



Effect of Sintering Temperature on Metal-Insulator Phase Transition in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ Perovskites

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Abstract: Lanthanum calcium based perovskites are found to be advantageous for the possible applications in magnetic sensors/reading heads, cathodes in solid oxide fuel cells, and frequency switching devices. In the present investigation $\text{La}_{0.5}\text{Ca}_{0.7}\text{MnO}_3$ perovskites were synthesised through solid state reaction and sintered at four different temperatures such as 900, 1000, 1100 and 1200° C. X-ray powder diffraction pattern confirms that the prepared $\text{La}_{0.5}\text{Ca}_{0.7}\text{MnO}_3$ perovskites have orthorhombic structure with Pnma space group. Ultrasonic in-situ measurements have been carried out on the $\text{La}_{0.5}\text{Ca}_{0.7}\text{MnO}_3$ perovskites over wide range of temperature and elastic constants such as bulk modulus of the prepared $\text{La}_{0.5}\text{Ca}_{0.7}\text{MnO}_3$ perovskites was obtained as function of temperature. The temperature-dependent bulk modulus has shown an interesting anomaly at the metal-insulator phase transition. The metal insulator transition temperature derived from temperature-dependent bulk modulus increases from temperature 352° C to 367° C with the increase of sintering temperature from 900 to 1200° C.

Keywords: Sintering, Perovskite, Bulk modulus, Transition temperature

1.0 Introduction

Mixed-valent $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ perovskite manganites (R- Rare earth element and A- Alkaline element) are of great importance due to their special properties such as colossal magneto resistance (CMR), ferromagnetic (FM) to paramagnetic (PM) phase transition, metal-insulator (MI) phase transition charge ordering (CO), etc [1]. The applications of such materials include solar cells, switching devices, and magnetic storage devices. The dopant and its concentration has considerable impacts on the transport properties, Jahn-Teller (JT) induced strains and structural changes [2]. The MI transition temperature for $(\text{La}_{0.5}\text{Pr}_{0.5})_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ is 130 K. But the doping of 2% of copper in the above poly crystalline sample makes it an insulator over the temperature range 60 to 300 K [3]. Therefore, by changing the doping element, its level and its ionic radii one can modify the properties of the perovskite materials. In addition, the sintering temperature

of the sample also has an effect on the properties of the materials. Sintering is the process that helps to enhance purity and homogeneity of materials and also to increase the rate of diffusion of particles in the material. Sintering causes changes in the size of the particles, density, etc. The optimum sintering temperature is useful in balancing the properties of the materials [4]. Survey of literature suggests that the effect of sintering temperature on a wide variety of materials has been studied. The Curie temperature (T_c) of $\text{Ni}_{0.55}\text{Zn}_{0.45}\text{Fe}_2\text{O}_4$ ferrites increases from 321 to 323 K when the sintering temperature of the sample increases from 1250 to 1300 K. The density of the samples also increases when the sintering temperature increases from 1160 to 1250 °C and begins to decrease beyond 1250 °C [5]. The XRD spectra of ZnO particles shows that their size increases from 11.3 to 31.7 μm as the sintering temperature increases from 980 to 1380 °C [6].

The phase transition in the perovskite can be detected using in-situ ultrasonic measurement, an effective nondestructive technique. The interaction of ultrasonic waves with the perovskite leads to the structural/phase changes that are associated with lattice displacement and is reflected in the measurement of ultrasonic parameters [7-8]. The calcium substituted LaMnO_3 perovskite material exhibits metal-insulator phase transition at elevated temperatures depending on the level of calcium composition. Hazama et al., investigated the temperature dependence of elastic constants of perovskite manganite material $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.30, 0.40$ and 0.50). It has been observed that the samples show softening in the wide temperature range between 400 and 250 K. In addition for $x = 0.50$, the compound exhibits considerable softening around the charge ordering temperature $T_{co} = 240$ K. This indicates the fluctuation of charge carried with concentration and the concentration ratio $\text{Mn}^{3+}/\text{Mn}^{4+}$ is 1, and softening decreases as the value of x decreases. This shows that the charge order in the samples deviates from the position $x = 0.50$ [10].

In this study, LCMO perovskite samples were prepared to study the temperature dependence of the phase transition of sintered at different temperatures. The phase transition properties of the samples were studied by performing in-situ measurements of ultrasonic parameters over a temperature range of 27 °C to 427 °C. The bulk modulus of the perovskite was determined at various temperatures. The results obtained were used to discuss the impact of sintering temperature on the perovskite samples.

2.0 Experimental procedure

$\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ perovskite was synthesized in the form of pellets using solid state reaction technique. The prepared perovskite pellets were sintered at four different temperatures at 900, 1000, 1100 and 1200 °C. Hereafter the perovskite manganite samples will be called LCMO900, LCMO1000, LCMO1100 and LCMO1200 respectively for the sintering temperature 900, 1000, 1100 and 1200 °C. The crystalline nature of the prepared perovskite samples was revealed by the recorded X-ray diffraction (XRD) patterns using a powder X-ray diffractometer (X'PERT PRO PANalytical, Netherland). The longitudinal and shear ultrasonic velocity were measured as a function of temperature at the fundamental frequency of 5 MHz employing through

transmission method discussed in our earlier studies [7]. The bulk modulus of the samples at different temperatures have been determined using the standard formula [7].

3.0 Results and Discussion

XRD spectra of the prepared LCMO900, LCMO1000, LCMO1100 and LCMO1200 perovskite was shown in Fig.1 which shows that the samples belong to orthorhombic crystal structure with $pmnma$ space group. The observation is in close agreement with JCPDS file 51-1586. The crystalline size of the prepared samples as determined by Scherrer's equation [7] are 52 ± 3 , 60 ± 4 , 71 ± 3 , 78 ± 3 nm for the samples LCMO900, LCMO1000, LCMO1100 and LCMO1200 respectively and it reveals that the crystalline size increases with the increase of sintering temperature of the sample.

The temperature dependent measurement of shear and longitudinal ultrasonic velocities were performed out to determine the bulk modulus (K) of the perovskite. The values of K are used to understand the characteristic studies on the phase transition in the prepared LCMO900, LCMO1000, LCMO1100 and LCMO1200 perovskite samples. In perovskite manganite materials, such measurements are marked by an anomaly at the structural/phase transition temperature [12].

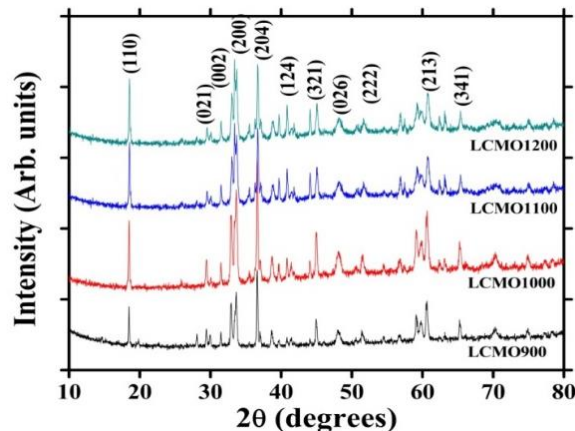


Figure 1. XRD pattern of the sintered LCMO samples

The variation of bulk modulus with temperature is plotted in **Fig. 2**. To understand the behaviour of K at different temperatures, the graph shown in **Fig. 2** can be considered into three zones. In the graph of LCMO900, we have Zone I (from 27° to 347° C), Zone II (from 347 to 357° C) and Zone III (from 357° to 447° C). The value of K decreases gradually with the increase of temperature in Zone I and Zone III which confirms the absence of structural/phase transition in the range of temperature.

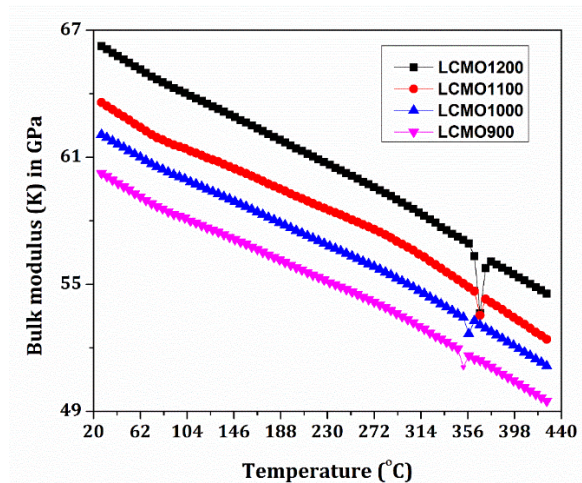


Figure 2. Temperature dependence of bulk modulus in the sintered LCMO samples

However, in Zone II (called anomalous region), there is a sudden drop in bulk modulus and the value becomes 51.95 GPa at 347° C comes down to a minimum of 51.08 GPa at 352° C followed by a steep rise up to 357° C where K becomes 51.64 GPa. Thus an anomalous behaviour is exhibited in Zone II called anomalous region. Similarly, the anomalous/ asymmetric region noted for LCMO1000, LCMO1100 and LCMO1200 were noted in Table 1 along with anomalous region noted for LCMO900 for easy comparison.

Table 1. Temperature range of anomalous region of the sintered LCMO samples

Sample	Anomalous region (°C)		
	Start	Dip/peak	End
LCMO900	347	352	357
LCMO1000	347	357	362
LCMO1100	362	367	372
LCMO1200	357	367	377

The temperature at which K becomes minimum (352° C) is called the anomalous temperature. From the curves shown in Fig. 2, it is observed that for the sample LCMO1000 the anomalous temperature is 357° C and for both LCMO1100 and LCMO1200 perovskites is 367° C. The temperature dependent K determined using the in-situ ultrasonic measurement helps to explore the phase transition in perovskite materials [13]. The comparison of the above results with the previous investigations confirms that the anomalous temperatures obtained in the

sintered samples are metal-insulator transition temperature (T_M) [14]. Thus the value of T_M is 352, 357 for LCMO900 and LCMO1000 samples respectively and is 367° C for both LCMO1100 and LCMO1200 perovskites. The result shows that T_M of the prepared LCMO samples increases from 325° to 367° C as the sintering temperature increases from 900° C to 1200° C. For the further increase of the sintering temperature to 1100° C, the value of T_M attains saturation.

4.0 Conclusions

In this study, $\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$ perovskite samples were synthesized. The sintering temperature of the samples were done at 900, 1000, 1100 and 1200° C. The XRD spectra of the samples show that the samples have orthorhombic structure with *pnma* space group. The crystalline size was found to increase with the sintering temperature. The temperature dependent bulk modulus of the samples shows sharp anomaly at the metal-insulator transition temperature (T_M) in the sintered samples. The value of T_M attains saturation at higher sintering temperature of the sample.

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Conflict of interest: NIL

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