

Structural Properties of Nd-Ca-Mn-O Bulk and Thin Film

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Abstract: Mixed-valent manganites perovskites have caught the eye of the researches over the past few years due to their captivating properties such as colossal magnetoresistance (CMR) effect and industrial purpose such as magnetic field sensing devices. In this study, Nd_{0.67}Ca_{0.33}MnO₃ (NCMO) compounds have been synthesised into bulk by sol-gel method and fabricated into thin film via Pulsed Laser Deposition and were characterized by using X-ray diffraction (XRD) to study the structural properties of the compounds. Based on the XRD results, all bulk samples showed single phase formation with orthorhombic crystal structure but the thin film samples showed monoclinic structure type. The crystallite size of the samples increases as the sintering temperature increases because higher temperature promotes crystallite growth.

Keywords: NCMO, Sol-gel route, Metal-insulator transition, Sintering temperature

In 1950, Jonker and van Santen have discovered the colossal magnetoresistance (CMR) in perovskite manganites which then has attracted many researches due to the industrial purpose such as magnetid field sensing devices. From the previous study, it was proven that by using sol-gel method, the grain growth will be restricted due to low sintering temperature and has broader metal-insulator transition (T_{MI}) compared to solid state reaction method [6]. On the other hand, the crystallite size that are in nanometer range are found to be decreased as sintering temperature decreased and has high magnetoresistance (MR) value [9]. However, there is only a few study on the neodymium calcium manganite (NCMO) bulk and thin film and thus this research is to investage and study about the structural properties of the NCMO system using sol-gel route by varying the sintering temperature for the bulk samples and Pulsed Laser Deposition for the thin film samples by varying the post-annealing temperature.

Nd_{0.67}Ca_{0.33}MnO₃ (NCMO) sample was prepared by sol-gel method. A stoichiometric amount of the precursors La(NO₃)₃.6H₂O, Ca(NO₃)₃.4H₂O and Mn(NO₃)₂.4H₂O were mixed together and dissolved in distilled water. The nitrate solution was mixed with citric acid (CA) and ethylene glycol (EG), heated up to 110°C to remove the moisture and sent to calcination at 500°C. Finally, the NCMO powder was sintered at various temperatures starting at 550°C, 600°C, 700°C, 800°C, 900°C and 1000°C. NCMO sample that was sintered at 800°C was then taken to thin film preparation by Pulsed Laser Deposition and was deposited for 1 hour and post annealed at 700°C and 800°C for 2 hours. Finally, the samples were characterized by an X-ray diffractometer (XRD; Philips PW 3040/60 X'Pert PRO) to study the structural properties of the samples.

The Rietveld analysis of the XRD data in Fig. 1 shown that all Nd_{0.67}Ca_{0.33}MnO₃ samples were fully crystalline in single phase without any detectable impurities and exhibited orthorhombic

crystal structure with space group Pnma. The highest peak (121) was taken into reference to determine the crystallite size of the samples using Scherrer's formula. As the sintering temperature increases from 550°C to 1000°C, the intensity of the X-ray peaks also increases. This indicates the growth of crystalline phase as the crystallite size increases along with the increasing sintering temperature. However, the lattice parameter and cell volume for all samples are not having any significant changes. The average calculated crystallite size for all samples are ~23.1 nm, ~25.7 nm, ~27.9 nm, ~33.3 nm, ~51.5 nm and ~93.1 nm for sintering temperature 550°C, 600°C, 700°C, 800°C, 900°C and 1000°C respectively. The variation of the crystallite size calculated was plotted in Fig. 2. Therefore, the higher the sintering temperature, the higher the crystallite growth due to congregation of the grains [4].

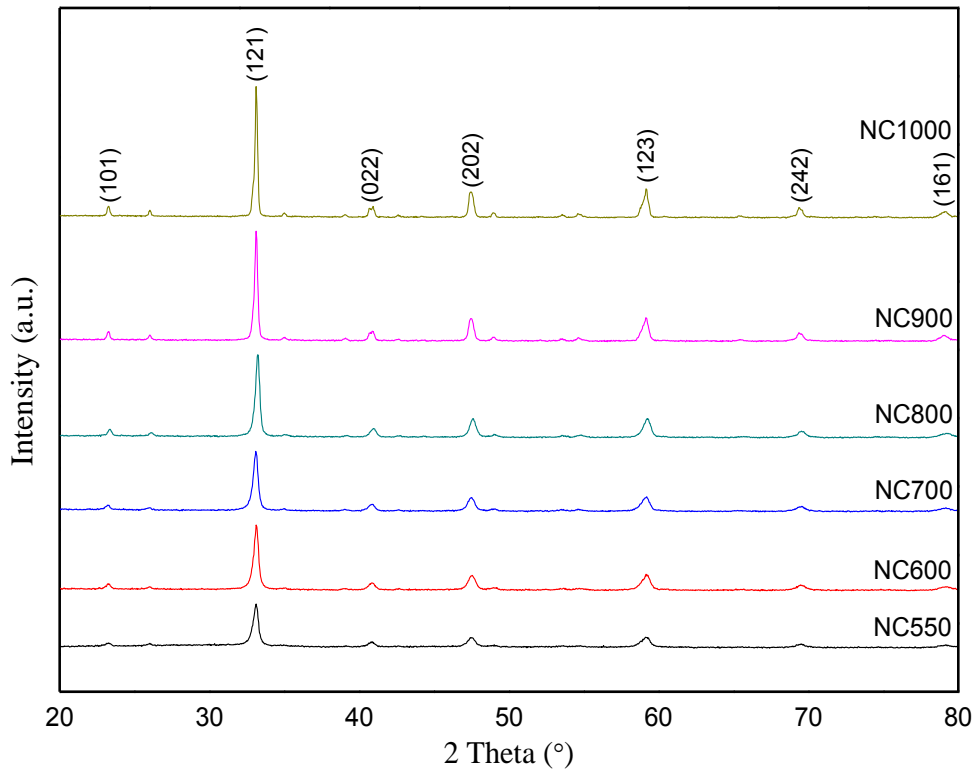


Figure 1. XRD pattern of $\text{Nd}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ at different sintering temperature

Table 1. Lattice parameter and Rietveld refinement data of $\text{Nd}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$

Sample code	NC550	NC600	NC700	NC800	NC900	NC1000
Structure type	orthorhombic					
Space group	Pnma					
a (Å)	5.39751	5.4472	5.44355	5.44691	5.45286	5.45163
b (Å)	7.62233	7.6305	7.63227	7.63864	7.65278	7.64855
c (Å)	5.44163	5.40214	5.4027	5.40534	5.41177	5.4088
Volume (Å ³)	223.8774	224.5391	224.4641	224.9001	225.8307	225.5312
R _P (%)	3.51197	2.8918	3.07927	2.92131	3.17624	3.53832
R _{WP} (%)	4.48071	3.6797	3.85398	3.72596	4.01985	4.53696
R _{EXP} (%)	3.84111	3.66977	3.74556	3.78064	3.83929	4.14898

Goodness of fit (S)	1.36076	1.00542	1.05873	0.97128	1.09627	1.19577
Crystallite size (nm)	23.1	25.7	27.9	33.3	51.5	93.1

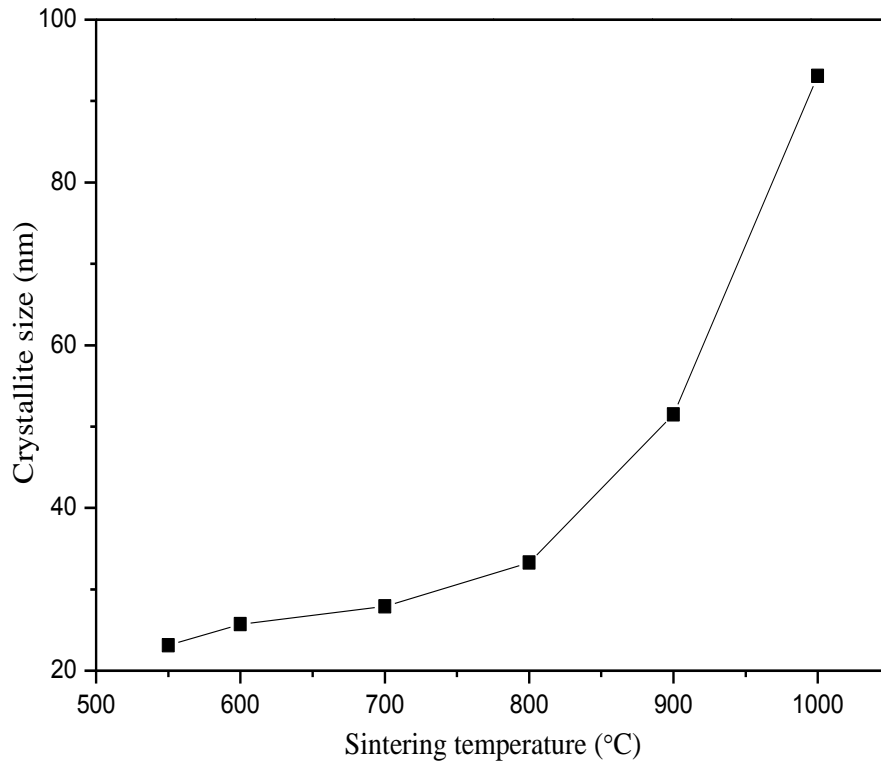


Figure 2. Crystallite size dependence on sintering temperature

Single layer of NCMO thin film was deposited for 1 hour with different post-annealing temperature via Pulsed Laser Deposition method. The XRD pattern of the NCMO thin films was shown in Fig. 3. All samples showed monoclinic structure type with space group P 1 21/c 1. There was no significant change on the lattice parameter and cell volume of the samples. However, the peak shown is much broader compared to bulk system due to much smaller range of crystallite size.

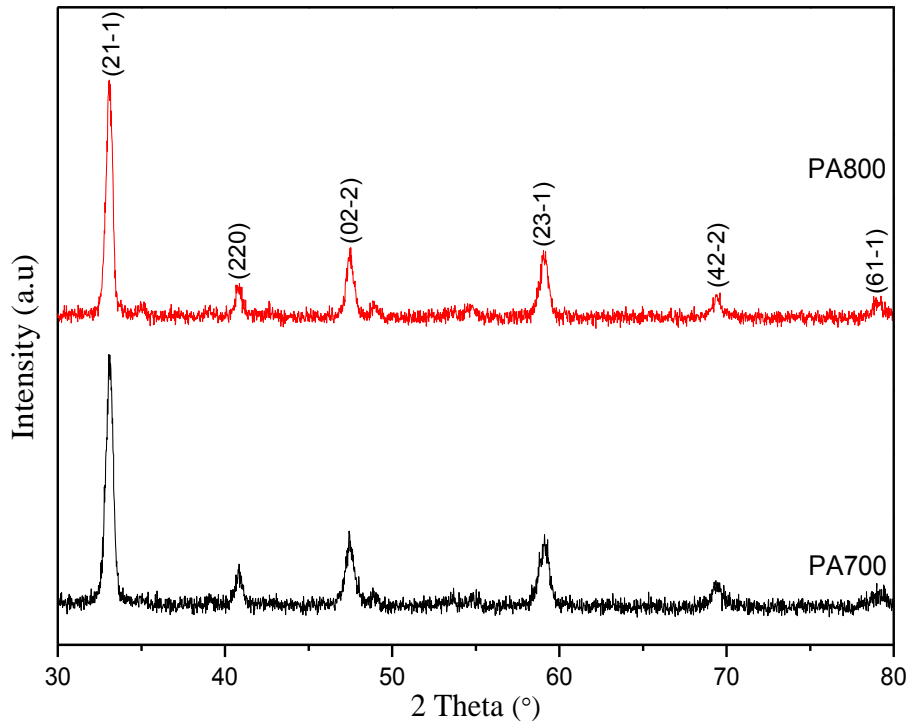


Figure 3. XRD pattern of NCMO thin film at different post-annealing temperature in 1 hour deposition

Table 2. Lattice parameter and Rietveld Refinement data of NCMO thin film with different post-annealing temperature in 1 hour deposition

Sample code	PA700	PA800
Structure type	Monoclinic (beta)	
Space group	P 1 21/c 1	
a (Å)	7.63895	7.64114
b (Å)	5.41148	5.40736
c (Å)	5.45158	5.44749
Volume (Å ³)	225.3577	225.0813
R _P (%)	7.55606	7.85777
R _{WP} (%)	9.6394	10.04215
R _{EXP} (%)	9.59334	10.30664
Goodness of fit (S)	1.00962	0.94933
Crystallite size (nm)	18.4	21.4

In conclusion, Nd_{0.67}Ca_{0.33}MnO₃ compound has been synthesized using sol-gel route with different sintering temperature starting from 550°C up until 1000°C. Rietveld’s refinement data shows that NCMO compound is single phase with orthorhombic crystal structure. It also shows that the crystallite size has a strong dependence on sintering temperature as it will increase when the sintering temperature increases. Based on AC susceptibility graph, the sample undergoes a PM to AFM (weak FM) transition at temperature lower than charge ordering transition ($T < T_{CO}$) at zero magnetic field.

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References

- [1] Hsu, D., Shih, Y. C., Wang, W. T., & Lin, J. G. (2009). Magnetotransport Behavior and the Phase Diagram of $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ Manganites, **45**(10), 4345–4347.
- [2] Lim, K. P., Halim, S. A., Chen, S. K., Awang Kechik, M. M., Ng, S. W., & Wan Jusoh, W. N. W. (2018). Grain Size Effect on Electrical and Magnetotransport Properties of Grain Size Effect on Electrical and Magnetotransport of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ synthesized via Sol-Gel Method. *J. Phys.: Conf. Ser.* **1083**: 012059.
- [3] Reshi, H. A., & Shelke, V. (2014). Grain Size Induced Metal-insulator Transition in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Compounds, **5**(4), 12–14.
- [4] Sudakshina, B., Chandrasekhar, K. D., Yang, H. D., & Vasundhara, M. (2017). Observation of complex magnetic behaviour in calcium doped neodymium manganites. **50**(6): 065004
- [5] Venkataiah, G., Lakshmi, Y. K., & Reddy, P. V. (2003). Influence of Sintering Temperature on Magnetotransport Behavior of Some Nanocrystalline Manganites. 10.5772/34099.