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Fine representation of dielectric properties by impedance spectroscopy

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ABSTRACT

Dielectric spectroscopy is used as a quick, precise and nondestructive examination tool of macroscopical dielectric properties for dielectrics. However, if the information of the microstructure and the location of a certain dielectric relaxation can be learned also by dielectric spectroscopy, it will help to reveal point defect structure and macroscopic and microscopic mechanisms of conduction and dielectric relaxation. Fine representation of dielectric properties by impedance spectroscopy (IS) is analyzed carefully in this paper. It is found that IS is not a good tool to describe a uniform system because a pseudo relaxation peaks exists at low frequency limit corresponding to direct current (DC) conductivity, and two relaxation peaks appears simultaneously corresponding to only one relaxation process for a high loss system with $\tan\delta>1$. However it is very convenient to describe a multiple phase system with IS for that only one Cole-Cole arc with some distortion appears for every phase with several relaxations, therefore it is very easy to distinguish different phases from each other. Especially, the location of a true relaxation process can be deduced by IS without any uncertainly according to pseudo relaxation theory which is built in this paper. Furthermore, when dielectric properties are shown with specific impedance spectroscopy (SIS), the information of the microstructure can be obtained conveniently. Based on these theoretical results above, dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics with giant dielectric constant (GDC) are investigated. It is found that GDC comes from pseudo relaxation of grain.

1. Introduction

Except for macroscopic electrical properties, microscopic mechanisms of polarization and conduction, point defect structure and the microstructure of dielectrics can be obtained also by dielectric spectrometer [1–9]. Therefore, it becomes more and more important for today's dielectric physics to realize the fine representation of dielectric properties and to reveal the inherent physical meanings of dielectric representation methods [9].

Generally speaking, there are four representation methods of dielectric properties, including dielectric spectroscopy (DS), impedance spectroscopy (IS), modulus spectroscopy (MS) and admittance spectroscopy (AS) [10–12]. Although the four representation methods are equivalent in nature to each other, they focus on different sides of dielectric properties and develop along different routes. How to use them to judge a dielectric as a uniform system or a non-uniform one? How to deduce the location of a certain dielectric relaxation? How to distinguish an intrinsic relaxation from Maxwell-Wagner (MW) polarization? These are the most important problems which have to be settled before the analysis of a complex system.

Among the four representation methods, IS may be the most popular method for the scientists in different science and technology fields to analyze dielectric response of different materials [13]. The interpretation of IS experimental data is usually realized by the distribution of relaxation time (DRT) method or equivalent circuit (EC) method. Since DRT method is related to IS data via a Fredholm integral equation, the problem of DRT is intrinsically an ill-posed inverse problem that the solution may be strongly unstable depending on experimental errors or even numerical truncation errors [14,15]. Although many solutions have been proposed to obtain the distribution of relaxation time [16–22] or restrain experimental errors [23,24], the correspondence of DRT results to

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structural characteristics of the material is indirect. For a complex system, the first problem have to be solved is the number of phases in the system. As for EC method, it is a direct approach and lots of structural information can be learned from it.

In this paper, fundamental principles of IS analysis by EC method is discussed in detail. It is found that an extra relaxation peak appears at low frequency limit in IS, which is induced by DC conductivity. Furthermore, for high loss dielectric with tanδ>1, two relaxation peaks appears which correspond to only one relaxation. If dielectric properties are shown with Cole-Cole equation, only one Cole-Cole arc forms for every phase. Therefore, the number of phases can be obtained easily with IS. As an application, dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics (CCTO) with giant dielectric constant are discussed. Although CCTO ceramics have been investigated by many kinds of methods [25–29], the origin of GDC is not clear so far for the complexity of crystal structure [30–37].

2. Theoretical analysis

2.1. Impedance spectroscopy or specific impedance spectroscopy for a uniform system

In order to analyze dielectric properties of dielectric, simple physical models of parallel circuit of resistance and capacitor are often used. According to this model, dielectric properties of a uniform system can be shown in IS as follows

$$Z' = \frac{R}{1+\omega^2R^2C^2} = \frac{R}{1+\omega^2\tau_P^2} \quad (1)$$

$$Z'' = R\frac{\omega RC}{1+\omega^2R^2C^2} = R\frac{\omega\tau_P}{1+\omega^2\tau_P^2} \quad (2)$$

where R and C are the resistance and capacitor of the dielectric respectively, ω is angle frequency, $\tau_p = RC$ is circuit responding time. In consideration of relaxation conductivity g and DC conductivity γ at the same time, τ_p can be expressed as

$$\tau_P = RC = \rho\frac{l}{S}\frac{\varepsilon_0\varepsilon' S}{l} = \rho\varepsilon_0\varepsilon' = \frac{\varepsilon_0\varepsilon'}{\gamma+g} = \frac{\varepsilon_0\varepsilon'}{\omega\varepsilon_0\varepsilon''} = \frac{1}{\omega\tan\delta} \quad (3)$$

where ε_0 is permittivity of free space, ε' and ε'' are real and imaginary parts of permittivity respectively, ρ is resistivity, l is the thickness, S is electrode area and tanδ is loss tangent. It is clear from Eqn. (2) that a relaxation peak will appear in Z''-f curve when $\omega\tau_p = 1$. This condition is equivalent to that tan$\delta = 1$. For a dielectric relaxation with $(\tan\delta)_m > 1$, there will be two frequency points corresponding to tan$\delta = 1$. In this case, two relaxation peaks will be observed in Z''-f curve which correspond to only one relaxation process. At low frequency limit, DC conductance is the main process and dielectric relaxation can be ignored, then IS can be shown as

$$Z' = \frac{R_0}{1+\omega^2R_0^2C_0^2} = \frac{R_0}{1+\omega^2\tau_{P0}^2} \quad (4)$$

$$Z'' = R_0\frac{\omega R_0C_0}{1+\omega^2R_0^2C_0^2} = R_0\frac{\omega\tau_{P0}}{1+\omega^2\tau_{P0}^2} \quad (5)$$

where R_0 and C_0 are DC resistance and geometric capacitance respectively and τ_{p0} is

$$\tau_{p0} = R_0C_0 = \frac{\varepsilon_0\varepsilon_s}{\gamma} \quad (6)$$

It can be known from Eqn. (5) that a peak will appear in Z''-f curve at low frequency limit when $\omega\tau_{p0} = 1$. This implies that DC conductivity can induce a peak in IS, which is called pseudo relaxation peak in this paper. Therefore, for a uniform system with n kinds of dielectric relaxations, $2n$+1 relaxation peaks may be obtained at most by IS.

What is the relationship between circuit responding time τ_p and dielectric relaxation time τ? If DC conductivity can be ignored, we have

$$\omega\tau_P = \frac{\varepsilon_s+\varepsilon_\infty\omega^2\tau^2}{(\varepsilon_s-\varepsilon_\infty)\omega\tau} \quad (7)$$

According to Eqn. (7), a relaxation peak in Z''-f curve will be observed when the following condition is satisfied

$$\frac{\varepsilon_s+\varepsilon_\infty\omega^2\tau^2}{(\varepsilon_s-\varepsilon_\infty)\omega\tau} = 1 \quad (8)$$

The premise of real solution of the equation above is that $k = \varepsilon_s/\varepsilon_\infty > 3+2\sqrt{2}$. Under this condition, we have $\omega\tau = [(k-1)\pm\sqrt{k^2-6k+1}]/2 > 1$. This implies that relaxation peak in IS moves to high frequency compared with that in DS. However, no relaxation peak will be observed in IS if $k = \varepsilon_s/\varepsilon_\infty < 3+2\sqrt{2}$.

IS can be shown in the form of Cole-Cole equation as follows

$$Z''^2 + \left[Z' - \frac{1}{2(G_0+G_r)}\right]^2 = \left[\frac{1}{2(G_0+G_r)}\right]^2 \quad (9)$$

where G_0 and G_r are DC conductance and relaxation conductance respectively. When no dielectric relaxation exists the equation above represents a standardized circular arc with radium of $R_0/2$ and the center at $(R_0/2, 0)$. However, if one or more dielectric relaxation exists in the system, the Cole-Cole arc is no longer a circular one for the variation of effective conductance with frequency. The arc varies with frequency gradually form the circle defined by DC resistance R_0 to the circle defined by dielectric relaxation process. Whether the arc is circular or not, the intersection points at Z' axis are $(0, 0)$ and $(R_0, 0)$. From this information, DC conduction process can be learned. Based on the analysis above, it can be concluded that only one Cole-Cole arc can be formed for every phase no matter how many dielectric relaxations exist in the phase. How many phases in a complex non-uniform system is the most important problem which has to be solved when we are facing a complex uniform system. With the help of IS, the problem is solved conveniently. The number of phases can be deduced from the number of Cole-Cole arcs.

In fact, for a uniform system with dielectric relaxations, IS as shown in Eqns. (1) and (2) are not a convenient tool for the variation of R with frequency. In order to learn the intrinsic characteristics of dielectric, the influence of physical dimension has to be removed. After the elimination of physical dimension from IS, specific impedance spectroscopy (SIS) can be expressed as follows

$$z' = \frac{1}{\omega\varepsilon_0}\frac{\varepsilon''}{\varepsilon'^2+\varepsilon''^2} \quad (10)$$

$$z'' = \frac{1}{\omega\varepsilon_0}\frac{\varepsilon'}{\varepsilon'^2+\varepsilon''^2} \quad (11)$$

At low frequency limit, the influence of dielectric relaxation can be ignored and SIS can be expressed as