# Physical meaning of conductivity spectra for ZnO ceramics*

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(Received 11 January 2012; revised manuscript received 3 March 2012)

With the help of broadband dielectric spectroscopy in a wide temperature and frequency range, conductivity spectra of ZnO polycrystalline ceramics are measured and direct-current-like (DC-like) conductivity and relaxation polarization conductivity are observed successively along the frequency axis. According to classical Debye theory and Cole–Cole equation, the physical meanings of the two conductivities are discussed. It is found that the DC-like conductivity corresponds to electron transportation over Schottky barrier at grainboundary. The relaxation polarization conductivity corresponds to electronic trap relaxation of intrinsic point defects (zinc interstitial and oxygen vacancy). When it is in the high frequency region, relaxation conductivity obeys the universal law with the index $n$ equal to the index $\alpha$ in Cole–Cole equation as an indictor of disorder degree.

**Keywords:** ZnO ceramics, conductivity spectra, Schottky barrier, relaxation polarization

**PACS:** 72.20.–i, 73.30.+y, 77.22.Gm, 77.55.hf **DOI:** 10.1088/1674-1056/21/9/097201

## 1. Introduction

Two kinds of charges exist in materials, one is free charge, and the other is bounded charge. It is believed that the former corresponds to DC conduction through the body from one electrode to the other, while the latter corresponds to relaxation polarization between two equilibrium positions. Recently, the so-called hopping conduction was investigated extensively and the internal relationship between conduction and relaxation polarization was recognized. Since free charge is activated from localized state to conduction band or valence band by the stimulation of temperature, free charge and bounded charge are the same in nature. In fact, the excitation of bounded charge is an electrical relaxation process with a time constant $\tau$, accompanied by a distortion of polarized electron cloud. If the time period of the applied electrical field is far shorter than $\tau$, the effect of the applied field on relaxation polarization averages out. For a far longer time period than $\tau$, the relaxation of the polarization cloud is in phase with the applied electrical field. In this case, the field supports the propagation of charge transport. In the case that the time period of the applied electrical field is near to $\tau$, relaxation polarization is expected to be observed. Hence, there exists an internal relationship between conduction process and polarization process. Although some important results have been obtained,[1−6] such as universal law for hopping conductivity, investigations of conductivity and polarization are habitually separated apart intentionally and the correlation of them is not clear now.

In this paper, conductivity spectra of ZnO varistor ceramics are analysed and DC-like conduction and relaxation polarization conduction are identified. An interesting phenomenon is found that relaxation polarization behaves as hopping-like conductivity following the universal law in high frequency region. According to classical dielectric theory, the origins of DC-like conduction and relaxation polarization conduction in conductivity spectra are discussed. In the end, the physical meaning of the index $n$ in the universal law for hopping-like conductivity is explained.

*Project supported by the Scientific Research Plan of the Education Department of Shaanxi Province, China (Grant No. 12JK0434) and the Doctoral Scientific Research Foundation, China (Grant No. BS0814).

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## 2. Experiment

Zinc oxide polycrystalline ceramics were prepared by traditional electronic ceramic process and sintered at 1150 °C for 2 h. The formula of ZnO polycrystalline ceramics is composed of $Bi_2O_3$, $Sb_2O_3$, $Co_2O_3$, $Cr_2O_3$, and $MnO_2$. The percentages of these dopants are all 0.5 mol%. The finally formed samples are of disks each with a diameter of 10 mm and a thickness of about 2 mm. Gold is sputtered on both sides of the samples as electrodes for electrical measurement. The dielectric properties were measured using a Novocontrol broadband dielectric spectrometer with an Alpha-A high performance frequency analyzer in a frequency range of 0.1 Hz–0.1 MHz. The measurement temperatures were in a range of from −160 °C to 200 °C in steps of 10 °C.

## 3. Results and discussion

Conductivity spectra of ZnO ceramics at different temperatures are shown in Fig. 1 within a frequency range from 0.1 Hz to 0.1 MHz. It is clearly observed that a DC-like conductivity appears in a low frequency region when temperature is higher than 90 °C, which is called low frequency dispersion.[2−4] In a high frequency region, the linear increase of hopping-like conductivity with frequency (double logarithmic coordinates) can be observed clearly as predicted by the universal law.[2−6] However, as is well known, the universal law is applicable to an extreme disorder glass-like system, so high frequency conductivity for a common polycrystalline ceramics needs to be investigated. If the measurement temperature is low enough, step-like effective conductivity introduced by relaxation polarization can be spotted. According to the activation nature of relaxation polarization, the relaxation peak will appear between low frequency DC-like conductivity and high frequency hopping-like conductivity as shown in Fig. 1. The little distortion of the step in Fig. 1 is introduced by the high frequency hopping-like conductivity. With the increase of measurement temperature, relaxation polarization shifts toward high frequency region and is submerged by hopping-like conductivity.

According to the Debye theory, the total conductivity can be expressed as $\sigma' = \sigma_{\rm DC} + g_{\rm r}$, where $\sigma_{\rm DC}$ is DC conductivity and $g_{\rm r}$ is relaxation polarization conductivity. Considering that only very few systems show ideal Debye-like relaxations,[7] relaxation polarization conductivity should be expressed according to Cole–Cole equation, so the total conductivity is expressed as follows:

$$\sigma' = \sigma_{\rm DC} + \frac{\varepsilon_0(\varepsilon_{\rm s} - \varepsilon_\infty)\cos(\pi\alpha/2)\omega^{2-\alpha}\tau^{1-\alpha}}{1 + 2(\omega\tau)^{1-\alpha}\sin(\pi\alpha/2) + (\omega\tau)^{2(1-\alpha)}}, \tag{1}$$

where $\alpha$ is an index indicating distribution degree of relaxation time. The value of $\alpha$ is in a range of 0–1.

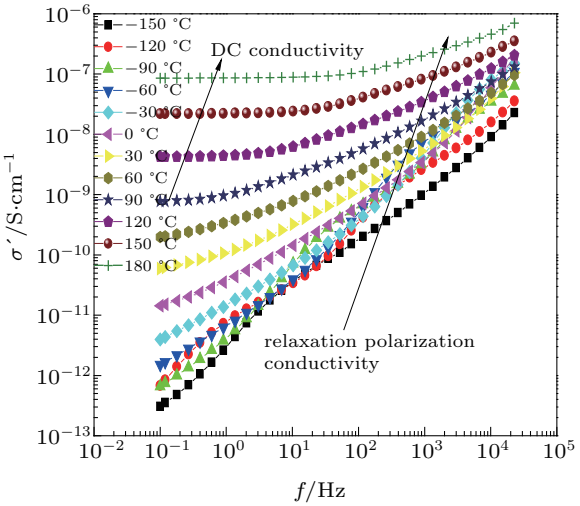



**Fig. 1.** (colour online) Conductivity spectra of ZnO ceramics at different temperatures. Two different regions can be indentified as shown in the figure.

When the temperature is higher than 90 °C, relaxation polarization conductivity can be ignored at low frequency, for $\omega\tau$ is far less than 1 and DC conductivity becomes the most important part in total conductivity. The DC conductivity activation energy refers to the energy needed for a charged carrier to overcome the highest barrier along its way through a sample from one electrode to another. In ZnO polycrystalline ceramics, the most difficult process is electron emission across a Schottky barrier at grain-boundary. Hence, the activation energy of DC-like conductivity in ZnO ceramics refers to Schottky barrier height at grainboundary.

In order to improve accuracy, the data at 0.1 Hz at higher temperature than 90 °C are chosen as DC conductivity and the corresponding activation energy is obtained to be 0.77 eV as shown in Fig. 2. This value has a very good coincidence with those reported for ZnO polycrystalline ceramics. Schottky barrier height is always measured by $I$–$T$ characteristics according to thermionic emission mechanism.[8−10] However, whether thermionic emission is the most important conduction mechanism for a specific sample under experimental conditions is not clear at all. In this

paper, it is clearly shown that when the measurement temperature is higher than 90 °C, the influence of relaxation polarization can be omitted. Therefore, conductivity spectra offer a better way to measure Schottky barrier at grainboundary.

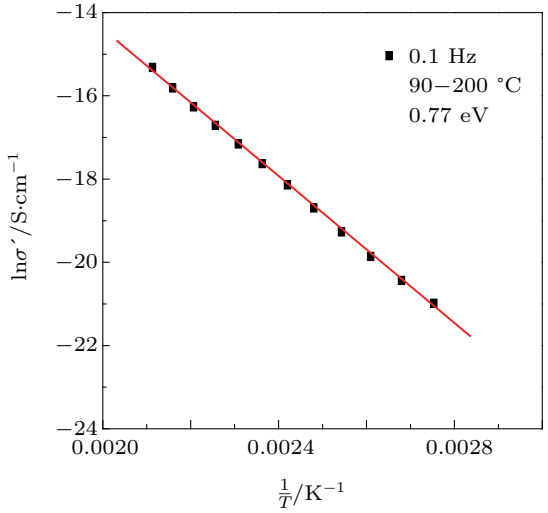



**Fig. 2.** (colour online) DC conductivity activation energy of ZnO ceramics. The data are chosen from the conductivity value at 0.1 Hz when the temperature is higher than 90 °C.

When measurement temperature decreases enough, the DC conductivity decreases more rapidly than the relaxation polarization conductivity for its bigger activation energy. In this case, conductivity peaks of relaxation polarization will rise up in the curve of $\sigma'$–$T$ as shown in Fig. 3. If we omit DC conductivity in Eq. (1) and let the derivative of conductivity with respect to $\omega\tau$ equal 0, while in the condition that the relaxation polarization conductivity comes to its maximum value, let $\omega\tau$ equal 1. According to the slope of the curve of $\ln(1/f_{\rm m})$–$1/T$, where $f_{\rm m}$ is the frequency of the conductivity peak in Fig. 3, the activation energy for the two peaks are obtained to be 0.22 eV and 0.35 eV, respectively.

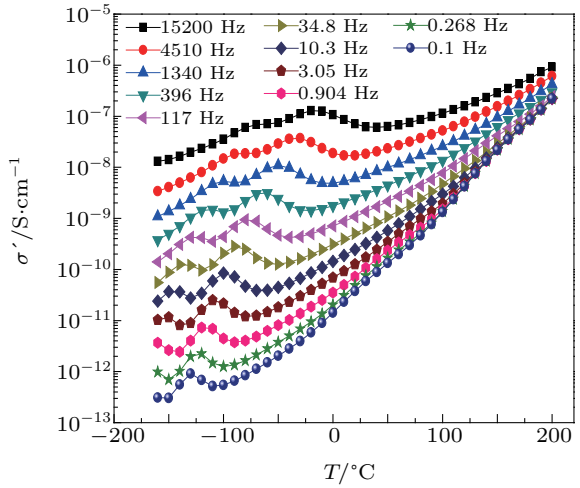



**Fig. 3.** (colour online) Temperature spectra of conductivity at different frequencies. Two conductivity peaks can be observed clearly, which correspond to electronic trap relaxations of intrinsic donor defects of zinc interstitial and oxygen vacancy in ZnO, respectively.

Defect structure, especially intrinsic defect structure of ZnO has been investigated widely and deeply, of which the most convenient method is developed by dielectric spectroscopy.[11,12] This method is very similar to our method here. If we transform this figure of $\sigma'$–$T$ into a figure of $\varepsilon''$–$f$ at different temperatures, the dielectric loss peaks are sharper as shown in Fig. 4. The peaks in Fig. 4 correspond to the peaks in Fig. 3 exactly. According to Refs. [11] and [12], the two loss peaks in Fig. 4 come from the electronic trap relaxation process of intrinsic point defects of ZnO. The corresponding activation energies are 0.22 eV and 0.35 eV for zinc interstitial and oxygen vacancy, respectively. Therefore, the peaks in curve of $\sigma'$–$T$ as shown in Fig. 3 origin from intrinsic defects of ZnO. Once Schottky barrier height and defect structure of ZnO have been obtained from the conductivity spectra, more accurate theory results about electronic structure at grainboundary will be obtained.[12]

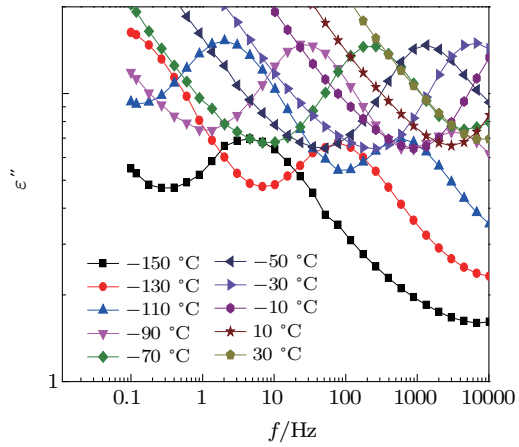



**Fig. 4.** (colour online) Dielectric frequency spectra of ZnO polycrystalline ceramics at different temperatures. The sharp dielectric loss peaks are attributed to electronic trap relaxation of zinc interstitial and oxygen vacancy, respectively.[11,12]

At high frequency limit for relaxation conductivity, namely for the case that $\omega\tau$ tends to be infinite, another equation can be obtained from Eq. (1) as

$$\sigma' = \varepsilon_0(\varepsilon_{\rm s} - \varepsilon_\infty)\cos(\pi\alpha/2)\tau^{\alpha-1}\omega^{\alpha}. \qquad (2)$$

It is clear that in the high frequency region the conductivity obeys the universal law in the expression of $\sigma' = A\omega^n$, where index $n$ is replaced with $\alpha$. For an

ordered system, high frequency relaxation conductivity tends to be a constant as predicted by the Debye theory for the case that $\alpha$ is zero. While for a disordered system, $\alpha$ is in a range of 0–1, and relaxation conductivity will obey the universal law as shown in Fig. 1. From Eq. (2), it is clear that the index $n$ in the universal law is an indicator of disorder degree as index $\alpha$ in Cole–Cole equation.

## 4. Conclusion

In the present paper, conductivity spectroscopy is a powerful and useful tool because that DC behaviours and dielectric relaxation characteristics can be obtained in different frequency regions at the same time. According to classical Debye theory and Cole–Cole equation, the DC conductivity and relaxation polarization conductivity are identified clearly in the conductivity spectra. It is found that, for a practical material with disorder degree less than 1, high frequency relaxation conductivity obeys the universal law with index $n$ equal to $\alpha$ in Cole–Cole equation.

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