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DIELECTRIC PROPERTIES OF $La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_3$ WITH x = 0.4 and 0.6

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ABSTRACT

The dielectric properties of Ti-substituted $La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_3$ with x = 0.4 and 0.6 as a function of frequency and temperature have been investigated. The samples have been prepared using the conventional solid state reaction method at 1300°C. Both samples showed rhombohedral structure with *R3C* space group. The grain size of x = 0.4 and 0.6 are ~2.5 to 3.3 μm and ~0.4 to 0.9 μm respectively. The dielectric constant, ε' of the samples decreases with frequency but increases with temperature. We have successfully obtained very high dielectric constant material. The highest ε' value for LSMT with x = 0.4 and 0.6 are at frequency of 10 Hz and temperature 300 K, which are ~5.7 x 10^6 and ~2.4 x 10^6. The tan δ increases with temperature for x = 0.6 but shows a peak at a certain temperature for x = 0.4. Sample with x = 0.4 has better dielectric properties compared to x = 0.6 sample because it has higher ε' and lower tan δ value. At 175 K and 1 kHz sample with x = 0.4 shows the best dielectric properties with a high ε' value and low tan δ which are 1.1 x 10^5 and 0.8 respectively.

Keywords: LSMO; dielectric properties;

INTRODUCTION

Hole-doped rare earth manganite perovskite with general formula $R_{1-x}A_xMnO_3$ (R is a trivalent rare earth metal ion such as La, Nd, Pr and A is the divalent alkaline earth ion such as Ca, Sr, Ba) have been studied extensively for several years due to the interesting colossal magnetoresistance (CMR), electronic transport and magnetic properties of the material. Apart from that there are also a few studies on the dielectric properties of this type of material [1-4]. Gutierrez et al. [1] found that $La_{0.85}Sr_{0.15}MnO_3$ showed a quite stable dielectric constant in a relatively high value of 10^6 orders. Currently it was discovered that substantial substitution of Ti at Mn site in lanthanum manganite produced unusually high dielectric constant material [3, 4], which can be utilized in the

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electronics devices for technological applications.

Recently we reported on the magnetic, electrical transport and impedance spectroscopy of Ti substituted $La_{0.67}Sr_{0.33}MnO_3$ at room temperature [5]. In this work we investigated the dielectric properties of the compound as a function of frequency and temperature with the intention of obtaining more useful properties from the manganite material.

EXPERIMENTAL DETAILS

As in our previous work [5] $La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_3$ (henceforth referred to as LSMT) samples with x = 0.4 and 0.6 were prepared using the solid state reaction technique. Stoichiometric mixture of La_2O_3, $SrCO_3$, MnO_2 and TiO_2 powders were ball milled in acetone medium and then dried and ground. The well mixed powders were then calcined at 900 ^oC for 12 hours to remove CO_2. Finally the powders were pressed into pellets and sintered at 1300 ^oC for 24 hours. The phase and crystal structure analysis of the final products were done using Philips 7602 EA Almelo X'pert Pro Pw 3040 x-ray diffractometer (XRD). LEO 1450VP variable pressure scanning electron microscope (SEM) was used to examine the microstructure of the samples. The flat surfaces of the pellet were thinly electroded with gold and dielectric measurement was carried out using a HP4192 LF Hewlett-Packard Impedance Analyzer in a frequency range of 5 Hz to 10 MHz at different temperature from 100 K to 300 K.

RESULTS AND DISCUSSION

The x-ray diffraction (XRD) patterns in Figure 1 shows that sample with x = 0.4 is in single phase whereas a few extra impurity peaks emerge from the formation of $La_2Ti_2O_7$ phase at very high Ti substitution of x = 0.6. The data is indexed on the basis of a hexagonal unit cell using CHEKCELL software [6] and is found to crystallize in rhombohedral structure with *R-3C* space group. The lattice parameter, *a* and *c*, and unit cell volume, *V* are 5.5258 Å, 13.4407 Å and 355.42 $Å^3$ respectively for x = 0.4 sample and 5.5204 Å, 13.4904 Å and 356.04 $Å^3$ for x = 0.6. Figure 2 exhibits microstructure of both LSMT samples with denser and larger grains (~2.5 to 3.3 μm) with clear and excellent connectivity grain boundary for x = 0.4 compared to sample with x = 0.6 which is more porous and has smaller grain size (~0.4 to 0.9 μm).

The frequency dependence of the real part of the relative permittivity (ε') or can also be referred to as the dielectric constant is plotted in double logarithmic form as in Figure 3. Both LSMT samples show a decrement of ε' with frequency due to the relaxation process. In manganite the relaxation of ε' is correlated with a frequency dependent space charge or interfacial polarization that can be explained from the hopping rate of the electron double exchange mechanism between Mn^{3+} and Mn^{4+} ions [3]. The electron can hop following the field at low frequency. However at higher frequency the field change is too quick for the electron exchange to occur hence they are trapped and pile up at physical barriers or lattice defects and decreases the ε'. Larger space charge

polarization at lower frequencies can be explained by the accumulation of charge carriers at the sample-electrode interface or at the grain boundaries [1]. A sluggish decrement of ε' can be observed around 10^2 to 10^5 Hz for x = 0.4 at 250 K showing a nearly frequency independent behaviour. The much lower ε' at higher frequency is due to grain polarization effect [4].

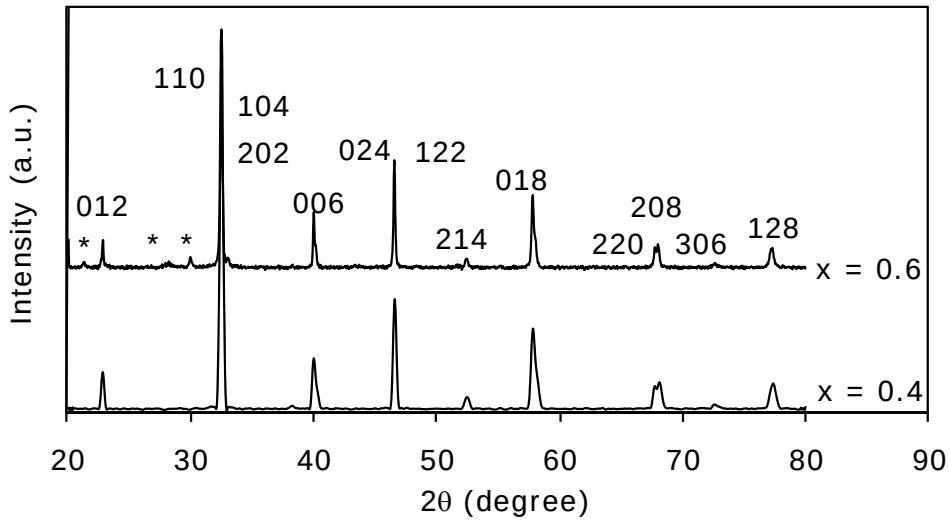
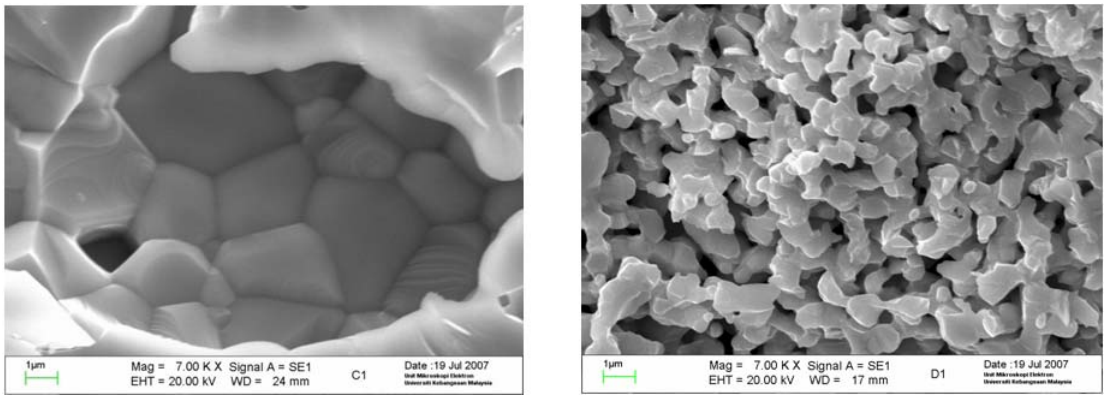


Figure 1: XRD patterns of $La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_3$ with x = 0.4 and 0.6. * indicates impurity phase of $La_2Ti_2O_7$



(a) x = 0.4 (b) x = 0.6

Figure 2: SEM micrographs of $La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_3$ with x = 0.4 and 0.6

Figure 4 shows the frequency dependence of loss tangent, tan δ which is the ratio of the stored energy with the dissipated energy (tan δ = ε''/ε') of the LSMT. For sample with x = 0.4, at 150 K a loss peak can be observed at $10^{4.5}$ Hz and at 250 K a shallow peak with higher tan δ emerges at lower frequencies due to the interfacial polarization produced in grain boundaries or between the sample and electrode contact [2]. For sample with x = 0.6, the loss peak exists but the amplitude is too small and become so

shallow and appears as virtually flat loss at T = 150 K and 200 K. The peak appears when jumping frequency of the localized electron more or less become equal to that of the externally applied electric field.

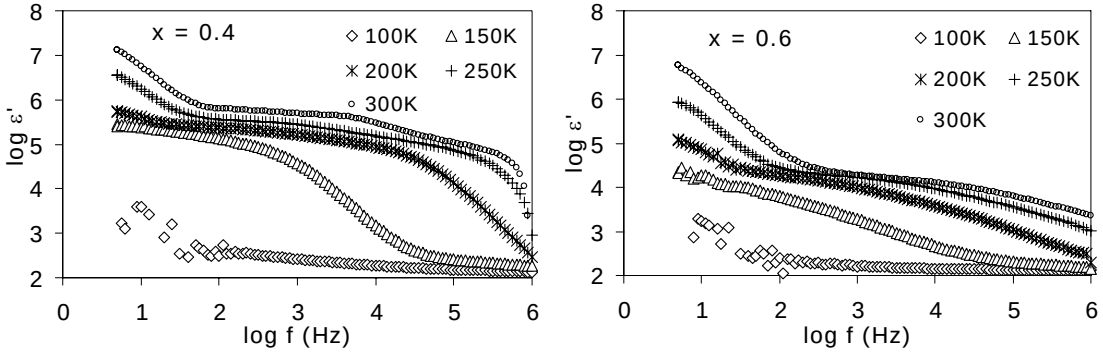


Figure 3: ε' variation with frequency for $La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_3$ with x = 0.4 and 0.6

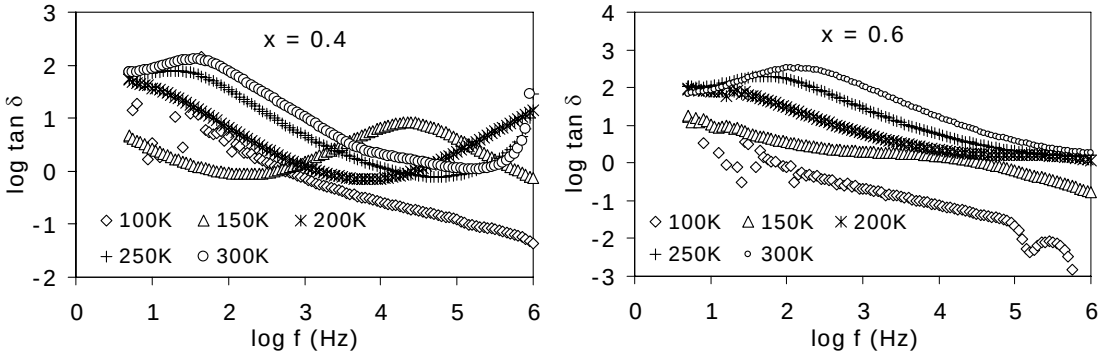


Figure 4: Tan δ variation with frequency for $La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_3$ with x = 0.4 and 0.6

The variation of ε' and tan δ are plotted in a semi logarithmic form in Figure 5 with temperature range of 100 K to 300 K at frequency of 0.01 kHz, 1 kHz and 100 kHz for the LSMT with x = 0.4 and 0.6. ε' for both samples increases with temperature showing the reduction of the polarization process when charge carriers gain energy from the applied heat., Although LSMT with x = 0.4 has larger grains with better connectivity, at all frequencies it has higher dielectric constant, ε' and lower tan δ compared to when x = 0.6 may be because it has more Mn^{3+}-Mn^{4+} ions. LSMT with x = 0.6 shows a rise of tan δ with temperature that is contributed by the scattering of the thermally activated charge carriers. Larger DC conduction at higher temperature increases ε", thus increasing tan δ [7]. LSMT with x = 0.4 shows quite different behavior with a peak at a certain temperature. From this work the highest ε' value achieved for LSMT with x = 0.4 and 0.6 is at frequency of 10 Hz and temperature 300 K, which are ~5.7 x 10^6 and ~2.4 x 10^6. The high ε' occurs at the dispersion region of log ε' versus log f graph in

Figure 3. The best dielectric properties of the studied LSMT is when x = 0.4 at 175 K and 1000 K with a quite high ε' value of 1.1 x 10^5 and low tan δ of 0.8. Table 1 shows the ε' and tan δ value at temperature of 300 K and frequency of 0.01 kHz, 1 kHz and 100 kHz for LSMT samples with x = 0.4 and 0.6.

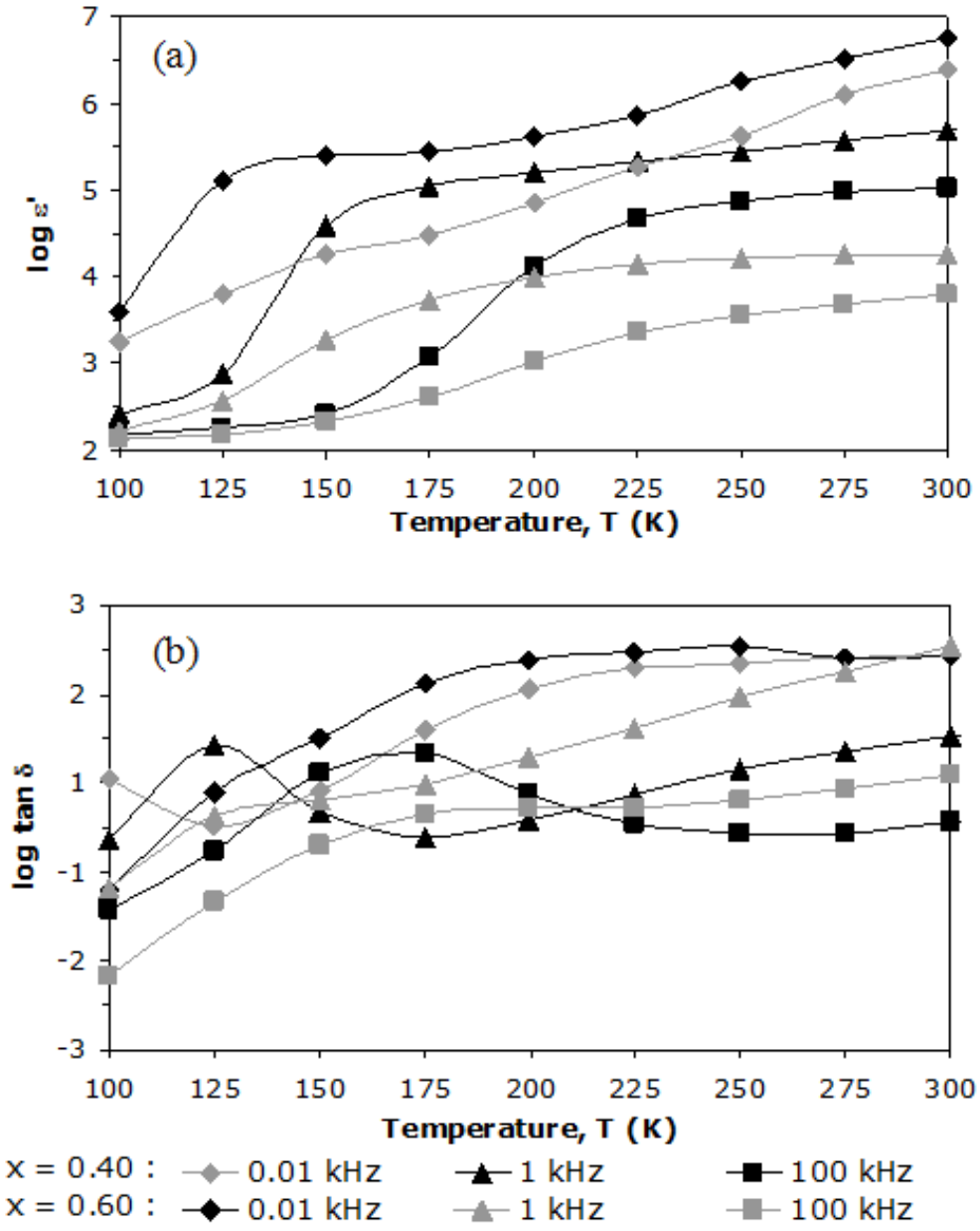


Figure 5: (a) ε' and (b) tan δ variation with temperature at different frequency for $La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_3$ with x = 0.4 and 0.6

Table 1: Values of ε' and tan δ at 300 K.

(x)		0.01 kHz	1 kHz	100 kHz
0.4	ε'	5.7×10^6	4.9×10^5	1.1×10^5
	tan δ	86	10	1
0.6	ε'	2.4×10^6	1.9×10^4	6.3×10^3
	tan δ	85	111	4

CONCLUSIONS

We studied the dielectric properties of Ti-substituted $La_{0.67}Sr_{0.33}Mn_{1-x}Ti_xO_3$ with x = 0.4 and 0.6 as a function of frequency and temperature. Both samples shows that the dielectric constant, ε' decreases with frequency and increases with temperature. We have successfully obtained very high ε' value at 300 K from this work. The highest ε' are ~5.7 x 10^6 and ~2.4 x 10^6 at 10 Hz and 300 K for sample with x = 0.4 and 0.6 respectively. We also found that Ti substitution with x = 0.4 have better dielectric properties compared to x = 0.6.

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