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Microstructural engineering of microwave dielectric ceramics

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Abstract

Temperature stable, low loss dielectric ceramics find application as resonators in communication systems operating at microwave frequencies. Candidate materials need to exhibit high relative permittivity, high dielectric Q value and near zero temperature coefficient of resonant frequency. Current materials include a range of complex perovskites, predominantly titanate-based, with $Q \times f_o$ (product of Q value and resonant frequency) values of 250,000 GHz or more. An overview is given in the ways in which the microstructures of microwave dielectric ceramics have been 'engineered' at the levels of the grain, grain boundary, sub-grain and the lattice to optimise the critical dielectric parameters. This is primarily accomplished by either (a) modifying the processing conditions, or (b) modifying the powder formulation (from dopants to major compositional changes). The outcomes provide a series of ground rules to maximise the performance of new materials.

Keywords: Dielectric properties; Microwave dielectrics; Sintering; Perovskites

1. Introduction

Microwave dielectric ceramics are crucial components in mobile telephone systems. In the form of dielectric resonators they enable the filter units in the mobile telephone base stations to remove unwanted sidebands and secondary signals, ensuring transmission of high quality primary signals with minimum interference. The concept of using a solid dielectric as a resonator in place of the traditional air-filled metal cavity is generally attributed to Richtmyer[1] in 1939. The ceramic resonator offers significant advantages in terms of space saving and signal selectivity over the traditional structure. Based upon the original Richtmyer model, a monomode ceramic resonator is cylindrical in shape, with a central, axial cavity, allowing standing waves to be set up within the outer solid 'doughnut'. In spite of the simplicity of the solid resonator model, it was almost 30 years before the first ceramic resonators were realised[2] and a further decade[3,4] before high quality components became commonly available.

For a material to be considered as candidate for a microwave dielectric resonator, there are three critical requirements:

(i) The relative permittivity (ε_r) should be as large as possible, since the size of a resonator is inversely proportional to the square root of relative permittivity. In reality the range of materials is restricted to approximately $20 < \varepsilon_r < 100$, in order that other conditions can be met.
(ii) The dielectric losses ($\tan\delta$) should be as small as possible to ensure maximum signal discrimination. This is more commonly described in terms of the dielectric Q value ($1/\tan\delta$) which should be maximised. However, Q is not an independent parameter, as experience has shown[5] that for a given material the product of Q and the resonant frequency (f_o) is approximately constant (known as the figure of merit) and therefore statements on the Q value of a material should always refer to the measurement (resonant) frequency. For many practical applications today, $Q > 30{,}000$ at 1 GHz is essential.
(iii) To ensure temperature stability in communications systems, the resonator needs to have a temperature coefficient of resonant frequency (τ_f) $\sim \pm 2$ ppm/°C, so that the signal does not drift during device operation.

Titania (TiO_2) was one of the materials explored[6] for resonator applications in the 1960s. With a relative permittivity of ~100 and high Q value it immediately met criteria (i) and (ii), but failed the final criteria (iii) with very poor temperature stability ($\tau_f \sim +450$ ppm/°C). Since τ_f is linked to the temperature coefficient of relative permittivity (τ_ε) and the coefficient of thermal expansion (α_L) by

$$\tau_f = -\left(\frac{\tau_\varepsilon}{2+\alpha_L}\right) \quad (1)$$

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then τ_f needs to be small, but non-zero to compensate for the thermal expansion of the resonator.[7]

Hence for the development of new and improved microwave dielectrics the objectives are (i) high or increased ε_r, (ii) high or increased $Q \times f_o$, and (iii) near zero τ_f. There are various strategies to achieve such changes in the materials, and here we will explore the potential offered by 'microstructural engineering'. In the case of ZnO varistors, where the non-linear electrical properties are controlled by the defect chemistry of the grain and the grain boundary regions, Gupta[8] applied the concept of 'microstructural engineering' through donor and acceptor doping of the grains and grain boundaries. He identified three levels of engineering the microstructure, in terms of (i) the types of dopants (grain/grain boundary specific), (ii) whether the dopant acts as donor or acceptor, and (iii) whether the dopant sits on a lattice or interstitial site. In the case of microwave dielectric ceramics we will consider four levels of engineering: the grain level, the grain boundary, the sub-grain, and the lattice (or point defect) level. To set this work in context, the following section provides a brief historical introduction.

2. Historical development

The earliest studies of resonator materials commenced with the work of Cohn[6] on titania in the 1960s (which exhibited high τ_f as noted above), but also included pioneering investigations by Bolton[2] on high permittivity tungsten bronze-structured $BaTiO_3$–Ln_2O_3–TiO_2, which achieved temperature stability and relative permittivities of 60–80. Negas et al.[9] noted that the work of Bolton is rarely acknowledged in subsequent literature, but provided the technical foundation for a host of investigations of tungsten bronze structure materials.

By the late 1970s and early 1980s there was interest in a range of materials including $MgTiO_3$–$CaTiO_3$, $(Zr,Sn)TiO_4$ and $BaTi_4O_9$. Plourde and Ren[10] in 1981 reported that the maximum $Q \times f_o$ available was around 36,000 GHz, with maximum ε_r of 40 (again overlooking the work of Bolton[2]). Data for typical microwave dielectric ceramics in 1981 are summarised in Table 1. The growth of the mobile communications market in the 1990s stimulated research in microwave dielectrics, particularly for high relative permittivity materials ($\varepsilon_r \sim 75$–90) for mobile telephone handset applications, and very high Q materials ($Q \sim 30{,}000$ at 3 GHz) for base station applications.[7] For the former group, the high ε_r tungsten bronze-structured materials (for example $BaTiO_3$–Nd_2O_3–TiO_2) remained the primary choice,

Table 1
Typical properties of microwave dielectric ceramics in 1981 (from references[2,9–11])

	ε_r	$Q \times f_o$ (GHz)	τ_f (ppm/°C)
$Ba_2Ti_9O_{20}$	40	36,000	+2
$(Zr,Sn)TiO_4$	34–37	36,000	∼20
$(Sc,Ca)\{(Li,Nb)Ti\}O_3$	36–46	38,000	+30 to −70
$BaTi_4O_9$	38	34,000	+15
$(Ca,Sr)\ (BaZr)O_3$	29–32	27,500	±50
$BaTiO_3$–Nd_2O_3–TiO_2	62–80	[a]	

[a] Properties measured at 1 MHz.

Table 2
Typical examples of temperature stable ($\tau_f \sim 0$) microwave dielectric ceramics available in 2007 (after Reaney and Iddles[7])

	ε_r	$Q \times f_o$ (GHz)
$BaMg_{1/3}Ta_{2/3}O_3$	24	250,000–300,000
$BaZn_{1/3}Ta_{2/3}O_3$	29	150,000
$Ba(Co,Zn)_{1/3}Nb_{2/3}O_3$	34	90,000
$SrTiO_3$–$LaAlO_3$	39	60,000
$CaTiO_3$–$NdAlO_3$	45	48,000
$ZrTi_2O_6$–$ZnNb_2O_6$	44	40,000–48,000
$Ba_{6-3x}R_{8+2x}Ti_{18}O_{24}$	80–90	7,000–13,000

whilst complex perovskites (for example $BaMg_{1/3}Ta_{2/3}O_3$, ε_r 24–29) provided the highest Q values for the base stations. Between these two families there was still a significant gap in terms of relative permittivities; the simple perovskites (for example $CaTiO_3$–$LaAlO_3$, ε_r ∼45) and the two-phase α-PbO_2-structured $ZrTiO_4$–$ZnNb_2O_6$ ($\varepsilon_r \sim 44$) with $Q \times f_o$ values around 48,000 GHz have gone some way for providing 'mid-range' materials. A summary of typical materials available in 2007 is presented in Table 2. A striking feature is still the gap in the available materials with ε_r in the range 45–75. Reaney and Iddles[7] highlighted the fact that materials with ε_r of 45–75, with high Q value and zero τ_f do not currently exist. The following sections examine ways in which the microstructures of microwave dielectric ceramics have been 'engineered' *at different levels* to optimise the critical dielectric parameters. The outcomes provide a series of ground rules to maximise the performance of new materials. They may ultimately provide a way forward to develop materials with both high Q and high ε_r in the permittivity 45–75 gap.

There are two principle routes to engineer the microstructure, either (a) modifying the processing conditions, or (b) modifying the powder formulation (from dopants to major compositional changes). Both are relevant to microwave dielectric ceramics and achieve effects at different levels.

3. Engineering at the grain level

For a given formulation the optimum relative permittivity can be achieved by maximising density and eliminating porosity, as for all ceramics. If the base composition is itself not temperature stable, then cations can be substituted, until $\tau_f \sim 0$ is achieved. When the substitution gives rise to an increase in polarizability, then there is further benefit of an increase in relative permittivity as well. For example $MgTiO_3$ and $CaTiO_3$ have very different properties; $MgTiO_3$ has negative τ_f (−45 ppm/°C), low ε_r (17) and high Q (22,000 at 7 GHz), whilst $CaTiO_3$ has a large positive τ_f (+800 ppm/°C) high ε_r (170), and low Q (1800 at 7 GHz). When they are combined in the ratio $MgTiO_3$:$CaTiO_3$ of 95:5, then a temperature-stable dielectric is achieved, which has a higher ε_r (21) than the base $MgTiO_3$, but a Q value (8000 at 7 GHz) which is inevitably lower than that of the pure $MgTiO_3$.

The possibility of combining two dielectrics of different relative permittivity or temperature dependence to obtain a material with the desired properties has long been known. There are many empirical relationships to describe the interaction of two