

EFFECT OF SINTERING DURATION ON MAGNETIC PROPERTIES OF $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ PEROVSKITE

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ABSTRACT

$\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) powder has been prepared by conventional solid state method. The evolution of structure formation on magnetic properties via single-stage and multi-stage sintering process were studied. X-ray diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) analysis showed that better crystallinity was observed in multi-stage sintered sample. The enhancement of crystallinity in multi-stage sintered sample is due to intermediate grinding process which provides more homogenous size, better diffusion and grain connection between particles. The increasing of crystallinity enhanced the magnetization for multi-stage sintered sample.

Keywords: crystallinity; magnetization; grain size

INTRODUCTION

Novel physical properties of perovskite manganites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A= Sr, Ba, Ca, Pb or vacancies) system have been extensively studied nowadays. Besides fundamental understanding of colossal magnetoresistance (CMR) mechanisms, the study have also been motivated to enhance CMR effect through doping or addition and different sintering routes. Previous investigations show that physical properties (particle size) of La-Sr-Mn-O system are dependent on sintering effect which could influence magnetic and electrical properties of materials [1,2,3]. A substantial decrease in the insulator-metal transition temperature and an enhancement in resistivity are found on lowering the sintering temperature [2,3]. Moreover, the magnetization decrease as sintering temperature decreases [4,5]. Hence, the crystallite as well as particle size shows strong dependence on sintering temperature or duration. However, controllable of desirable structural, microstructure, grain size and other is challenging in this method due to the diffusion of components occurred at high temperature and longer sintering time [6]. In this work, evolution of structure formation was improved by intermediate grinding process. A more homogenous diffusion rate is provided which will changes the magnetic properties.

METHODS

Bulk samples of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) were prepared using conventional solid-state synthesis technique. Stoichiometric amounts of La_2O_3 (99.9%), SrCO_3 (99.9%) and MnO_3 (99.9%) powders with high purity were mixed, ground and then calcined for at 900°C for 12 hours. Two sets of samples which are multi-stage sintered series (M8, M16 and M24) and single-stage sintered (S24) were synthesized at 1300°C . M8 sample was reground and sintered for 8 hours without any intermediate grinding. M16 sample was reground sintered for 16 hours with one intermediate grinding at 8 hours. M24 sample was reground and sintered for 24 hours with twice intermediate grinding at 8 hour and 16 hour respectively. However for S24, it was reground and sintered for 24 hours without any intermediate grinding. Evolution of structure formation due to different sintering route on magnetic properties was investigated. The structure of the samples was characterized by X-ray diffraction (Philips PW 300/60 Xpert Pro) using a Cu $K\alpha$ radiation at room temperature. Scanning electron microscope (LEO 1455VPSEM) was used to investigate the microstructure. Magnetic properties at room temperature from 0-1T were obtained using vibrating sample magnetometer (Lake Shore model 7407).

RESULTS AND DISCUSSIONS

X-ray diffraction patterns of all samples are shown in Figure 1(a). The results reveal that all samples matched $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ phase (ICSD code: 98-010-7027) correspond to hexagonal structure (R-3c). No other obvious phases was detected showing that all starting powders were fully reacted to form pure LSMO phase after sintered at 1300°C . Peak's intensity of (110) and (104) for multi-stage sintered and single-stage sintered samples is shown in Figure 1(b). Obviously M24 sample shows the highest peak intensity while peaks for M16, S24 and M8 were much lower and quite close to each other. As compared, the peak's intensity increases with the number of intermediate grinding, from M8 to M24. The higher peak intensity implies that the sample becomes more crystallized as the grinding stage is prolonged [7]. Intermediate grinding which carried out in multi-stage sample would break the agglomerated particles into more homogeneity and smaller powders which would enhance the reaction and resulting better crystallinity. Hence, the crystallinity for M24 sample is much higher than S24 sample although both samples were sintered in the same duration due to the effect of intermediate grinding process for M24 sample.

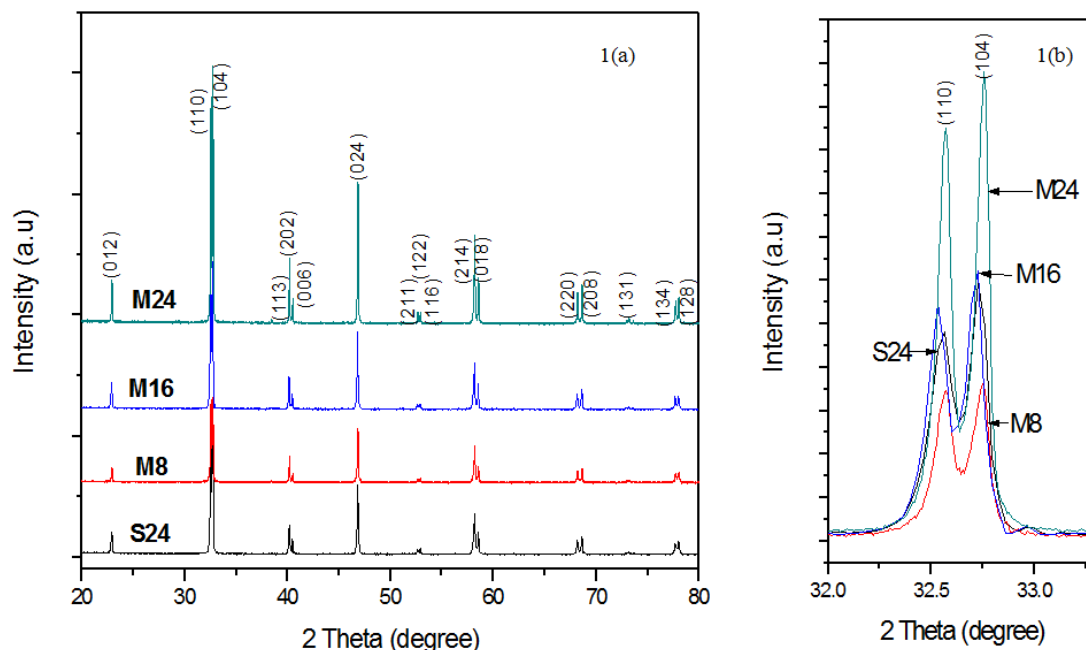


Figure 1: (a) X-ray diffraction pattern for LSMO for all samples and (b) increase of peak intensity due to the different sintering process

SEM images of all samples are shown in Figure 2. With the increase of sintering duration in multi-sintered stage samples (M8, M16, and M24), the average grain sizes become larger which is $0.556\mu\text{m}$ (M8), followed by $0.616\mu\text{m}$ (M16) to $0.816\mu\text{m}$ (M24). The grain boundaries become clearer too. This is due to the different in diffusion rate and particle connections were formed across different sintering process. For single-stage sample (S24), uneven and agglomerated grain particles with bigger grain sizes ($0.908\mu\text{m}$) were observed. Neck growth with grain boundary between connected particles which was due to coalesce of two particles into single particles was observed obviously. As shown, without any intermediate grinding process, sample caused irregular grain formation due to the inhomogeneity of agglomerated particles. Hence, S24 sample ($0.908\mu\text{m}$) is larger than M2 sample ($0.816\mu\text{m}$).

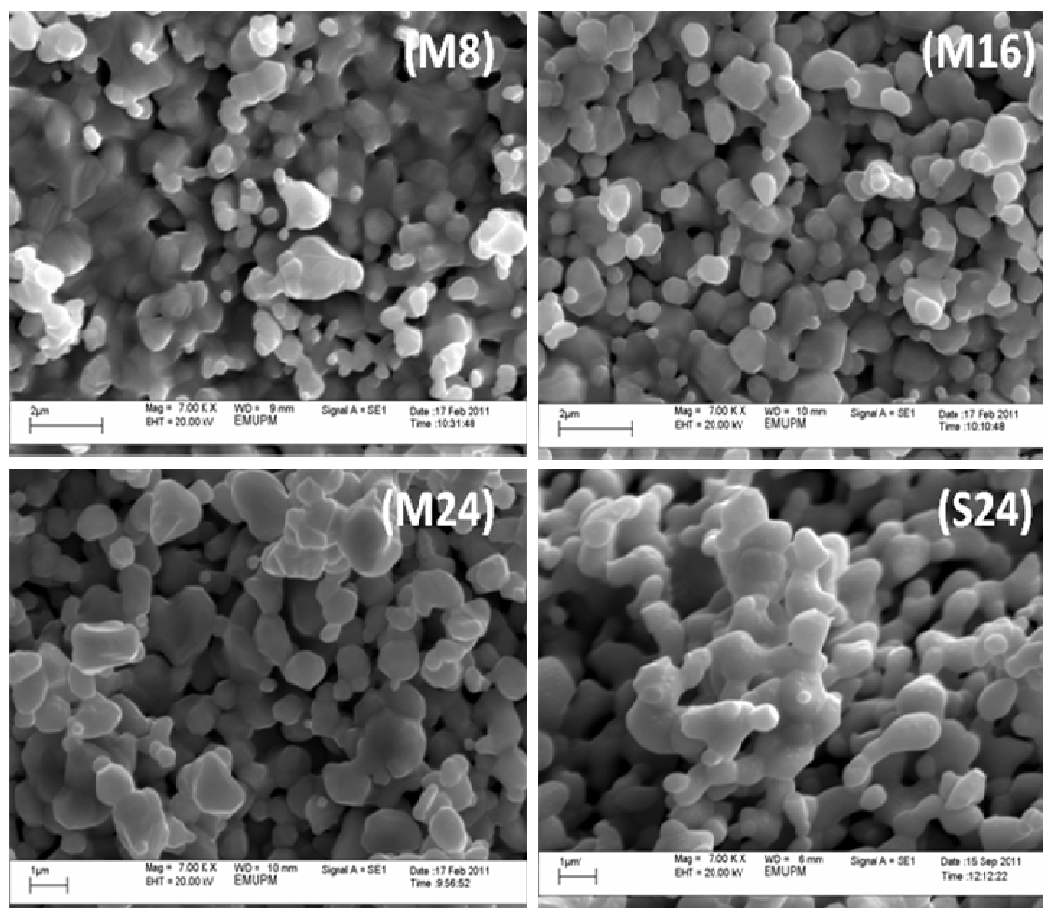


Figure 2: SEM micrograph of LSMO studied samples

Hysteresis loop of all samples at room temperature are shown in Figure 3. All LSMO samples exhibited ferromagnetic with a quick rise in magnetization due to magnetic domain rotation under low applied field and then saturated at higher applied field. For multi-stage sample, it is found that saturation magnetization, M_s increase from M8 (47.3 emu/g), followed by M16 (62.9 emu/g) and M24 (148.9 emu/g). However, saturation magnetization for single-stage sintered (S24) is 51.3 emu/g, which is lower than that of M16 and M24 samples but higher than that of M8 sample. This magnitude is quite consistent with the relative height of peak intensity (crystallinity) from XRD analysis. Hence, these suggested that an increase of crystallinity by reducing the fraction of amorphous region outside the grain through intermediate grinding might increase the M_s . A better crystalline structure will enhance the alignment of magnetic moments when magnetic field is applied. Single-stage sample (S24) shows lower M_s which is quite similar with M8 and M16 samples. Besides that, lower gradient indicated that it is a weaker ferromagnetic sample as compared to multi-sintered samples.

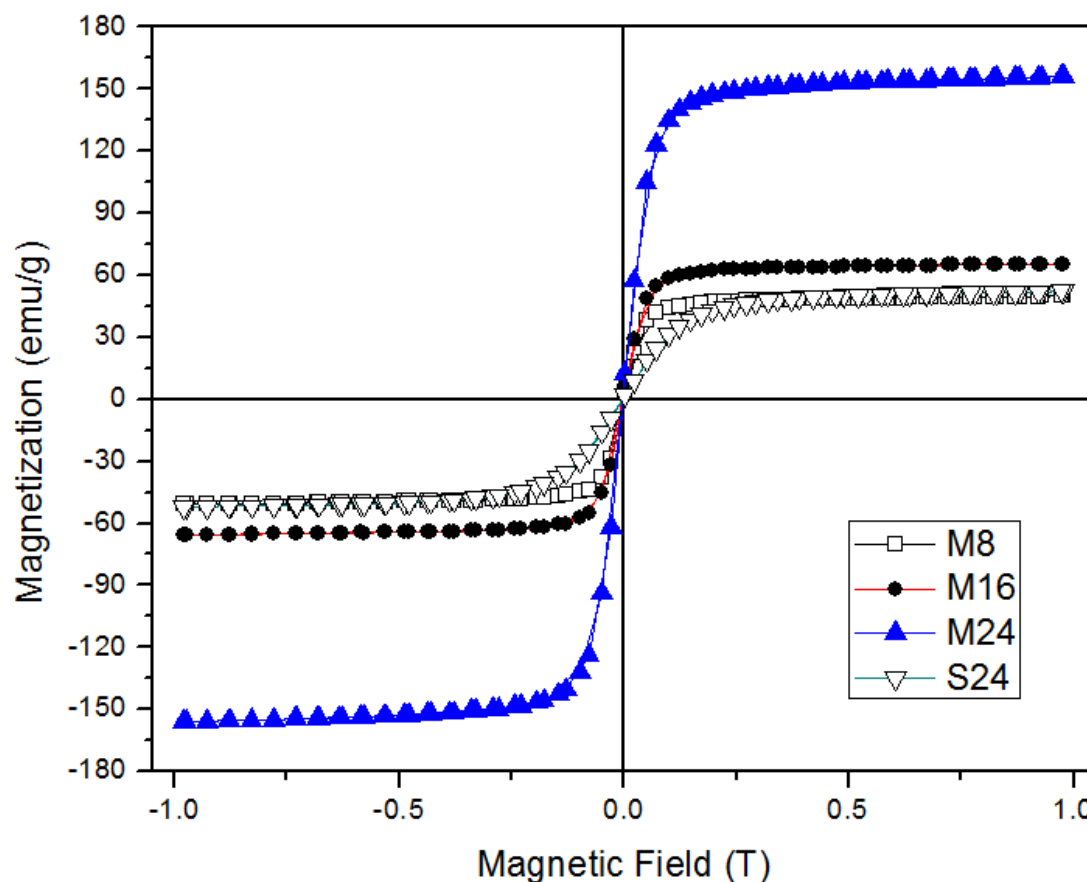


Figure 3: Magnetization as a function of applied external magnetic field at room temperature

CONCLUSION

In summary, single-stage and multi-stage sintering of LSMO samples had been fabricated successfully via solid-state method. Magnetic properties which are strongly dependent on the evolution of structure formation by different sintering route have been studied. All the samples show pure LSMO perovskite phase with hexagonal structure (R-3c). Through XRD and SEM analysis, multi-stage sintering would promote a higher crystallinity and smaller particles size than single-stage sintering. Enhancement of the crystallinity will increase the magnetization value.

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REFERENCES

- [1] Pham Thanh Phong, Do Hung Manh, Lee Van Hong, Nguyen Xuan Phuc, *Communications in Physics*, **18**, (1) (2008) 48-57
- [2] V.Dyakonov, A.Slawaska-Waniewska, J.Kazmierczak, K.Piotrowski, O.Iesenchuk, *Low Temperature Physics*, **35** (7) (2009) 568-576
- [3] M.Z.Iqbal, S.Ali, M.A.Mirza, Coden JNSMAC, **4**, (1&2) (2008) 51-63
- [4] Yun-Hui Huang, Zhi-Gang Xu, Chun-Hua Yan, Zhe-Ming Wang, Tao Zhu, *Solid State Communication* **114** (2000) 43-47
- [5] Anurag Guar and G D Varma, *J.Phys: Codens. Matter* **18** (2006) 8837-8846
- [6] V Dayal and S Keshri, *Solid State Commun.* **142** 63 (2007)
- [7] Y.Waseda, A.Muramatsu, "Morphology Control of Materials and Nanoparticles", Springer, Berlin, 2003.