Physica B 459 (2015) 105–109

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Modulus spectroscopy of grain–grain boundary binary system

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ARTICLE INFO

Article history:
Received 6 October 2014
Received in revised form
2 December 2014
Accepted 3 December 2014
Available online 5 December 2014

Keywords:
Modulus spectroscopy
Non-uniform system
Grain–grain boundary binary system
Maxwell–Wagner polarization
Intrinsic polarization

ABSTRACT

Understanding various polarization mechanisms in complex dielectric systems and specifying their physical origins are key issues in dielectric physics. In this paper, four different methods for representing dielectric properties were analyzed and compared. Depending on the details of the system under study, i.e., uniform or non-uniform, it was suggested that different representing approaches should be used to obtain more valuable information. Especially, for the grain–grain boundary binary non-uniform system, its dielectric response was analyzed in detail in terms of modulus spectroscopy (MS). Furthermore, it was found that through MS, the dielectric responses between uniform and non-uniform systems, grain and grain boundary, Maxwell–Wagner polarization and intrinsic polarization can be distinguished. Finally, with the proposed model, the dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics were studied. The colossal dielectric constant of CCTO at low frequency was attributed to the pseudo relaxation process of grain.

1. Introduction

Dielectric spectroscopy is a very powerful and widely used method to explore the dielectric properties of dielectric. Through dielectric spectra under various fields, including frequency, temperature, direct current (DC) bias and so on, the polarization mechanisms, conduction process, point defect structure, microstructure and other information can be obtained [1–9].

In fact, parameters obtained by dielectric spectroscopy are overall apparent parameters, implying that the dielectric is assumed to be a uniform system. Nevertheless, for a non-uniform system such as grain–grain boundary binary system, a large difference between apparent dielectric parameters and those of each component makes further analysis rather difficult. Especially for a multi-component dielectric with complex microstructure, it is not easy to know in advance whether its properties within a limited frequency and temperature region originate from some certain component or well-known polarization mechanisms. For example, $CaCu_3Ti_4O_{12}$ (CCTO) ceramics with giant dielectric constant have very complex microstructure, including grain, grain boundary, [10, 11] nano-scale domains, [12–15] surface layer, [16, 17] and so on. Although it is very clear that giant dielectric constant comes from high frequency relaxation with activation energy of about 0.1 eV, but the corresponding relaxation component is still not clear, which makes the further analysis of relaxation mechanism rather difficult. Therefore, representation methods of dielectric properties have to be studied in detail to reveal the relationship between dielectric properties and microstructure.

Generally speaking, there are four methods for representing dielectric properties, which are dielectric spectroscopy (DS), admittance spectroscopy (AS), electric modulus spectroscopy (MS), and impedance spectroscopy (IS) [18–20]. Although these methods are equivalent to each other theoretically, [21] they are different in application because different microstructure information is contained in them. In this paper, differences between the characterizing of dielectric properties by these four methods were discussed firstly, and then the theoretical analysis method of MS was elaborated. The similarities and differences between MS for uniform and non-uniform systems were compared, and the essence of Maxwell–Wagner (MW) polarization, the difference between MW polarization and intrinsic polarization were investigated with a simple grain–grain boundary binary system. Finally, as a real application, the dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics were investigated by MS and the results exhibit good agreements with our proposed model.

2. Representation methods for dielectric properties

For a uniform system with several relaxation processes, parallel model is convenient and the equivalent circuit is shown in Fig. 1.

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http://dx.doi.org/10.1016/j.physb.2014.12.001
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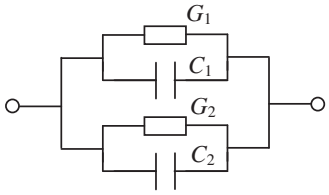

Fig. 1. Parallel equivalent circuit model for uniform system.

The dielectric properties can be expressed with admittance as follows

$$Y^* = G_1 + G_2 + j\omega(C_1 + C_2) \tag{1}$$

$$Y' = G_1 + G_2 = (g_1 + g_2)\frac{S}{l} = \omega\varepsilon_0(\varepsilon_1'' + \varepsilon_2'')\frac{S}{l} = \omega\varepsilon_0\varepsilon''\frac{S}{l} \tag{2}$$

$$Y'' = \omega(C_1 + C_2) = \frac{\omega\varepsilon_0\varepsilon_1' S}{l} + \frac{\omega\varepsilon_0\varepsilon_2' S}{l} = \frac{\omega\varepsilon_0\varepsilon' S}{l} \tag{3}$$

where G is the conductance, C is the capacitor, ω is angle frequency, s is electrode area, l is sample thickness, ε_0, ε' and ε'' are dielectric constant of vacuum, relative dielectric constant and dielectric loss respectively. Removal of the geometric factors, dielectric properties of uniform system can be represented as follows

$$\varepsilon' = \varepsilon_1' + \varepsilon_2' = \varepsilon_\infty + \frac{\Delta\varepsilon_1'}{1 + \omega^2\tau_1^2} + \frac{\Delta\varepsilon_2'}{1 + \omega^2\tau_2^2} \tag{4}$$

$$\varepsilon'' = \varepsilon_1'' + \varepsilon_2'' = \frac{\gamma_1 + \gamma_2}{\omega\varepsilon_0} + \frac{\Delta\varepsilon_1'\omega\tau_1}{1 + \omega^2\tau_1^2} + \frac{\Delta\varepsilon_2'\omega\tau_2}{1 + \omega^2\tau_2^2} \tag{5}$$

where γ is DC conductivity, τ is relaxation time, $\Delta\varepsilon$ is the variation of dielectric constant for a certain polarization from optical frequency to quasi-DC steady state. If a certain polarization originates from the ionization of point defect, for example electronic relaxation, [1, 2] DC conductance and dielectric polarization will have the same micro-origin.

As for a non-uniform system, series model is more convenient as show in Fig. 2. The impedance of the system can be shown as follows:

$$Z^* = Z_1^* + Z_2^* = \frac{1}{Y_1^*} + \frac{1}{Y_2^*} = \frac{R_1(1 - j\omega R_1 C_1)}{1 + \omega^2 R_1^2 C_1^2} + \frac{R_2(1 - j\omega R_2 C_2)}{1 + \omega^2 R_2^2 C_2^2} \tag{6}$$

where Z^* and R are complex impedance and resistance respectively. The corresponding specific impedance is

$$z^* = \frac{l_1}{l}z_1^* + \frac{l_2}{l}z_2^* = k_1 z_1^* + k_2 z_2^* \tag{7}$$

$$z' = \frac{1}{\omega\varepsilon_0}\left(\frac{k_1\varepsilon_1''}{\varepsilon_1'^2 + \varepsilon_1''^2} + \frac{k_2\varepsilon_2''}{\varepsilon_2'^2 + \varepsilon_2''^2}\right) = k_1 z_1' + k_2 z_2' \tag{8}$$

$$z'' = \frac{1}{\omega\varepsilon_0}\left(\frac{k_1\varepsilon_1'}{\varepsilon_1'^2 + \varepsilon_1''^2} + \frac{k_2\varepsilon_2'}{\varepsilon_2'^2 + \varepsilon_2''^2}\right) = k_1 z_1'' + k_2 z_2'' \tag{9}$$

where l_1 and l_2 are the thickness of the first and second components, l is the thickness of the non-uniform system, $k_1 = l_1/l$, $k_2 = l_2/l$. In the same way, series model can be expressed with specific modulus as follows:

$$m' = \omega\varepsilon_0 z'' = \frac{k_1\varepsilon_1'}{\varepsilon_1'^2 + \varepsilon_1''^2} + \frac{k_2\varepsilon_2'}{\varepsilon_2'^2 + \varepsilon_2''^2} = k_1 m_1' + k_2 m_2' \tag{10}$$

$$m'' = \omega\varepsilon_0 z' = \frac{k_1\varepsilon_1''}{\varepsilon_1'^2 + \varepsilon_1''^2} + \frac{k_2\varepsilon_2''}{\varepsilon_1'^2 + \varepsilon_2''^2} = k_1 m_1'' + k_2 m_2'' \tag{11}$$

From the analysis above, it can be seen that it is more convenient for uniform system to be represented with DS or AS. Under this condition, dielectric response can be exhibited separately according to dielectric relaxations. While, IS or MS is more convenient for non-uniform system and dielectric properties can be represented individually according to components. In the following text, we will discuss representation of dielectric properties by MS only.

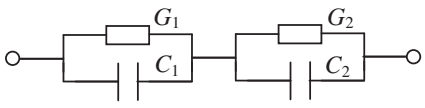

Fig. 2. Series equivalent circuit model for non-uniform system.

3. Distinguish between uniform and non-uniform systems by modulus spectroscopy

3.1. Modulus spectroscopy for uniform system

To the first approximation, different polarization is considered to be separated completely along the frequency axis. The effect of DC conductance is much higher than polarization at low frequency limit, and then the modulus induced by DC conductivity can be expressed as

$$m' = \frac{\omega^2\varepsilon_0^2\varepsilon_s^2/\gamma^2}{\varepsilon_s(1 + \omega^2\varepsilon_0^2\varepsilon_s^2/\gamma^2)} = \frac{\omega^2\tau_p^2}{\varepsilon_s(1 + \omega^2\tau_p^2)} \tag{12}$$

$$m'' = \frac{\omega\varepsilon_0\varepsilon_s/\gamma}{\varepsilon_s(1 + \omega^2\varepsilon_0^2\varepsilon_s^2/\gamma^2)} = \frac{\omega\tau_p}{\varepsilon_s(1 + \omega^2\tau_p^2)} \tag{13}$$

where $\varepsilon_0\varepsilon_s/\gamma$ is regarded as a new equivalent relaxation time τ_p. The equations above are very similar to those of Debye equations and a "relaxation peak" will appear at low frequency limit in m''–f curve also. However, the "relaxation peak" is not induced by dielectric relaxation, but by DC conduction, so we call it a pseudo relaxation. The pseudo relaxation is presented as an increasing line with a slope of 2 at low frequency side of m'–f curve, and then m' turns to be the reciprocal of the dielectric constant with the increase of frequency, as shown in Fig. 3(a) for a uniform system without relaxations. If there are several relaxations in a uniform system, there will be several steps as shown in Fig. 3(b). Generally, the variation of dielectric constant induced by polarization is less than 10 times, so there is very little difference between the neighboring steps. In addition, the activation energy for pseudo relaxation should be same as DC conductance.

3.2. Modulus spectroscopy for non-uniform system

Grain–grain boundary binary system is the simplest non-uniform system and it is also the basic microstructure of electronic ceramics; therefore we adopt grain–grain boundary structure as the typical non-uniform system in the following text.

3.2.1. Non-uniform system without polarization

At low frequency limit, dielectric polarization can be omitted and MS can be expressed as

$$m_{10}' \approx \frac{k_1}{\varepsilon_1'}\left(\frac{\omega\varepsilon_0\varepsilon_1'}{\gamma_1}\right)^2,\ m_{20}' \approx \frac{k_2}{\varepsilon_2'}\left(\frac{\omega\varepsilon_0\varepsilon_2'}{\gamma_2}\right)^2 \tag{14}$$

where subscripts 1 and 2 represent the first component, grain boundary and the second component, grain respectively. Generally