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Article

Dielectric Properties of $La_{0.4}Ca_{0.6}Mn_{0.4}Ti_{0.6}O_3$ Ceramic Oxide

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ABSTRACT

The dielectric properties of $La_{0.4}Ca_{0.6}Mn_{0.4}Ti_{0.6}O_3$ ceramic oxide was investigated under various temperatures. A Debye-like behaviour was observed although the dc conduction effects at low frequencies almost overlapping the relaxation peak in the imaginary part. This feature of dielectric behaviour was explained using trapping mechanism. An equivalent circuit modeling was proposed to represent the electrical behaviour of this sample using universal capacitor, $C^*(\omega) = B(i\omega)^{n-1}$. The circuit modeling is consisting of two series of dispersive capacitors in parallel with conductance and high frequency capacitance.

| Dielectric properties | Ceramic | Universal capacitor |

1. Introduction

A Debye-like behaviour in ceramic samples is widely observed and reported to possess high dielectric property at low frequency region, typically below microwave region, e.g. $(Ca_{0.25}Cu_{0.75}TiO_3)_4$ (CCTO) being reported to show a colossal dielectric properties ~ 10,000 (1 kHz) at room temperature [1,2]. However, this property is due to the grain boundaries effect [3] which differs to that of the bulk property $BaTiO_3$ and no ferroelectric character have been found [4]. With this properties, CCTO has opened a new dimension for fabricate on of new barrier layer capacitors. Recently, a cubic structure (Pm-3m) of manganate-base doped with 60% of Ti, $La_{0.4}Ba_{0.4}Ca_{0.2}Mn_{0.4}Ti_{0.6}O_3$ has been reported [5]. It shows an unusual high dielectric constant (6980 at 1 kHz) and coupled with the long-range magnetic interaction. However, the magnetic property detected is very small and required high magnetic field which is not significantly and compatible to be measured. In further investigation of the origin of the high dielectric constant is due to the grain boundary effect and not from the intrinsic bulk effect arising from hopping conduction between Mn^{3+} and Mn^{4+} [6].

The approach with immitance spectroscopy (IS) analysis by plotting the data in a variety of complex plane formalisms, e.g., capacitance, C*, impedance, Z*, or spectroscopic plots of the real and/or imaginary components are very useful either physically and/or electrochemically. The information that obtained from IS analysis can be used to model the electrical properties via equivalent circuit modeling. Experimentally, the ac electrical data obtained can not be represented by a simple RC circuit's due to the complexity properties of the material under investigation. Thus, a dispersive response are used consist of universal capacitor. The universal capacitance, $C^*(\omega)$ equation can be expressed mathematically as complex capacitance with relation,

$$C^*(\omega) = B(\omega)^{n-1}[\sin(n\pi/2) - i\cos(n\pi/2)] \quad (1a)$$
$$= C'(\omega) - iC''(\omega) \quad (1b)$$

where B is constant, ω is angular frequency and n is the values from 0 to 1 [7]. For single dispersive processes of bound quasi-free charges, the response model required two universal capacitors arrange in parallel. One of it, the n-1 is replace with $-p$ and is given by

$$C(\omega) \propto C_o(i\omega/\omega_c)^{-p} \qquad \omega \ll \omega_c \quad (2)$$

and

$$C(\omega) \propto C_o(i\omega/\omega_c)^{n-1} \qquad \omega \gg \omega_c \quad (3)$$

where ω_c is the characteristic frequency [8,9,10]. Usually the low frequency conductance, G with high frequency capacitance, C_{inf} is added in parallel with the universal capacitor response. To represent the grain boundary and bulk regions, the electrical model are consisting of three parallel elements arrange in series.

In this article, the dielectric properties of $La_{0.4}Ca_{0.6}Mn_{0.4}Ti_{0.6}O_3$ sample under applying frequency and temperature are examined and the results of complex capacitance are presented in normalize form. An electrical model is also presented based on the normalized complex capacitance data.

2. Methodology

$La_{0.4}Ca_{0.6}Mn_{0.4}Ti_{0.6}O_3$ (LCMT) sample was prepared by the conventional solid state reaction technique. A stoichiometric amount of La_2O_3, CaO, MnO_2 and TiO_2 were thoroughly mixed for 24 hours. The dried mixed powders were then calcined at 950°C and fired at 1300°C for 72 hours with three times of intermediate grinding. Finally, the powders were pressed into pellets at a pressure of 6 tons and sintered at 1300 °C for 3 hours. The analyzed x-ray powder diffraction (XRD) data shows a single phase with tetragonal form. The pellet samples were polished on both sides to get flat surfaces and coated with silver paste and dried at 100 °C before the dielectric measurement is conducted using an impedance analyzer (HP 4192A LF, Hewlett Packard, USA) ranging from 5 Hz to 1 MHz at -125°C up to 125°C with increment of 25°C.

3. Results and Discussion

Normalized plots of the complex capacitance of LCMT sample against frequency from (a) -125 to -50°C and (b) -25to 125 °C are shown in Figure 1. The locus of the normalization for (a) and (b) are -50 °C and 125 °C respectively. The advantage of plotting data in normalized form gives a broad picture of the dielectric behaviour instead of obtaining the activation energy from the shifted data. Roughly, the shape of the curve in Figure 1(a) resembles a Debye-like behaviour where the peak wings $\omega > \omega_p$ of the imaginary curve gives the gradient of 0.95 (1 for Debye). At relative low frequencies, the peak wings $\omega < \omega_p$ is dominated by dc conduction as the reflection of conductance, G with gradient -1. Both of the normalized data have the plateaus magnitude of ~8.8 nF and ~63 pF, at low and high frequencies respectively, and with small gradient ~ - 0.03 and ~ -0.11. The high capacitance plateau is known as grain boundary effect whiles the lower plateau of C' is due to the bulk effect. The gradient of G/ω below ω_c at the grain boundary region is -1 and - 0.95 at bulk region.

As mentioned earlier, the high frequencies capacitance curve is weakly dependent with frequency with gradient -0.11 whereas high frequencies capacitance is respond independently with frequency. Moreover, the bound charge response only suitable for dipolar materials and certainly not in the ceramic materials that consisting of grain and grain boundary. Since, this sample is dominated by electronic carrier and has semiconducting properties, the Debye-like behaviour arising might be due to the electrons from Mn^{4+} in the trap process. In this process, the charges making transitions between localized levels act as a manner similar to the dipoles turning abruptly between preferred positions and since these transitions are delayed with respect to the exciting signal they register as a complex permittivity [11]. The proposed equivalent circuits modeling response is consisting of two quasi-dc response in series (that differ with the Debye-like) were the quasi-dc response is in parallel with the conductance and high frequencies capacitance.

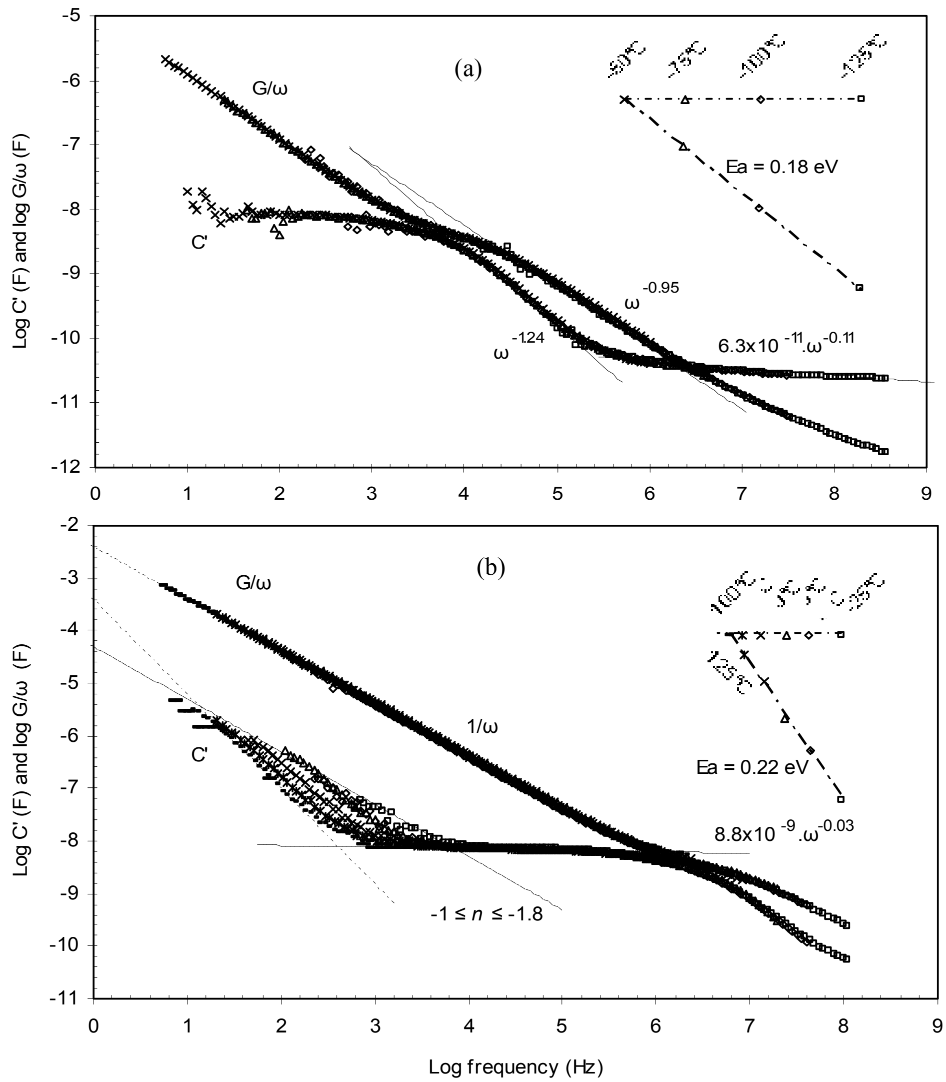

Figure 1: Normalized plots of the complex capacitance of LCMT sample against frequency from -125 to -50°C (a) and -25to 125 °C (b). The locus of the normalization for (a) and (b) are -25°C and 125°C respectively. The insert plot is the activation energy plots of the horizontal shift of the normalization points against a 1000/T(K) scale.

The activation energy (inserted plot) obtained by the horizontal shift of data in Figure 1a is 0.18 eV. At higher temperatures, the sample is dominated by dc conductivity, σ_o as shown in Figure 1b. The gradient of the real part of complex capacitance at 10^3 to 10^6 Hz is observed almost independent of frequency (-0.03) and hence the value of the capacitance is about 8.8 nF. The risen of the interfacial effect is observed to increase with the power law n from n=-1.8 to -1. Large thermally activated energy with 0.22 eV was observed at this range of temperatures applied.

The dielectric response using universal law which is used to fit the dielectric data in Figure 1a are consisted of three parallel circuits (quasi-dc response, conductance and high frequency capacitance) in series as shown in inserted picture in Figure 2. The first quasi dc response is due to the grain boundaries effect with additional conductance and high frequency capacitance arrange in parallel. The second quasi dc response is due to the bulk effect, also in parallel with conductance and high frequency capacitance. For each quasi-dc response, the real and imaginary part is crossing at 100 Hz and 3.4 MHz. The fitting parameters are listed in Table 1. A peak-like feature at the imaginary part occurred as the universal capacitor arrange in series where the grain boundary is dominated by capacitance effect and the bulk effect is dominated by conductance effect. Series combination modeling are suitable in all systems where a barrier region is present adjacent to the bulk conducting or semiconducting material – the barrier accumulates the charge carriers and appears as a capacitance, while the bulk looks like a series resistance.

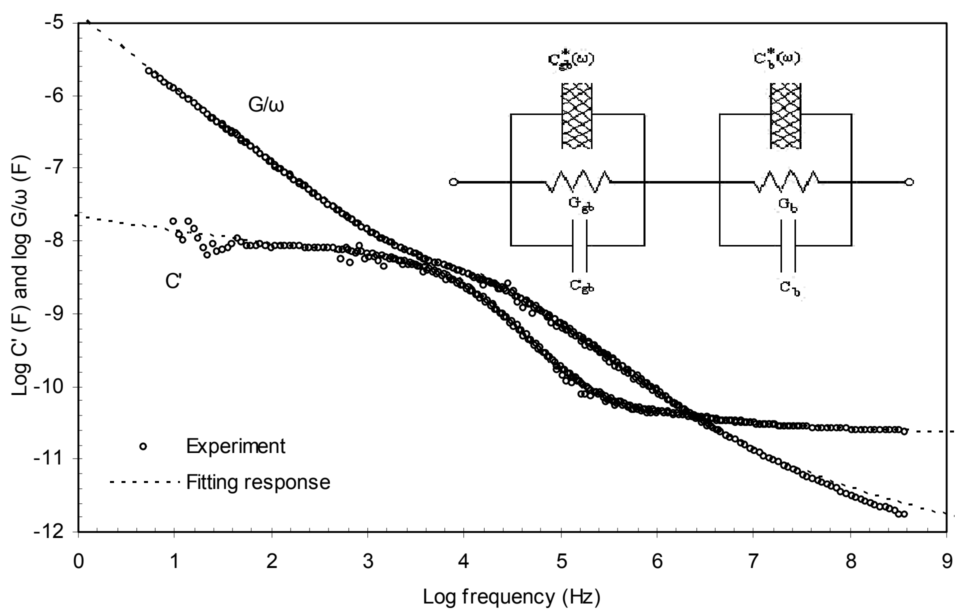

Figure 2: The normalization data of the real and imaginary part of LCMT sample fitted with universal capacitor response. The electrical circuit modeling corresponds to the parameters fitting are inserted.

Table 1: Fitting parameter with the normalized data in Figure 2 corresponding to the bulk and grain boundary regions.

Parameters	Grain boundary	Bulk
p	1	1
n	0.75	7
C_o (F)	9 nF	20 pF
f_c (Hz)	100 Hz	3.4 MHz
G (Ω^{-1})	90 μ/Ω	40 μ/Ω
C (F)	5 nF	10 pF

4. Conclusions

The normalized frequency dependence of dielectric properties of LCMT sample under a range of temperatures has been studied. A Debye-like behaviour was seen in this ceramic sample due to the trapping process of the charge carrier. Two regions have been identified corresponding to the grain at low frequencies and grain boundary at higher frequencies. An electrical circuit model was proposed consisting of quasi free charge response in parallel with conductance and high frequency capacitance representing each grain and grain boundary effects.

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6. References

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