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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

Contents

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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.