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Low-temperature microwave and THz dielectric response in novel microwave ceramics

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Abstract

Low-temperature dielectric properties of $BaZn_{1/3}Nb_{2/3}O_3$-based ceramics, CeO_2-based ceramics and Ruddlesden–Popper $Sr_{n+1}Ti_nO_{3n+1}$ ($n = 1$–4) ceramics has been studied in microwave, THz and infrared frequency range down to 10 K. Extrinsic dielectric losses originating probably from diffusion of charged defects are observed in two families of compounds by a minimum in the temperature dependence of microwave quality Q. The rise of microwave permittivity and dielectric losses at low temperatures in $Sr_{n+1}Ti_nO_{3n+1}$ ($n = 2$–4) ceramics was explained by softening of an optical polar mode in $SrTiO_3$, which is in the $Sr_{n+1}Ti_nO_{3n+1}$ ($n = 3$, 4) ceramics contained as a second phase.

Keywords: Dielectric properties; Spectroscopy; Perovskites; Microwave ceramics

1. Introduction

Modern communication systems have moved to the microwave (MW) frequency region, where advanced dielectric ceramics are frequently used in resonators and filters. Miniaturization requires high relative permittivity (ε') materials (since the size of resonators is inversely proportional to $\sqrt{\varepsilon'}$) with a small or zero temperature coefficient of resonance frequency τ_f ($|\tau_f| < 10\,\text{ppm}\,\text{K}^{-1}$). Furthermore, ceramics with low dielectric loss ε'' (often described in terms of high dielectric quality, $Q = \varepsilon'/\varepsilon''$) are needed for the high selectivity and optimized bandwidth of the filters. Within the last 20 years many new suitable ceramics with high ε' and low τ_f were described. However, it was shown that although the two former parameters are not very dependent on the method of sample preparation, the quality Q is extremely sensitive on conditions of sample preparation. It is not rare that in some cases the Q value varies within 2 orders of magnitude depending on sintering temperature, cooling rate, atmosphere of annealing, etc. Technologists spent much time with improvement of sample processing to obtain losses as low as possible (highest Q), but the methods used were purely empirical, without knowing the lowest limit of the losses (intrinsic losses) with an origin in multi-phonon absorption.

Almost 20 years ago, Wakino et al.[1,2] proposed infrared (IR) reflectivity spectroscopy as a tool for investigating the intrinsic MW dielectric properties of dielectric resonators. It is well known that the main infrared dispersion of the permittivity is given by the sum of polar phonon contributions

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - \mathrm{i}\omega''(\omega) = \sum_{j=1}^{n} \frac{\Delta\varepsilon_j \omega_j^2}{\omega_j^2 - \omega^2 + \mathrm{i}\omega\gamma_j} + \varepsilon_\infty \qquad (1)$$

where ω_j and γ_j are the frequency and damping of the jth polar phonon, respectively; $\Delta\varepsilon_j$ denotes the mode contribution to the static permittivity $\varepsilon'(0)$ and ε_∞ denotes the electronic part of the permittivity. We note that this formula is as a rule valid in dielectrics with $\varepsilon'(0) \leq 100$. In higher permittivity materials (e.g. ferroelectrics) an additional dispersion occurs below polar phonon frequencies, in the simplest case modelled by a Debye relaxation $\Delta\varepsilon_r\omega_r/(\omega_r + \mathrm{i}\omega)$ ($\Delta\varepsilon_r$ and ω_r are the dielectric strength and relaxation frequency, respectively), which should be added into Eq. (1).

Wakino et al.[1,2] mentioned that extrapolation of Eq. (1) from IR down to MW range, i.e. 2–3 orders of magnitude below ω_j's

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gives constant real part of the permittivity

$$\varepsilon' = \varepsilon_\infty + \sum_{j=1}^{n} \Delta\varepsilon_j, \tag{2}$$

while the dielectric losses ε'' are proportional to frequency

$$\varepsilon''(\omega) \propto \omega \sum_{j=1}^{n} \frac{\Delta\varepsilon\gamma_j}{\omega_j^2}. \tag{3}$$

At high temperatures (around and above room temperature) the phonon damping should be linearly temperature dependent so that one can expect

$$\varepsilon''(\omega, T) \propto \omega \times T \tag{4}$$

This implies that the dielectric loss could be linearly extrapolated from the THz range (0.1–3 THz) down to the MW region. Later on it was shown[3,4] that for an accurate determination of the complex permittivity in the THz range it is more suitable to use the THz transmission spectroscopy than IR reflectivity, because it is much more sensitive to weak absorption effects. Simultaneously, it was shown that the extrinsic absorption mechanisms contribute only slightly to the THz and IR absorption, therefore, the linear extrapolation from THz to the MW range allows us to estimate predominantly the intrinsic dielectric losses stemming from the multi-phonon absorption.[3,4]

The method described above was used in the study of many MW ceramics[3,4] and it was shown that it gives rather good estimate of intrinsic MW losses, although the Eq. (1) is valid only in the range near phonon frequencies and the use of this formula is not theoretically justified for frequencies much lower than ω_j, i.e. in MW range.

Gurevich and Tagantsev[5–7] developed a comprehensive microscopic phonon transport theory and have shown that depending on crystalline symmetry, temperature interval, frequency range and some parameters of the phonon spectrum, the temperature and frequency dependence of intrinsic dielectric loss can be described by a power law.[6]

$$\varepsilon''(\omega, T) \approx \omega^n \times T^m \tag{5}$$

where $n = 1$–5 and $m = 1$–9. In the MW range, far below the frequencies of mean phonon damping, two-phonon difference decay processes dominate at room and medium–high temperatures and the theory predicts

$$\varepsilon''(\omega, T) \approx \omega \times T^2. \tag{6}$$

Both approaches, the damped oscillator model as well as microscopic phonon transport theory, give in some limited cases, the linear frequency dependence of $\varepsilon''(\omega)$, but the temperature dependence in Eq. (4) is not the same (it agrees only for crystals of symmetry 4/*m* and 6/*m*).[7] We note that at low temperatures Eq. (6) is not valid and more general Eq. (5) with steeper temperature dependences is theoretically expected.

As was already mentioned, the total MW dielectric loss consists of intrinsic and extrinsic contributions. Extrinsic losses are caused by lattice defects and therefore can be in principle removed by proper material processing. Various types of defects can play a role: point defects (isotopes, dopant atoms, vacancies, defect pairs, positional disorder in complex systems), linear defects (dislocations), planar defects (grain boundaries, domain walls) and volume defects (pores, inclusions, secondary phases).[8] Depending on the kind of defects, frequency and temperature dependence of extrinsic losses can be different.

(1) *Defect induced one-phonon absorption*: In the case of static disorder the momentum conservation is relaxed due to breaking of the translation symmetry and a linear part of the acoustic branches activates in the MW and THz spectra. As long as the concentration of defects is temperature independent, the losses are also temperature independent. The microscopic calculations yield[6] $\varepsilon''(\omega) \propto \omega$ for uncorrelated charged point defects and uncharged planar defects; $\varepsilon''(\omega) \propto \omega^2$ for uncharged linear defects and $\varepsilon''(\omega) \propto \omega^3$ for uncharged point defects. In the case of correlated charged point defects $\varepsilon''(\omega) \propto \omega^3$ up to the frequency $\omega_c \approx v/\xi$ where v is the mean transverse acoustic velocity and ξ the correlation length.[9] Realistic estimates give 1–10 nm so that $\omega_c \approx 10^{10}$–10^{12} Hz.

(2) *Phonon scattering on defects*: This reduces the phonon lifetime, i.e. increases the phonon damping (independent of *T*). The main effect on the loss spectrum concerns the enhanced damping of polar phonon modes, which enhances also the THz and extrapolated MW losses.

(3) *Absorption associated with localized defect vibrations*: This may influence the THz losses in the case of heavy or weakly bound defects which give rise to so called resonant modes (local defect modes coupled with acoustic vibrations).[10] Their direct influence on MW losses is probably negligible, but a two-resonant-phonon absorption can give rise to a quasi-Debye[6] type absorption in the case when the defect environment lacks inversion symmetry.

(4) *Losses connected directly with strongly anharmonic motion (diffusion) of charged defects*: As a rule, such a motion gives rise to broad relaxation-like loss maxima with thermally activated relaxation frequencies and strengths. Such relaxation was observed for example in $LaAlO_3$ single crystals.[11] In weakly disordered dielectrics these effects dominate mostly below the MW range, but no systematic experimental studies are available because an extremely broad frequency and temperature range should be covered to elucidate the corresponding loss mechanism.

It is the aim of this short paper to review temperature dependences of MW and THz dielectric response in various MW ceramics down to 20 K and try to show how one can distinguish the intrinsic and extrinsic dielectric losses from the spectra.

2. $BaZn_{1/3}Nb_{2/3}O_3$-based ceramics

$BaZn_{1/3}Ta_{2/3}O_3$ ceramics are popular as resonators in mobile telephone base station filters because of their excellent dielectric properties ($\varepsilon' = 30$, $Q \times f = 150$ THz, $\tau_f = 1$ ppm K^{-1}). However, there is a long-term effort to replace expensive Ta-containing compounds by much cheaper Nb analogues. $BaZn_{1/3}Nb_{2/3}O_3$