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Dielectric properties of grain–grainboundary binary system

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ABSTRACT

Dielectric properties of grain–grainboundary binary system are analyzed theoretically and compared with unary system and classical Maxwell–Wagner (MW) polarization in binary system. It is found that MW polarization appears at higher frequency compared with intrinsic polarization for grain–grainboundary binary system, which is abnormal compared with classical dielectric theory. This dielectric anomaly is premised on the existence of electronic relaxation at grainboundary. The origin of giant dielectric constant of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics is also investigated on the basis of the theoretical results. It is proposed that low frequency relaxation originates from electronic relaxation of oxygen vacancy at depletion layer, while high frequency relaxation comes from MW polarization. The results of this paper offer a quantitative identification of MW polarization from intrinsic polarization at grainboundary and a judgment of the mechanism and location of a certain polarization in grain–grainboundary binary system.

1. Introduction

Grain–grainboundary binary system is the basic structural unit of electronic ceramics. It is declared by most researches on microstructure of electronic ceramics that almost no additional foreign atoms exist between grains except for the juncture of more than three grains, so grainboundary is in fact depletion layer on the surface of grain. Because of inhomogeneous distribution of space charges, Schottky barrier is built across depletion layer. Several kinds of polarizations exist in this binary structure, such as intrinsic polarizations in grain or depletion layer and Maxwell–Wagner (MW) polarization. Especially, when there are more than one intrinsic polarization organs, the judgment about the mechanism and location of a certain relaxation becomes more complicated. For example, there are only two main relaxation processes in $CaCu_3Ti_4O_{12}$ ceramics (CCTO), but the mechanism and the location of the polarizations are still in debate so far [1–9]. Although MW polarization is proposed by Sinclair [1,2] that giant dielectric constant comes from the inhomogeneous binary structure [10–16], no theoretical explain for the contradiction that MW polarization always has the longest relaxation time compared to other polarizations according to classical dielectric theory, while giant dielectric constant of CCTO comes from high frequency relaxation. Furthermore, the model cannot get rid of the probability of intrinsic polarization at grainboundary which can give rise to a huge dielectric constant too according to boundary layer capacitors (BLC) effect [17]. In this paper, after the theoretical analysis of dielectric properties of grainboundary binary system, the contradiction in Sinclair's theory is solved and quantitative identification of MW polarization with intrinsic polarization at grainboundary is realized. In the end, the mechanism and the location of polarizations in CCTO is discussed.

2. Theoretical analysis of dielectric properties

2.1. Unary system

For a simple unary system with only one polarization organ, dielectric properties can be described by famous Debye equations as

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+\omega^2\tau^2} \quad (1)$$

$$\varepsilon'' = \frac{\gamma+g}{\omega\varepsilon_0} = \frac{\gamma}{\omega\varepsilon_0} + \frac{(\varepsilon_s-\varepsilon_\infty)\omega\tau}{1+(\omega\tau)^2} \quad (2)$$

When there are more than one polarizations, dielectric constant and dielectric loss can be expressed as the sum of the contribution of all the polarizations for the linearity of the system

$$\varepsilon' = \varepsilon_\infty + \sum_i \frac{\varepsilon_{si} - \varepsilon_{\infty i}}{1+\omega^2\tau_i^2} \quad (3)$$

$$\varepsilon'' = \frac{\gamma+g}{\omega\varepsilon_0} = \frac{\gamma}{\omega\varepsilon_0} + \sum_i \frac{(\varepsilon_{si}-\varepsilon_{\infty i})\omega\tau_1}{1+(\omega\tau_i)^2} \quad (4)$$

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where ε' and ε'' are dielectric constant and loss, respectively, ε_0 is vacuum dielectric constant, ε_s an ε_∞ are static state dielectric constant and light frequency dielectric constant, respectively, ω is angular frequency, τ is relaxation time, and γ and g are direct current conductivity and relaxation conductivity, respectively. Subscribe i represents the ith polarization. Dielectric loss peaks will appear when $\omega\tau_i = 1$. The peak values are determined by the polarization strength itself. For a common dielectric material, $\varepsilon_\infty < 10$ and $\varepsilon_s/\varepsilon_\infty < 10$, then the apparent dielectric constant is no more than 100.

2.2. Grain–grainboundary binary system

If the resistance and capacity of grainboundary and grain are denoted as R_1, C_1 and R_2, C_2, respectively, dielectric properties of grain–grainboundary binary system can be described with impendence as followings

$$Y_1 = \frac{1}{R_1} + j\omega C_1 = \frac{1 + j\omega\tau_1}{R_1} \tag{5}$$

$$Y_2 = \frac{1}{R_2} + j\omega C_2 = \frac{1 + j\omega\tau_2}{R_2} \tag{6}$$

$$Y = \frac{Y_1 Y_2}{Y_1 + Y_2} = \frac{1 + [(\tau_1 + \tau_2)\tau - \tau_1\tau_2]\omega^2}{R(1 + \omega^2\tau^2)} + j\frac{(\tau_1 + \tau_2 - \tau)\omega + \tau_1\tau_2\tau\omega^3}{R(1 + \omega^2\tau^2)} \tag{7}$$

where $R = R_1 + R_2$, $\tau = \varepsilon_0(d_1\varepsilon_2 + d_2\varepsilon_1)/[d_1(\gamma_2 + g_2) + d_2(\gamma_1 + g_1)]$, $\tau_1 = R_1C_1 = \varepsilon_0\varepsilon_1/(\gamma_1 + g_1)$, $\tau_2 = R_2C_2 = \varepsilon_0\varepsilon_2/(\gamma_2 + g_2)$. Subscripts 1 and 2 denote grainboundary and grain, respectively. Dielectric constant and loss of the system can be expressed as

$$\varepsilon'' = \frac{(1/\omega) + [(\tau_1 + \tau_2)\tau - \tau_1\tau_2]\omega}{1 + \omega^2\tau^2} \times \frac{d}{\varepsilon_0((d_1/\gamma_1 + g_1) + (d_2/\gamma_2 + g_2))} \tag{8}$$

$$\varepsilon' = \frac{(\tau_1 + \tau_2 - \tau) + \tau_1\tau_2\tau\omega^2}{1 + \omega^2\tau^2} \times \frac{d}{\varepsilon_0((d_1/\gamma_1 + g_1) + (d_2/\gamma_2 + g_2))} \tag{9}$$

where d_1, d_2 and d are the thickness of grainboundary, grain and binary system, respectively, γ and g are direct current conductivity and relaxation conductivity, respectively. For a practical electronic ceramics, we have $d_1 \ll d_2 \approx d$.

2.2.1. Grain and grainboundary with same polarizations

Generally, polarization mechanism is same for grain and grainboundary because they own same crystal structure, thus $\varepsilon_1 = \varepsilon_2 = \varepsilon = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/(1 + \omega^2\tau_0^2)$ and $g_1 = g_2 = g_0 = \varepsilon_0(\varepsilon_s - \varepsilon_\infty)\omega^2\tau_0/(1 + \omega^2\tau_0^2)$, where τ_0 is intrinsic polarization time and g_0 is intrinsic relaxation conductivity. For this situation, relaxation time can be expressed as $\tau_1 = \varepsilon_0\varepsilon/(\gamma_1 + g)$, $\tau_2 = \varepsilon_0\varepsilon/(\gamma_2 + g)$ and $\tau \approx \varepsilon_0 d\varepsilon/[d_1(\gamma_2 + g) + d_2(\gamma_1 + g)]$. If a dielectric relaxation can be observed experimentally, the precondition $g_{0\infty} > \gamma_i$ when $\omega\tau_i = 1$ must be satisfied, where $g_{0\infty}$ is the maximum value or high frequency limit value of intrinsic relaxation conductivity g_0 and $g_{0\infty} = \varepsilon_0(\varepsilon_s - \varepsilon_\infty)/\tau_0$. Therefore, only the situation $g > \gamma_i$ when $\omega\tau_i \geq 1$ is considered in this paper. Generally, $\gamma_2/\gamma_1 \gg d_2/d_1$ is tenable for grain–grainboundary binary system. Dielectric properties of the binary system will be discussed in different frequency regions as follows

(1) $\omega \gg \omega_0$ (where ω_0 is the most probable frequency of intrinsic relaxation).
We have $\tau_1 \approx \tau_2 \approx \tau \approx \varepsilon_0\varepsilon_\infty/g_{0\infty}$, $\varepsilon' \approx (\tau + \tau^3\omega^2)g_{0\infty}/\varepsilon_0(1 + \omega^2\tau^2) = \varepsilon_\infty$ and $\varepsilon'' \approx (\omega^{-1} + \tau^2\omega)g_{0\infty}/\varepsilon_0(1 + \omega^2\tau^2) = g_{0\infty}/\omega\varepsilon_0 = (\varepsilon_s - \varepsilon_\infty)/\omega\tau_0$. The dielectric properties in this frequency region present the high frequency response of the binary system.

(2) $\omega \to \omega_0$.
Under this condition, $g_1 = g_2 = g_0 \approx \varepsilon_0(\varepsilon_s - \varepsilon_\infty)\omega^2\tau_0/(1 + \omega^2\tau_0^2) > \gamma_2 \gg \gamma_1$, so $\tau_1 \approx \tau_2 \approx \tau \approx \varepsilon_0\varepsilon/g_0$, so we have $\varepsilon' \approx (\tau + \tau^3\omega^2) g_0/\varepsilon_0(1 + \omega^2\tau^2) = \varepsilon = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/(1 + \omega^2\tau_0^2)$ and $\varepsilon'' \approx (1/\omega + \tau^2\omega)g_0/\varepsilon_0(1 + \omega^2\tau^2) = (\varepsilon_s - \varepsilon_\infty)\omega\tau_0/(1 + \omega_2\tau_0^2)$. When $\omega\tau_0 = 1$, dielectric relaxation peak appears with the value of about $(\varepsilon_s - \varepsilon_\infty)/2$, which represents the intrinsic relaxation process of the material and no boundary layer capacitors (BLC) effect can be observed.

(3) $\omega \ll \omega_0$.
Under this condition, $g_0 \approx 0$, $\tau_1 \approx \varepsilon_0\varepsilon_s/\gamma_1$, $\tau_2 \approx \varepsilon_0\varepsilon_s/\gamma_2$, $\tau \approx \varepsilon_0 d\varepsilon_s/d_1\gamma_2$, thus we have $\tau_1 \gg \tau \gg \tau_2$. The sequence order of relaxation times along frequency axis is shown in Fig. 1, where ω_1 and ω_2 are turning frequency from one dielectric relaxation to another. So dielectric properties can be expressed as $\varepsilon' \approx (\tau_1 + \tau_1\tau_2\tau\omega^2)d\gamma_1/(1 + \omega^2\tau^2)d_1\varepsilon_0$ and $\varepsilon'' \approx (1/\omega + \tau_1\tau\omega) d\gamma_1/(1 + \omega^2\tau^2)d_1\varepsilon_0$. It is very clear that dielectric properties under this situation are modulated by the size ratio of grain and depletion layer.

If $\omega < \omega_1$, we have $\varepsilon' \approx d\gamma_1\tau_1/d_1\varepsilon_0$, $\varepsilon'' \approx d\gamma_1/d_1\omega\varepsilon_0$. Dielectric properties here present the dielectric properties of dielectric at very low frequency.

If $\omega_1 < \omega < \omega_2$, we have $\varepsilon' \approx d\varepsilon_s/d_1(1 + \omega^2\tau^2)$ and $\varepsilon'' \approx d\varepsilon_s\omega\tau/d_1(1 + \omega^2\tau^2)$. A peak appears in ε''–f curve when $\omega\tau = 1$, which is introduced by MW polarization. The corresponding peak value is $d\varepsilon_s/2d_1$. It is obvious that activation energy of MW polarization is exact the activation energy of direct current conduction of grain. It is not surprising that the same result can be obtained by BLC model, because BLC model is a special example of MW polarization.

If $\omega_2 < \omega$,we have $\varepsilon' \approx d\tau_1\tau_2\gamma_1/d_1\varepsilon_0\tau = \varepsilon$ and $\varepsilon'' \approx d\varepsilon_1/d_1\omega\tau = d\varepsilon/d_1\omega\tau$, this is the continuation of the situation above.

From the analysis above, it can be concluded that when grain and grain boundary have the same polarization, intrinsic polarization exists at higher frequency, while MW polarization at lower frequency. Dielectric constant varies from ε_∞ to ε_s for intrinsic polarization and ε_s to $d\varepsilon_s/d_1$ for MW polarization, which are the results of a traditional MW polarization.

2.2.2. Grain and boundary with different polarizations

Since grain resistance is much less than grainboundary, if electric field is applied, energy band at grainboundary varies with electric field, but energy band in grain does not change at all. Electronic traps originating from intrinsic point defects are forced to emit or capture electrons with the variation of energy band, thus an additional polarization of electronic relaxation occurs at grainboundary [18–22]. For this situation, considering $g_1 > \gamma_1$, $g_1 \ll \gamma_2$, $\tau_1 = \varepsilon_0\varepsilon_1/(\gamma_1 + g_1)$ and $\tau_2 = \varepsilon_0\varepsilon_2/\gamma_2$, we have $\tau = \varepsilon_0(d_1\varepsilon_2 + d_2\varepsilon_1)/[d_1(\gamma_2 + g_2) + d_2(\gamma_1 + g_1)] \approx d\varepsilon_0\varepsilon_1/d_1\gamma_2$, namely $\tau_1 > \tau_{10} \gg \tau \gg \tau_2$, so dielectric constant and dielectric loss can be expressed as following Eqs. (10) and (11). In order to offer a clear physical images, dielectric properties of the binary system will be discussed in different frequency regions as follows

$$\varepsilon' = \frac{\tau_1 + \tau_1\tau_2\tau\omega^2}{1 + \omega^2\tau^2} \times \frac{d(\gamma_1 + g_1)}{d_1\varepsilon_0} \tag{10}$$

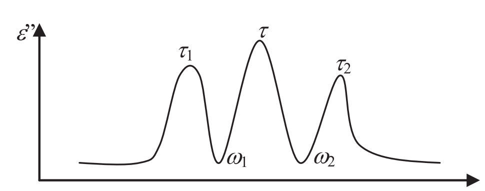

Fig. 1. Sequence order of relaxation times.