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The role of dopants in tailoring the microwave properties of $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$ R = (La–Gd) Ceramics

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Microwave dielectric ceramics with a high dielectric constant need to satisfy very high technical demands. They should possess extremely low losses to achieve high Q-values (Quality factor) a small temperature coefficient of resonant frequency (τ_f), and a relative permittivity (ε_r) higher than 80. Industrial applications require very stringent electrical and dimensional tolerances, typically ± 0.5–1.0 ppm K^{-1} for a specified τ_f and $\pm 0.25\%$ for a specified ε_r. To meet such requirements ceramics based on $BaO–R_2O_3 - TiO_2$ (R = La–Gd) are used. The investigation of this type of ceramic was stimulated by the observation that ceramics based on compositions in the TiO_2-rich region of the system exhibit highly temperature stable electrical properties. Especially interesting are compositions within the solid solubility region with the general formula $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$. As the ionic radius of the rare earth decreases the extent of the solid solubility region becomes narrower, i.e., $0 < x < 3$ for La and $x = 0.5$ for Gd. Further improvements in the dielectric microwave properties can be achieved by combining different rare earth oxides, and by partial replacement of Ba^{2+} with other alkaline earth atoms such as Ca^{2+} and Sr^{2+}. Typically such ceramics meet the requirements for Q and ε_r; however, τ_f must be additionally adjusted by the use of dopants. Most commonly bismuth and lead oxides or titanates are used. In the present contribution the role of different dopants and their influence on the resulting microwave dielectric properties of $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$ based ceramics are discussed.

1. Introduction

The unique electrical properties of ceramic dielectric resonators have revolutionized the microwave-based wireless communications industry by reducing the size and cost of filter and oscillator components in systems ranging from cellular telephones to global positioning technologies. Ceramics are used mostly as metallized, TEM mode, coaxial filters and inductors. Less frequently they serve as unmetallized TE_{OI} resonators or as substrate platforms for thin/thick film circuits.

Three basic requirements for microwave ceramics can be defined:

(1) the ceramics should exhibit a high dielectric constant, since the resonator size is in inverse proportion to the square root of the material's relative permittivity (ε_r);
(2) they should possess a low dielectric losses, a high Q-value (Quality factor) in the microwave region ($Q \approx 1/tg\delta \geqslant 5000$), and
(3) they should possess a near-zero temperature coefficient of resonant frequency (dissipation factor). τ_f, ($\tau_f \approx \tau_k/2 - \alpha$), of the dielectric constant τ_k and of the capacitance τ_c ($\tau_c \approx -2\tau_f + \alpha$) (linear expansion coefficient).

Over the last two decades several ceramics have been found that meet these criteria. Some of them, listed in Table I, have also found widespread commercial application [1–3].

As one can see from Table I, high permittivity microwave ceramics are obtained in the solid solution series $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$, where the value of x depends on the lanthanide (R). Despite industrial development and market acceptance of these ceramics, mainly in wireless communication circuits, the open literature data relating to the structure, composition and properties of these phases are not consistent and in fact they are often in disagreement.

Therefore the aim of this work is to contribute to a better understanding of such phenomena by a study in which we investigate the beneficial role of different dopants on the microwave properties of $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$ based ceramics.

2. Phase relations and crystal chemistry in the $BaO–R_2O_3–TiO_2$ systems

The crystal structure of a ceramic is the most important parameter in the tailoring of its microwave properties using various dopants. The main function of doping is to retain a high relative permittivity (ε) and low losses while tuning τ_f to zero.

TABLE I Properties of some typical commercial microwave ceramics

System	ε_r	Q(at f_r)	τ_f (ppm K^{-1})
$Ba_3Ta_2MeO_9$(Me = Zn/Mg/Ni)	28–30	> 20 000 (at 10 GHz)	0
$(Zr_{1-x}Sn_x)TiO_4$	35–40	10 000 (at 4.5 GHz)	0
$BaTi_4O_9$	38	13 000 (at 4.5 GHz)	13
$Ba_2Ti_9O_{20}$	40	12 500 (at 4.5 GHz)	3
$Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$	85–90	2 000 (at 3 GHz)	0

For such tailoring three basic concepts are used:

(1) the combination of different rare earth analogues of 114 solid solutions,
(2) the formation of isotypical solid solutions by the introduction of isovalent or aliovalent ions, and
(3) the formation of multiphase ceramics.

In all of three cases the crystal structure determines the efficiency of the dopants used to improve the microwave dielectric properties.

Investigation of the crystal chemistry and phase relations of the ceramics based on the $BaTiO_3$–Nd_2TiO_5–TiO_2 system has been stimulated [1, 4, 5] by the observation of the very promising dielectric properties of these ceramics in the vicinity of the 114 composition [4]. These vital investigations have spread to other systems containing rare earths. It has been confirmed that isotypical 114 solid solutions are also formed with Pr_2O_3 [7], Sm_2O_3 [8, 9], La_2O_3 [10], Eu_2O_3 [11] Gd_2O_3 [12]. As the rare earth ionic radius decreases the extent of the $Ba_{6-x}R_{8+2/3x}Ti_8O_{54}$ solid solution becomes narrower. For a La-containing solid solution it extends from x = 0 (3:2:9) through x = 1.5 (1:1:4) to x = 3 (3:5:18) [13]. For Nd and Pr, $0 \leqslant x \leqslant 2.25$, for Sm and Eu, $0 \leqslant x \leqslant 1.5$ [11] and for Gd, x = 1.5 [12].

While it is generally accepted that the composition of so-called 114 solid solutions plays a key role in determining the electrical properties no concensus exists about the crystal structures of these solid solutions.

The crystal structure of the 114 isotypical solid solution has been studied by several authors, using powders and single crystals [6, 14–19]. Matveeva *et al.* [7] determined the crystal structure using the Pr_2O_3 analogue ($Ba_{3.75}Pr_{9.5}Ti_{18}O_{54}$). The structure was described as orthorhombic with the space group *Pba2*, built up as an infinite network of TiO_6 octahedra, linked by their corners. In between there are pentagonal channels along the (001) direction that are filled with Ba ions. Nd ions lie in the perovskite-like column (rhombic), surrounded by TiO_6 octahedra. The pentagonal channels are only 80% occupied and the perovskite-like columns contain randomly distributed rare earth ions and the remaining Ba ions. The same structure has been reported for the Nd_2O_3 analoge [19] for which very faint superstructure reflections, indicating a possible doubling of the *c*-axis have been reported. The structure described differs only slightly from that described by Matveeva *et al.* [7]. The major dispute has arisen over the occupancies of the pentagonal and rhombic sites. It was found that on the special positions (1/2, 0, *z*), and (0, 1/2, *z*), the occupancy is $\approx 2/3$. Recently Rawn [9] has taken into account the superstructure reflections, which has already been observed but previously neglected in the structural determination. She refined the Sm-analogue ($Ba_{5.19}Sm_{8.54}Ti_{18}O_{54}$), using the doubled cell corresponding to the *Pnma* space group and revealed that the pentagonal channels are fully occupied by Ba ions, one rhombic channel is fully occupied by Sm, one is partially occupied by Sm and one is shared by Ba and Sm ions (Fig. 1). The concentration of vacancies and the Ba/Sm ratio in the shared channel depend on the composition (x) of the solid solution.

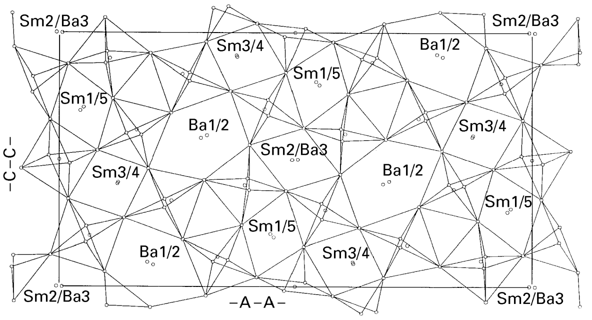

Figure 1 $x - z$ projection of the crystal structure of $Ba_{5.19}Sm_{8.54}Ti_{18}O_{54}$ [9].

Details of the structure remain unclear. Experimental observations that the solid solution limits of La to Nd based solid solutions extend beyond $x \geqslant 2$ [11, 13] cast doubt on the assumption of Roth *et al.* [18] and Rawn [9] that the pentagonal A-sites contain exclusively Ba^{2+} ions. On the other hand, superlattice reflections [19, 20] indicate an ordering that was not taken into account in the structural model proposed by Matveeva *et al.* [7].

It is expected that using new analytical methods (for example extended X-ray fine absorption structure (EXAFS) and high resolution neutron diffraction) that the details of the structure will be clarified at a future date.

3. Dielectric properties at high frequencies

The basic phase relations of the ceramics of current interest are represented in Fig. 2. A particularly interesting part of the diagram with regard to the microwave dielectric properties is represented by the $Ba_{6-x}Nd_{8+2/3x}Ti_{18}O_{54}$ solid solution composition ($0 \leqslant x \leqslant 2.25$) and its vicinity. As previously mentioned the Nd 114 isotypical solid solutions are formed with the other rare earth oxides from La_2O_3 to Gd_2O_3. A decrease in the rare earth ionic radius decreases the extent of the $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$ solid solution and in addition the microwave electrical

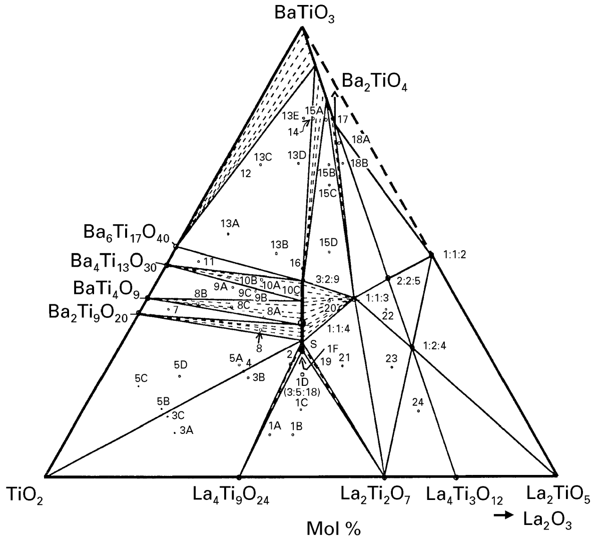

Figure 2 Phase relations in the $BaTiO_3$–La_2TiO_5–TiO_2 system (at ≈ 1300 °C) [32].

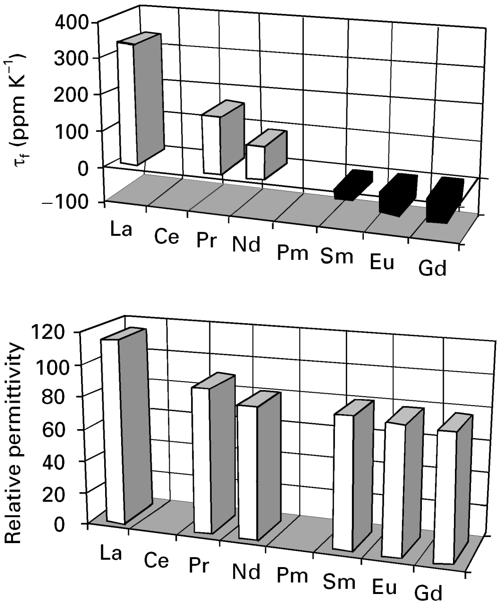

Figure 3 The τ_f and relative permittivities of $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$ solid solutions (R = La − Gd) (at 1 GHz).

properties change. The change of relative permittivity, ε_r, and temperature coefficient of resonant frequency τ_f are shown in Fig. 3.

It can be observed that both the relative permittivity and τ_f decrease as the rare earth changes from La to Gd. This decrease in the relative permittivity can be followed using the Clausius–Mosotti equation:

$$\varepsilon_r = \frac{3Vm + 8\pi\alpha_D}{3Vm - 4\pi\alpha_D}$$

where Vm is the molar volume and α_D is the net dielectric polarizability.

Thus the decrease can be ascribed to a decrease in the net dielectric polarizability α_D as a consequence of a decreased ionic polarization as we go from La to Gd [21]. The decrease in relative permittivity is accompanied by a decrease of τ_f, even though there is no valid explanation for the reverse value of τ_f for the Nd to Sm analogues of the 114 solid solution. (La, Nd based ceramics have a positive τ_f, Sm, Eu and Gd based ceramics a negative τ_f). However, this phenomenon is used for τ_f-compensation in Nd-based commercial microwave ceramics, following the previously discussed first concept of tailoring the microwave properties of these ceramics. Such a concept is based on the formation of mixed solid solutions, for example a combination of the Nd- and Sm-analogues of the 114 solution, which remain after sintering the single phase.

The microwave electrical properties of the Nd-based 114 solid solution with an $\varepsilon_r = 88$ and $\tau_f = +85\ \mathrm{ppm\,K^{-1}}$ can be improved by the addition of the Sm-based 114 solid solution which has an $\varepsilon_r = 70$ and $\tau_f = -8\ \mathrm{ppm\,K^{-1}}$. As a result of such a combination, the net relative permittivity will slightly decrease while at the same time a strong compensation of τ_f can be obtained. Some examples are given in Table II.

The second concept is based on the finding that partial occupancy of rare earth sites in the $Ba_{6-x8+2/3x}Ti_{18}O_{54}$ structure makes possible various substitutions with aliovalent ions, while preserving the electrical charge balance. For example the R^{3+} sites that are only 2/3 occupied, may be fully occupied by Me^{2+} ions (Me^{2+} = Ca, Sr). Similarly, since 1/2 (Ti^{4+}) is equivalent to ($La^{3+}_{1/3}Zn^{2+}_{1/2}$), part of the Ti^{4+} may be substituted by Zn^{2+}. Examples of the dielectric properties of samples obtained by the rule are listed in Table III.

It has already been mentioned that in the 114 isotypical solid solutions the relative permittivity and τ_f decrease with a decrease in the ionic size of the rare earth atom. The same tendency can also be observed from Table III for the alkaline earths. The smaller Ca^{2+} cation strongly decreases the relative permittivity of the La-114 solid solution as compared to the Sr^{2+} sample ($R_{Ca} = 0.099$ nm, $R_{Sr} = 0.113$ nm) but at the same time it is more efficient at improving τ_k in these ceramics. On the other hand the substitution of Ti^{4+} ($R_{Ti} = 0.068$ nm) by Zn^{2+} ($R_{Zn} = 0.074$ nm) shows the opposite tendency.

Of greater effectiveness in tailoring the microwave dielectric properties is the use of additives such as PbO or Bi_2O_3. The beneficial influence of Bi_2O_3 addition in improving τ_f and promoting the densification of 114 type ceramics has been reported by several authors [2, 22–24]. However, explanations as to the role of Bi_2O_3 in producing the improvement in the dielectric properties were incomplete and in disagreement until 1994, when the reaction mechanism for the incorporation of Bi^{3+} into the 114-Nd solid solution was described in detail [25–28]. According to these findings Bi^{3+} substitutes for Nd^{3+} in the crystal structure of the 114-Nd solid solution up to the solubility limit, which was determined to be 15%. The saturated phase can be written as $Ba_{6-x}(Bi_yNd_{1-y})_{8+2/3x}Ti_{18}O_{54}$. After exceeding the solid solubility limit, additional Bi_2O_3 concentrates as an enriched phase at the grain boundaries, causing a considerable reduction in the Q value and an increase in τ_f of these ceramics (Figs 4 and 5).

TABLE II Relative permittivities and temperature coefficients (ε_r/τ_k) of the rare earth family 114 compositions (at 1 MHz)

Composition	References				
	[16]	[22]	[4]	[8]	[12]
$BaLa_2Ti_4O_{12}$	100/ − 155[a]	110/ − 740			
$BaCe_2Ti_4O_{12}$		90/ − 410			
$BaPr_2Ti_4O_{12}$		91/ − 315			
$BaNd_2Ti_4O_{12}$	85/ − 160	85/ − 120	92/ − 113		
$Ba(Nd,Sm)_2Ti_4O_{12}$				83/ − (6 − 10)	
$BaSm_2Ti_4O_{12}$	81/ + 30	80/ + 40			
$BaEu_2Ti_4O_{12}$	76/ + 60	78/ + 100			
$BaGd_2Ti_4O_{12}$					68/ + 147

[a] ppm K^{-1}

TABLE III Dielectric properties of 114 isotypical solid solutions (1 MHz)

Composition	ε_r	$tg\ \delta\ 10^4$	$T_{k-30\ \mathrm{to}\ 115\ ^\circ C}$ (ppm K^{-1})
$Ba_{2.25}La_{4.5}Ti_9O_{27}$	114	1 − 2	− 833
$Ba_{2.25}Nd_{4.5}Ti_9O_{27}$	93	1 − 2	− 120
$Ba_{2.25}Nd_{4.5}Ti_9O_{27}$ + 10 wt % $Bi_2O_3 \cdot 2TiO_2$	100	1	− 24
$Ba_2La_4SrTi_9O_{27}$ + 10 wt % $Bi_2O_3 \cdot 2TiO_2$	110	1 − 2	− 560
$Ba_2La_4CaTi_9O_{27}$ + 10 wt %$Bi_2O_3 \cdot 2TiO_2$	92	1	− 520
$Ba_2La_5Zn_{0.5}Ti_{8.5}O_{27}$	64	1	− 450
$Ba_2La_5Zn_{0.5}Ti_{8.5}O_{27}$ + 10 wt % $Bi_2O_3 \cdot 2TiO_2$	79	1 − 2	− 275

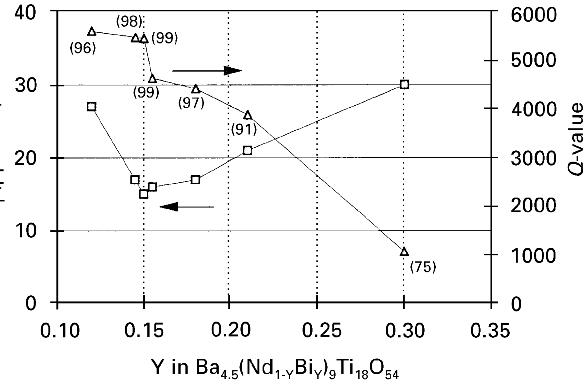

Figure 4 The microwave dielectric properties of ceramics based on the $Ba_{4.5}Nd_9Ti_{18}O_{54}$–$BaTi_4O_9$ system with various Bi_2O_3 contents.

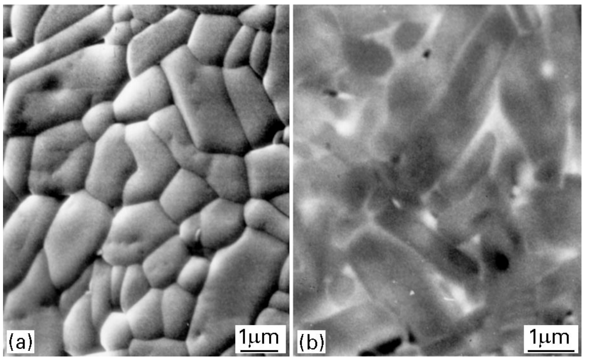

Figure 5 The microstructure of Nd-114 based ceramics sintered at 1320 °C for 15 min (a) with 2.4 mol % Bi_2O_3, and (b) with 5.0 mol % Bi_2O_3.

Similar improvements in the microwave properties were observed when the Nd-114 ceramics were doped with Pb^{2+}. Although several authors have suggested [1, 25] that the Pb^{2+} enters the Ba^{2+} sites, no detailed experimental evidence or solid solubility limit has been reported. Recent EXAFS investigations of the incorporation of Bi and Pb atoms into the crystal structure of $Ba_{4.5}Nd_9Ti_{18}O_{54}$ solid solution revealed [29] that neither Bi^{3+} nor Pb^{2+} substitute for Nd^{3+} or Ba^{2+} randomly on all possible sites. Instead Bi^{3+} selectively enters one of three possible channels; thus, the sites at $x = 0.9484$, $y = 0.2500$, $z = 0.2939$ and/or $x = 0.0455$, $y = 0.2500$, $z = 0.6928$ previously occupied by Nd^{3+}, while the Pb^{2+} selectively enters the site at $x = 0.4940$, $y = 0.2500$, $z = 0.4993$ previously shared by Ba^{2+} and Nd^{3+}.

Taking into account these findings, as well as the crystal structure proposed for the 114 type rare earth solid solutions, one can calculate a theoretical solid solubility limit for Bi^{3+} and Pb^{2+} in the crystal structure of $Ba_{6-x}Nd_{8+2/3x}Ti_{18}O_{54}$ solid solutions. A practical problem in the synthesis of these materials is related to the conditions necessary to maintain exact stoichiometry and reproducibility due to the high partial pressure of Bi_2O_3 and PbO at elevated temperatures. Slight changes in stoichiometry can lead to dramatic changes in the microstructural development during sintering. Namely, incomplete substitution of Pb^{2+} for Ba^{2+} and Bi^{3+} for Nd^{3+} due to the evaporation of PbO or Bi_2O_3 during sintering leads to the formation of multiphase ceramics. In such ceramics the additional phases are of lower relative permittivity or higher τ_f than the $Ba_{4.5}Nd_9Ti_{18}O_{54}$ solid solution, and therefore worsen the resulting microwave dielectric properties according to the contributions of each single phase (Table IV).

TABLE IV Dielectric properties of various compounds in the $BaTiO_3$–R_2TiO_5–TiO_2 systems

Phase	ε_r	τ_f(ppm K^{-1})	*Q*x f_r	*f_r*(GHz)	Reference
$Ba_2Ti_9O_{20}$	40	+ 4	8000	4.0	[30]
$BaTi_4O_9$	38	+ 30	8000	4.0	[30]
$Nd_4Ti_9O_{24}$	37.5	+ 65	3000	8.0	[31]
$Nd_2Ti_2O_7$	36	− 118	1800	9.1	[31]
TiO_2	104.1	+ 427	14 600	3.0	[1]
$La_4Ti_9O_{24}$	37	+ 15	3060	8.0	[31]
$La_2Ti_2O_7$	47	− 10	1090	7.8	[31]
114 − Nd	85	+ 88	6000	3.0	[25]

The negative effect of multiphase ceramic formation in some systems (La and Nd-based) can turn into a positive one in other systems, and this is the basic idea of the third concept. The beneficial influence of TiO_2 addition on tuning τ_f to 0 ppm K^{-1} in Sm-114 based ceramics has been reported [2, 8]. Namely, a small addition of TiO_2 turns a single phase ceramic into a multiphase one, containing, in addition to the 114-type solid solution, TiO_2 and $Ba_2Ti_9O_{20}$. The slightly negative τ_f of the Sm-based 114 solid solution ($\tau_f = -15$ ppm K^{-1}) is compensated for by the very positive τ_f of TiO_2, while the net relative permittivity remains nearly unchanged. The beneficial role of combined concepts was described for the 114 - Nd based ceramics [1]. The highly positive τ_f of this material was partially decreased by the introduction of the isovalent dopant Pb^{2+} and finally compensated for by the formation of multiphase ceramics (114 solid solution, $Nd_2Ti_2O_7$ and $Nd_2T_9O_{21}$). The same effect was achieved by combining Nd- and Gd- analogues of the 114-solid solutions, and subsequent doping these ceramics with Bi_2O_3 [12].

4. Summary

The rare earth ions from La to Gd form a series of isotypical solid solutions with the formula $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$ in which the Ba/R ratio may vary to some extent. The microwave dielectric properties of these ceramics critically depends on several parameters, such as the purity of the starting materials, the rare earth content and the Ba/Ti ratio in the starting materials, sintering conditions and most of all, on the crystal structure and phase relations of these ceramics. Significant improvements can be achieved by the use of additives and dopants. At least three effective concepts can be used to tailor the microwave properties.

In the first one significant improvements in τ_f are achieved by the use of solid solutions of rare earth isotypical compounds. By combining $Ba_{6-x}Nd_{8+2/3x}Ti_{18}O_{54}$ and $Ba_{6-x}Sm_{8+2/3x}Ti_{18}O_{54}$ the τ_f values of the solid solutions can be tuned to near 0 ppm K^{-1}. The second concept is based on the use of dopants, which partially replace individual cations in the 114 - solid solutions. When such additives are used, solid solubility limits must be considered in order to minimize the content of secondary phases. In contrast, the third concept uses the beneficial influence of the formation of multiphase ceramics. Therefore for the effective tailoring of microwave dielectric properties of high permittivity microwave ceramics the exact definition of the crystal structure, phase relations and formation mechanisms of various phases of multicomponent systems is required.

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