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DIELECTRIC CHARACTERIZATION OF $Ba_{0.6}La_{0.4}Sn_{0.6}Mn_{0.4}O_3$ CERAMIC

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ABSTRACT

The prepared $Ba_{0.6}La_{0.4}Sn_{0.6}Mn_{0.4}O_3$ ceramic sample using solid state technique has been studied and its dielectric behaviour as a function of frequency and temperature are presented in normalized form. At -25 to 75 ºC, the dielectric spectra displayed the behaviour of low frequency dispersion (LFD) where some of the charge carriers (electronic) are bound and some are moving freely. However, at elevated temperature above 75 ºC, the carrier's blockade occurred due to the rising up of interfacial and internal barrier effect at low and intermediate frequency, respectively.

INTRODUCTION

The dielectric dispersion of semi-insulating ceramic materials are usually displayed a Debye-like form e.g., gallium arsenide (GaAs) and iron-doped indium phosphate (Fe:InP) [1,2]. Physically, the behaviour appeared due to the effects of grains and grain boundaries region which have different thickness d, permittivity ε and conductivity σ. However, not all semi-insulator ceramic materials will show Debye-like dispersion.

A new feature of dielectric dispersion call anomaly low frequency dispersion (LFD) has been identified by Jonscher [3]. In this feature, the charges are weakly bounded and partially free to move. Dissado and Hill [4] have proposed a theory based on the many body interaction by the concept of cluster vibration. They define cluster as local groupings of interacting defects and distinguishes intra-cluster (at high frequency branch of spectra) and inter-cluster (at low frequency branch) transitions which results the LFD spectra [5]. The respond of LFD in complex susceptibility, $\chi^*(\omega)$ is given by

$$\chi^*(\omega) = \chi'(\omega) - i\chi''(\omega) \quad (1a)$$

$$= \chi_o F_O^{-1} [1 + (i\omega/\omega_c)]^{n-1} \times {}_2F_1\{1 - n, 1 + p, 2 - n, [1 + (i\omega/\omega_c)]^{-1}\} \quad (1b)$$

where p is the efficiency of charge transport between clusters, n is the measure of correlation degree within the cluster, χ_o denotes the amplitude, ω_c is the critical frequency, F_O^{-1} is the equivalent normalizing constant and equal to $\Gamma(2\text{-}n)\Gamma(1\text{-}p)[(p+n\text{-}1)/p\Gamma(2\text{-}n\text{-}p)]$. $\Gamma(\ )$ and ${}_2F_1\{\ ,\ ;\ ;\ \}$ are the gamma and gaussian hypergeometric function, respectively. As the efficiency of this process p approaches unity, the ac conductivity $\sigma(\omega)$ defined by $\varepsilon_o\omega\chi''(\omega)$ approaches a constant value such as would be appropriate to

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dc conductivity [3,6,7].

In the measurement, the data was obtained in complex capacitance $C^*(\omega)$ and its relation with the dielectric susceptibility is given by

$$\chi^*(\omega) = C^*(\omega) - C_\infty = C'(\omega) - iC''(\omega) - C_\infty$$

where C_∞ is high frequency capacitance. Mathematically, the real and imaginary part of the quasi-dc response of LFD in equation (1) can be represented analytically by the following equations,

$$C'(\omega) = C_o[(i\omega/\omega_c)^{-p}.\cos(p\pi/2) + (i\omega/\omega_c)^{n-1}.\sin(p\pi/2)] \quad (2a)$$
$$C''(\omega) = C_o[(i\omega/\omega_c)^{-p}.\sin(p\pi/2) + (i\omega/\omega_c)^{n-1}.\cos(p\pi/2)]. \quad (2b)$$

where C_o is the response amplitude.

In this paper, the prepared of semi-insulator $Ba_{0.6}La_{0.4}Sn_{0.6}Mn_{0.4}O_3$ (BLSN) sample has been studied in term of frequency and temperature effects on its dielectric capacitance properties. The obtained data is presented in normalize form by shifting the data to the locus point. Self-fitting and circuit modeling were also been proposed to represent the dielectric behaviour of the sample.

METHODOLOGY

$Ba_{0.6}La_{0.4}Sn_{0.6}Mn_{0.4}O_3$ (BLSN) sample was prepared by the conventional solid state reaction technique. A stoichiometric amount of BaO, La_2O_3, SnO_2 and MnO_2 were thoroughly mixed for 24 hours. The dried mixed powders were then calcined at 950 ºC and fired at 1300 ºC 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 ºC for 3 hours. The pellet samples were polished on both sides to get flat surfaces and coated with silver paste and dried at 100 ºC before the dielectric measurement is conducted using Impedance Analyzer Model 4192A LF Hewlett Packard ranging from 5 Hz to 1 MHz at -25 ºC up to 200 ºC with increment 25^{o}C. The sample thickness is 1.3 mm and the coated diameter is 8 mm.

RESULTS AND DISCUSSION

The normalized dielectric spectra of BLSM measured from -25 to 75 ºC and 75 to 200 ºC are shown in Figure 1a and 1b, respectively. In Figure 1a, generally, the dielectric spectra show LFD behaviour. The real and imaginary part below the crossing frequency f_c gives the similar gradient which is obeyed the universal law $C''(\omega) = C'(\omega)\cot(0.99\pi/2)$ [8,9]. To characterize the LFD behaviour, fitting approach was used using the dielectric response of capacitance in equation 2. The fitted data together with the equivalent circuit modeling and fitting parameters for Figure 1a are shown in Figure 2.

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In the response, the effects of C_∞ and conductance G are added in parallel by the relation

$$C^*(\omega) = C'(\omega) + C_\infty - i\,(C''(\omega) + G/\omega). \qquad (3)$$

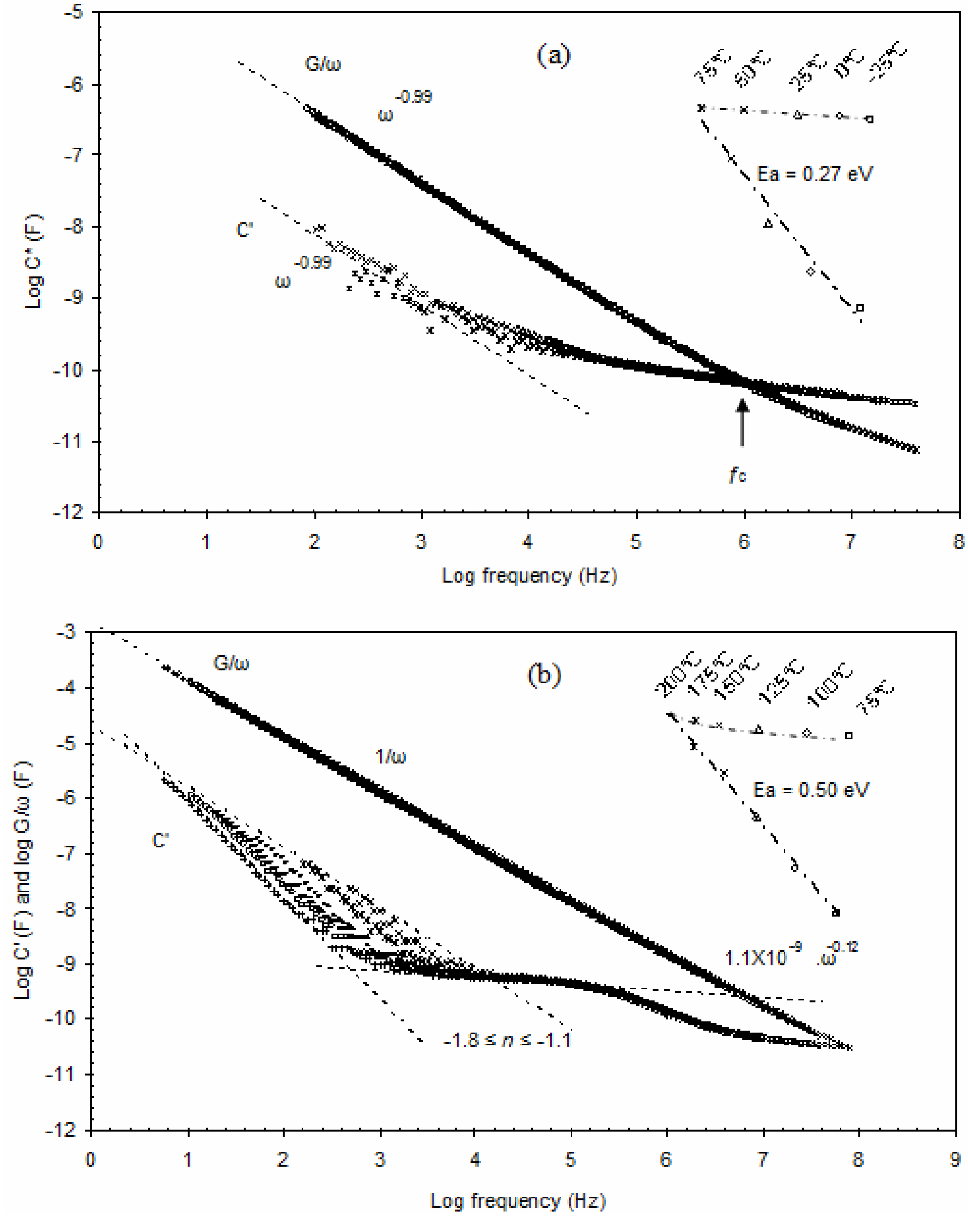

Figure 1: Normalized plots of the complex capacitance of BLSM sample against frequency from (a) -25 to 75 °C and (b) 75 to 200 °C. The locus of the normalization for (a) and (b) are 75 °C and 200 °C respectively. The insert plot is the activation energy plots of the horizontal shift of the normalization points against a 1000/T(K) scale.

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A direct information about the carriers from the spectra is that they are partially mobile as shown by the G/ω dispersion at below and above f_c. At lower frequency $f < f_c$, the charge explore the structure formed by the weak connections. In this case, some clusters will form part of a continues transport path to which the other will be connected by a single weak bond. The strongly frequency dependence of G/ω with p = 0.99 at below f_c comes very close to the dc transport but not a true dc behaviour since $\omega \neq 0$. The value of p = 0.99, indicates that the electrons motion in the sample is strongly correlated between clusters and behaves as a dc conduction process. Meanwhile, the G/ω above f_c is characterized as the bound carriers with the correlation degree n = 0.81. This can be easily seen when the G/ω is transformed into frequency dependent of conductivity plot. The shifted data to 75 °C give the activation energy value of 0.27 eV indicates internal bulk effect of electron hopping between Mn^{3+} and Mn^{4+} ions.

As the temperature increased from 75 to 200 °C, the normalized data in Figure 1b shows a $C'(\omega)$ plateau at ~10^3 to ~10^5 Hz with gradient -0.12 and the magnitude 1.1×10^{-9} F. The plateau is due to the grain boundary effect since it's appeared below the bulk effect in frequency range. At this excess of temperature, interfacial effect is also observed at ~10 to ~10^4 Hz with the gradient ranging $-1.8 \leq n \leq -1.1$. The risen of C' towards low frequency along with the decreases of its gradient to ~ -2 reflects the formation of Maxwell-Wagner behaviour due to imperfect contact between sample/electrode. The G/ω curve give the gradient -1 at almost the entire range of measured frequency indicates of strong dc conduction behaviour. The temperature dependence of the dielectric spectra gives the activation energy of 0.50 eV.

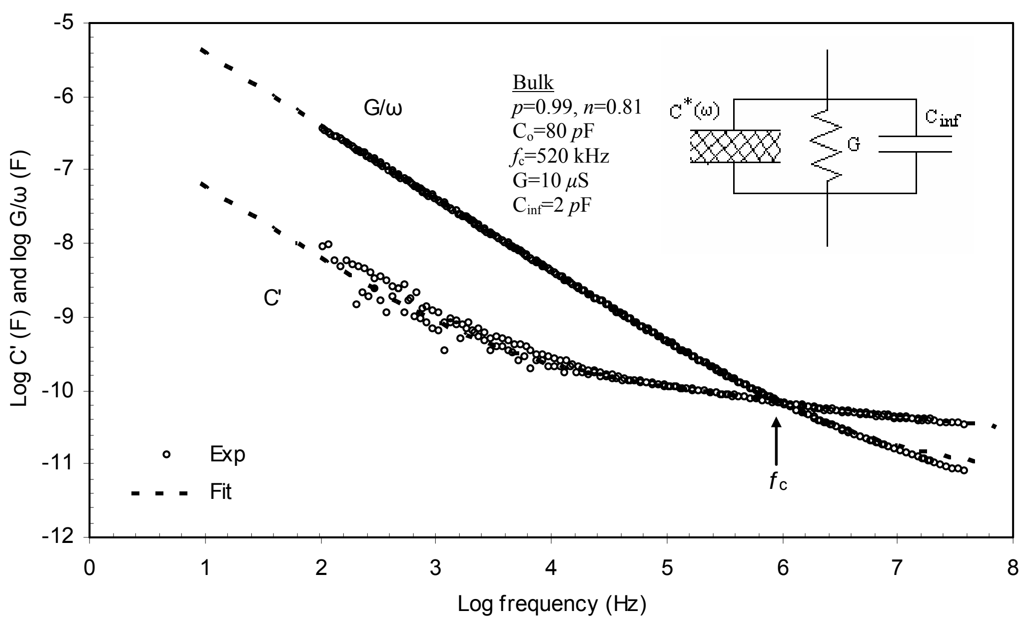

Figure 2: The normalization data of the real and imaginary part of BLSM sample fitted with fitting response. The electrical circuit modeling corresponds to the parameters fitting are inserted.

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From the dielectric dispersion observed in Figures 1a and 1b, it is clear that at low temperature the dielectric dispersion shows a quasi-dc shape of bulk properties and although at high temperature, the grain boundary region is dominated by the strong dc conductivity, the response is expected to have a similar response with the bulk one. Thus, in circuit modeling, the dielectric behaviour represented consisting of two series combination of quasi-dc, conductance *G* and high frequency capacitance C_{inf} in parallel as in Figure 3. In series combination, the capacitance of the bulk and boundary is given by the relation of:

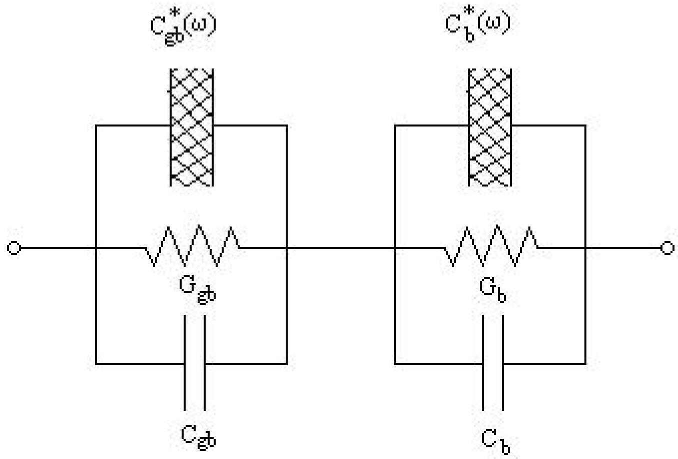

Figure 3: Equivalent circuit modeling consisting of two series combination of quasi-dc, conductance *G* and high frequency capacitance C_{inf} in parallel representing the dielectric behaviour at bulk (b) and grain boundary (gb) effects.

$$Z^* = \frac{1}{i\omega}\left(\frac{1}{C_b(\omega)+C_{gb}(\omega)}\right) \tag{4a}$$

$$= \frac{1}{i\omega}\left(\frac{C_b^*(\omega).C_{gb}^*(\omega)}{C_b^*(\omega)+C_{gb}^*(\omega)}\right). \tag{4b}$$

The interfacial effect is excluded in the circuit modeling.

CONCLUSION

The dielectric behaviour of BLSM sample has been studies and its behaviour has been modeled using equivalent circuit modeling. At temperature range -25 to 75 ºC normalized dielectric data shows a low frequency dispersion form and the other normalized data ranging from 75 to 200 ºC displayed the grain boundary effect located at below the bulk frequency range. A strong dc conduction effect is also observed at this temperature range with large activation energy 0.5 eV compared to the previous normalization activation energy 0.27 eV.

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