Solid State Communications 149 (2009) 2017–2020

Contents lists available at ScienceDirect

Solid State Communications

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

Pseudo-relaxor behaviour induced by Maxwell–Wagner relaxation

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ARTICLE INFO

Article history:
Received 13 August 2009
Received in revised form
20 August 2009
Accepted 21 August 2009 by A. Pinczuk
Available online 29 August 2009

PACS:
77.22.-d
77.22. Ch
78.20.Bh

Keywords:
A: Semiconductors
D: Dielectric response

ABSTRACT

We performed a further investigation on the Maxwell–Wagner (MW) relaxation-induced relaxor-like dielectric response characterized by a broad peak in the real part of the dielectric permittivity as a function of temperature. Based on the double-layer MW model formulated by Catalan et al. (2000) [10], an empirical formula was derived to describe the temperature dependence of the peak intensity. It was also found that the temperature dependence of the peak position can be characterized by an Arrhenius-like relation. The differences between the true relaxor and MW-related relaxor behaviours are also discussed.

1. Introduction

Relaxor ferroelectrics (relaxors) are of significant technological and scientific interest. They are characterized by a diffuse phase transition and a strong frequency dispersion, i.e., there is a broad peak in the real part of the dielectric permittivity (ε') as a function of temperature, with the peak decreasing in magnitude and shifting to higher temperature with increasing measurement frequency; and the low-temperature side of the peak shows strong frequency dispersion, whereas the high-temperature side exhibits frequency independence [1]. These features are generally regarded as fingerprints of relaxor ferroelectrics. This assumption is made despite the indications that a relaxor-like dielectric anomaly unrelated to ferroelectric polarization can be achieved in a variety of systems, including single-crystalline materials, thin films, ceramics and composite materials. The diffuse dielectric anomaly is a very common phenomenon in the temperature range 400–900 °C in titanate perovskites [2–7]. In $CaCu_3Ti_4O_{12}$, the anomaly was even observed at as low as around 340 K [8]. On the other hand, in the temperature range below room temperature, relaxor-like dielectric behaviour was reported in many systems [9–18]. Up to now, various mechanisms have been put forward to account for the underlying physics of the relaxor-like dielectric anomaly. These mechanisms can be classified into two types. One is the dipole model, associated with different mobile defects based on the universal feature that the anomaly is very sensitive to oxygen vacancies, especially for the titanate perovskites [4–6,8,19]. The other is the MW model, associated with the electrical inhomogeneity in the tested sample [2,3,9,10]. Based on the typical double-layer MW model (see the inset of Fig. 1) containing two *RC* (R = resistance and C = capacitor) circuits in series, Catalan et al. showed that a relaxor-like dielectric behaviour can be fully replicated by simply assuming that the intrinsic permittivities were temperature independent and only the resistivities changed [10]. However, an MW-type relaxation is widely evidenced to exhibit a Debye-like dielectric behaviour, namely, the dielectric constant (ε') exhibits a characteristic frequency dispersion kink accompanied by a peak in the corresponding dielectric loss (ε''). For example, the MW mechanism is believed to be the origin of the giant dielectric constants that show a steplike decrease from a higher temperature plateau to a lower temperature plateau found in $CaCu_3Ti_4O_{12}$ in recent years [20,21]. Since the Debye-like behaviour is quite alien to the relaxor-like behaviour, this raises a pertinent question of how the MW model can account for both different behaviours? Besides, several important facts about the relaxor-like behaviour caused by MW relaxation still remain unclear: (i) What are the main features of the relaxor-like behaviour? (ii) How can we distinguish between the relaxor-like behaviour and the real relaxor behaviour?

In this communication we present a further investigation of the MW model with the aim of providing some insights into the above questions. Since the relaxor-like behaviour displays a temperature-dependent anomaly, we therefore restrict our following discussion to the temperature domain.

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doi:10.1016/j.ssc.2009.08.031

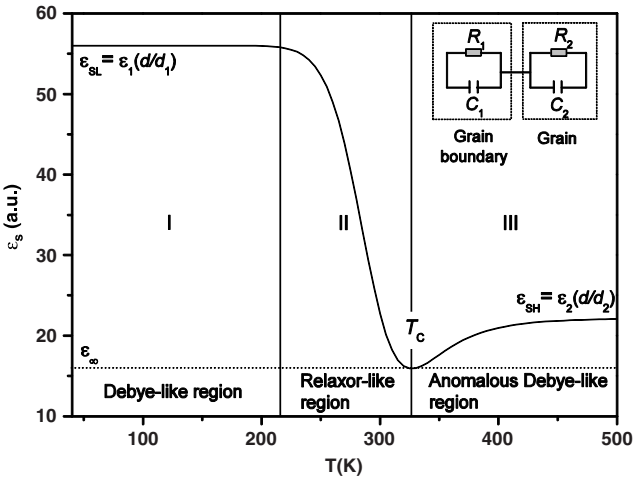

Fig. 1. The temperature dependence of ε_S calculated with the parameters $\sigma_{10} = 3.0 \times 10^{-11}$ S cm^{-1}, $E_1 = 0.98$ eV, $\varepsilon_1 = 5.6$ for the grain boundary, $\sigma_{20} = 1.0 \times 10^{-5}$ S cm^{-1}, $E_2 = 0.59$ eV, $\varepsilon_2 = 20$ for the grain, and $d_1/d_2 = 1/9$. The inset shows the double-layer model for MW relaxation.

2. Results and discussion

The real (dielectric constant, ε') and imaginary (dielectric loss, ε'') parts of the complex permittivity of the double-layer system can be characterized by the conductivities σ_i ($i = 1, 2$) (or resistivities ρ_i), permittivities ε_i (unit-free), and thicknesses d_i [9,22],

$$\varepsilon'(T) = \varepsilon_\infty + (\varepsilon_S - \varepsilon_\infty)/[1 + (\omega\tau)^2] \quad (1)$$

$$\varepsilon''(T) = d\sigma_1\sigma_2/[\omega\varepsilon_0(d_1\sigma_2 + d_2\sigma_1)] + (\varepsilon_S - \varepsilon_\infty)\omega\tau/[1 + (\omega\tau)^2] \quad (2)$$

with

$$\varepsilon_S = \varepsilon'(\omega = 0) = d(d_1\varepsilon_1/\sigma_1^2 + d_2\varepsilon_2/\sigma_2^2)/(d_1/\sigma_1 + d_2/\sigma_2)^2 \quad (3)$$

$$\varepsilon_\infty = \varepsilon'(\omega \to \infty) = d/(d_1/\varepsilon_1 + d_2/\varepsilon_2) \quad (4)$$

$$\tau = (\varepsilon_1 d_2 + \varepsilon_2 d_1)/(\sigma_1 d_2 + \sigma_2 d_1) \quad (5)$$

where $d = d_1 + d_2$, T is the absolute temperature, and ω and ε_0 are the angular frequency and the permittivity of free space, respectively. Except for an additional term (the first term in Eq. (2)) that forms an exponential increasing background with increasing temperature in $\varepsilon''(T)$, the MW relaxation follows similar relaxation equations to those of the Debye relaxation. This is the reason why the MW relaxation is always found to exhibit Debye-like behaviour. In order to describe the relaxor-like anomaly, detailed information about the temperature dependences of σ_i and ε_i is required. Following the assumptions made by Catalan et al. [10], the conductivity obeys the thermally activated law, i.e., $\sigma_i = \sigma_{i0}\exp(-E_i/k_BT)$ ($i = 1, 2$), while ε_i ($i = 1, 2$) is relatively temperature independent. Under these assumptions, $\varepsilon_\infty =$ constant; hence, the MW relaxation properties are completely dominated by ε_S and τ. As seen from Eq. (5), τ varies with temperature following a quasi-exponential relation; it increases steeply at low temperatures. In terms of $d\varepsilon_S/dT = 0$, it is easy to clarify that ε_S, as shown in Fig. 1, shows a minimum at the critical temperature (T_C), where $\varepsilon_1\rho_1 = \varepsilon_2\rho_2$. In this case, $\varepsilon_S = \varepsilon_\infty$; this means that the relaxation term in Eqs. (1) and (2) equals zero and the MW relaxation disappears. At temperatures lower than T_C, two cases should be considered: $\varepsilon_1\rho_1 > \rho_2\varepsilon_2$ and $\varepsilon_1\rho_1 < \rho_2\varepsilon_2$. The first case implies that $E_1 > E_2$, and the resistivity of the grain boundary will be greater than the resistivity of the grain at low enough temperatures; thus, ε_S can be written as [22]

$$\varepsilon_S = A_1/[B_1 + C_1\exp(-E/k_BT)] \quad (6)$$

where $A_1 = (d_1/d)\varepsilon_1$, $B_1 = (d_1/d)^2$, $C_1 = 2d_2d_1\sigma_{10}/d^2\sigma_{20}$, and $E = E_1 - E_2$. The low-temperature branch saturates at low enough temperatures with a value of $\varepsilon_{SL} = \varepsilon_1(d/d_1)$. Meanwhile, at temperatures higher than T_C, ε_s can be written as

$$\varepsilon_S = A_2/[B_2 + C_2\exp(E/k_BT)] \quad (7)$$

where $A_2 = (d_2/d)\varepsilon_2$, $B_2 = (d_2/d)^2$, $C_2 = 2d_2d_1\sigma_{20}/d^2\sigma_{10}$. The high-temperature branch achieves a saturation value of $\varepsilon_{SH} = \varepsilon_2(d/d_2)$. The low- and high-temperature saturation values define ε_∞ by the relation $1/\varepsilon_\infty = 1/\varepsilon_{SL} + 1/\varepsilon_{SH}$.

The second case ($\varepsilon_1\rho_1 < \rho_2\varepsilon_2$) simply causes the exchange of ε_{SL} and ε_{SH}. It has no effect on the discussion and the final conclusions; we therefore do not consider this case. This is also because: (1) in most practical cases, the grain boundary resistivity is much larger than that of the grain; and (2) the well-known effective permittivity of non-uniform materials, $\varepsilon_{eff} \sim \varepsilon_1(d/d_1)$, is simply the low-temperature saturation value ε_{SL}. This implies that the grain boundary actually plays a decisive role in the dielectric properties.

The dielectric constant $\varepsilon'(T)$ depends on the ratio of $(\varepsilon_S - \varepsilon_\infty)/(1 + (\omega\tau)^2) \sim \varepsilon_S/(1 + (\omega\tau)^2)$, which can be qualitatively described by a graphic method, as illustrated in Fig. 2. According to the position where the $1 + (\omega\tau)^2$ curve intersects the ε_S curve, three dielectric regions can be classified (I, II, and III, as indicated by the vertical lines in Fig. 1. ε_S is almost temperature independent in region I and decreases drastically in region II, while in region III ε_S increases with temperature following Eq. (7). We therefore have three dielectric behaviours:

(1) If the $1+(\omega\tau)^2$ curve intersects ε_S in region I [Fig. 2(a)] at the temperature θ_I, $\varepsilon'(T)$ tends to ε_S, showing a higher temperature plateau at temperatures higher than θ_I due to $\varepsilon_S \gg 1 + (\omega\tau)^2$, whereas at temperatures lower than θ_I, $\varepsilon'(T)$ tends to ε_∞, giving a lower temperature plateau due to $\varepsilon_S \ll 1 + (\omega\tau)^2$ [Fig. 2(b)]. At θ_I, one has $\varepsilon_S = 1 + (\omega\tau)^2$, i.e., $\omega\tau = \sqrt{\varepsilon_S - 1}$; thus $\omega\tau = 1$ will be achieved at a temperature somewhat higher than θ_I. In this case,$\varepsilon''(T)$, as seen from Eq. (2), will show a relaxation peak [Fig. 2(c)]. This dielectric behaviour is the well-known Debye-like behaviour; therefore, region I is termed a

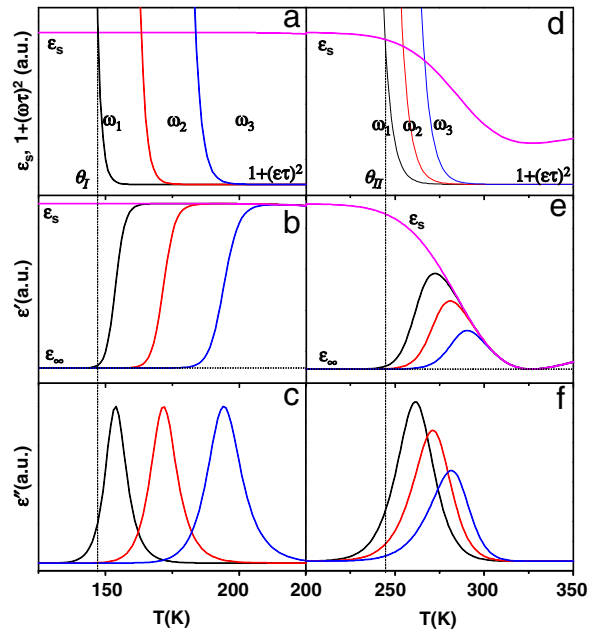

Fig. 2. Debye-like (left) and relaxor-like (right) dielectric behaviours predicated by MW relaxation. (a) and (d): The temperature dependence of ε_S and $1 + (\omega\tau)^2$ at three frequencies with $\omega_1 < \omega_2 < \omega_3$. (b) and (e): The temperature dependence of ε'. (c) and (f): The temperature dependence of ε'' without background. The dotted lines in the left and right panels indicate, respectively, the temperature θ_I and θ_{II} where the $1 + (\omega_1\tau)^2$ curve intersects the ε_S curve.