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Maxwell–Wagner relaxation in the $CaMn_7O_{12}$ perovskite

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Abstract

In this work we have measured the complex dielectric permittivity of a polycrystalline material using samples of different thickness (frequency range 20–1 MHz). The results reveal that the $CaMn_7O_{12}$ material is electrically heterogeneous as it consists of regions of different conductivities.

In this kind of electrically heterogeneous materials the variation of the dielectric permittivity as a function of temperature can be fitted to a Maxwell–Wagner model. In the case of the $CaMn_7O_{12}$ sample this model fits only partially the experimental data and we need to include three regions of different conductivities to explain the obtained dielectric response.

Keywords: Perovskites; Manganese oxides; Charge ordering; Dielectric response; Impedance spectroscopy; Maxwell–Wagner relaxation

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1. Introduction

Recently, the possible existence of alternative dielectric materials is an attractive topic, specially after the recent discovery of multiferroic materials [1,2] and the room temperature frequency independent "colossal" dielectric constant in the complex mixed-oxide $CaCu_3Ti_4O_{12}$ [3,4]. The giant dielectric constant displayed by this compound is not a bulk effect. Sinclair et al. have reported that this material is electrically inhomogeneous and comprise semiconducting grains and insulating grain boundaries that give rise to an internal barrier layer capacitor [5,6]. Lukenheimer et al. suggested that the colossal dielectric response would be due to a Maxwell—Wagner (M—W) relaxation of depletion layers at the interface between sample and electrodes or at grain boundaries [7]. Maxwell—Wagner relaxation generally refers to interfacial polarization occurring in electrically inhomogenous systems. When an electric current passes through the interfaces between two media with different conductivities, surface charges pile up at the interfaces and give rise to a Debye-like relaxation process under an external alternating voltage. This effect can be described by an equivalent circuit and has been widely used to study the dielectric relaxations in many heterogeneous materials [7,8]. Techniques such as Impedance Spectroscopy (IS) are also useful tools to determine indirectly the electrical microstructure of these heterogeneous systems [6].

In a previous paper, we have described the dielectric behavior of the manganese mixed-oxide $CaMn_7O_{12}$, which is isostructural with the $CaCu_3Ti_4O_{12}$ material [9]. From the magnetic and electronic point of view this oxide is more complex as it shows a Charge/Orbital Ordering transition at 440 K and antiferromagnetic order below 80 K [10]. Surprisingly, this compound also presents a high dielectric constant $(\varepsilon_r' > 10^4)$ at room temperature. Our studies made on samples of different particle sizes and using different types of contacts revealed that, as in the $CaCu_3Ti_4O_{12}$ sample, the extrinsic effects had a strong influence on the dielectric response obtained. By impedance spectroscopy, we have separated the intrinsic and extrinsic contributions to the dielectric constant and we have concluded that the value of the intrinsic dielectric constant is $\varepsilon_r' \sim 30$. We have related this value, relatively high for this type of compound, to the presence of the electronic process of charge ordering that this material presents at $T_{CO} = 440$ K. Extrinsic effects enhance even further the dielectric response of this material and give rise to such high dielectric constant at room temperature.

In this work, we have focused on the features that give rise to the overall behavior observed. We have attempted to fit the dielectric response of the $CaMn_7O_{12}$ sample to the Maxwell—Wagner model, finding that this model describes only partially the behavior of this material.

2. Experimental

We have used the sol-gel method to prepare $CaMn_7O_{12}$ as polycrystalline material, as described elsewhere [9]. The final sintering temperature was 950 °C and the grain size obtained was 0.6 μm.

The complex dielectric permittivity was measured with a parallel-plate capacitor coupled to a precision LCR meter Agilent 4284 A, capable of measuring frequencies ranging from 20 to 10^6 Hz. The capacitor was mounted on an aluminium box refrigerated with liquid nitrogen, incorporating a mechanism to control the temperature up to 350 K.

Two samples in the form of pellets of different thickness (1.1 and 0.65 mm, respectively) were prepared to fit in the capacitor, and gold was sputtered on their surfaces to ensure good electrical contact. In order to check the influence of the contacts, sputtered silver was also used in some measurements.

Impedance complex plane analysis of the obtained impedance data was performed using the computer program LEVM [11].

3. Results

In Figs. 1(a) and 2(a), we show the ε'_r vs temperature curves obtained for the two samples at several frequencies. Fig. 1(a) refers to the pellet of thickness 1.1 mm and Fig. 2(a) to that of 0.65 mm. As it can be seen in both figures, after an initial slight increase that gives rise to a broad shoulder (peak 1), ε'_r increases by various orders of magnitude (peak 2). These two

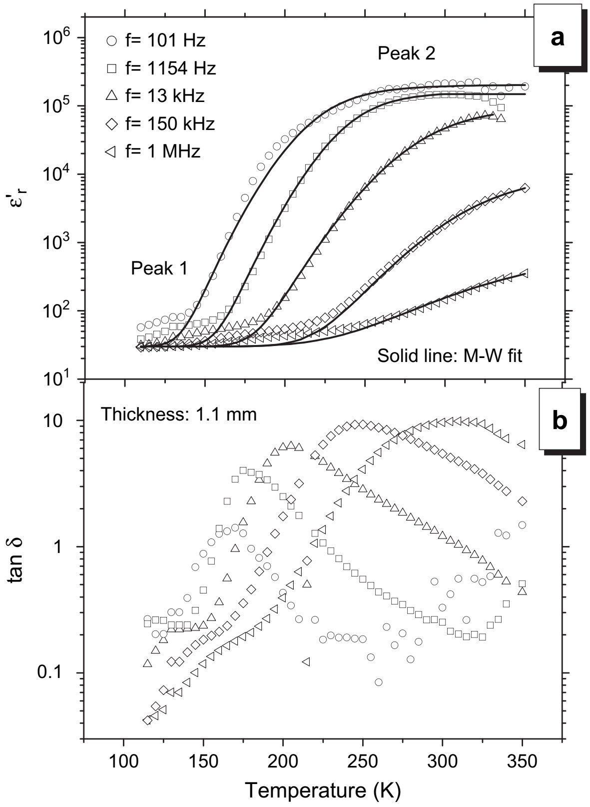

Fig. 1. (a) ε'_r vs T curve obtained at several frequencies for the sample of thickness 1.1 mm. The solid lines represent the fit to the M–W model. (b) Corresponding tan δ vs T curve.

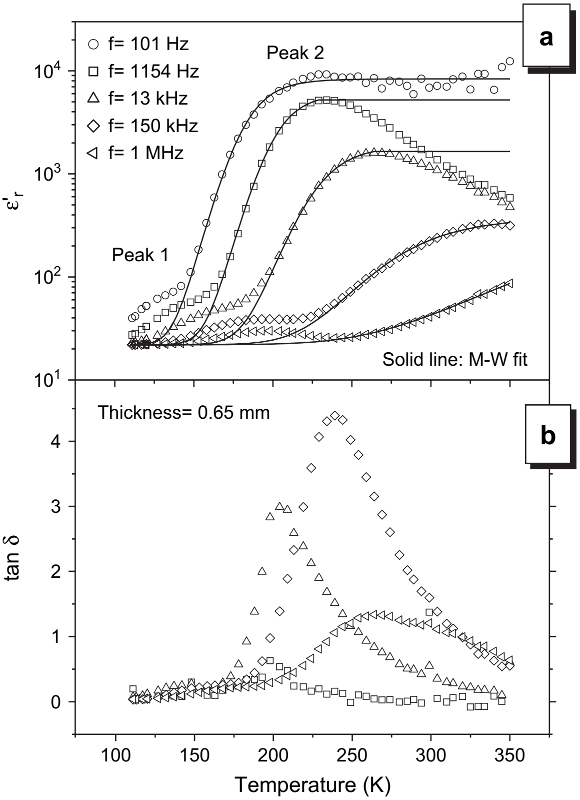

Fig. 2. (a) ε_r' vs T curve obtained at several frequencies for the sample of thickness 0.65 mm. The solid lines represent the fit to the M–W model. (b) Corresponding tan δ vs T curve.

step-like features shift to higher temperatures as frequency increases, displaying a typical relaxor behavior.

As we indicate in these figures the solid lines represent the fit to the Maxwell–Wagner expression for the real part of the dielectric permittivity:

$$\varepsilon_r' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2}$$

In this expression ε_∞ is the value of the dielectric constant at high frequency, ε_s is the value of the dielectric constant at low frequency, ω is the angular frequency and τ is the relaxation time.

In both cases the calculated data fit only partially the experimental data.

In Figs. 1(b) and 2(b), we show the tan δ vs temperature curves of the samples. As it can be seen, the loss tangent curves also show two peaks correlated with the increases in $\varepsilon_r'(T)$.

We have analyzed the shifts of the two maxima as a function of frequency and in both cases we found that they follow an Arrhenius law $\nu = \nu_0 \exp(E_a/k_BT)$. In both samples the obtained E_a values were ≈ 85 meV for peak 1 and ≈ 115 meV for peak 2. As an example we show in Fig. 3 the results obtained for the sample of thickness 0.65 mm.

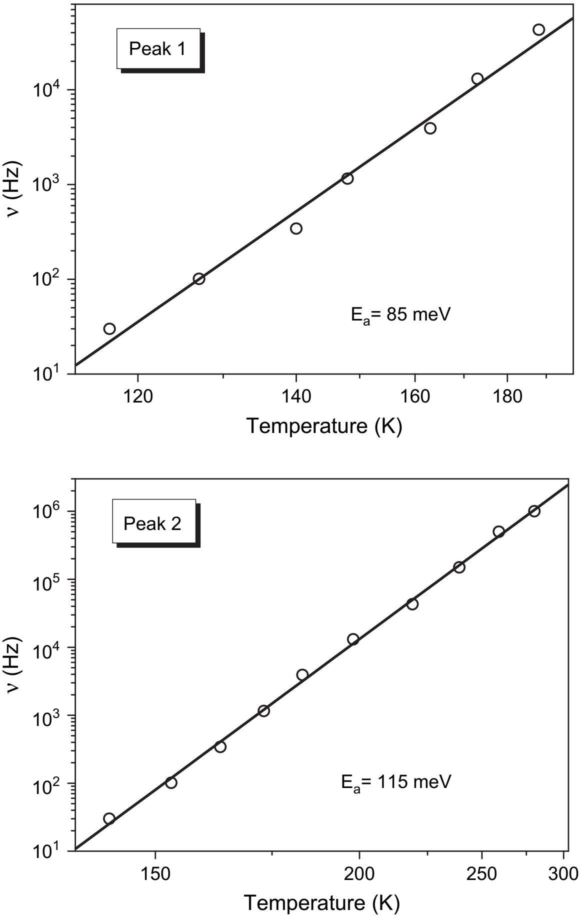

Fig. 3. Example of the Arrhenius plot of the shift of the two peaks as a function of frequency (sample of thickness 0.65 mm).

Also, we have to note that the temperatures at which the two maxima appear are independent of the pellet thickness; meanwhile, the ε'_r value of peak 2 is higher for the thickest sample.

In order to understand the dielectric behavior of this material IS analysis was carried out. Both samples showed very similar results. In Fig. 4 we show as example some impedance complex plane plots obtained for the sample of thickness 1.1 mm. Three different representative temperature intervals found were as follows:

- For $T \leq 180$ K the data give rise to an arc that intercepts the coordinates' origin (Fig. 4(a)). The large arc can be modeled by an equivalent circuit containing three elements connected in parallel: a resistance (*R*) and a capacitance (*C*) that are frequency independent, and a frequency-dependent distributed element (DE).
- In the temperature range $180 \leq T$ (K) ≤ 280 there are two arcs and one of it intercepts the coordinates' origin (Fig. 4(b)). The impedance complex behavior of these samples can be modeled by an equivalent circuit consisting of two parallel RC elements connected in series to a third element with an *R*, *C* and DE connected in parallel.

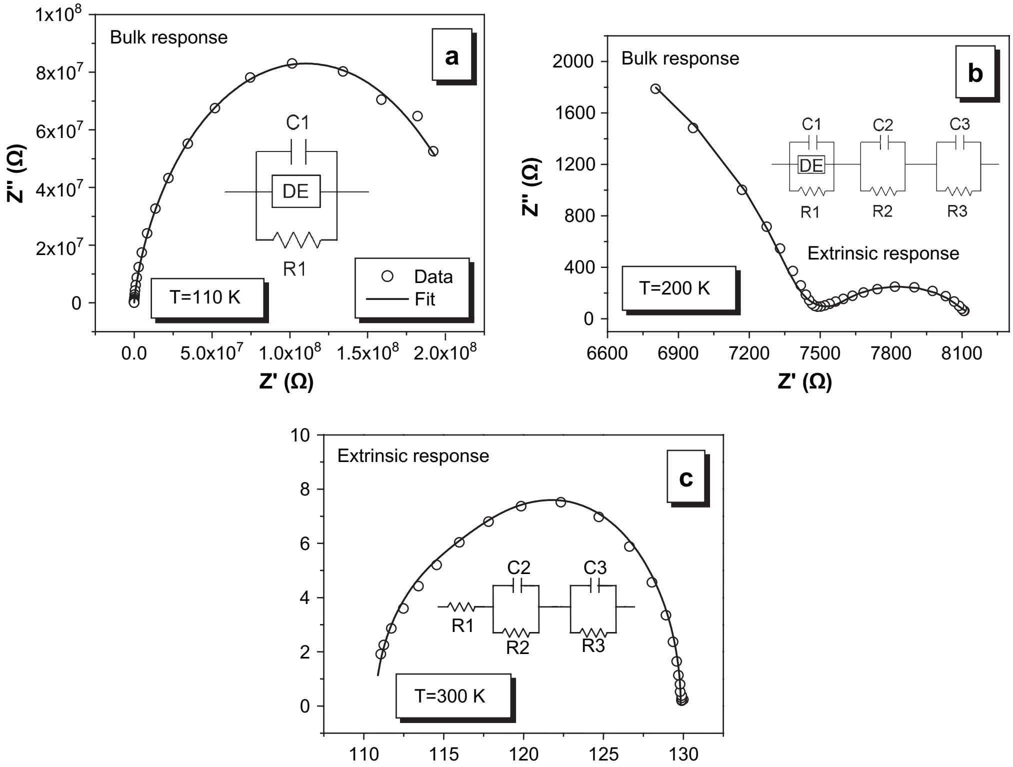

Fig. 4. Impedance complex plane plots and equivalent circuits obtained for the $CaMn_7O_{12}$ compound (sample of thickness 1.1 mm) at three different representative temperatures (110, 200 and 300 K).

- For $T \geq 280$ K the diagrams only show an asymmetric arc that does not intercept the origin (Fig. 4(c)). This plot can be modeled with two RC elements connected in series and one *R*.

4. Discussion

To explain the dielectric response of the $CaMn_7O_{12}$ compound we have applied the Maxwell–Wagner model that explains the dielectric behavior of electrically inhomogenous materials, as the $CaCu_3Ti_4O_{12}$ sample. In this case, as shown in Figs. 1(a) and 2(a), this model cannot explain the $\varepsilon_r'(T)$ plots in the whole temperature range studied. The model fits the pronounced increase of ε_r', but it does not explain the smaller and broad shoulder that appears at lower temperatures.

The impedance complex plane plots reveal that at lower temperatures $T \leq 180$ K, the arc obtained intercepts the zero, so it seems to be associated with the material bulk response [12]. For temperatures $T > 180$ K, in the low frequency range a new arc appears, which is associated with extrinsic contributions like grain boundaries or electrode effects. Analyzing the IS plot with the computer program LEVM, we have found out that this arc needs two RC elements connected in series to be modeled. This fact indicates that the extrinsic response is due to two different contributions that could be grain boundaries (GB) and Schottky barriers (SB) due to electrode effects.

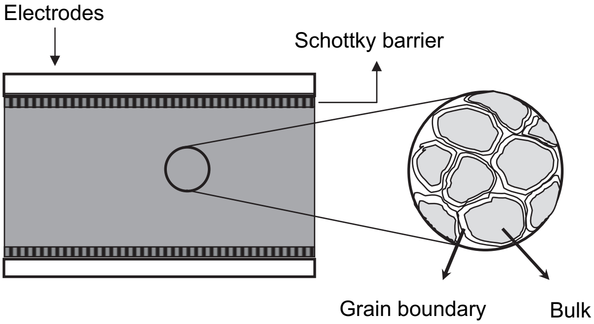

Fig. 5. Schematic representation of the three different regions proposed to explain the dielectric behavior obtained for this compound.

For the $CaCu_3Ti_4O_{12}$ sample, Sinclair et al. [5] have observed by IS two inhomogenous regions: insulating grain boundaries and a semiconducting bulk. In the $CaMn_7O_{12}$ sample, the IS reveal three inhomogenous regions: an insulating bulk, semiconductive grain boundaries and semiconductive Schottky layers (see Fig. 5). In this case, the bulk is more insulating than the grain boundaries, probably due to the fact that the charge ordered state that is present in the bulk of the material is destroyed in the grain boundaries.

Another important difference with the $CaCu_3Ti_4O_{12}$ compound is the presence of two different contributions in the extrinsic factors. This fact explains why the $\varepsilon_r'(T)$ curves cannot be fitted with the M–W model in the whole temperature range studied, in which only two regions of different conductivities are considered. Then, we relate the two step-like features observed in the ε_r' vs temperature curves to GB and SB contributions. To assign the nature of each peak, we compare the results of the experiments done changing only one parameter (Schottky layer or grain boundaries). The pellet thickness changes the number of grain boundaries without changing the Schottky layers. In this case, we have observed changes in the value of peak 2 but not in the value of peak 1. Also, we have changed the nature of the electrode. In Fig. 6, we show the ε_r' vs temperature curve at different frequencies of pellets with Ag and Au

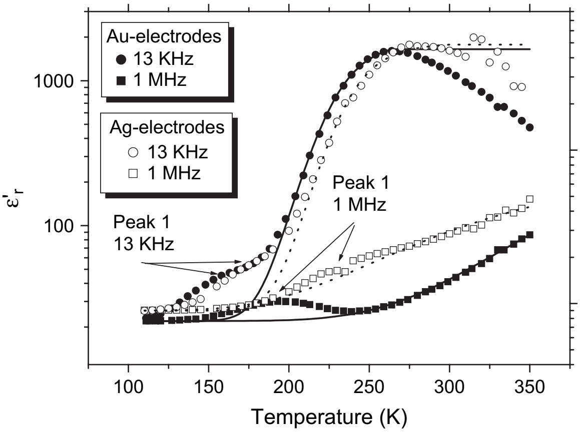

Fig. 6. Examples of ε_r' vs T curves obtained at 13 KHz and 1 MHz using two different electrode contacts: sputtered gold and sputtered silver (sample of thickness 0.65 mm).

electrodes. We observe that depending on the nature of the electrode the temperature at which the peaks appear changes. Both results indicate that peak 1 may be due to Schottky barriers and peak 2 may be due to grain boundaries.

In addition, we have already indicated that peaks 1 and 2 are shifted to higher temperatures as frequency increases. This fact reminds of the typical Debye relaxor state [13] in which dipolar entities that possess more than one equivalent orientation undergo dielectric relaxation in an applied ac field. In this case the dipolar entities may be surface charges at the interfaces, sample–electrode and bulk–grain boundary. The strong frequency dispersion in $\varepsilon_r'(T)$ on the low-temperature sides of the maxima is associated with the slowing down of these dipolar fluctuations. In our case, these shifts follow also an Arrhenius law $\nu = \nu_0 \exp(E_a/k_B T)$, as it can be seen in Fig. 3.

In summary, we have studied the ε_r' vs T curves of the $CaMn_7O_{12}$ sample with different thickness and electrode contacts. In combination with the IS analysis, we have found out that the sample contains at least three electrically inhomogeneous regions: bulk, grain boundaries and Schottky layers.

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