Synthesis, phase transition and structural properties of LPMO nanoperovskites with influence of grain size towards ultrasonic studies

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Synthesis, phase transition and structural properties of LPMO nanoperovskites with influence of grain size towards ultrasonic studies

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Abstract: In this present work, nanocrystalline powders of Pb-doped LaMnO3 or La0.64Pb0.36MnO3 (LPMO) have been synthesized with various grain sizes by a solid-state reaction method followed by ball milling technique. Based on the dependence of crystallite size, the magnetic properties of the LPMO nanoperovskites have been investigated. The nanoperovskites have been structurally characterized. Further, the synthesized nanoperovskite manganite materials with various grain sizes are systematically studied for ultrasonic longitudinal velocity ($U_L$), shear velocity ($U_S$) and longitudinal and shear attenuation ($\alpha_L$ and $\alpha_S$) in wide range of temperatures. All the nanoperovskites revealed an anomalous behaviour in concern with ultrasonic velocities and attenuation towards the phenomenon of phase transition.

Keywords: nanoperovskites; manganite materials; phase transition; structural; ultrasonic studies

ABOUT THE AUTHORS

M. Vigneswari has an in-depth knowledge in fundamental and advanced Physics. She also has a vast experience in the synthesis of perovskites for the past three years. She has also provided several important international research works in this field. Presently, she is working on the synthesis of luminous nanoperovskites by collaborating with S Sudharsan and guided by S Sankarrajan.

S. Sudharsan has provided several vital international research contributions in the synthesis and multifacetal applications of various nanomaterials for the past six years. Recently, he has aided few research works on the synthesis of luminous nanoperovskites. Currently, he is working on the synthesis of bioactive dielectric glass.

S. Sankarrajan has a wide background in the synthesis and applications of perovskites for the past 15 years. He has also provided several imperative international research articles in the above field. Presently, his group is working on the synthesis of luminous nanoperovskites.

PUBLIC INTEREST STATEMENT

In this present work, our group has synthesized nanocrystalline powders of Pb-doped LaMnO3 or La0.64Pb0.36MnO3 (LPMO) with various grain sizes by a solid-state reaction followed by a facile ball milling technique. The manganite nanoperovskites are structurally characterized and systematically studied in wide range of temperatures. All the nanoperovskites revealed an anomalous behaviour in concern with the phenomenon of phase transition.
1. Introduction
Perovskite manganites have been the subject matter of a large number of studies due to their exotic property (Arulraj, Dinnebier, Carlson, Hanfland, & van Smaalen, 2007; Jin et al., 1994; Martin, Chu, & Ramesh, 2010; Xu, Meier, Das, Koblishka, & Hartmann, 2002) along with extraordinary structural, electrical and magnetic properties. The parent compound LaMnO$_3$ (LMO) doped with divalent alkaline earth cation (A$^{2+}$) results in the conversion of a proportional number of Mn$^{3+}$ to Mn$^{4+}$ along with structural distortion due to the different ionic sizes in A and B sites. The metallic character and ferromagnetic (FM) properties of these materials have been attributed due to the interaction between Mn$^{4+}$ and Mn$^{3+}$ ion pairs through the double exchange (DE) mechanism (Zener, 1951). The grain or crystallite size is more important since the magnetic and transport properties of this material strongly depend on them. Owing to the persuade of structural and magnetic disorders at the grain surfaces predominantly in nanocrystalline systems, samples with smaller grain sizes perhaps demonstrate their effective electronic and magnetic properties (Zhang, Yang, Ding, Xing, & Du, 1999).

Nanostructured perovskites exhibit fascinating size-dependent optical, electronic, magnetic, thermal, mechanical and chemical properties, which are distinct from those of their corresponding bulk perovskites (Ma et al., 2002; Mao, Banerjee, & Wong, 2003; Newsms et al., 2000; Urban, Yun, Gu, & Park, 2002; Zhang, Li, & Jiang, 2000). La$_{1-x}$Pb$_x$MnO$_3$ (LPMO) perovskite manganite demonstrates a ferromagnetic metallic phase at room temperature besides large magnetoresistance. Similarly, due to their unique physicochemical and large giant magnetoresistant properties, LPMO nanophase manganites have shown potential for a wide range of applications such as magnetic field sensors, piezoelectric transducers and actuators, ultrasonic devices, fuel cells, infrared devices, magnetic reading heads for memory devices and non-volatility memory devices and microwave active components (Ling et al., 2005; Ramesh Babu et al., 2009; Zhang et al., 2006).

Though there are different methods used to synthesize the LPMO perovskite manganites at different grain size viz., ball milling method, sonochemical method, electrochemical deposition, magnetron sputtering, pulse laser deposition, sol-gel, hydrothermal and spray pyrolysis (Abrutis et al., 2004; Cuong, Dho, Park, & Kim, 2009; Panagiotopoulos, Moutis, Ziese, & Bollero, 2006; Pang et al., 2003; Rostamnejadi, Salamati, Kameli, & Ahmadvand, 2009), ball milling method is best suited here due to its ease to other techniques, that has established much concentration as a dominant tool for the synthesis of several advanced functional materials (Zhang et al., 2010).

Even though different techniques are known to explore structural/phase transition temperatures of perovskite manganite materials, the ultrasonic measurement is an important tool owing to its precise online evaluation of structural/phase transitions, non-destructive method of measurement, accurate and reproducibility of results than any other experimental methods (Chau et al., 2003).

In this work, nanocrystalline powders of Pb-doped LaMnO$_3$ or La$_{0.64}$Pb$_{0.36}$MnO$_3$ (LPMO) are synthesized via solid-state reaction followed by the ball milling technique with various grain sizes. A systematic study has been made on ultrasonic longitudinal velocity ($U_L$), shear velocity ($U_S$) and longitudinal and shear attenuation ($\alpha_L$ and $\alpha_S$) in nanostructured LPMO perovskites manganite materials for different grain sizes with wide range of temperatures. The observed anomalous behaviour in ultrasonic velocities and attenuation has been discussed with the phenomenon of phase transition. Further, the structural properties along with the morphology of the prepared LPMO nanoperovskite samples have been characterized using different techniques.

2. Experimental details

2.1. Synthesis
The nanostructured La$_{0.5}$Pb$_{0.5}$MnO$_3$ perovskite samples of various grain sizes were prepared from high-purity lanthanum nitrate (99.9%, Sigma Aldrich), lead nitrate (99.0%, Himedia GR), manganese carbonate (99.9%, Sigma Aldrich) and citric acid (99.9%, Sigma Aldrich) by conventional solid-state reaction technique followed by the ball milling technique (Fritsch Planetary Monomill, Germany). The
stoichiometric ratio of the base materials was measured and grounded. The mixture was calcined twice at 723 K for 2 h in air (Lenton Wire Chamber Furnace, Germany). Further, the calcined powders were subjected to high-energy ball milling with intermediate grounding. Small amount of milled powder was taken out from the bowl after 2, 4, 6 and 8 h milling to check the formation of nanostructured material and the samples were denoted as LPMO2, LPMO4, LPMO6 and LPMO8, respectively. Finally, samples were pressed into pellets with a diameter of 13 mm and then sintered at 1,273 K for 12 h in atmospheric air. The sintered pellets were used for further characterization.

2.2. Instrumentation
The X-ray diffractograms of synthesized nano LSMO perovskites were recorded in BRUKER AXS D8 advance X-ray diffractometer, USA, with Cu–Kα radiation and amplitude wave \( \lambda = 1.5406 \text{ Å} \). The 2θ scans were performed with the steps of 0.05. The grain size (d) of LPMO nanoperovskites was determined using the Scherrer relation.

\[
d = \frac{0.94 \lambda}{\beta_{1/2} \cos \theta}
\]

where \( \beta_{1/2} \) and \( \theta \) are the full width half maximum and diffraction angle, respectively. The density of the synthesized LPMO nanoperovskite samples was determined using Archimedes principle. To understand the functional group, the synthesized LPMO nanoperovskites were analysed in a Shimadzu FTIR spectrophotometer IR Affinity-1 by employing KBr pellets and registering amplitude waves ranging from 400 to 4,000 cm\(^{-1}\). The surface area of the prepared LPMO nanoperovskites was determined using Brunauer–Emmett–Teller (BET) surface area analyser (Autosorb-1, Quantachrome, USA). Morphological characteristics of the synthesized LPMO nanoperovskites were evaluated by SEM (Quanta FEG 250, Netherlands). The images obtained using a TEM (CM 200; Philips, USA) were used to reveal the sub structural information and particle size of the samples. Ultrasonic velocities and attenuation measurements were obtained using through-transmission technique. The ultrasonic signal was transmitted into the specimen using a high-power ultrasonic Pulser Receiver (Olympus NDT, 5900 PR, USA). A high-frequency (1 GHz) digital storage oscilloscope (Lecroy, Wave Runner 104 MXi, USA) with a built-in computer was used to record digital ultrasonic (rf) signals. The ultrasonic velocities and attenuation measurements were taken at the temperature range of 300–600 K at a heating rate of 0.5 K min\(^{-1}\). A programmable temperature controller (Eurotherm, 2604, USA) was used to control the required temperature under a dynamic mode of operation.

3. Results and discussion

3.1. XRD analysis
The XRD pattern of nano LPMO perovskites with various grain sizes is shown in Figure 1. The observed diffraction peaks in the XRD pattern of nano LPMO samples were used to explore the crystalline nature of the prepared samples. The peaks of the prepared sample have emerged out as a uniform crystalline phase with the maximum intensity planes at [0 1 1]. The synthesized samples were indexed and well matched with rhombohedral phases (JCPDS files No: 4-095-1256) as reported elsewhere (Chau et al., 2003). The grain size of nano LPMO perovskite samples has been obtained using Scherrer’s formula and the values are, respectively, 63, 48, 25 and 12 nm for LPMO2, LPMO4, LPMO6 and LPMO8. Hereafter, the samples were renamed as LPMO63, LPMO48, LPMO25 and LPMO12. Further, the XRD peaks of smaller grain size of nano LPMO perovskite samples shifted towards a lower diffracted angle when compared with the higher grain size samples. A shift in diffraction angle (2θ = 33.114) to a lower value (2θ = 32.20) from LPMO63 to LPMO12 has been observed. And the nano LPMO12 perovskite sample has a large full width half maximum value (0.6635) when compared with nano LSMO63 perovskite sample (0.1998). Since the grain size is reduced, the \( \beta \) value is increased due to the weakening of DE interaction between Mn\(^{3+}\) and Mn\(^{4+}\).

3.2. FTIR analysis
The observed FTIR spectra of LPMO63 nano perovskite sample are shown in Figure 2. The observed broad peak in the low wavenumber range, i.e. 450–600 cm\(^{-1}\), is ascribed to Mn–O bonds because of
the Jahn–Teller effect (JT) in the prepared perovskite sample (Keshri, Joshi, & Rout, 2009). The observed broad band in the high wavenumber range of 3,410 cm⁻¹ can be attributed to the O–H stretching vibration of water molecules (Kolat, Gencer, Gunes, & Atalay, 2007). The intense band observed at 1,634 cm⁻¹ corresponds to the H–O–H bending mode, characteristic of water molecules (Keshri et al., 2009).

3.3. Density measurement
The density of nano-sized LPMO perovskite with different grain sizes was measured. The physical parameter like density of the samples has played a vital role in determining the structural, electrical and magnetic properties. The grain size-dependent density is shown in Figure 3. The values of the densities are 6,387, 6,128, 5,926 and 5,729 kg/m³ for LPMO63, LPMO48, LPMO25 and LPMO12, respectively. The density of the nano-sized LPMO perovskite manganite material is significantly decreased with a decrease in grain size. It is interesting to observe that the reduction of grain size has led to a decrease in the density.

3.4. BET surface area analysis
The surface area of the synthesized LPMO nanoperovskite samples has been measured and the values are 15, 20, 40 and 87 m² g⁻¹, respectively, for LPMO63, LPMO48, LPMO25 and LPMO12. It has inferred that the surface area increases with a decrease in grain size. The equivalent spherical diameter ($D_{BET}$) has been determined by measuring the surface area and the density of perovskite samples and the values are 61, 50, 24 and 13 nm, respectively, for LPMO63, LPMO48, LPMO25 and LPMO12. The $D_{BET}$ of the samples decreases with an increase in the milling time. This is in close agreement with the grain size from XRD results.

3.5. Morphological analysis
The SEM image of the LPMO nanoperovskite samples is shown in Figure 4(a–d). From the figure, it is revealed that there is a small-sized particle with diameter between 90 and 10 nm, which could be seen in the magnified image. And it is also clear that the size distribution of the particles has not been quite even due to the synthesis process since all the prepared LPMO perovskite samples have irregular boundaries due to the homogeneity during synthesis at different milling time. Further, all the images have been intrinsically homogenous and have exposed an agglomerated spherical-like morphology with undistributed pores. In addition, the crystallite size from XRD result is compared with the particle size
from SEM image owing to the bunching of strappingly relating grains in SEM images. And it is also clear that both crystallite and particle size of prepared LPMO nanoperovskites decrease with increase in milling time.

The TEM image of LPMO nanoperovskite samples has been shown in Figure 5(a–d). It is clear that the synthesised LPMO nanoperovskite samples are dissimilar and distributed in different sizes. The approximate particle size is estimated from TEM images. The particle sizes are 64, 51, 28 and 11 nm, respectively, for LPMO63, LPMO48, LPMO25 and LPMO12, respectively. Further, it is clear from the TEM images that the particle size decreases with an increase in milling time. This is in close concurrence with the results of BET study.
3.6. Ultrasonic measurement

The longitudinal, shear ultrasonic velocities and attenuation measurements of LPMO nanoperovskite samples were carried out at room temperature. The grain size-dependent ultrasonic parameters of LPMO nanoperovskites have been shown in Figure 6(a–b). A linear increase in longitudinal ultrasonic velocity ($U_L$) is observed with a decrease in grain size. Consequently, for attenuation ($\alpha_L$), it decreases with a decrease in grain size. A similar trend has been observed in shear velocity ($U_S$) and its attenuation ($\alpha_S$) of $U_L$ and $\alpha_L$, respectively, of LPMO nanoperovskite samples. An increase in ultrasonic velocity and a decrease in attenuation have been obtained with a decrease in grain size. The LPMO nanoperovskites having disordered surface layers and uniform morphology as their grain size are reduced (Godfrey & Philip, 1996).

The temperature dependencies within the region 300–400 K of $U_L$ and $U_S$ of LPMO nanoperovskites with various grain sizes are shown, respectively, in Figures 7 and 8. It is interesting to note from the observed results that there is an anomalous behaviour in the variation of both $U_L$ and $U_S$ rather than an expected linear variation as a function of temperature. The phase transition temperature of LPMO nanoperovskite samples is examined through ultrasonic studies. The ultrasonic velocities and attenuation as a function of temperature have been used to reveal information about the various temperature-dependent phase transitions and their behaviour during the transition in LPMO nanoperovskite samples.

It is evident from Figures 7 and 8 that the monotonic decrease in velocity is 300–341 K and 363–400 K, 300–340 K and 359–400 K, 300–338 K and 356–400 K and 300–336 K and 355–400 K noted, respectively, for LPMO63, LPMO48, LPMO25 and LPMO12. An anomalous behaviour is noted in the temperature ranging from 341 to 363 K and it is used to study the structural/phase transitions in LPMO nanoperovskite samples. It is clearly seen that at the temperature of 341 K, there is a sharp dip in velocity and reaches a minimum at 353 K and a further increase in temperature beyond 353 K leads to a sharp rise in velocity up to 363 K. Similarly, the dip in velocities for LPMO48, LPMO25 and LPMO12 is observed at 349, 347 and 345 K, respectively. A similar behaviour in $U_L$ is observed as that of $U_L$, $\alpha_L$ and $\alpha_S$ as a function of temperature have shown a reverse trend to the velocities as shown in Figures 9 and 10.

The observed anomalous temperature in ultrasonic velocity/attenuation measurements is in agreement with the temperature at which FM–PM phase transition takes place in LPMO perovskite samples (Mao et al., 2003; Singh et al., 2007). It is inferred that the temperature at which the minima in
velocities is related to the FM–PM transition temperature of LPMO nanoperovskite samples. Thus, the temperature 353, 349, 347 and 345 K are denoted as $T_c$ for LPMO63, LPMO48, LPMO25 and LPMO12, respectively. It is clear that the $T_c$ value decreases with a decrease in grain size. As the grain size is reduced, the short-range magnetic interaction between Mn$^{3+}$ and Mn$^{4+}$ ions is distorted due to the large number of grain boundaries. It has been responsible for the suppression of $T_c$ and reduction in magnetization (Zheng, Zhu, & Li, 2001).

As the grain size is reduced, the broad FM transition has been observed in the prepared LPMO nanoperovskite samples. This is in line with the observation made from the XRD pattern for nanocrystalline samples. To explain the observed behaviour, Curie temperatures ($T_c$) and transition width ($\Delta T_c$) of all samples were noted and are given in Table 1. It is seen that the broadened transition observed in smaller grain size LPMO nanoperovskite samples indicate a diffused FM phase transition. Further, a broad transition with large peaks was considered to be due to the existence of small grain size attributed to the coexistence of orbitally disordered (OD) and OO phases (Shankar & Raychaudhuri, 2006; Trukhanov, Trukhanov, Szymczak, Botez, & Adair, 2007).

One can directly correlate the occurrence of peak height at transition temperature to lattice softening. Generally, a decrease in velocity and an increase in attenuation are due to the occurrence of lattice softening, whereas an increase in velocity and decrease in attenuation are mainly due to lattice hardening (Sankarrajan, Sakhipandi, & Rajendran, 2011). An abrupt change in coupling between spin, charge, orbital and lattice degrees of freedom and interactions at transition temperature is responsible for the observed anomaly in ultrasonic velocities and attenuations (Ling et al., 2005; Sankarrajan et al., 2011).

From Figures 7 and 8, it is seen that the lattice hardening and lattice softening are gradually increased from LPMO63 to LPMO12 nanoperovskite samples. The observed larger magnitude in smaller grain size LPMO nanoperovskite samples is not only attributed to a conventional FM spin fluctuation near FM–PM transition but is also related to the existence of strong electron–lattice interactions via Jahn–Teller distortion of Mn$^{3+}$O$_6$ and the spontaneous spin ordering below FM–PM transition (Zheng, Zhu, Xie, Huang, & Li, 2002). The large softening below $T_c$ in velocities is attributed to the significant change in lattice parameters or the Mn–O bond length (Ramesh Babu et al., 2009). The local distortion of MnO$_6$ determines the transport properties and CMR properties of perovskite materials. Thus, it leads to a significant reduction in the Jahn–Teller distortion of the Mn$^{3+}$O$_6$ octahedral because of spin-lattice

Figure 5. TEM micrograph of prepared LPMO nanoperovskites (a–d).
coupling below the transition temperature (Bose, Raychaudhuri, Banerjee, Vasa, & Ayyub, 2005). This indicates a direct evidence for weak magnetic coupling between the grains below $T_c$ in smaller grain size nanoperovskites manganite materials (Bose et al., 2005; Zheng et al., 2002).

The grain size-dependent $T_c$ of synthesized LPMO nanoperovskite samples is shown in Figure 11. It is evident from the figure that when the grain size is reduced from LPMO63 to LPMO12 nanoperovskite samples, the $T_c$ value decreases from 353 to 345 K. Further, one can easily identify the unknown size of the particles from the plot of grain size-dependent $T_c$. Thus, the ultrasonic measurements have been useful in exploring the structural and phase transition behaviour in LPMO nanoperovskite manganite materials. Further, it is interesting to note that as the grain size is decreasing, the $T_c$ is also decreasing.
4. Conclusion

This research work addressed the investigation of grain size effect on phase transition and structural properties of LPMO nanoperovskite samples towards ultrasonic studies. Herein, the LPMO nanoperovskite samples are prepared by solid-state reaction followed by the ball milling method. From the XRD analysis, the synthesized samples were indexed and well matched with rhombohedral phases. Further, increase in $\beta$ value and decrease in $2\theta$ with decrease in grain size due to the weakening of DE interaction between Mn$^{3+}$ and Mn$^{4+}$ are observed. And the surface area analysis from the BET study is in close agreement with the grain size from XRD results. Further, the morphological analysis is in close agreement with the BET results. From the ultrasonic measurement, it is clearly seen that there exists an anomalous behaviour in the variation of ultrasonic parameters (velocity and attenuation) rather than an expected linear variation as a function of temperature. The $T_c$ values of synthesized LPMO nanoperovskites were obtained from the observed maxima/minima in $U_L$, $U_S$ and $\alpha_L$ and

![Figure 7. Temperature dependence of ultrasonic longitudinal velocity.](image)

![Figure 8. Temperature dependence of shear ultrasonic velocity.](image)
α$_s$. Lower $T_c$ and broader transition are observed from the nano LPMO63 to LPMO12 due to the reduction of grain size and distribution of grain boundaries. The diffusion of the FM–PM phase transition along with a decrease in $T_c$ is correlated due to the effect of grain size. It is also clear that as the grain size is reduced, the occurrence of lattice softening and hardening is more and wider because of the

Table 1. Temperature range of anomalous region of LPMO nanoperoxide sample

| Anomalous temperature | LPMO63 | LPMO48 | LPMO25 | LPMO12 |
|-----------------------|--------|--------|--------|--------|
| Start (K)             | 341    | 340    | 338    | 336    |
| End (K)               | 363    | 359    | 356    | 355    |
| Anomaly (K)           | 353    | 349    | 347    | 345    |

Figure 9. Temperature dependence of ultrasonic longitudinal attenuation.

Figure 10. Temperature dependence of shear ultrasonic attenuation.
existence of strong electron–phonon interaction and involvement of disordered surface layers, which is acting as a significant task when the grain size is reduced. Moreover, the observation made from the XRD pattern for LPMO nanoperovskite samples is in line with the peak broadening in ultrasonic studies at phase transition. Finally, the ultrasonic parameters perform as central tools to achieve unambiguous facts about structural/phase transitions of the prepared LPMO nanoperovskites.

Figure 11. Grain size-dependent transition temperature of LPMO nanoperovskites.
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