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Polarization Mechanisms in Thermal Stable Microwave BLT Ceramics
Part 1: “Hard” Paraelectrics Peculiarities

The "hard" paraelectrics as a material with a high dielectric constant and low loss at microwave frequencies are considered. The impact of different types of polarization on the dielectric and thermal properties of paraelectric is described. The tetragonal rutile structure is considered and the influence of the oxygen octahedrons TiO_6 on the dielectric constant of the paraelectric is established. References 5, figures 2.

Keywords: *dielectric permittivity ε; temperature coefficient of dielectric permittivity TCε; thermal stability; paraelectric; rutile; barium-lanthanum tetratitanate.*

I. Introduction

High dielectric constant ceramics with good thermal stability of their parameters have many compositions that use in various areas of electronics. At that, there is a sharp distinction between sintering methods of relatively low frequency and microwave high-ε dielectrics. In both cases some solid solutions or mixtures are produced.

Used as capacitors, actuators or pyroelectrics, relatively low frequency ceramics are built up on the base of diffuse phase transition in ferroelectrics that have $\varepsilon > 10^4$ due to the presence disordered ionic type polar clusters. These clusters are characterized by a broad distribution of relaxation times that expands up to the microwave region and leads to high dielectric loss. Enhanced loss factor is unwanted for majority of microwave applications.

The microwave dielectric usually requires a very high thermal stability, and their production requires a rather complicated technology. Thermostable low loss microwave dielectrics are often used as dielectric resonators and filters: low loss provides their high quality factor: $Q \sim (\tan\delta)^{-1}$. So the physical nature of those ceramics thermal stability and losses is of great importance. The possibility of combination in one microwave dielectric small loss ($\tan\delta < 10^{-3}$) and high permittivity ($\varepsilon \sim 100$) which is practically independent on temperature ($TC\varepsilon = \varepsilon^{-1}\, d\varepsilon/dT < 10^{-5}$) needs physical ground. In all known physical models [2, 3, 4], the requirements of low loss and zero temperature coefficient of ε are in a contradiction with very high microwave permittivity. However, limiting data of possible high ε and low tanδ for microwave thermostable ceramics are still unknown. That is why the main question of this work is the explanation of nature of high-ε microwave dielectrics thermal stability as well as the nature of their loss.

II. “Hard” paraelectrics as a basic material for microwave dielectrics

High value ε without significant absorption electrical energy at frequencies of 1...100 GHz in the crystals and ceramics can be realized only at the expense of quick-response mechanisms of polarization, but they (with rare exceptions) can not provide it on condition independence permittivity from temperature.

Fast mechanisms of polarization are optical (electronic) and infrared (lattice) polarization. Other polarization mechanisms cannot contribute substantially to the ε_{mic} or accompanied by the ε dispersion that is the cause of significant dielectric loss. That is why $\varepsilon_{mic} = \varepsilon_{opt} + \varepsilon_{inf}$. Large ε_{mic} is possible only in the ferroelectrics and in paraelectrics of the displace type in which high permittivity is formed mainly by soft lattice vibration frequency mode ω_{TO}.

However, ferroelectrics due to their domain structure and correspondent ε(ω) dispersion have large microwave losses that is unacceptable for technical application. So for very high ε microwave dielectrics the only paraelectric-based material should be used.

Paraelectrics might be as the "hard" paraelectrics (rutile TiO_2 or perovskite $CaTiO_3$) so the "soft" paraelectrics ($SrTiO_3$, $KTaO_3$, $CdTiO_3$ or $(Ba,Sr)TiO_3$, etc). All of them are a priori nonthermostable ($\varepsilon \sim C/(T-\theta)$ due to their “soft” lattice vibration mode which frequency critically changes with temperature: $\omega_{TO} = A(T-\theta)^{1/2}$, where θ is Curie-Weiss temperature and *A* is soft mode temperature constant [1].

It is vital to note that the “soft” paraelectrics of $SrTiO_3$ type have $\theta > 0$ K and, therefore, could be transformed into ferroelectrics by the additives, electrical or mechanical fields, etc. As a result, in the “soft” paraelectrics microwave losses at 300 K are not very small: $\tan\delta \geq 10^{-2}$ due to the possible existence or fluctuations of polar phase.

In contrast, the "hard” paraelectrics of TiO_2 or $CaTiO_3$ type could be described by the artificial Curie-Weiss parameter $\theta < 0$. Neither doping nor strong electric fields can transform such a “hard” paraelectrics into a polar phase (which is the main reason of microwave losses [3]). That is why, "hard” paraelectrics have sufficiently low microwave losses ($\tan\delta \sim 10^{-3}$); nevertheless, they are highly non-thermostable ($TC\varepsilon \sim 1000$ *ppm*/K).

In the displace type paraelectrics (that belong to the ionic crystals) the electronic polarization with its dielectric contribution $\varepsilon(\infty) = \varepsilon_{opt}$ has noticeable influence on the frequencies of the infrared vibrations: on the longitudinal mode ω_{LO} and, especially, on the transverse mode ω_{TO}. For these two frequencies and for dielectric contribution from infrared polarization the following expressions were obtained [3]:

$$\omega_{TO}^2 = \frac{c}{m} - \frac{nq^2}{3\varepsilon_0 m}\frac{\varepsilon(\infty)+2}{3};$$

$$\omega_{LO}^2 = \frac{c}{m} + \frac{2nq^2}{3\varepsilon_0 m}\frac{\varepsilon(\infty)+2}{3}; \qquad (1)$$

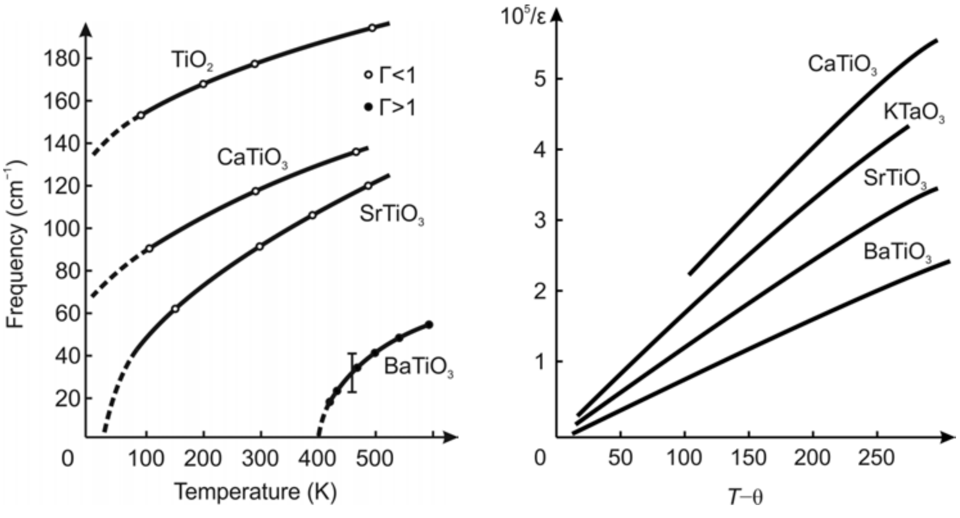
$$\varepsilon(0)-\varepsilon(\infty) = \frac{nq^2}{\varepsilon_0 m\omega_{TO}^2}\frac{\left(\varepsilon(\infty)+2\right)^2}{9}.$$

These formulas correspond to the Lorentz oscillator model, so *c* is elastic constant, *m* is effective mass, *n* is the number of oscillators in the on unit volume and *q* is ionic charge. It is important to indicate that the expression for ω_{LO} is the sum; therefore, the impact of the electron polarization hardly changes the value of the longitudinal frequency. That is why, in practice, the frequency ω_{LO} is temperature independent.

On the contrary, transverse lattice frequency ω_{TO} is characterized by the difference between the minuend *c/m* in the Eq. (1) and the subtrahend that contains electronic dielectric contribution $\varepsilon(\infty)$. That is why lattice frequency ω_{TO} is strongly temperature variable, especially if the said difference is small. At that, any alteration in the ω_{TO} results in a very big modification of the $\varepsilon_{inf} = \varepsilon(0) - \varepsilon(\infty) \sim (\omega_{TO})^{-2}$.

The obtained relations allow provide various opportunities in the temperature dependence of the ionic crystals permittivity. For most of ionic crystals that have value of permittivity $\varepsilon_{mic} < 10$ the temperature coefficient is positive: $TC\varepsilon > 0$. However, the ionic dielectrics that are characterized by predominantly electronic polarization have $\varepsilon_{mic} > 30$ and $TC\varepsilon < 0$. This is confirmed that, if temperature is changed, even a small alteration in the value of ω_{TO} can lead to a noticeable modification in the ε_{mic}.

Reducing the lattice frequency ω_{TO} with decreasing temperature is described by the Cochran law: $\omega_{TO} = A\sqrt{T-\theta}$, where *A* is the temperature coefficient of frequency. Direct connection of the transverse mode frequency and permittivity of displace type paraelectrics is confirmed by the experimental data in Fig. 1.



a) b)

Fig. 1. Temperature dependence of frequency ω_{TO} (a) and inverse permittivity (b) for paraelectrics TiO_2, $CaTiO_3$, $SrTiO_3$ and ferroelectric $BaTiO_3$ (in its paraelectric phase); cm^{-1} = 30 GHz

To any paraelectric the Curie-Weiss law can be applied: $\varepsilon(T) = \varepsilon_1 + C/(T - \theta)$, where θ is characteristic temperature, C is Curie-Weiss constant, and ε_1 is independent on the temperature part of the permittivity (given by the electronic polarization and by higher vibration modes). For example, in the perovskite ($CaTiO_3$) the $\varepsilon(T)$ dependence can be described in a wide range of temperatures, if one put $\varepsilon_1 = 60$, $C = 4{\cdot}10^4$ K, $\theta = -90$ K and $A = 170$ GHz·K$^{1/2}$. However, from the typical ("soft") displace type paraelectrics, for example the $SrTiO_3$ in which $\theta > 0$ K, the $CaTiO_3$ is distinguished by the fact that characteristic temperature $\theta < 0$ K.

Since we need to discuss the possibility of reducing the temperature dependence of ε_{mic}, it is desirable to express the Curie-Weiss constant through the parameters of the discussed model. Approximate form of Curie-Weiss law $\varepsilon(T) \approx C/(T - \theta)$ can be obtained if in the equation (1) put

$$\frac{m\omega_{TO}^2}{c} = 1 - \frac{nq^2\left(\varepsilon(\infty)+2\right)^2}{9c\varepsilon_0} = \gamma\left(T-\theta\right).$$

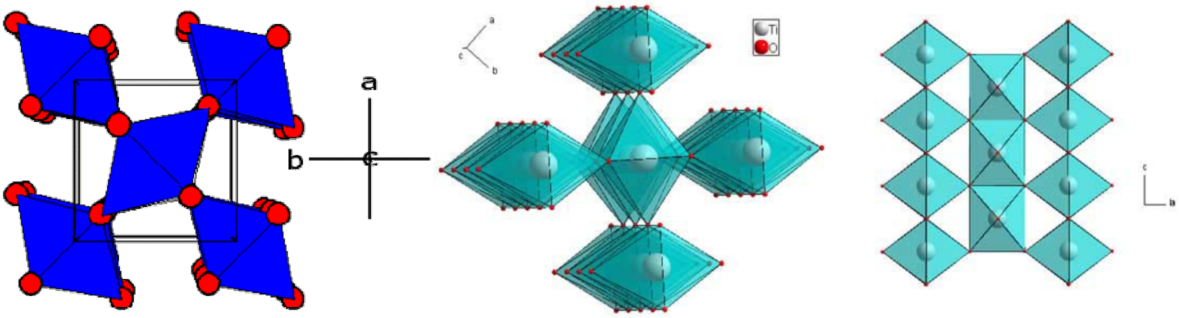
Substituting this value in the expression for the dielectric constant in the formulas (1), it is possible to obtain

$$\varepsilon(0) - \varepsilon(\infty) = \frac{nq^2\left(\varepsilon(\infty)+2\right)^2}{9c\gamma\varepsilon_0}\,\frac{1}{T-\theta};$$

$$A = \sqrt{\frac{c\gamma}{m}}; \qquad C = \frac{nq^2\left(\varepsilon(\infty)+2\right)^2}{9c\gamma\varepsilon_0}.$$

The main obstacle why paraelectrics cannot be applied in the microwaves is the ε_{mic} temperature instability. Since the nature of this instability is the electronic subsystem of the crystal, the ways to overcome this instability should be sought in the methods of the impact on this subsystem. The main contribution to the ε_{mic} gives infrared polarization. Formally it is mentioned as ionic polarization, but in fact it is associated with susceptibility of the ions electronic orbitals (external shells). It is found that most part of the ε_{mic} in the rutile and perovskite is caused by highly polarizable oxygen octahedrons TiO_6 which are connected at the vertices. In this case, the electronic clouds that linked ions in the system of the octahedrons provide enough freedom for easy polarization, and just this leads to the $\varepsilon_{mic} > 100$.

As an example, Fig. 2 demonstrates a tetragonal rutile (TiO_2) structure. Due to anisotropy, in rutile crystal $\varepsilon_c = 170$ and $\varepsilon_a = \varepsilon_b = 80$ (to average out, in the rutile ceramics $\varepsilon_{mic} \approx 100$). Rutile structure can be represented as infinite columns of edge-sharing TiO_6 octahedrons; the each edge-shared oxygen is corner-shared with an adjacent infinite chain. As such, each ion Ti^{+4} are coordinated to six ions O^{-2}, and each of oxygen is coordinated to three titaniums: two within a column, and one within the adjacent column. It is obvious, that electronics clouds density is bigger in the tetragonal axis, so $\varepsilon_c > \varepsilon_a$.



a) b)

Fig. 2. Rutile structure simplified representation

As it is shown in the rutile structure (Fig. 2), there are many possibilities to impact on crystal properties by the allocation between the octahedron various additives. That is why it is possible to govern dielectric properties by the degree of the electronic shells interaction and their reciprocal displacement by means of different ions implementation to the structure.

By this way, it is possible significantly weaken the critical $\varepsilon(T)$ dependence (according to the Curie-Weiss low) and maintain a high polarizability.

In the second part of the article will be considered an increase in the thermal stability of the paraelectrics, especially BLT ceramics, at microwave frequencies by its doping rare-earth ions [5].

Conclusions

Large ε_{mic} is possible only in the ferroelectrics and in paraelectrics of the displace type. But ferroelectrics due to their domain structure and correspondent $\varepsilon(\omega)$ dispersion have large microwave losses. So for very high ε microwave dielectrics the only paraelectric-based material should be used.

The "hard" paraelectrics have sufficiently low microwave losses ($\tan\delta \sim 10^{-3}$); nevertheless, they are highly non-thermostable ($TC\varepsilon \sim 1000$ *ppm*/K).

Most part of the ε_{mic} in the rutile and perovskite is caused by highly polarizable oxygen octahedrons TiO_6 which are connected at the vertices. It is possible to govern dielectric properties by the degree of the electronic shells interaction and their reciprocal displacement by the allocation between the octahedron various additives. By this way, it is possible significantly weaken the critical $\varepsilon(T)$ dependence.

References

1. *Kniazev A. S., Zakharov V. P., Mitiureva I. A., Poplavko Y. M.* (1973), “Vibrational spectra of rutile”. Solid State Physics. Vol. 15, no. 8, pp. 2371–2377. (Rus)
2. *Narytnik T. N., Voitenko A. G., Rotenberg B. A. [et al.]* (1978), “Investigation of thermostable dielectrics for high-Q microwave dielectric resonators”. Electronic technique. Series Microwave Electronics. No. 10, pp. 102–106. (Rus)
3. *Poplavko Y.M.* (2013), “Dielectric spectroscopy of Solids”. Saarbrücken, Lambert Academic Publishing, P. 253. (Rus)
4. *Poplavko Y. M., Pashkov V. M., Bovtun V. P.* (1982), “Dielectrics with high dielectric constant in the microwave technology”. Kiev, Znanie, P. 20. (Rus)
5. *Tamura H., Sagala D., Wakino K.* (1986), “Lattice vibration of Ba(Zn1/3Ta2/3)O3 crystal with ordered perovskite structure”. Jap. Journ. Appl. Phys. Vol. 25, part 1, no. 6, pp. 787–791.

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Механізми поляризації у термостабільній БЛТ кераміці на надвисоких частотах Частина 1: Особливості «жорстких» параелектриків

Розглянуто «жорсткі» параелектрики як матеріал з високою діелектричної проникністю і малими втратами на НВЧ. Описано вплив різних видів поляризації на діелектричні та температурні властивості параелектриків. Описана тетрагональна структура рутила й встановлено вплив кисневих октаедрів TiO6 на діелектричну проникність параелектриків. Бібл. 5, рис. 2.

Ключові слова: *діелектрична проникність ε; температурний коефіцієнт діелектричної проникності ТКε; термостабільність, параелектрик; рутил; барійлантаноідний тетратітанат.*

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Механизмы поляризации в термостабильной БЛТ керамике на сверхвысоких частотах Часть 1: Особенности «жестких» параелектриков

Рассмотрены «жесткие» параэлектрики как материал с высокой диэлектрической проницаемостью и малыми потерями на СВЧ. Описано влияние различных видов поляризации на диэлектрические и температурные свойства параэлектриков. Описана тетрагональная структура рутила и установлено влияние кислородных октаэдров TiO6 на диэлектрическую проницаемость параэлектриков. Библ. 5, рис. 2.

Ключевые слова: *диэлектрическая проницаемость ε; температурный коэффициент диэлектрической проницаемости TKε; термостабильность; параэлектрик; рутил; барийлантаноидный тетратитанат.*

Список использованных источников

1. *Князев А. С.* Колебательные спектры рутила / А. С. Князев, В. П. Захаров, И. А. Митюрева, Ю. М. Поплавко // ФТТ. – 1973. – Т. 15, № 8. – С. 2371–2377.
2. *Нарытник Т. Н.* Исследование термостабильных диэлектриков для высокодобротных СВЧ диэлектрических резонаторов / Т. Н. Нарытник, А. Г. Войтенко, Б. А. Ротенберг [и др.] // Электронная техника. Сер. Электроника СВЧ. – 1978. – № 10. – С. 102–106.
3. *Поплавко Ю. М.* Диэлектрическая спектроскопия твердых тел : монография / Ю. М. Поплавко. – Germany, Saarbrucken: LAMBERT Academic Publishing, 2013. – 253 с.
4. *Поплавко Ю. М.* Диэлектрики с высокой диэлектрической проницаемостью в технике СВЧ / Ю. М. Поплавко, В. М. Пашков, В. П. Бовтун. – К. : Знание, 1982. – 20 с.
5. *Tamura H.* Lattice vibration of Ba(Zn1/3Ta2/3)O3 crystal with ordered perovskite structure / H. Tamura, D. Sagala, K. Wakino // Jap. Journ. Appl. Phys. – 1986. – Vol. 25, Part 1, No. 6. – PP. 787–791.