectrics in the microwave range are characterized by a considerable

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temperature instability of electrophysical properties and cannot be used in microwave technology. Therefore, the combination of low dielectric loss, high permittivity and temperature stability in one substance is a complicated scientific-technical problem.

Microwave dielectrics can be developed in several different ways, for example on the basis of monophase systems and by creating multiphase compositions. Monophase microwave dielectrics are developed on the basis of solid solutions[3–6] using aliovalent substitution in one of the crystal sublattices[7] and by making one of the sublattices mobile.[8,9] At the same time, microwave dielectrics based on multiphase compositions can be developed by creating gradient (composite) materials and elements based on them[10,11] and by using volume temperature compensation.[12,14] Let us discuss briefly the above methods for developing microwave dielectrics in terms of literature data and the results by the author.

2. Results and discussion

Microwave dielectrics are made most often on the basis of solid solutions.[3–6] In this way are made microwave materials, which are widely used in engineering, for example on the basis of $Ba(Zn, Mg)_{1/2}(Nb, Ta)_{2/3}O_3$,[4,15–17] $Ba_{6-x}Ln_{8+2/3x}Ti_{18}O_{54}$,[18–21] $(La,Ca)(Ti, Al)O_3$,[3,22] etc. The essence of this approach is that solid solution is formed by the interaction of phases, which have in the microwave range different trends of the plot of permittivity against temperature and a low dielectric loss. Paraelectrics, which are characterized by low dielectric loss, for example $CaTiO_3$ in the system $CaTiO_3$–$LaAlO_3$, can be used as phase having a negative temperature coefficient of permittivity ($\tau_\varepsilon < 0$).[3] $LaAlO_3$[23] and $Ba_{6-x}Ln_{8+2/3x}Ti_{18}O_{54}$ (Ln = Sm, Gd) are used as phases having $\tau_\varepsilon > 0$ in the microwave range.[19–21,24] Positive τ_ε in the microwave range might indicate the existence of an internal field due to spontaneous polarization, as in ferroelectrics and antiferroelectrics. However, no dielectric hysteresis loop was observed in $LaAlO_3$;[23] there is no evidence for the presence of hysteresis loops in $Ba_{6-x}La_{8+2/3x}Ti_{18}O_{54}$ (Ln = Sm,Gd), either. It should be noted that in $BaSm_2Ti_4O_{12}$ anomalies were observed in plots of $\varepsilon(T)$ in the microwave range.[19] However, the nature of these anomalies remains unexplained as yet.

The possibility of developing microwave dielectrics using the effect of aliovalent substitution in cation sublattices on τ_ε was studied for the system $La^{3+}_{2/3}M^{+}_{3x}TiO_3$ (where M = Na,K).[25] In the dielectric spectrum of lanthanum metatitanates, two characteristic regions can be distinguished: the first region, up to 10^8 Hz and the second region, 10^8–2×10^{11} Hz (Fig. 1). Up to 10^8 Hz, dispersion is of relaxation character, and the function $\varepsilon(\omega)$ for $La_{1/2}Na_{1/2}TiO_3$ can be defined by the Cole–Cole dispersion relation:

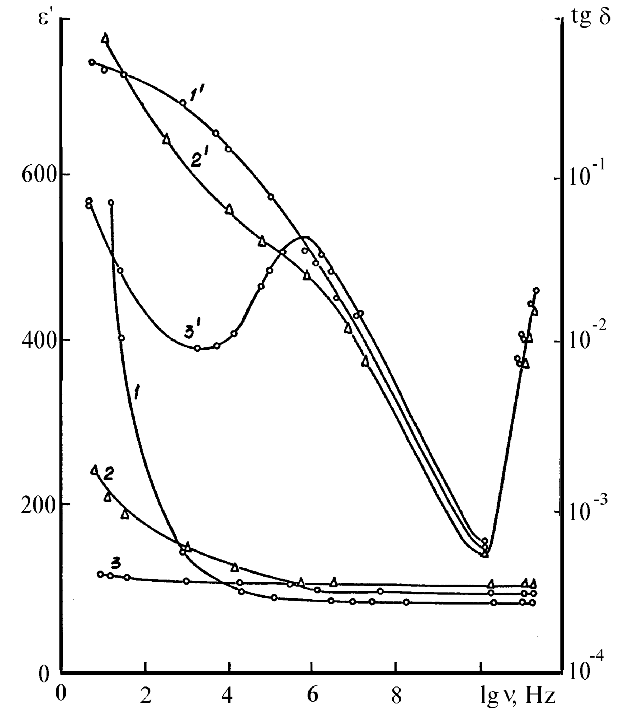

Fig. 1. Frequency dependence of permittivity (1, 2, 3) and loss (1′, 2′, 3′) for the compounds $La_{7/12}Na_{2/4}\square_{1/6}TiO_3$ (1, 1′), $La_{1/2}Na_{1/4}K_{1/4}TiO_3$ (2, 2′) and $La_{1/2}Na_{1/2}TiO_3$ (3, 3′) at 295 K.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-2}}$$

where ε_s is the static permittivity, ε_∞ the permittivity above relaxation frequency, τ the relaxation time and α the parameter characterizing relaxation time.

In the frequency range 10^8–2×10^{11} Hz there is no ε dispersion, and tg δ is determined by high-frequency polarization mechanisms.[25] At 1.2×10^{10} Hz, the minimum tg δ value, which changes slightly with rising temperature, is observed in $La_{1/2}Na_{1/4}K_{1/4}TiO_3$ and is 5–6×10^{-4} (Fig. 2). The dynamic properties of lanthanum metatitanates $La_{2/3-x}M_{3x}TiO_3$ in the microwave range are determined mainly by the $La_{2/3}TiO_3$ matrix, as evidenced by a small difference in tg δ between some compounds. In the submillimeter-wave band, a similar trend of plots of ε and tg δ against frequency is observed, but dielectric loss increases by more than an order of magnitude as against SHF band.

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

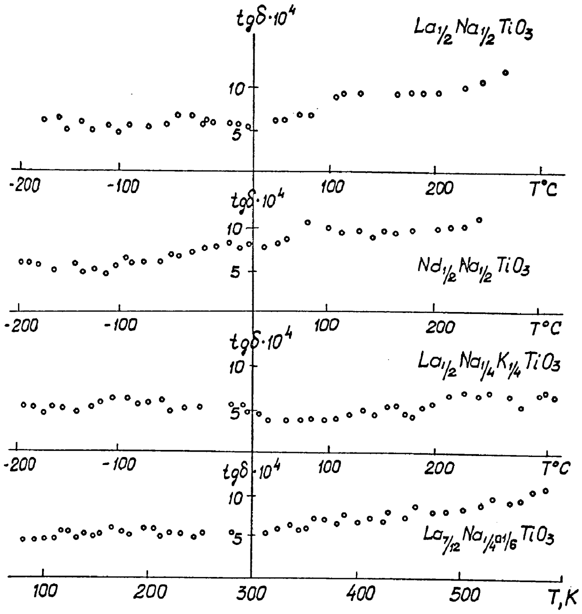

Fig. 2. Temperature dependence of dielectric loss for $(La_{2/3-x}M_{3x}\square_{1/3-2x})TiO_3$ compounds at 1.2×10^{10} Hz.

Table 1
Parameters of dispersion oscillators $(La_{2/3-x}M_{3x}\square_{1/3-2x})TiO_3$

N	$La_{1/2}Na_{1/4}K_{1/4}TiO_3$				$La_{7/12}Na_{1/4}\square_{1/6}TiO_3$			
	$\varepsilon=106$				$\varepsilon=87$			
	ω_{TO} cm^{-1}	ω_{LO} cm^{-1}	$\Delta\varepsilon$	g	ω_{TO} cm^{-1}	ω_{LO} cm^{-1}	$\Delta\varepsilon$	g
1	116	163	74	0.75	133	178	55	0.64
2	198	258	22	0.44	201	224	19.5	0.31
3	267	334	3	0.21	230	265	4.1	0.3
4	336	375	0.2	0.33	270	343	1.8	0.26
5	381	489	0.4	0.16	345	490	0.2	0.1
6	554	747	1.2	0.1	563	694	1	0.11
7	785	816	0.1	0.12	789	860	0.3	0.3
		$\varepsilon\infty=5.1$				$\varepsilon\infty=5.1$		

Aliovalent substitutions in the cation sublattice affect greatly 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.[26] Owing to the small deviation of the structure from the ideal one in $La_{2/3-x}M_{3x}TiO_3$ perovskites, vibrational spectra with rhombic and tetragonal distortions are very similar. Differences pertain only to the stretching vibration region of the oxygen octahedron of TiO_6. Whereas in $La_{1/2}Na_{1/2}TiO_3$ or $La_{1/2}Na_{1/4}K_{1/4}TiO_3$ they have a practically regular shape, in $La_{7/12}Na_{1/4}TiO_3$ one more vibration of low intensity is observed at over 750 cm^{-1}. A similar high-frequency band splitting was observed for the first time by Last in $BaTiO_3$ on lowering crystal symmetry from cubic to rhombic one and is due to a partial elimination of vibration degeneracy.[27]

As a result of processing experimental reflection spectra by dispersion analysis,[28] the parameters of dispersion oscillators were determined, by means of which experimental reflection spectrum is described (Table 1). It is known that one low-frequency vibration is responsible for the high permittivity values in the microwave range in compounds with perovskite structure.[29] As can be seen from the results given in Table 1, aliovalent substitution gives rise to a second vibration, which makes a noticeable contribution to permittivity. This fact can be employed in the development of novel microwave dielectrics, in which it is necessary to combine high permittivity with high temperature stability and low dielectric loss.

Let us discuss the development of microwave dielectrics by creating a mobile crystal sublattice in rare-earth titanates with perovskite structure, in which structure stabilization is effected by large alkali metal ions (Na, K) and which are characterized by negative temperature coefficient of permittivity ($\tau_\varepsilon<0$) and low dielectric loss in the microwave range.[25] At the same time, when we substituted lithium ions for rare-earth elements, we obtained for the first time lithium ion-conducting perovskites,[30] of which positive temperature coefficient of permittivity at high frequencies, including submillimeter-wave band, is typical.[31] This is due to the relaxation of small lithium ions within the limits of voids formed by oxygen octahedra, which makes an additional contribution to the permittivity value on temperature increase. Dielectric loss (tg δ) in cationic conductors $La_{2/3-x}Li_{3x}TiO_3$ in the SHF and millimeter-wave bands is high. However, by reducing the size of conducting channels and crystallographic voids, in which lithium ions are situated, and by substituting smaller rare-earth ions for La ions, the state can be achieved in which lithium relaxation persists in relatively small voids, and positive temperature coefficient of permittivity is obtained at relatively low dielectric loss values. This makes it possible to obtain solid solutions having high permittivity and temperature stability in the microwave range at relatively low dielectric loss on the basis of lithium-containing and, for example, sodium-containing rare-earth titanates with perovskite structure, which have a different character of permittivity variation with temperature.[8,9]

The development of temperature stable microwave dielectrics using volume temperature compensation consists in the creation of multiphase systems, where each of the phases has a different character of the temperature dependence of permittivity (τ_ε). When investigating $BaTi_4O_9$ ceramics, which is characterized by $\tau_\varepsilon<0$, it was shown[12] that addition of zinc oxide (ZnO) improves the temperature stability of the permittivity of the ceramics (Fig. 3). It was found that when zinc oxide is introduced in barium tetratitanate ($BaTi_4O_9$), a phase of the composition $3BaO{\cdot}12TiO_2{\cdot}7ZnO$ appears, which has a rhombic crystal system of the cell ($a=0.6390$ nm, $b=0.6875$ nm, $c=0.7045$ nm). The phase $3BaO{\cdot}12TiO_2{\cdot}7ZnO$ has a positive temperature coefficient of ε ($\tau_\varepsilon>0$). This makes it possible to control temperature

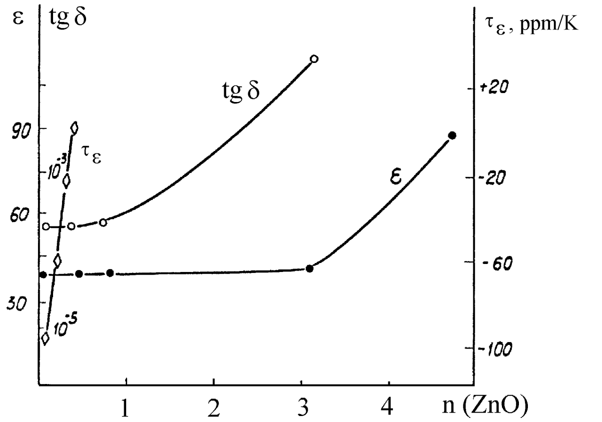

Fig. 3. Variation of the electrophysical properties of $BaTi_4O_9$–nZnO materials as a function of ZnO concentration (10^{10} Hz).

stability at practically constant ε and low dielectric loss (Fig. 3). It should be noted that the authors of ref 13 also point out the formation of the phase $3BaO{\cdot}12TiO_2{\cdot}7ZnO$, which is formed by the interaction of $BaTi_4O_9$ with ZnO. At the same time, Refs. 14 and 32 point out that this phase probably corresponds to $BaTi_4Zn_2O_{11}$. Independent of this, however, it should be noted that the improvement of the temperature stability of $BaTi_4O_9$-based materials on the addition of ZnO is due to the formation of a multiphase system with different character of the temperature dependence of permittivity of each phase.

One of the methods for the development of temperature stable microwave materials with high ε_{eff} seems to be the manufacture of gradient dielectrics and elements (for example, dielectric resonators, dielectric substrates) consisting of two layers of high-Q dielectrics with temperature coefficients of permittivity (τ_ε) different in sign.[10] The temperature coefficient of frequency of such materials depends on the size of the constituent parts and ε and τ_ε of the dielectrics of which they are made. Whereas a large number of dielectrics with $\tau_\varepsilon < 0$ (mainly paraelectrics) are known at present, expensive single-domain lithium niobate ($LiNbO_3$) and lithium tantalate ($LiTaO_3$) crystals are used as dielectrics with $\tau_\varepsilon > 0$.[10] The use of the latter does not allow questions connected with the microminiaturization of microwave circuits to be effectively solved since the ε value of these crystals, which determines the dielectric resonator (DR) size, is low (about 40–50). We endeavoured to clear up whether tellurium-containing compounds with perovskite structure of the general composition A_2BTeO_6 can be used as microwave dielectrics with $\tau_\varepsilon > 0$. According to Ref. 33, some of the compounds are antiferroelectrics (AFE). The fact that AFEs, which possess temperatures of transition to vapour phase that are higher than room temperature, have promise as materials for making microwave devices was pointed out in Ref. 34. The technical characteristics of AFE-based microwave elements, however, were not studied before. Lead–cobalt tellurate (Pb_2CoTeO_6) was chosen for investigations from a large number of ceramic compounds of the general composition A_2BTeO_6. Fig. 4 shows the temperature dependence $\varepsilon(T)$ for Pb_2CoTeO_6, which was measured at 10^9 Hz. In the temperature range 220–350 K, the dependence $\varepsilon(T)$ is close to linear one; the average τ_ε value is $700\times10^{-6}\ K^{-1}$.

Composite dielectric resonators were made from the following pairs of ceramic materials: Pb_2CoTeO_6–TiO_2, Pb_2CoTeO_6–$CaTiO_3$, Pb_2CoTeO_6–$SrTiO_3$, $LiNbO_3$–TiO_2. DR parts were cemented with varnish KO-8. Table 2 lists ε_{eff} and Q values ($Q = 1/\text{tg}\ \delta$) for composite DRs at temperature coefficient of frequency (τ_f) tending to zero. Fig. 5 shows plots of ε_{eff} of composite DR's against τ_ε for different pairs of materials.

As is evident from Table 2 and Fig. 5, the effective permittivity of composite DRs formed by the pair Pb_2CoTeO_6–$SrTiO_3$ is almost 3times higher than ε_{eff} of DRs formed by $LiNbO_3$–TiO_2. Thus, the use of lead–cobalt tellurate as material with $\tau_\varepsilon > 0$ for making gradient DRs makes it possible to increase ε_{eff} of DRs and hence to reduce the size of microwave circuit elements. On the other hand, the change of the linear dimensions of composite DRs formed by Pb_2CoTeO_6 and paraelectrics leads to a change in τ_ε from -2500×10^{-6} to $+350\times10^{-6}$ K^{-1}. This allows the temperature range of the use of some microwave circuits to be widened since gradient

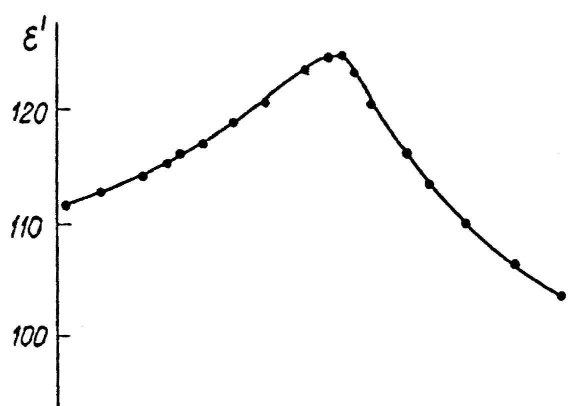

Fig. 4. Temperature dependence of the permittivity of lead–cobalt tellurate at 6×10^8 Hz.

Table 2
Electrophysical characteristics of gradient DRs at 10^{10} Hz at τ_f values tending to zero

Material of gradient DRs	Q_{eff}	ε_{eff}
Pb_2CoTeO_6–TiO_2	1000	110
Pb_2CoTeO_6–$CaTiO_3$	900	125
Pb_2CoTeO_6–$SrTiO_3$	900	135
$LiNbO_3$–TiO_2	3000	49

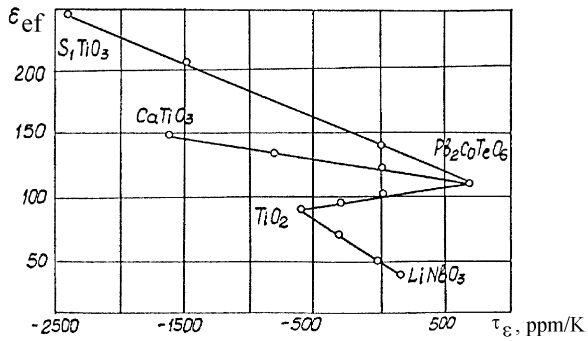

Fig. 5. Effective permittivity (ε_{eff}) of gradient (composite) DRs as a function of τ_f for different pairs of materials at 10^{10} Hz.

DRs with known τ_f can be used in microwave devices to compensate the temperature instability of semiconductor elements in use and the thermal expansion of metallic circuit parts.[35]

3. Conclusion

Thus, various methods for developing MW dielectrics, which would have in the MW range high permittivity and low dielectric loss and possess a high temperature stability of electrophysical properties, have been considered in terms of literature date the experimental results obtained by the author. Examples are given of the development of MW dielectrics based on monophase systems (by using solid solutions and aliovalent substitution in one of the crystal sublattices or by making one of the sublattices mobile) and multiphase compositions (by creating gradient materials or using volume temperature compensation).

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