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$(La_{0.5-x}Pr_xBa_{0.5})(Mn_{0.5}Ti_{0.5})O_3$ PEROVSKITE: MICROSTRUCTURAL AND ELECTRICAL PROPERTIES

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ABSTRACT

A new perovskite of titano-manganite based $(La_{0.5-x}Pr_xBa_{0.5})(Mn_{0.5}Ti_{0.5})O_3$ has been prepared by ceramic solid-state technique at sintering temperature 1300 °C. The concentration of Pr, x, in molar proportion in A site has been varied as x = 0.0, 0.1, 0.2, 0.3 and 0.4. Analysis has been carried out to determine microstructure and electrical properties of the synthesized material. It is found that at sintering temperature 1300 ˚C, only sample with x=0.1 produce a better diffused condition with low dielectric loss.

INTRODUCTION

In recent years, there are major interests in exploring for new applications and development of a new form multifunctional hybrid for next generation devices such as a new form of memory storage or novel miniaturized sensor that may be applied in medical and automotive industries. In multiple state memory elements for example, data is stored both in the electric and magnetic polarizations, or novel memory media, which might allow writing of ferroelectric data bit, and reading of the magnetic field association [1,2].

The perovskite structure has been the most explored in tailoring the properties of oxide material. The material can show properties ranging from colossal magnetoresistance (CMR), superconductivity and ferroelectricity [1,3,4]. The ferroelectric and dielectric behaviour of this material are important in electronic industry. To note that there will be a continuing demand in studying dielectric material for electronic system which is cheaper, small in size, more reliable, less loss and with the capability of increased functionality.

Perovskite structures possess a property in which its central atom A does not touch its coordination neighbours. This structure arrangement is responsible for strange ferroelectricity property of the material. Such materials include the manganites of the rare earths and yttrium, and a few Bi compounds in which Bi is the largest cation [5,6].

Mixed valence manganites, with general formula $A_{1-x}B_xMnO_3$ have been widely studied

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in the past 50 years due to their interesting complex behaviour and properties [1-4,7,8]. By changing the cation dopant concentration, x, it gives a diverse formation of phases, changing from insulating antiferromagnetic, to ferromagnetic metallic, passing through change of orbital ordered region. This diverse physical behaviour is as a result of substitution of rare earth and alkali metal cations into the polycrystalline structure and by controlling parameter x.

$LaMnO_3$ oxide based material is well known for their ferromagnetic and giant-magnetoresistance behaviour [9]. Jonker and Van Santen first studied these types of perovskite lanthanum manganese oxides back in 1950 [10] due to its profound colossal magnetoresistivity effect. Oxides in the A site (i.e La) that has been substituted with other cation like Ca, Ba and Pb are found to show ferromagnetism and magnetoresistance behaviour. For example the $La_{1-x}Ca_xMnO_3$ with x = 0.6 and 0.8 were reported to demonstrate magnetic properties over large temperature range [11]. Other material reported is a new titano manganite oxide $(La_{0.4}Ba_{0.4}Ca_{0.2})(Mn_{0.4}Ti_{0.6})O_3$ [8] that shows the presence of high dielectric constant, coupled with the long-range anti ferromagnetic interaction near 5K. Another type is $La_{0.7}Ca_{0.3}MnO_3$ [12] which showing an electron spins ordering behavior along with magnetoresistance.

In this study a titano manganite based material $(La_{0.5-x}Pr_xBa_{0.5})(Mn_{0.5}Ti_{0.5})O_3$ has been synthesised by solid-state reaction at temperature 1300 °C as to investigate its microstructural and electrical properties. The Pr concentration in molar proportion in A site has been varied as x = 0.0, 0.1, 0.2, 0.3 and 0.4.

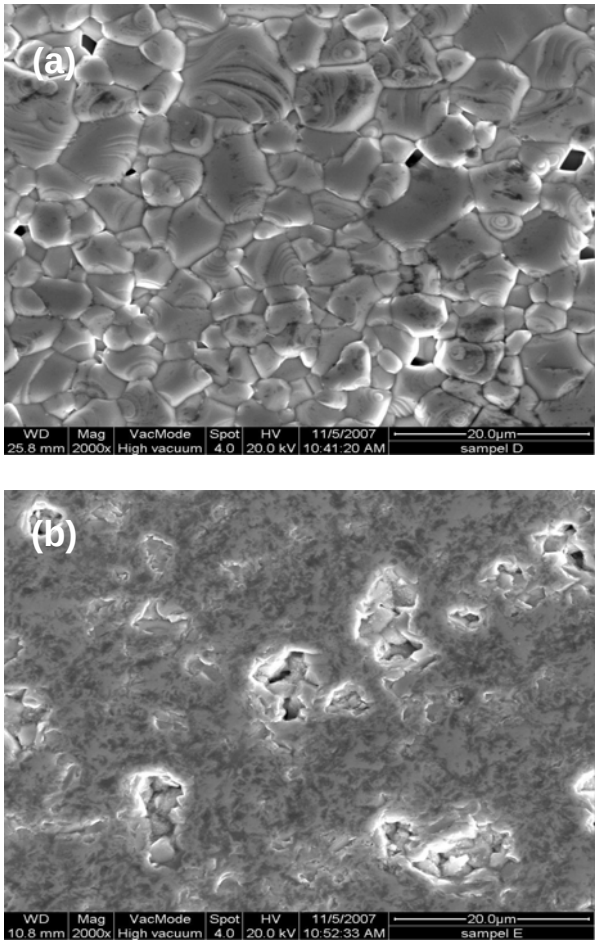
EXPERIMENTAL

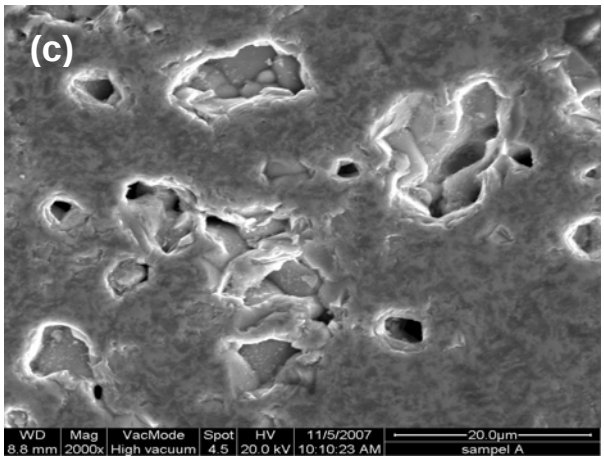
Polycrystalline samples of manganite based materials with nominal composition $(La_{0.5-x}Pr_xBa_{0.5})(Mn_{0.5}Ti)O_3$ have been prepared by solid-state reaction technique. Basic oxides were mixed together in molar proportion at concentration x = 0, 0.1, 0.2, 0.3 and 0.4. The mixture was then mixed by wet milling, followed by drying to produce powder. The resultant powder was then pre-sintered at 900 °C for 12h. This followed with grinding and compacting into green pellets. The green pellets were finally sintered in air for 1300 ˚C for 24h. The sintered pellets are named as sample X1(x=0), X2(x=0.1), X3(x=0.2), X4(x=0.3) and X5 (x=0.4) respectively. Microstructural and electrical effect of dopant concentration was investigated by using Scanning Electron Microscopy (SEM) and Impedance Analyzer at frequency 5 Hz to 1M Hz in room temperature.

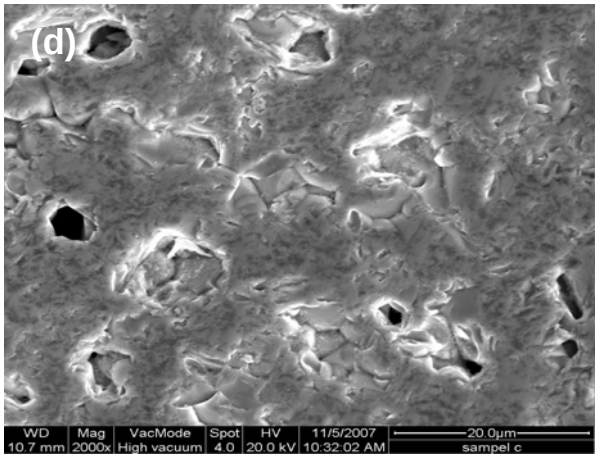
RESULTS AND DISCUSSION

Scanning electron microscopy of sample results are shown in Figure 1. As observed in Figure 1(a), the undoped sample X1(x=0) possess a prominent grain boundary with irregular grain size and exhibited some grain growth. From Figure 1(b) to 1(e), it is observed that Pr addition would allow sintering diffusion process where the grain centers moving towards each other leading to the smoothing of the grain surfaces.

Further diffusion and melting resulted in partial elimination of boundary and thus no clear grain boundary is observed. Increased content of Pr would somehow inhibit the complete diffusion process. As a result, some of the diffusion area generated coarse surfaces of agglomerated grains with pores as shown in Figure 1(c) to 1(e). Compared to others, X2(x=0.1), the only sample shows better diffused condition of sample with less porosity. Therefore it can be suggested that sintering temperature 1300 ˚C is fairly adequate for x=0.1, giving a dense microstructure with less porosity.







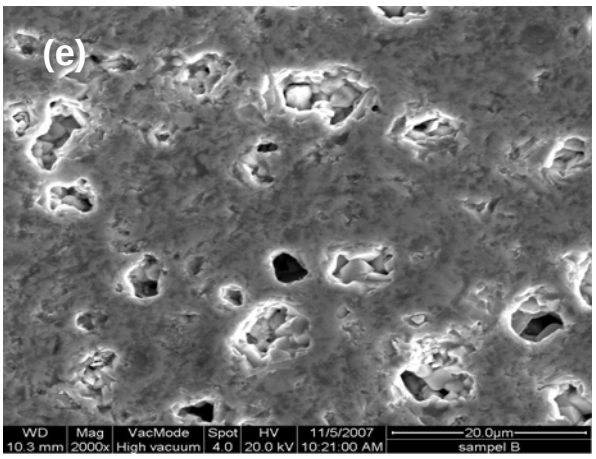


Figure1: SEM micrographs of doped concentration of Pr (a) X1(x=0); (b) X2(x=0.1); (c) X3(x=0.2); (d) X4(x=0.3) and (e) X5(x=0.4).

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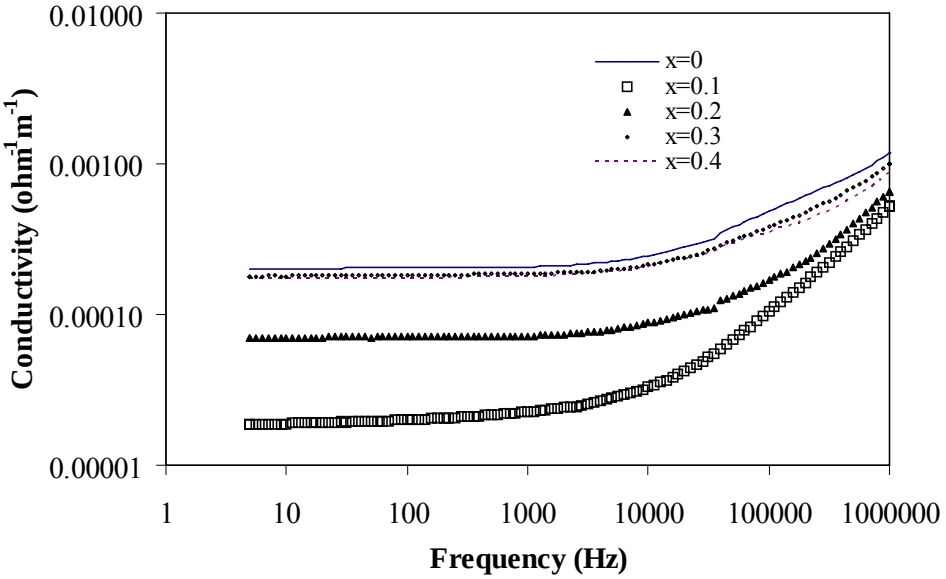

Figure 2: Plot of conductivity (σ) vs. frequency at room temperature.

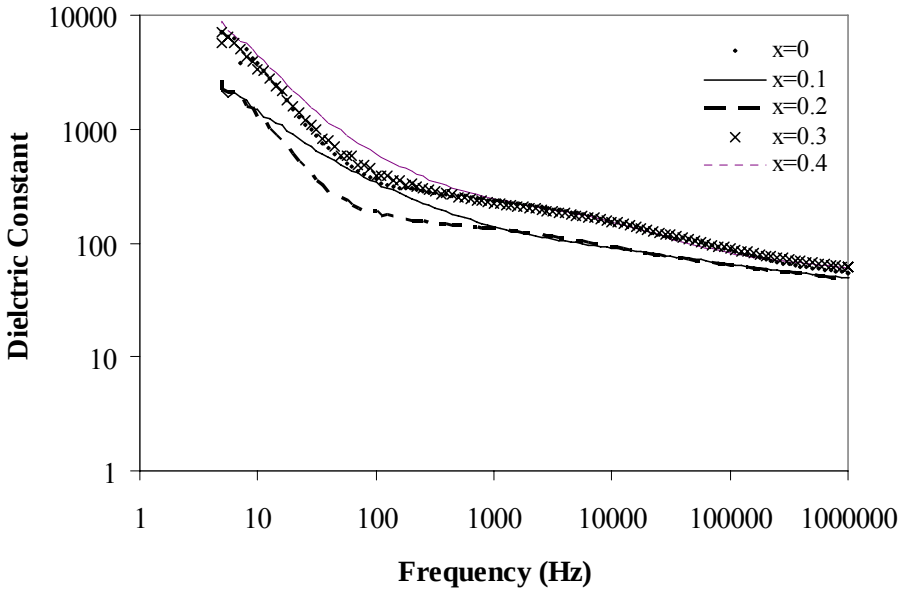

Figure 3: Plot of dielectric constant vs. frequency at room temperature.

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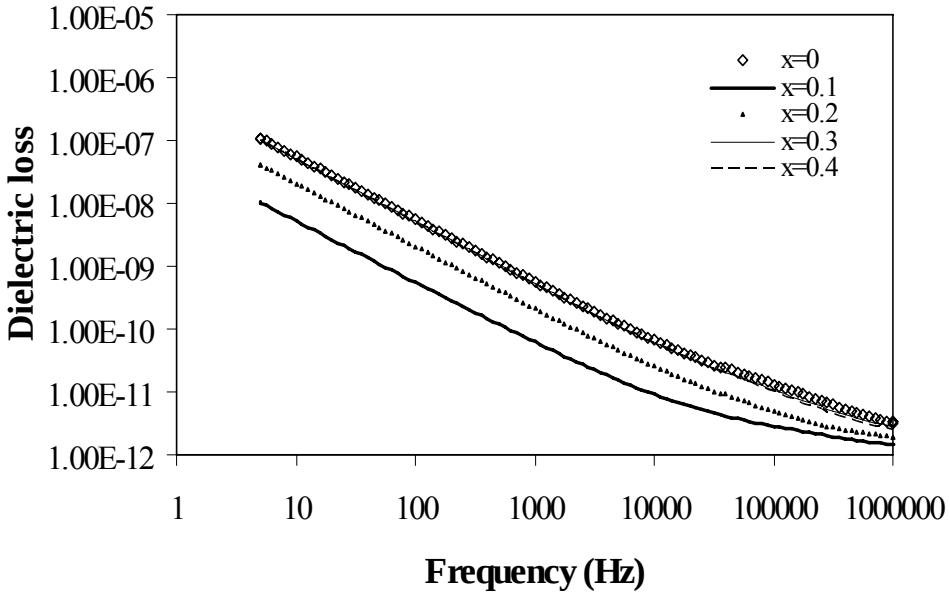

Figure 4: Plot of dielectric loss vs. frequency at room temperature.

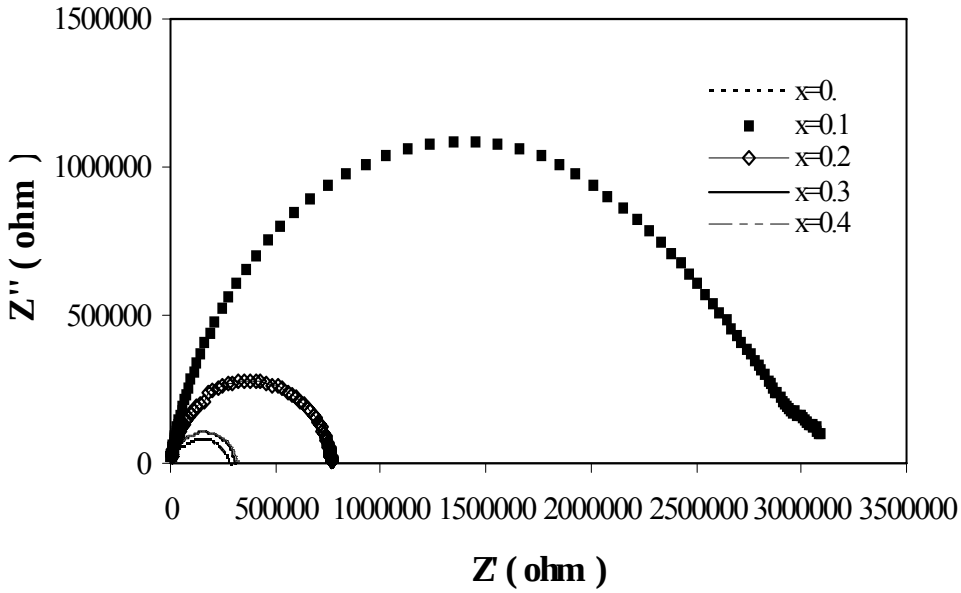

Figure 5: Complex impedance Nyquist plot at different x concentration.

The graphs of electrical properties of Pr, x concentration variation have been plotted in Figure 2-5. From Figure 2, all of the samples conductivity increases with increase frequency but with addition of Pr the conductivity value decreases. It is also observed that there is no significant changes in conductivity value for X4(x=0.3) and X5(x=0.4). Sample X2 with concentration x=0.1 is having the lowest conductivity value followed by sample X3(x=0.2). At frequency > 100000Hz the conductivity value for sample X2(x=0.1) appear to merge into single curve line with sample X3(x=0.2). Figure 3 demonstrates that there is no significant change in dielectric constant values due to Pr addition. The dielectric constant values drop to around 50 with increasing frequency. This value is considered high for dielectric material. From Figure 4 it can be depicted that sample X2(x=0.1) has the lowest loss value followed by sample x=0.2. For all samples, the dielectric loss also decreases with increased frequency. Pr addition would also increase the resistivity value pronouncedly in sample X2(x=0.1) followed by X3(x=0.2) as shown in Figure 5. Such pattern in complex impedance Nyquist plot would give us the correlation between microstructure and the electrical behaviour in the material when modeled in terms of an electrical equivalent circuit [13, 14]. From the analysis, the results thus presented clearly indicated that Pr addition at x= 0.1 is significant to promote sintering diffusion process at 1300 ºC, but the effect for lesser amount of Pr added need to be investigated. Further analysis should be carried out for Pr addition at x<0.1.

CONCLUSION

Prominent grain boundary is only exhibited in undoped sample sintered at 1300 ˚C. The sample x=0.1 shows dense and well diffused sample. This sample also displays low dielectric loss and low conductivity value. As the Pr content increases it tends to promote agglomeration and porosity. Thus, coarse and porous surface microstructures are formed with decreased conductivity. Further studies has to be done for sample with x<0.1 in order to establish optimum concentration of Pr (x), with the lowest dielectric loss and better microstructural properties.

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REFERENCES

[1]. V. K Wadhawan, Introduction to Ferroic Materials, (2000); (Gordon & Breach, UK.)
[2]. A. Aizu, (1969); J. Phys. Soc. Japan, Vol. **27**, 387.
[3]. S. H. Curnoe, I. Munawar, (2006); Magnetic Phases of Rare Earth Hexagonal Manganites, (Pre print submitted to Elsevier Science)
[4]. H. Schmid, (1994); Ferroelectrics **162**, 317.

[5]. G. A. Swolensky, V. A. Isupov, N. N Krainik and A. I. Agranovskaya, Isvest. Akad. Nauk SSSR, (1961); Sev. Fiz **25**, 1333.
[6]. V. L. Mathe, K. K. Patankar, M. B. Kothale, S. B. Kulkarni, P. B. Joshi and, S. A. Patil, (2002); Preparation Structural Analysis and Dielectric Properties of Bi_xLa_{1-x} FeO_3 Perovskite, Pramana Journal of Physics, Vol **58** (5 & 6), 1105-1113
[7]. P. Schiffer, A.P. Ramirez, W. Bao and S.-W. Cheong, (1995); Physical Review Letters **75** 3336.
[8]. Pika Jha, sarita Rai, Kandalam V. Ramanujachany, Samuel E. Lofland and Ashok K. Ganguli, (2004); Journal of Solid State Chemistry **177,** 2881-2888
[9]. H. Asano, J. Hayukawa, M. Matsui, (1997); Phys. Rev. B **56**, 5395
[10]. G. H. Jonker, J. H. Van Santen, (1950); Physica **16,** 337.
[11]. C. Himcinshi, E. Burzo, R. Tetean, D. Ristoiu, V. Pop, (2003); Mod. Phys. Lett. B **17** 263.
[12]. R. Laiko, K.G. Lisomov, E. Lahderanta, P.A. Petrensko, J. Salminen, V. N. Stamov, Y. P. Stepsnov, V. S. Zakhvalinskii, (2003); J. Phys Chem. Solids **64** 2313
[13]. D.K. Pradhan, B.K. Samantary, R.N.P. Chaudhary, A.K. Thakur, (2005); Mater. Sci. Eng. B **116,** 7.
[14]. M. Nadeem, M.J. Akhtar, A.Y. Khan, (2005); Solid State Commun. **134,** 431.