

Structural and physical properties of $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-x}\text{Sn}_x\text{O}_3$ ceramic samples

C. P. Walter, S. A. Halim, Z. Zalita, Z. A. Talib, Z. A. Hassan, W. M. Daud W. Yusoff and M. Mazni
Department of Physics, Faculty of Science, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

(Received 6 December 2006)

A titano-manganate based, $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-x}\text{Sn}_x\text{O}_3$ ($x = 0.0, 0.2, 0.4$ and 0.6) ceramic systems have been prepared using conventional solid state method at 1300°C . For sample with $x = 0$, this oxide shows cubic structure with “a” = 3.9712 \AA (space group Pm-3m) and volume of 62.63 \AA^3 . As Ti sites are completely substituted with Sn, the cubic structure co-exists with the second phase $\text{La}_2\text{Sn}_2\text{O}_7$, cubic structure (pyrochlore-type). All samples show weak ferromagnetic properties. The unusual high dielectric constant of $\sim 14,000$ at 1 kHz and decreasing to ~ 480 at 100 kHz were observed at room temperature for $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ sample. However, introducing Sn in the titano-manganate system has decreased the dielectric constant to ~ 1100 at 1 kHz for $x = 0.6$. By using impedance spectroscopy technique, the unusual high dielectric constant is originated from grain boundary effect. An equivalent circuit model has been done to represent the intrinsic (bulk) and extrinsic (grain boundary) effect of the sample.

I. INTRODUCTION

A well known manganate systems $A_{1-x}B_x\text{MnO}_3$ ($A = \text{La, Pr, Nd, Dy, B} = \text{Ba, Ca, Sr, Pb}$) exhibit colossal magnetoresistance (CMR) at near room temperature has attract interest in experimental and theoretical for a long time [1-4]. The CMR properties arise from the mixture of Mn^{3+} and Mn^{4+} with the fraction of Mn^{4+} determined by the Ca dopant level for $x = 0.3$, that is 30% of the Mn sites would be Mn^{4+} . Zener [2] explained magnetism in these materials due to the double exchange (DE) mechanism where the only way charge transport between Mn^{4+} and Mn^{3+} can happen via the simultaneously hopping of an e_g -electron from Mn^{3+} to the connecting O^{2-} and from the O^{2-} to the $\text{Mn}^{4+} e_g$ band. However, there is argument that this mechanism alone cannot explain the unusual electronic behaviour of the samples. Millis *et al.* [5] suggest that electron-phonon coupling arising from the distortion of the MnO_6 octahedron due to the Jahn-Teller effect should play an important role in CMR compounds. For $x > 0.5$, the manganate systems are antiferromagnetic due to the superexchange interaction while substituting Ti or Sn on Mn decreasing the density of Mn^{4+} holes [6]. Replacement of Mn^{4+} (0.54 \AA) ions with Ti^{4+} (0.605 \AA) and Sn^{4+} (0.69 \AA) cause a large lattice distortion due to the larger ionic radii [7]. Beside that, removing the Mn^{3+} site removes four magnetic electrons while removing Mn^{4+} , only removes three magnetic electrons [8]. Recently, a cubic structure (Pm-3m) of manganate-base doped with 60% of Ti, $\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ has been reported [9] shows an unusual high dielectric constant ($\epsilon' = 6980$ at 1 kHz) and coupled with the long-range magnetic interaction. However, 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+} [10]. In this article, the structural and dielectric properties of Sn doped on Ti site of $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ (LBMT) samples have been studies.

Impedance spectroscopy methods of Cole-Cole plot (Z' Vs Z'') are widely used to characterize the inter particle interactions like grain, grain boundary effects etc. The complex impedance, $Z^* (= Z' - iZ'')$ is related with relative dielectric permittivity, $\epsilon^* (\epsilon'(\omega) - i\epsilon''(\omega)) = 1/i\omega C_0 Z^*$ where $\omega (= 2\pi f)$ is the angular frequency, $C_0 (= \epsilon_0/k)$ is the vacuum capacitance of the measuring cell, ϵ_0 is the permittivity of free space ($8.854 \times 10^{-14} \text{ F/cm}$), and $k = d/A$, the cell constant where d is the thickness and A is the area). The complex capacitance $C^* (= C'(\omega) - iC''(\omega))$ is given by multiply ϵ^* with $\epsilon_0 A/d$. The conductivity, σ of the sample is equal to $\omega \epsilon_0 \epsilon''(\omega)$. For fitting purpose, the universal capacitor, $C^*(\omega) = B(i\omega)^{n-1}$ equation [11] are used to fit the experimental data. Connections between two universal capacitor in parallel give the quasi d.c response. The quasi-dc can be express by the Eqs. (1a) and (1b) below as shown in Fig. 1, where the n measures of the degree of correlation within the cluster and the p value is the fractional correlation index for the transport of the quasi-free charge between clusters [12].

$$C^*(\omega) \propto (i\omega/\omega_c)^{-p} \text{ for } \omega \ll \omega_c \quad (1a)$$

and

$$C^*(\omega) \propto C(\omega_c)(i\omega/\omega_c)^{n-1} \text{ for } \omega \gg \omega_c. \quad (1b)$$

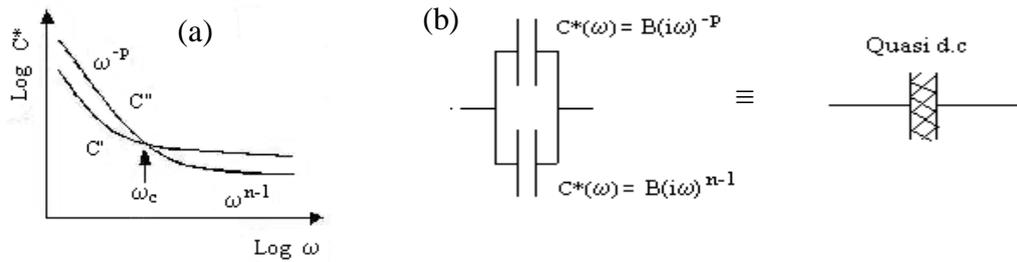


FIG. 1. The frequency dependence of the quasi d.c response (a) and (b) is the electrical equivalent circuit representing the quasi-dc response.

II. EXPERIMENTAL

(La_{0.4}Ba_{0.6})(Mn_{0.4}Ti_{0.6-x}Sn_x)O₃ samples with x = 0.0, 0.2, 0.4 and 0.6 (abbreviated with LBMT, LBMTS0.2, LBMTS0.4 and LBMS, respectively) were prepared by the conventional solid state reaction technique. A stoichiometric amount of La₂O₃, CaO, BaO, MnO₂, TiO₂ and SnO₂ were thoroughly mixed for a day. The dried mixed powders were then calcined at 950°C and fired at 1300°C for 48 hours in pellets from with intermittent grinding. Again the pellets were crushed, compacted into pellets form at a pressure of 6 tons and sintered at 1300°C for 24 hours to obtain the single phase. Powder X-ray diffraction (XRD) was carried out using Philips X’pert diffractometer with CuKα radiation in the 2θ range 20 to 80°. Pellet samples were polished to get flat surfaces for the dielectric measurement using impedance analyzer Model 4192A LF Hewlett Packard ranging from 5 Hz to 13 MHz at room temperature.

III. RESULTS AND DISCUSSIONS

From Fig. 2, the x-ray diffraction of LBMT shows a single phase cubic structure with “a” = 3.9712 Å (space group Pm-3m) and volume of 62.63 Å³. The structure retain until 40% of Sn. However, substituting of Ti with Sn has lead to the existence of second phase formation of La₂Sn₂O₇, pyrochlore-type compound. This pyrochlore have a cubic structure with “a” = 10.580 Å (space group Fd-3m) and volume of 1184.30 Å³ (see Table I). As Sn dopan increases to x = 0.4, the lattice parameter elongated and the cell volume become larger due to the large ionic radii 0.69 Å compared with Ti ionic radii (0.605 Å).

Fig. 3 shows, the magnetization of all samples measured at room temperature are field dependent. The magnetization curve is evidence of weak ferromagnetic.

However, there is no sign that the magnetization will saturate within the applied field. The dielectric properties of the samples are shown in Fig. 4. The dielectric constant versus frequency in Fig. 4(a) shows that doping with Sn decreased the dielectric constant especially at low frequency

The decreasing of the dielectric constant with elongated of lattice parameter and the increasing of cell volume are controlled by ionic radius of Sn⁴⁺ and the formation of the second phase. For LBMT sample, the dielectric constant ~14,000 at 1 kHz and decreasing to ~480 at 100 kHz was observed at room temperature. The dielectric constant value is much higher than BaTiO₃ (~1200 at 1 kHz) and CaCu₃Ti₄O₁₂ (~10,000 at 1 kHz) at room temperature. In Fig. 4(b), the dielectric loss for all samples is very with the applied frequency. At low frequency, the dielectric loss of all samples has the gradient of ~ -1 may be due to the dc conduction of Mn ions.

Two semi-circles are observed from Cole-Cole impedance plot in Fig. 5. The first large semi-circle is observed at low frequency and the second semi-circle at high frequency (insert picture). The high dielectric constant at low frequency is due to the grain boundary effect and the high frequency semi-circle is due to the bulk effect. These explain the origin of the high dielectric constant as also observed by M. Li *et al.* [10] for La_{0.4}Ba_{0.4}Ca_{0.2}Mn_{0.4}Ti_{0.6}O₃ ceramic sample.

By using universal capacitor, we have modeled the electrical behaviour of the samples consist of two quasi d.c. connected in series (Fig. 6). This model is fixed for all samples. The values of the fitting are tabulated in Table II consisting of p, n, C(ω_c) and f_c parameters. The current behaviour at high frequency in the grain boundary region follow from the resistive path and at low frequency in the bulk region, it is follow from the capacitive path.

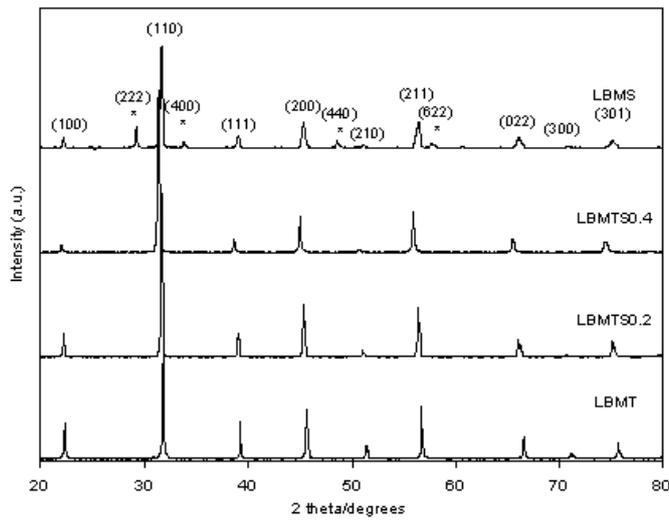


FIG. 2. X-ray diffraction pattern of $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-x}\text{Sn}_x\text{O}_3$ samples with $x = 0.0, 0.2, 0.4$ and 0.6 . The asterisk (*) sign is the second phase diffractions pattern.

TABLE I. The structure, space group, lattice parameter and cell volume obtained from XRD for all samples.

Samples	Structure and space group	Lattice parameter "a" (Å)	Cell volume (Å ³)
LBMT	Cubic (Pm-3m)	3.9712	62.63
LBMTS0.2	Cubic (Pm-3m)	3.9944	63.73
LBMTS0.4	Cubic (Pm-3m)	4.0252	65.22
LBMS	1) Cubic (Pm-3m) 2) *Cubic (Fd-3m)	3.9897 10.5800	63.51 1184.30

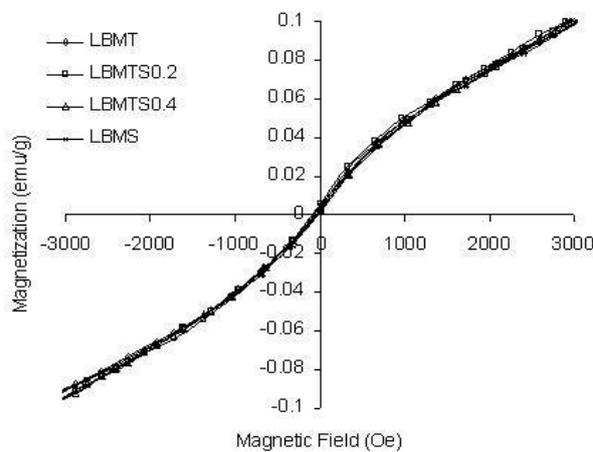


FIG. 3. Field dependent magnetization of $(\text{La}_{0.4}\text{Ba}_{0.6})(\text{Mn}_{0.4}\text{Ti}_{0.6-x}\text{Sn}_x)\text{O}_3$ at room temperature.

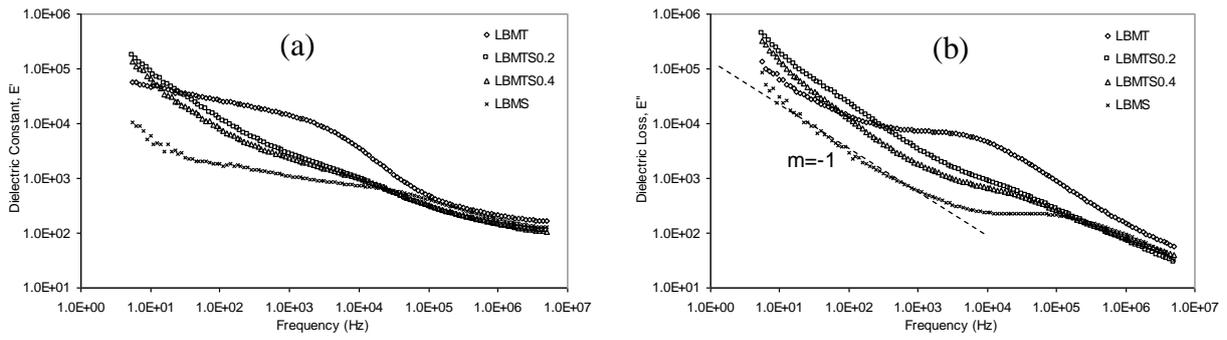


FIG. 4. Relative dielectric permittivity versus frequency at room temperature where a) is dielectric constant versus frequency and b) is dielectric loss versus frequency for $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-x}\text{Sn}_x\text{O}_3$ ($x = 0.0, 0.2, 0.4$ and 0.6) samples.

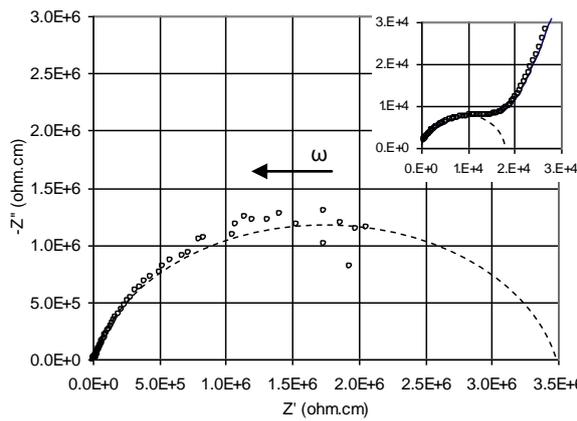


FIG. 5. Cole-Cole impedance plot for $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ samples shows two semi-circles. The low frequency semi-circle was due to the grain boundary effect and the high frequency semi-circle is due to the bulk effect (insert picture).

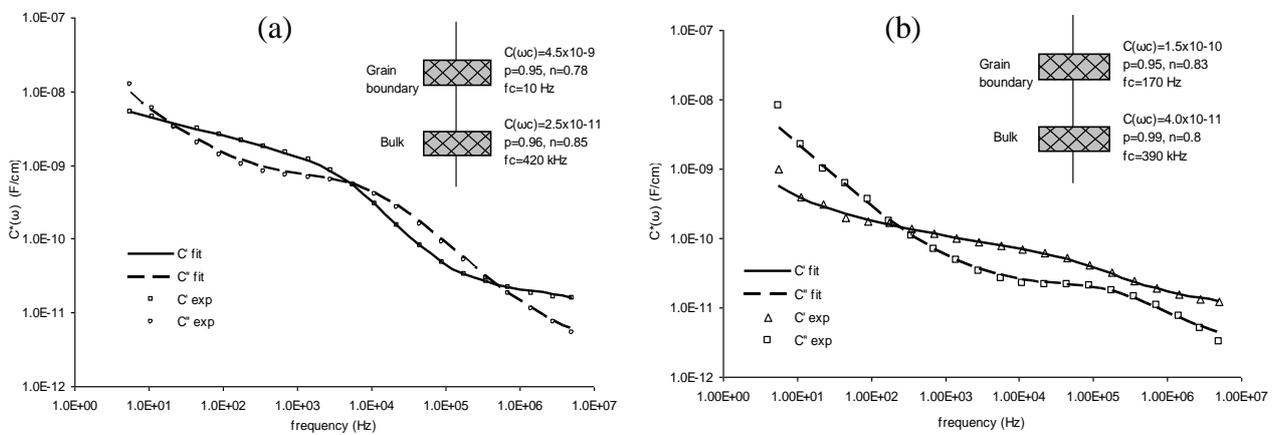


FIG. 6. Fitting of (a) LBMT and (b) LBMS using universal capacitor. The electrical behaviour of the samples has been modeled consisting of two quasi d.c. connected in series.

TABLE II. The fitting values of all samples regarding bulk and grain boundary region.

Samples	Bulk				Grain boundary			
	p	n	$C(\omega_c)$ (F/cm)	f_c (Hz)	p	n	$C(\omega_c)$ (F/cm)	f_c (Hz)
LBMT	0.95	0.78	4.5×10^{-9}	10	0.96	0.85	2.5×10^{-11}	420,000
LBMTS0.2	0.74	0.95	1.9×10^{-10}	2800	0.9	0.78	1.8×10^{-11}	200,000
LBMTS0.4	0.85	0.99	3.5×10^{-10}	900	0.62	0.87	1.2×10^{-11}	500,000
LBMS	0.95	0.83	1.5×10^{-10}	170	0.99	0.8	4.0×10^{-11}	390,000

IV. CONCLUSION

The $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-x}\text{Sn}_x\text{O}_3$ ceramic samples ($x = 0.0, 0.2, 0.4$ and 0.6) have been prepared by the conventional method and its structure and dielectric properties being studied. All samples show cubic structure with space group Pm-3m except for $x = 0.6$ co-exists with the second phase $\text{La}_2\text{Sn}_2\text{O}_7$ pyrochlore-type cubic structure (Fd-3m). All samples show weak ferromagnetic properties. The unusual high dielectric constant of $\sim 14,000$ at 1 kHz and decreasing to ~ 480 at 100 kHz was observed at room temperature for undoped sample. However, the unusual high dielectric constant is originated from grain boundary effect. Introducing Sn in the titanate-manganate system has decreased the dielectric constant to ~ 1100 at 1 kHz for $x = 0.6$. An equivalent circuit model has been done to represent the intrinsic (bulk) and extrinsic (grain boundary) effect of the sample. The decreasing of the dielectric constant with elongated of lattice parameter and the increasing of cell volume are due to the larger ionic radius of Sn^{4+} .

ACKNOWLEDGMENTS

We would like to acknowledge the Ministry of Science and Technology, under the IRPA vote: 09-02-04-0456-EA001 for the financial support and also to Miss Yusnita Othman for XRD analysis.

REFERENCES

- [1] G. H. Jonker and J. H. Von Santen, "Ferromagnetic compounds of manganese with perovskite structure", *Physica*, **16**, 337 (1950).
- [2] C. Zener, "Interaction between d-shells in the transition metals. ii ferromagnetic compounds of manganese with perovskite structure", *Physical Review*, **82(3)**, 403 (1951).
- [3] P. A. Anderson and H. Hasegawa, "Considerations on double exchange", *Physical Review*, **100(2)**, 675 (1955).
- [4] P. -G. De Gennes, "Effects of double exchange in magnetic crystals", *Physical Review*, **118(1)**, 141 (1960).
- [5] A. J. Millis, P. B. Littlewood and B. I. Shraiman, "Double exchange alone does not explain the resistivity of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ", *Physic Review Letter*, **74(2)**, 5144 (1995).
- [6] R. -W. Li, Z. -H. Wang, X. Chen, Sun and B. -G. Shen, "Magnetic properties and colossal magnetoresistance of the perovskites $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ ", *J. Physic D: Applied Physic*, **87(9)**, 5597 (2000b).
- [7] R. -W. Li, J. -R. Sun, Z. -H. Wang, S. -Y. Zhang and B. -G. Shen, "Magnetic and transport properties of Sn-doped $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ", *J. Physic D: Applied Physic*, **33**, 1982 (2000a).
- [8] D. Cao, F. Bridges, M. Anderson, A. P. Ramirez, M. Olapinski, M. A. Subramanian, C. H. Booth and G. H. Kwei, "Local distortions in (A = Ti and Ga) colossal magnetoresistance samples: correlation with magnetization and evidence for cluster formation", *Physical Review B*, **64**, 184409 (2001).
- [9] P. Jha, S. Rai, K. V. Ramanujachary, S. E. Lovland and A. K. Ganguli, " $(\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2})(\text{Mn}_{0.4}\text{Ti}_{0.6})\text{O}_3$: A new titanate-manganate with a high dielectric constant and antiferromagnetic interactions", *J. Solid State Chemistry*, **177**, 2881 (2004).
- [10] M. Li, A. Feteira D. C. and Sinclair, "Origin of the high permittivity in $(\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2})(\text{Mn}_{0.4}\text{Ti}_{0.6})\text{O}_3$ ceramics", *J. Applied Physics*, **98**, 084101 (2005).
- [11] A. K. Jonscher, *Dielectric Relaxation in Solids*, Chelsea Dielectrics Press, London (1983).
- [12] R. M. Hill and C. Pickup, "Barrier effects in dispersive media", *Journal of Materials Science*, **20**, 4431 (1985).

