Journal of the European Ceramic Society 26 (2006) 1775–1780

www.elsevier.com/locate/jeurceramsoc

Microwave dielectric losses caused by lattice defects

Hiroshi Tamura

Murata Manufacturing Co., Ltd., Kyoto 617-8555, Japan

Abstract

Dielectric loss tangent at microwave frequency is mainly determined by the anharmonic terms in the crystal's potential energy. In addition, there is a kind of lattice defect that increases the dielectric loss tangent seriously. This paper presents the experimental results for two materials; the system $Ba(Zn,Ta)O_3$–$BaZrO_3$ and $(Zr,Sn)TiO_4$. The dielectric loss tangents of the system $Ba(Zn,Ta)O_3$–$BaZrO_3$ increases seriously when the B-site ions distribute disorderedly in the crystal. The doping of oxygen vacancies and acceptor ions in $(Zr,Sn)TiO_4$ increase $\tan\delta$ by the way they increase the gradient and intercept of linear frequency dependency of $\tan\delta$. These experimental results are reasonably explained by Schlömann's theory. He predicted that the dielectric loss tangent increases when the ions are distributed disorderedly in a way that they break the periodic arrangement of charges in the crystal, and that the increase of $\tan\delta$ is negligible if the disordered charge distribution maintains the charge neutrality within a short range of the lattice constant in the crystal.

Keywords: Dielectric properties; Defects; Dielectric loss

1. Introduction

Since the 1970s, many dielectric resonator materials have been developed and put into practical use for filters and oscillators in microwave frequency, miniaturizing these components and saving costs.

The origins of dielectric losses at microwave frequency have been and are still the main subject for discussions by material researchers of dielectric resonator materials. As has been well discussed, main origin of dielectric loss tangent is the anharmonic terms in the crystal's potential energy. Actual dielectric ceramics, however, have many kinds of lattice defects and they increase $\tan\delta$.

In 1964, Schlömann presented a theory for the dielectric loss tangent in nonconducting ionic crystals where he gave an important prediction that the dielectric loss tangent increases when the ions are distributed disorderedly in such a way that they break the periodic arrangement of charges in the crystal, and that the increase of $\tan\delta$ is negligible if the disordered charge distribution in the crystal maintains the charge neutrality within a short range with the order of lattice constant.

Until now, his work has not been introduced well in the literatures, but his theory explains many experimental results on $\tan\delta$ of dielectric resonator ceramics reasonably. This paper introduces his theory and shows that the reasonable explanation is given for the experimental results on $\tan\delta$ of two materials; the system $Ba(Zn,Ta)O_3$–$BaZrO_3$ and $(Zr,Sn)TiO_4$.

2. Frequency dependence of dielectric loss tangent

Dielectric resonator materials are made of paraelectric dielectric ceramics. It is well known that their complex permittivity follows the classical dielectric dispersion equation.

$$\dot{\varepsilon}(\omega) - \varepsilon(\infty) = \frac{\omega_T^2(\varepsilon(0) - \varepsilon(\infty))}{\omega_T^2 - \omega^2 - j\gamma\omega}, \qquad (1)$$

where $\dot{\varepsilon}(\omega)$ is the complex permittivity at an angular frequency ω, $\varepsilon(\infty)$ is the permittivity caused by the electronic polarization, ω_r and γ are the resonance frequency and damping constant of the infrared active lattice vibration modes, respectively.

As the condition $\omega^2 \ll \omega_T^2$ is adopted reasonably at microwave frequency, following equations are derived from Eq. (1):

$$\varepsilon'(\omega) - \omega(\infty) = \varepsilon(0) - \varepsilon(\infty) \qquad (2)$$

$$\tan\delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = \frac{\gamma}{\omega_T^2}\omega \qquad (3)$$

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.09.080

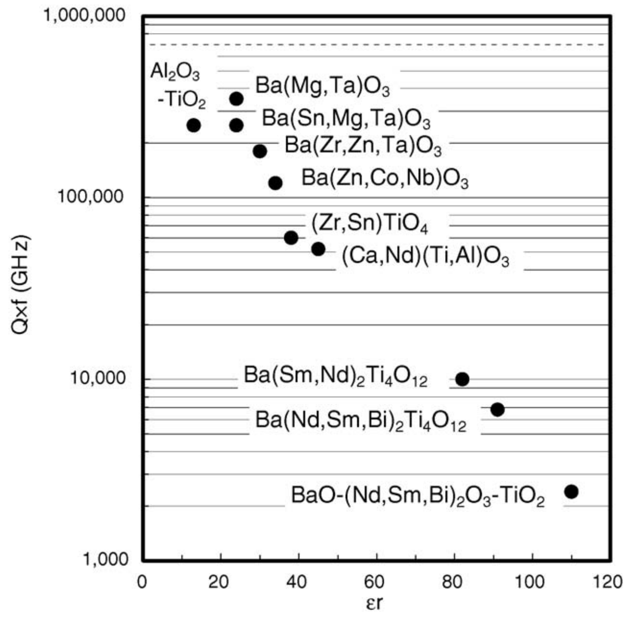

Fig. 1. $\varepsilon_r - Qf$ characteristics of dielectric resonator materials.

these equations show that the dielectric constant is independent of frequency, and the dielectric loss tangent increases proportionately to frequency. The damping constant γ is determined by the anharmonic terms in the crystal's potential energy. The anharmonic terms allow the energy in the infrared-active lattice vibration modes to transfer into those in the thermal phonon modes. Maradudin and Fein derived the equation, which relates the damping constant γ to the third anharmonic term of the crystal's Hamiltonian.[1]

Fig. 1 shows the $\varepsilon_r - Qf$ relation for available dielectric resonator materials; $Q = 1/\tan\delta$. By the contribution of anharmonic terms in the crystal's potential energy, the lower-ε_r material has higher-*Qf* value.

Eq. (3) is adopted for the idealized ceramics without any other origins that increase $\tan\delta$. In this case, $\tan\delta$ is zero at zero Hz and *Qf* product is constant. But, actual ceramics have many kinds of lattice defects that increase $\tan\delta$. Fig. 2 shows the frequency dependence of $\tan\delta$ that we usually observe for the actual ceramics. The dielectric loss tangent has linear frequency dependence with some value of intercept and the gradient increases by lattice defects. Precisely speaking, the *Qf* product is not constant for actual ceramics. The example of this kind of frequency dependence of $\tan\delta$ is shown in Section 4.2.

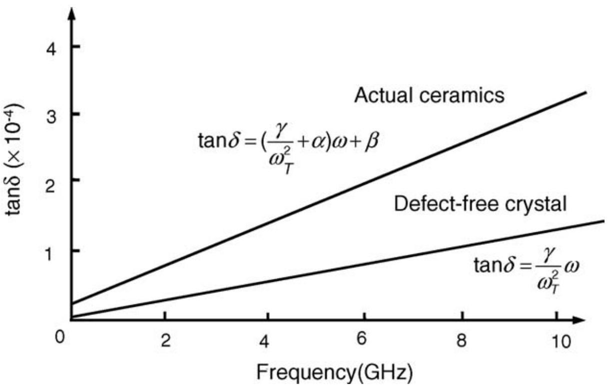

Fig. 2. Frequency dependence of dielectric loss tangents of defect-free crystal and actual ceramics.

3. Schlömann's theory

Dielectric ceramics have many kinds of structural or lattice defects such as grain boundaries, voids, dislocations, point defects and substitutional ions. Among these defects, disordered charge distribution in the crystal has the most serious contribution to increase $\tan\delta$, that is, $\tan\delta$ increases seriously when the ions are distributed disorderedly in a way that they break the periodic arrangement of charges in the crystal.

Schlömann predicted this phenomenon in 1964 and derived the following equation:[2]

$$\tan\delta \propto \frac{\omega}{C_t^3}\left\{1 - \frac{1}{(1 + (\omega/\omega_0)^2)^2}\right\} \tag{4}$$

where C_r is the transverse sound velocity and ω_0 is the characteristic frequency given by $\omega_0 = C_t/l$. This l is an important index defined as the "correlation distance", which is the length necessary to maintain charge neutrality.

Fig. 3 shows a frequency dependence of $\tan\delta$ calculated by Schlömann for crystals with the inverse spinel structure, in which two- and three-valent ions occupy equivalent sites in a random fashion. When the two- and three-valent ions distribute disorderedly in a complete way, he noted it zero correlation, $\tan\delta$ increases by the order of 10^{-4} at 1 GHz. When the disordered distribution is more localized and the charge neutrality is maintained within the correlation distance of $l = 64$ nm, characteristic frequency $\omega_0/2\pi$ is 10 GHz, and the increase of $\tan\delta$ is about 10^{-6} at 1 GHz. The $\omega_0/2\pi = C_t/2\pi l = 10^{10}$ was calculated by

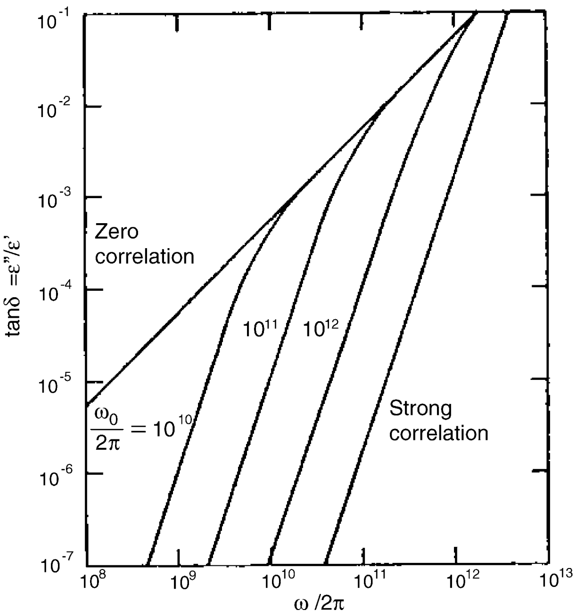

Fig. 3. Predicted $\tan\delta$ of inverse spinels as a function of frequency for various correlation frequencies ω_0.[2]

using the value 4000 m/s for the transverse sound velocity C_r, which Schlömann used in the paper.

It is predicted from this figure that the disordered charge distribution increases $\tan\delta$ in a way that increases the gradient of linear frequency dependence of $\tan\delta$, and that the increase of $\tan\delta$ is negligible if the disordered charge distribution maintains the charge neutrality within a short correlation distance with an order of nano-meter. This correlation distance l is an important indicator to be taken account for controlling the $\tan\delta$ of microwave dielectrics.

4. Experimental results and discussions

4.1. Dielectric loss tangent of $Ba(Zr,Zn,Ta)O_3$ ceramics

The dielectric loss tangents of the system $Ba(Zn,Ta)O_3$–$BaZrO_3$ is discussed in this section. Fig. 4 shows the ordering structure of Zn and Ta ions in $Ba(Zn_{1/3}Ta_{2/3})O_3$ crystal. Kawashima et al. investigated the contribution of sintering time on the Q-value of this ceramics. He proved that the Q-value improves drastically accompanying the formation of superstructure.[3]

This improvement of Q-value is explained reasonably by Schlömann's theory. As Fig. 5a shows, when the superstructure is formed, Zn^{2+} plane and Ta^{5+} plane form the tripling periodicity; Zn–Ta–Ta planes. This is the condition for $Ba(Zn_{1/3}Ta_{2/3})O_3$ crystal to have the minimum $\tan\delta$. When the sintering-time is insufficient, the superstructure is not fully formed. Some Zn ions get the sites of Ta ion and Ta ions get the sites of Zn ion. As shown in Fig. 5b, this forms the disordered distribution of two- and five-valent ions, which increase the $\tan\delta$.

We investigated the system $Ba(Zn,Ta)O_3$–$BaZrO_3$ and found this system having the high-Q value around the composition of 4 mol% $BaZrO_3$.[4] As shown in Fig. 6, the Q-value is as high as that of the $Ba(Zn,Ta)O_3$ sintered for long time. The X-ray diffraction pattern showed that the $Ba(Zr_{0.04}Zn_{0.32}Ta_{0.64})O_3$ ceramic forms the solid solution with the cubic perovskite structure. But, the high Q-value of this solid solution is unreasonable if we accept the Schlömann's theory. Because, whether the Zr^{4+} ion substitutes with Zn^{2+} ion or Ta^{5+} ion, Zr^{4+} ions create the disordered charge distribution that breaks the charge periodicity of the tripling superstructure.

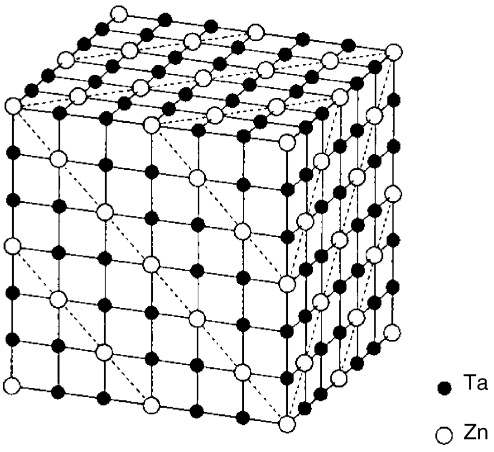

Fig. 4. Ordering of B site ions in $Ba(Zn,Ta)O_3$ crystal.

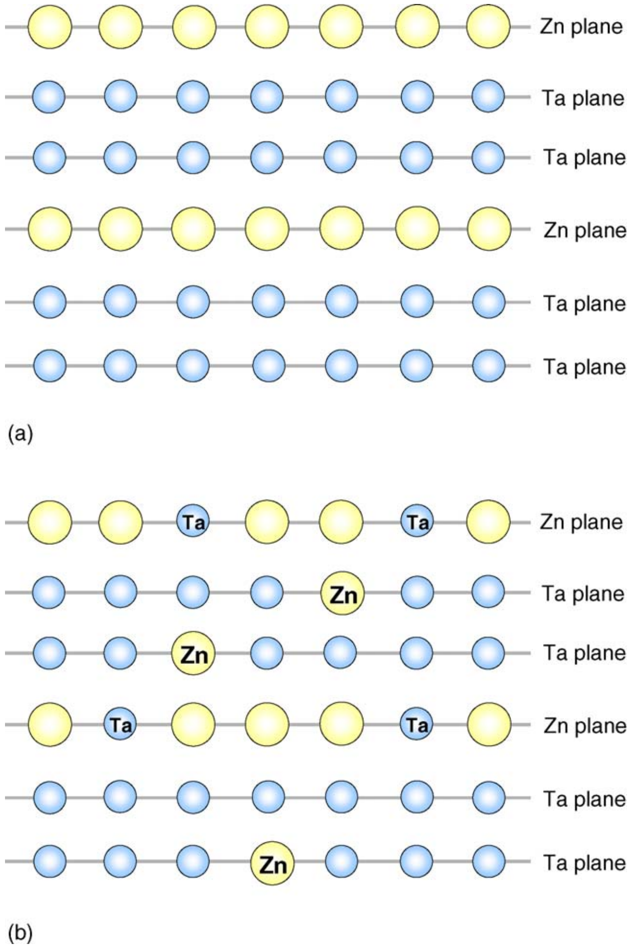

Fig. 5. Simplified model of: (a) ordering and (b) disordering of B site ions in $Ba(Zn,Ta)O_3$ crystal.

To investigate the lattice vibration of this system, we measured their far infrared reflection spectra.[5] Fig. 7 shows the measured and calculated far infrared reflection spectra for $Ba(Zn,Ta)O_3$, $Ba(Zr_{0.04}Zn_{0.32}Ta_{0.64})O_3$, and $BaZrO_3$ ceramics. The reflectance spectrum of $Ba(Zn,Ta)O_3$ and $BaZrO_3$ were fitted well by giving the 14 and 4 resonance modes, respectively. Numbers of the infrared-active lattice vibration modes are 18 for $Ba(Zn,Ta)O_3$ with hexagonal superstructure[6] and 3 for $BaZrO_3$ with cubic perovskite structure. The reflectance spectrum of $Ba(Zr_{0.04}Zn_{0.32}Ta_{0.64})O_3$ is rather similar to that of $Ba(Zn,Ta)O_3$ compared with $BaZrO_3$. The continuously increasing part of the spectrum from 150 to 400 cm^{-1} is difficult to analyze by giving the discrete resonance frequency. As a mathematical mean, this part was fitted by giving the resonance modes, as much as 250 modes, with narrow separation. It is expected that Zr ions bring about some continuum states in the lattice vibrations of the superstructure.

In 1998, Davis and Tong presented a paper about the crystal structure of the system $Ba(Zn,Ta)O_3$–$BaZrO_3$.[7] By using the high-resolution TEM, they proved that the solid solution with 3 or 4 mol.% $BaZrO_3$ does not have the tripling superstructure, but

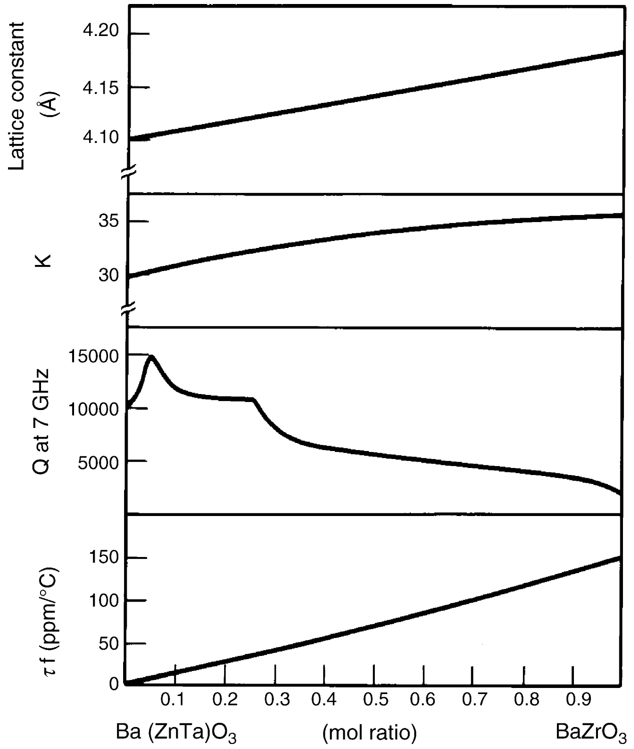

Fig. 6. Dielectric properties of system $Ba(Zn_{1/3}Ta_{2/3})O_3$–$BaZrO_3$.[4]

has the doubling superstructure. Fig. 8 shows a simplified image of this structure. The doubling superstructure is made of a Ta plane and a plane containing Zr, Zn and Ta ions. The combination of Zr, Zn and Ta ions in the latter plane has the average charge of 3+, and the crystal forms doubling superstructure with the Ta^{5+}-plane.

In this paper, they showed another important evidence that each grain of $Ba(Zr,Zn,Ta)O_3$ has many micro domains with the size of about 40 nm. It would not be unreasonable to expect that the doubling superstructure of $Ba(Zr,Zn,Ta)O_3$ maintains the charge neutrality within each micro domain and the charge neutrality within the short correlation distance of 40 nm restrains the increase of tan δ of $Ba(Zr,Zn,Ta)O_3$.

4.2. Dielectric loss tangent of (Zr,Sn)TiO$_4$ ceramics

The role of lattice defects such as oxygen vacancy, substituting acceptor ion and donor ion on the frequency dependence of dielectric loss tangent of $(Zr,Sn)TiO_4$ is discussed in this section.[8] Four specimens were prepared. Specimen A was made as a benchmark, which was sintered in air atmosphere. Specimen B was sintered in air and subsequently annealed in a deoxidized atmosphere. This annealing produced the oxygen vacancies of about 1000 ppm in specimen B, which was calculated from the weight loss by the annealing. Specimen C was doped with 1.3 mol% $FeO_{3/2}$ and specimen D was doped with 0.5 mol.% $TaO_{5/2}$.

Fig. 9 shows the frequency dependence of tan δ of specimens A and B. The dielectric loss tangent of both specimens has the linear dependency to frequency. Their frequency dependencies of tan δ are expressed by the following equations.

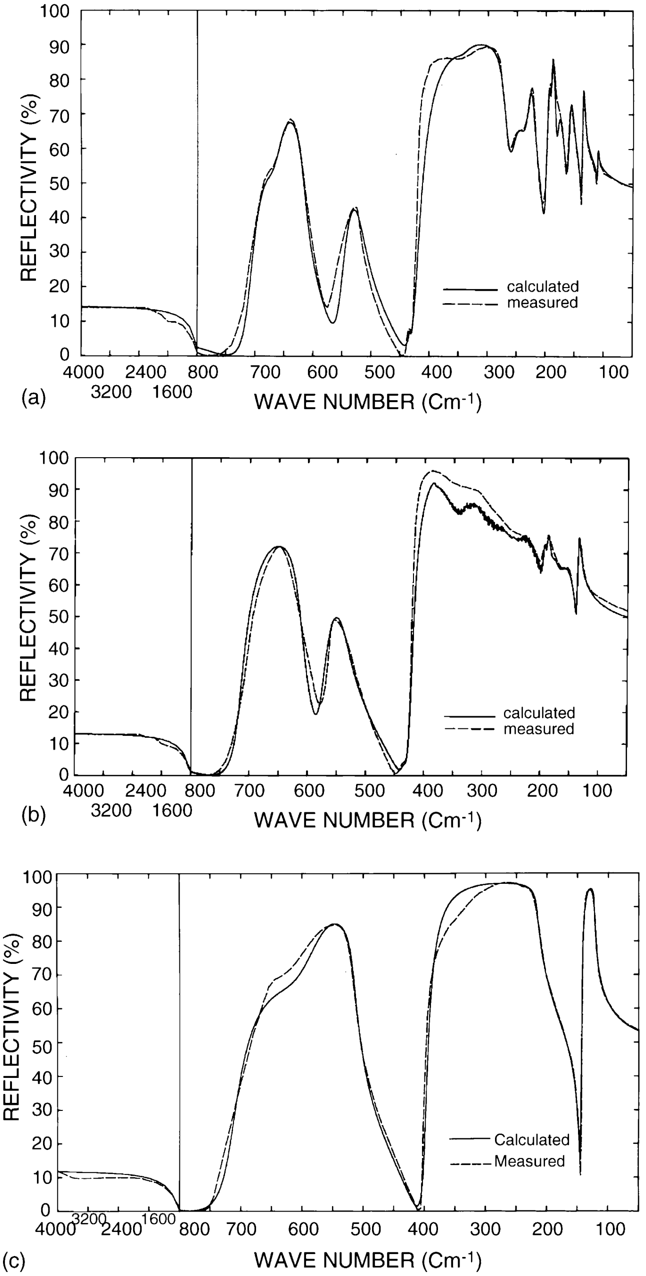

Fig. 7. Far infrared reflection spectra of: (a) $Ba(Zn_{1/3}Ta_{2/3})O_3$; (b) $Ba(Zr_{0.04}Zn_{0.32}Ta_{0.64})O_3$ and (c) $BaZrO_3$.[5]

Specimen A: $\tan\delta = (0.16f + 0.07) \times 10^{-4}$
Specimen B: $\tan\delta = (0.18f + 0.18) \times 10^{-4}$

it is shown that the gradient and intercept in the frequency dependence of tan δ increased in specimen B compared with specimen A. This increase was caused by the creation of 1000 ppm oxygen vacancies in specimen B, which distribute disorderedly in $(Zr,Sn)TiO_4$ crystal.

Fig. 10 shows the tan δ for specimens A, C and D. The frequency dependencies of tan δ for specimens C and D are expressed as follows:

Specimen C: $\tan\delta = (0.64f + 7.48) \times 10^{-4}$
Specimen D: $\tan\delta = (0.17f + 0.01) \times 10^{-4}$

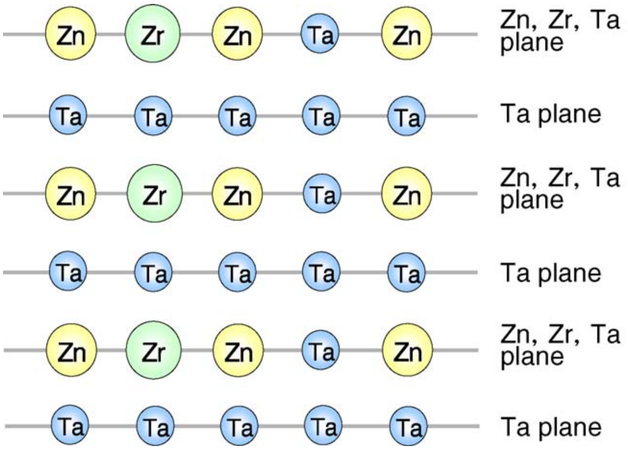

Fig. 8. Simplified model of doubling ordering of B site ions in Ba(Zr,Zn,Ta)O_3 crystal.

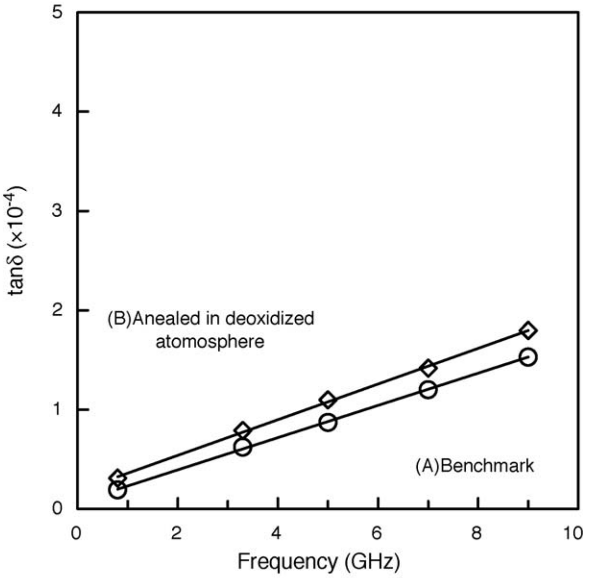

Fig. 9. Role of oxygen vacancy on tan δ of (Zr,Sn)TiO_4 ceramics.

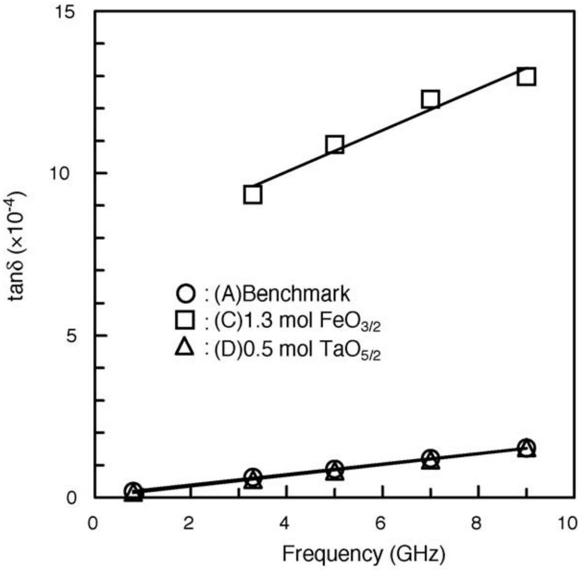

Fig. 10. Role of Fe and Ta ions on tan δ of (Zr,Sn)TiO_4 ceramic.

Table 1
tan δ at 7 GHz caused by anharmonic terms of crystal's potential energy and lattice defects

	tan δ at 7 GHz
tan δ caused by anharmonic terms of potential energy	
Ba(Zn,Ta)O_3	0.5×10^{-4}
(Zr,Sn)TiO_4	1.2×10^{-4}
tan δ caused by lattice defects	
Disordered charge distribution in Ba(Zn,Ta)O_3	10×10^{-4}
1000 ppm oxygen vacancies in (Zr,Sn)TiO_4	0.2×10^{-4}
0.5 mol.% Ta ions in (Zr,Sn)TiO_4	0.0×10^{-4}
1.3 mol.% Fe ions in (Zr,Sn)TiO_4	10×10^{-4}

doping of Fe^{3+} ions increased the gradient and intercept drastically. Great amount of Fe ions such of 1.3 mol.% was doped in this ceramic and the Fe ions, which work as acceptor ions in the (Zr,Sn)TiO_4 crystal, creates oxygen vacancies in the crystal. It could be expected that these great number of Fe ions and oxygen vacancies distributes disorderedly in the crystal and increases the tan δ of (Zr,Sn)TiO_4.

Comparing the frequency dependence of tan δ for specimens D and A, the doping of Ta ions decreased the tan δ, especially the intercept was decreased. This reason is not clearly explained. But, it could be assumed that the Ta^{5+} ions, donor ions, reduce the number of oxygen vacancies in the crystal of (Zr,Sn)TiO_4, and the Ta^{5+} ions might cause the charge shift for the adjacent Ti^{4+} ion to Ti^{3+} in a way that they maintain the charge neutrality within the nano-scale region. Further investigation is needed to prove this assumption.

5. Conclusion

The dielectric loss tangent at microwave frequency is mainly caused by the anharmonic terms in the crystal's potential energy, and increased by the lattice defects. Among many kinds of lattice defects, disordered charge distribution in the crystal contributes seriously to increase tan δ.

This paper introduced the Schlömann's theory and showed this theory explaining the experimental results obtained for the system Ba(Zn,Ta)O_3-BaZrO_3 and (Zr,Sn)TiO_4 ceramics reasonably. Table 1 shows the tan δ discussed in this paper. The dielectric loss tangent caused by the lattice defects can be eliminated by controlling the experimental condition. It is effective to minimize the disordered charge distribution in the crystal for decreasing the dielectric loss tangent of microwave dielectrics.

References

1. Maradudin, A. A. and Fein, A. E., Scattering of neutrons by an anharmonic crystal. *Phys. Rev.*, 1962, **128**, 2589–2608.
2. Schlömann, E., Dielectric losses in ionic crystals with disordered charge distributions. *Phys. Rev.*, 1964, **135**, A413–A419.
3. Kawashima, S., Nishida, M., Ueda, I. and Ouchi, H., Ba(Zn,Ta)O_3 ceramic with low dielectric loss. *J. Am. Ceram. Soc.*, 1983, **66**, 421–423.
4. Tamura, H., Konoike, T. and Wakino, K., Improved high-*Q* dielectric resonator with complex perovskite structure. *J. Am. Ceram. Soc.*, 1984, **67**, C59–C61.

5. Wakino, K., Murata, M. and Tamura, H., Far infrared reflection spectra of Ba(Zn,Ta)O_3–$BaZrO_3$ dielectric resonator material. *J. Am. Ceram. Soc.*, 1986, **69**, 34–37.
6. Tamura, H., Sagala, D. A. and Wakino, K., Lattice vibration of $Ba(Zn_{1/3}Ta_{2/3})O_3$ crystal with ordered perovskite structure. *Jpn. J. Appl. Phys.*, 1986, **25**, 787–791.
7. Davis, P. K. and Tong, J., Effect of ordering-induced domain boundaries on low-loss $Ba(Zn_{1/3}Ta_{2/3})O_3$–$BaZrO_3$ perovskite microwave dielectrics. *J. Am. Ceram. Soc.*, 1998, **80**, 1727–1740.
8. Michiura, N., Tatekawa, T., Higuchi, Y. and Tamura, H., Role of donor and acceptor ions in the dielectric loss tangent of $(Zr_{0.8}Sn_{0.2})TiO_4$ dielectric resonator material. *J. Am. Ceram. Soc.*, 1995, **78**, 793–796.