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Oxygen-deficiency-dependent Seebeck coefficient and electrical properties of mesoporous $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-x}$ films

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The thermoelectric power factor of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) is closely related to its oxygen-deficient nature. In this study, the oxygen content of mesoporous LSMO films was controlled using various annealing atmospheres (oxygen, nitrogen, air, and argon) to investigate the relationship between oxygen deficiency and power factor. The effect of the mesoporous structure on the power factor of the prepared LSMO films was also studied through analyses of structural and electrical properties. The oxygen-deficient state induces an increase in the lattice parameter of LSMO, which results in an increase in the electrical resistivity and enhanced Seebeck coefficient. This phenomenon was emphasized upon the introduction of a pore structure in LSMO because of an increase of unstable surface area. The oxygen-deficient state results in an increase in the amount of manganese in the Mn^{3+} valence state and in an increase of the lattice parameter; these effects were confirmed through photoemission spectroscopic analysis. As a result, LSMO can be applied as a thermoelectric material because of the successful preparation of LSMO films with a mesoporous structure and because of the enhancement of the power factor as a consequence of increased oxygen deficiency.

Introduction

Currently, thermoelectric generators are attracting intensive attention because they can convert waste heat into electricity [1]. The efficiency of a thermoelectric material is determined by its dimensionless figure of merit, $Z = S^2\sigma/\kappa$, where S , σ , and κ are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively [2]. According to this equation, a good thermoelectric material should possess a large power factor ($\text{PF} = S^2\sigma$) and low thermal conductivity. A large power factor and low thermal conductivity have been achieved in thermoelectric materials with layered structures [3] and nanostructures [4, 5] and in single-crystalline metals [6]. However, the large-scale growth of metals with high ZT values is generally difficult; metals are not cost-effective and usually exhibit poor thermal stability. Thus, fabricating thermoelectric devices with high-ZT metal materials is difficult. However, recent advancements have enabled the application

of metal oxides to thermoelectric materials to improve their cost-effectiveness and thermal stability [7, 8]. Several perovskite materials have been studied [9, 10]; among them, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) has received extensive attention because of its good conductivity and high thermal stability [11, 12]. However, LSMO has a low Seebeck coefficient and high thermal conductivity compared to other thermoelectric materials [13, 14]. Thus, for LSMO to function as an effective thermoelectric material, its Seebeck coefficient needs to be enhanced and its thermal conductivity needs to be reduced while maintaining its electrical conductivity.

The studies related to the reduction of thermal conductivity in ceramics have focused on secondary-phase formation [15], pore-structure formation [16], and layer-structure adoption [17]. Among the reported studies of reduced thermal conductivity in ceramics, that involving the preparation of ceramics with mesoporous structures is particularly interesting [18]. When a material is prepared with a mesoporous structure, its electrical conductivity is expected to decrease because of electron scattering by pores; however, the thermal conductivity is decreased even more by the additional phonon scattering by pores. Thus, the introduction of mesoporous structural features could be more effective in reducing thermal conductivity than in reducing electrical conductivity; furthermore, the inelastic mean free path of the phonon is longer than that of the electron [19–21]. In addition, as a consequence of carrier filtering or a change in the band structures by pore structuring, the Seebeck coefficient is expected to enhance [22–24]. Studies related to enhancements of the Seebeck coefficients of perovskite materials through

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cation substitution [25], changes in oxygen content [26], and the preparation of low-dimensional systems [27] have been conducted. Having reviewed the results of previous studies related to Seebeck coefficient enhancement, we concluded that controlling the oxygen content is the best approach among the investigated methods because the electronic structure and carrier concentration are closely related to oxygen content [28]. Thus, in this work, we controlled the oxygen content in LSMO to enhance its thermoelectric power factor.

In this study, LSMO films were synthesized using metal propionate [29], and the oxygen content of LSMO films was controlled via control of the atmospheric gas composition (air, Ar, N₂, and O₂) during the annealing process. The effects of the mesoporous structure and oxygen content of LSMO on the Seebeck and electrical properties of LSMO films were investigated.

Experimental

Metal acetates (La(CH₃CO₂)₃·3H₂O (Aldrich), Mn(CH₃CO₂)₂ (Aldrich), and Sr(CH₃CO₂)₂ (Aldrich)) were used to synthesize metal propionate powder as an LSMO precursor. Propionic acid (C₃H₆O₂, Duksan) and *n*-butyl alcohol (CH₃(CH₂)₃OH, Duksan) were used as solvents, and Brij-S10 (C₅₈H₁₁₈O₂₁, Aldrich, MW 711) was used as a surfactant for templating. The weights of propionates of La, Mn, and Sr were adjusted to the composition of LSMO and were dissolved in propionic acid under stirring for 1 h. Then, the Brij-S10 surfactant was dissolved in *n*-butyl alcohol under stirring for 1 h. After stirring, the LSMO precursor was mixed with the surfactant solution. The final product had a composition of LSMO:Brij-S10:propionic acid:*n*-butyl alcohol in molar ratios of 1:0.014:15:20. Mixed solutions were aged for 4 h, and the LSMO sol was spin-coated onto SiO₂/Si substrates at 3000 rpm for 30 s. The coated LSMO films were annealed at 650 °C for 2 h to induce crystallization. To vary the oxygen deficiency in the films, we used air, Ar, N₂, and O₂ as the annealing atmospheric gas. The thickness of the films were measured around 123 nm (Fig. S1) by using scanning electron microscopy (SEM: JEOL, JSM 7001F, Tokyo, Japan). The microstructures and surface morphology of the LSMO films were also analyzed by using SEM. The surface topography of the films was analyzed using atomic force microscopy (AFM: Bruker NanoscopeV). X-ray diffraction (XRD: Ultima IV, Rigaku) with Cu Kα radiation (λ = 1.5418 Å) was used to study the pore ordering and crystalline structure of the fabricated mesoporous LSMO films. X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo VG, U.K.) was used for elemental analysis by using an instrument equipped with a monochromated Al Kα source (1486.6 eV); the accelerating voltage and emission current of the X-ray source were 12 kV and 3 mA, respectively. The chemical states of the films were analyzed using the high-resolution photoemission spectroscopy (HRPES) system installed on beam line 4D of the Pohang Light Source (PLS) in the Republic of

Korea. The Seebeck coefficients and electrical resistivity of mesoporous LSMO films were measured by detecting the Seebeck voltage in the temperature range 50–400 °C, under a He atmosphere. The procedure was repeated twice to check that the material did not evolve upon temperature increase and that the electrical properties were stable.

Results and discussion

Various atmospheric gases such as air, Ar, N₂, and O₂ were used during the crystallization treatment of LSMO films to control the films' oxygen deficiency. To confirm the oxygen deficiency of the films, we performed XPS composition analysis. As shown in Fig. 1, the composition of mesoporous LSMO films depended on the annealing atmosphere. The films treated under Ar and N₂ atmospheres exhibited a relative increase of metal-ion content because of a decrease in the oxygen-ion content, which resulted in an oxygen-deficient state. We carefully checked by XPS that no carbon neither nitrogen was implemented in the LSMO film upon treatment under the different atmospheres. (Fig. S2) Perovskite-structured materials heated under oxygen-deficient atmospheres are known to exhibit changes in their lattice parameter [30–32]. In addition, a change in the lattice parameter can cause a change in the pore structure.

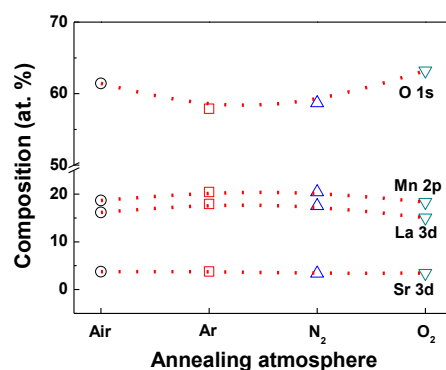


Figure 1. Variation in the composition of mesoporous LSMO films synthesized using various annealing atmospheres.

To clarify the change in the lattice parameter as a function of oxygen deficiency, we analyzed the LSMO films using wide-angle XRD over the 2θ range from 20° to 60°; the results are shown in Fig. 2. Furthermore, a confirmation of crystal structure is necessary to determine the relationship between the oxygen content and the valence state of the metals in the LSMO films. Figure 2 shows (a) wide-angle XRD patterns and (b) lattice parameters of the mesoporous LSMO films. The patterns in Fig. 2(a) confirm that skeleton-forming LSMO crystallized with polycrystalline nature [33]. Shifting and broadening of the diffraction peaks were observed with the mesoporous LSMO films annealed under Ar and N₂ atmospheres. To confirm the shift and broadening of the diffraction peaks precisely, accurate (110) diffraction data for mesoporous LSMO films were collected; the results are

presented in the inset table. The calculated lattice parameter is given in Fig. 2(b). The lattice of LSMO expanded in the case of samples annealed under Ar and N₂ atmospheres. The Mn ions of LSMO have mixed valence states of Mn³⁺ and Mn⁴⁺. The oxygen-deficient state resulted in increase in the concentrations of oxygen vacancies and Mn³⁺, and the effective ionic radius of Mn³⁺ (0.645 Å) is larger than that of Mn⁴⁺ (0.53 Å) [30, 31]. Normally, during the thermal treatment of ceramics in an oxygen-deficient atmosphere, generated oxygen vacancies induce a decrease in the lattice parameter of the ceramic. However, in the case of the LSMO samples, a contraction of the lattice was not observed because of coulombic repulsion from the large Mn³⁺ ions generated through the oxygen deficiency [30]. A similar oxygen-deficiency-induced lattice expansion of perovskite-structured oxides has been previously reported [30–32].

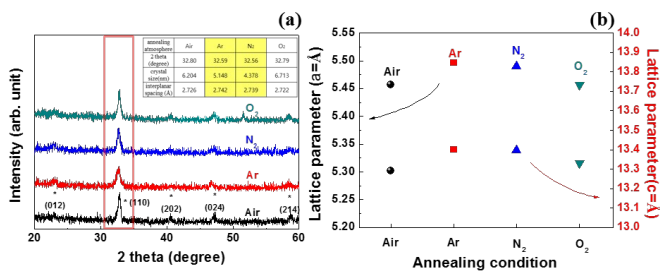


Figure 2. (a) Wide-angle XRD patterns and (b) lattice parameters of mesoporous LSMO films synthesized using various annealing atmospheres. The inset table presents the crystalline size and interplanar spacing obtained using the (110) peaks.

In order to confirm the change of the valence state on the basis of the change of the surface chemical bonding state according to the annealing atmosphere, we investigated the Mn 2p chemical states in the mesoporous LSMO films using XPS. Figs. 3(a) and (b) show the constitutional bonding peaks obtained from the deconvolution of the Mn 2p peaks before and after surface etching of air-atmosphere-annealed LSMO samples. The peak deconvolution results of all samples are summarized in Table 1. As shown in Fig. 3(a) and Table 1, the samples annealed under Ar and N₂ atmospheres exhibited a relative increase in the Mn³⁺ peak in the region near 641.7 eV because of the generation of oxygen vacancies. Peaks in the Mn²⁺ region near 640.9 eV were observed in the spectra of all samples; this Mn²⁺ component is known to be formed during the exposure of manganese-containing perovskite-structured samples to ambient atmosphere [34].

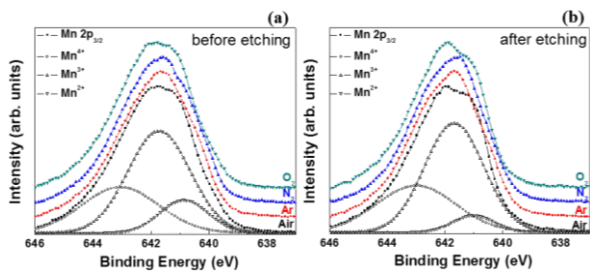


Figure 3. XPS Mn 2p core level spectra of mesoporous LSMO films synthesized using various annealing atmospheres (a) before and (b) after surface etching.

Table 1. The valence states of Mn ions in mesoporous LSMO films synthesized under various annealing atmosphere obtained by using XPS before and after surface etching.

Valence state	BE (eV)	Air		Ar	
		before etching	after etching	before etching	after etching
Mn ⁴⁺	643.0	30.5%	33.8%	25.1%	26.9%
Mn ³⁺	641.7	55.5%	59.6%	61.4%	68.2%
Mn ²⁺	640.9	14.0%	6.6%	13.5%	4.9%

Valence state	BE (eV)	N ₂		O ₂	
		before etching	after etching	before etching	after etching
Mn ⁴⁺	643.0	23.8%	23.9%	28.5%	36.8%
Mn ³⁺	641.7	63.1%	70.0%	54.8%	57.9%
Mn ²⁺	640.9	13.1%	6.1%	16.7%	5.3%

To confirm the surface presence of Mn²⁺, Mn 2p spectra were also obtained after surface etching; the results are presented in Fig. 3(b). A relative decrease in the constitutional bonding peak of Mn²⁺ was observed; on the basis of this result, we deduced that Mn²⁺ existed primarily on the surface of the samples. Table 1 also indicates a relative decrease in the Mn²⁺ concentration after the etching process.

To clarify modification of the pore structure from a change in the lattice parameter depending on the oxygen deficiency, the LSMO films were analyzed using small-angle XRD; the results are shown in Fig. 4(a).

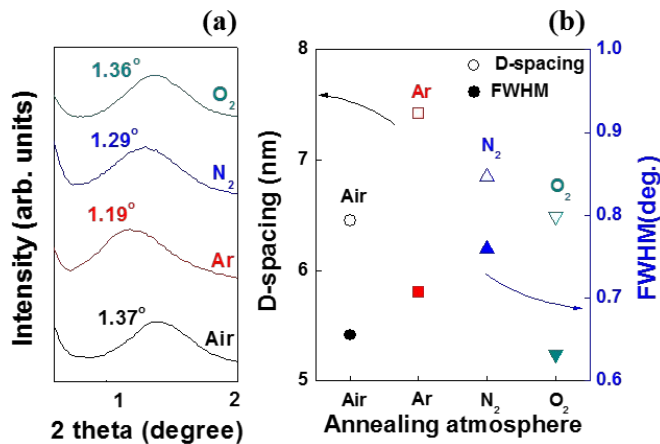


Figure 4. (a) Small-angle XRD patterns and (b) inter-pore distance of mesoporous LSMO films synthesized using various annealing atmospheres.

The presence of diffraction peaks at 1.19°–1.37° revealed that the LSMO films have an ordered pore structure. However, a shift in the peak positions of samples annealed under different atmospheres confirms that the pore structure of the ordered mesoporous LSMO films depends on the annealing atmosphere. In the case of samples annealed under Ar and N₂, the diffraction peak position shifted to a low-angle 2θ region. This shift in the peak position indicates a change in the

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interpore distance; we therefore calculated the interpore distances of the LSMO films; the results are presented in Fig. 4(b). The interpore distances were larger in the samples annealed under Ar and N₂ atmospheres than under air and O₂ atmospheres. Furthermore, as shown in the Fig. 4(b), peak broadening was also observed in the samples annealed under Ar and N₂ atmospheres; such peak broadening in small-angle XRD measurements is typically caused by a decrease in the ordering of pores.

The changes in the surface morphology of the LSMO films as a function of the annealing atmosphere were investigated by SEM and AFM; the results are given in Figs. 5(a, b). As shown in these figures, the mesoporous LSMO films exhibited roughened and crooked morphologies. This coarse surface morphology of the mesoporous films is attributed to opening of closed interior pores at the surface during the growth and agglomeration of pore-wall-structured LSMO grains. Finally, the surface area was increased by the increased exposure of closed interior pores to the surface. The root mean square (RMS) roughness and surface area obtained from the AFM micrographic results (Fig. 5(b)) are presented in Fig. 5(c, d). The RMS roughness and surface area increased in the case of LSMO films annealed under Ar and N₂ atmospheres. The difference in surface area of the films was obtained from the difference between the measurement area and the projected area. This sudden increase in the surface area difference and RMS might be due to collapse of the interior pore structure, as observed in the small-angle XRD results (Fig. 4(b)) as peak broadening.

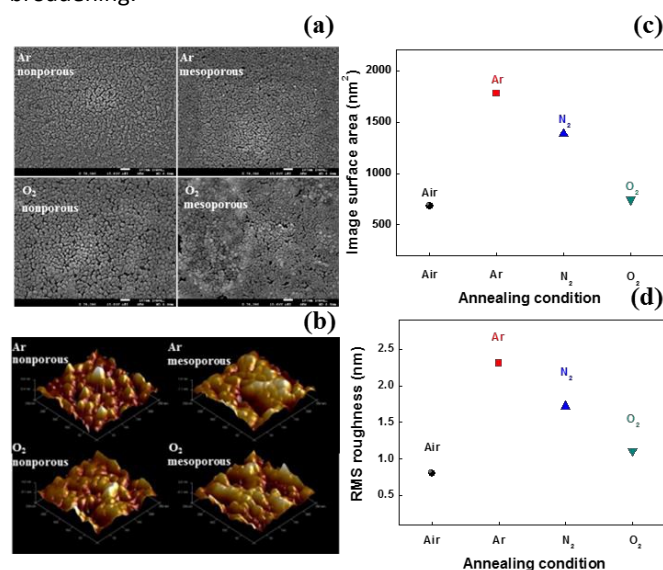


Figure 5. (a) Surface image, (b) AFM images, (c) AFM image surface area, and (d) AFM roughness mesoporous LSMO thin films synthesized using various annealing atmospheres.

Chemical bonding state related to the surface might be also changed, and this altered chemical bonding state might cause a change in thermoelectric properties. The chemical bonding state of mesoporous LSMO films were investigated using PES; the results are shown in Fig. 6. In the case of the samples annealed under Ar and N₂ atmospheres, the region of SrO_x increased compared with the lattice Sr region [35]. Segregation

of SrO_x occurred on the surface of LSMO by Sr²⁺ ions being partially expelled from lattice due to the ionic size mismatch between the host La³⁺ cations and the Sr²⁺ dopant cations [36]. The Sr²⁺ cations partially ejected from the lattice and formed SrO_x on the surface [37]. As shown in Fig. 2(b), the lattice expansion was induced by oxygen deficiencies. An increase in lattice strain from this lattice expansion corresponded to an increase in Sr 3d photoelectron intensity in the SrO_x region because of an increase in the amount of Sr²⁺ cations expelled from the lattice. Furthermore, the intensity of the high-binding-energy O 1s peak near 531 eV increased in the XPS spectra of the samples annealed under Ar and N₂ atmospheres. The O 1s peak at 531 eV is related to either a different surface oxide or oxygen associated with defects in the perovskite structure [38]. In LSMO, the high- and low-binding-energy peaks at approximately 531 and 529 eV in the O 1s spectrum correspond to the segregated SrO_x and lattice oxygen, respectively [39]. Therefore, we concluded that the oxygen-deficient atmospheres caused an increase in oxygen vacancies or surface segregation of SrO_x. A change in the A (La and Sr)-site-ion bonding state or in the oxygen ions influences the valence state of perovskite oxides [36].

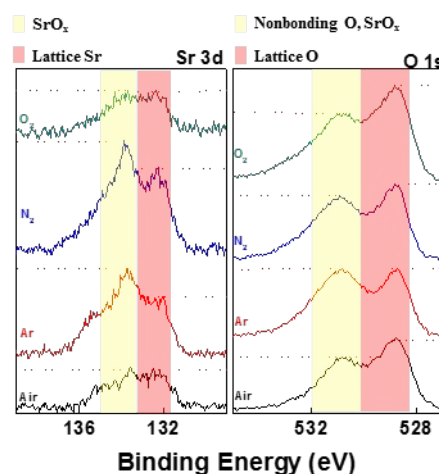


Figure 6. Photoemission spectra of Sr 3d and O 1s regions of mesoporous LSMO films synthesized using various annealing atmospheres.

The change in the valence state causes a change in the chemical bonding state and, finally, in the thermoelectric properties. To confirm the relation between the change in the valence state and the thermoelectric properties of LSMO films annealed in various atmospheres, we measured the thermoelectric properties of the films; the results are given in Fig. 7. As shown in Fig. 7(a), the electrical resistivity increased in the LSMO films annealed under Ar and N₂ atmospheres. The resistivities of the films decreased with increasing measurement temperature because of the semiconductor behavior of LSMO. The conduction mechanism of LSMO can be explained in terms of a double-exchange interaction between Mn³⁺ and Mn⁴⁺ [40]. As previously mentioned, the Mn³⁺ valence state can be increased in LSMO through the generation of oxygen defects and surface segregation of SrO_x. We thus attribute the higher electrical resistivity of the LSMO

films annealed under Ar and N₂ atmospheres compared with those of films annealed under O₂ and air atmospheres to the increased Mn³⁺/Mn⁴⁺ ratio in the Ar and N₂ films. When the ratio of Mn³⁺/Mn⁴⁺ becomes equal to one, the electrical conductivity will reach its maximum value via the maximized double-exchange interaction. As shown in Fig. 7(b), the Seebeck coefficients of the LSMO films annealed under Ar and N₂ atmospheres have more negative values than those of the films annealed under O₂ and air atmospheres. This behavior of the Seebeck coefficient is similar to the behavior of the electrical resistivity because the Seebeck coefficient is inversely related to the carrier concentration [41]. Hence, a diminished double-exchange interaction of LSMO would lead to an increase in Seebeck coefficient and in electrical resistivity. The Seebeck coefficient (S) is given by [41]

$$S = \left(\frac{8\pi^2 k_B^2}{3eh^2} \right) m^* T \left(\frac{\pi}{3n} \right)^{\frac{2}{3}}$$

where n is the carrier concentration, m^* is the carrier effective mass, k_B is the Boltzmann constant, h is Planck's constant, and T is the absolute temperature.

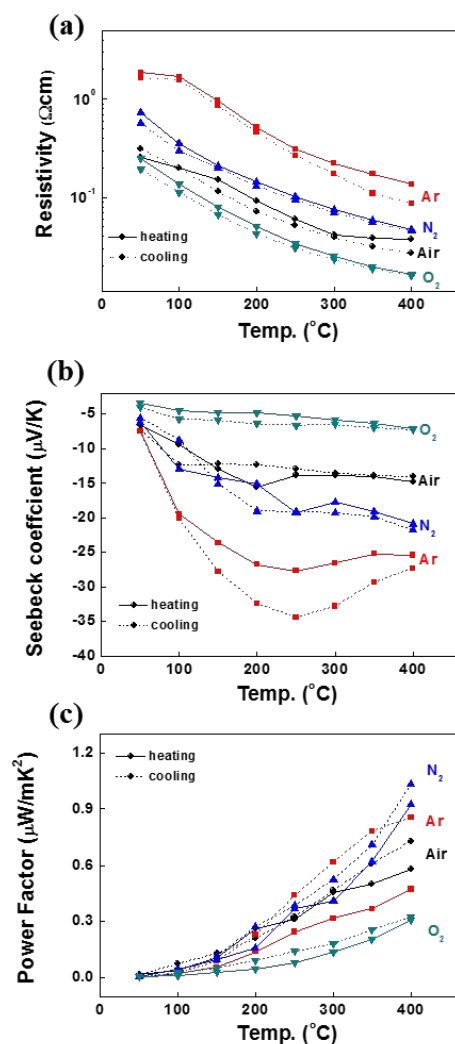


Figure 7. (a) Electrical resistivity, (b) Seebeck coefficient, and (c) power factor of mesoporous LSMO films synthesized using various annealing atmospheres.

The equation indicates the Seebeck coefficient depends on the absolute temperature, carrier effective mass, and carrier concentration. We confirm that the Seebeck coefficient tended to increase with increasing measurement temperature (absolute temperature T) via the phonon-drag effect [42].

As previously mentioned, an increase in the Mn³⁺/Mn⁴⁺ valence ratio causes a decrease in the electrical conductivity because of the decreased double-exchange interaction (carrier concentration). As a result, the carrier concentrations in LSMO films annealed under Ar and N₂ atmosphere were smaller than those in films annealed under O₂ and air atmospheres. Thus, the phonon-drag effect and Seebeck coefficient were more significant in the films annealed under Ar and N₂. However, at temperatures above 200 °C, the Seebeck coefficients remained almost constant because the phonon-drag effect was no more influential. The phonon-drag effect is known to minorly contribute to the Seebeck coefficient at temperatures above the Curie temperature, T_c (T_c of LSMO is 90 °C) [43]. As shown in Fig. 7(c), the LSMO films annealed under Ar and N₂ atmospheres showed a larger power factor than the other samples, as expected on the basis of the Seebeck coefficient values. In addition, the power factor values increased with increasing measurement temperature even after the Seebeck coefficient reached its saturation point because the power factor has a linear proportional relationship with electrical conductivity [2].

Conclusions

Mesoporous LSMO films were synthesized using a metal propionate powder as an LSMO precursor and Brij-S10 as a copolymer surfactant. The oxygen content of the prepared mesoporous LSMO films was controlled through the use of different atmospheres (air, Ar, N₂, and O₂) during the annealing process. The structural properties, bonding state, and thermoelectric properties of the LSMO were investigated as functions of the different annealing atmospheres; we also examined whether the films formed mesoporous structures. In an oxygen-deficient state, LSMO exhibits a lattice expansion because of the increase in the amount of manganese in the Mn³⁺ valence state and because of increased SrO_x segregation. These phenomena were also confirmed to apply to mesoporous structures because of the increase in unstable surface area. These changes led to changes in the bonding state of the LSMO, as confirmed by increases in the peak areas in the SrO_x region and the Mn³⁺ region in the PES spectra. As a result, the power factor was enhanced, although the electrical resistivity was increased. On the basis of the results of this study, we expect the application possibilities of LSMO as a thermoelectric material will be enhanced through the successful control of its characteristics through annealing under different atmospheres.

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Graphical Abstract

Oxygen-deficiency-dependent Seebeck coefficient and electrical properties of mesoporous $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-x}$ films

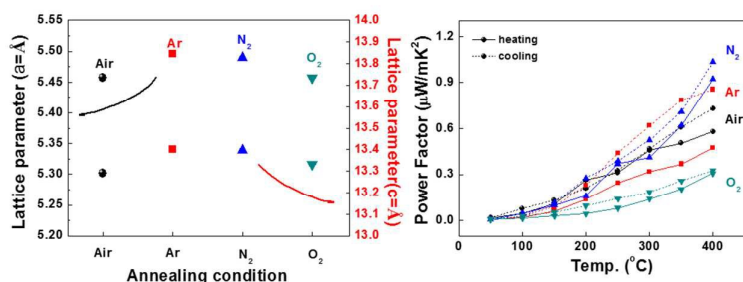
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The power factor of mesoporous LSMO films were enhanced with increase in the surface area.

Highlighting the novelty of the work

The effect of controlled the oxygen content on the mesoporous structure and thermoelectric properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-x}$ (LSMO) films were investigated. Normally oxygen deficiency induces an increase in specific surface area. Especially in case of LSMO films, the increase in oxygen deficiency induce in a band narrowing and filled Mn 3d state with electron-combined oxygen. As a result, the increase in oxygen deficient of LSMO film leads to a increased electrical resistivity with the filled Mn 3d states. However, the LSMO films annealed under oxygen deficient atmospheres has a larger enhanced Seebeck coefficient than increased electrical resistivity due to the pore structure and modified the band structure. On the basis of

the results of this study, we expect the application possibilities of LSMO as a thermoelectric material will be enhanced through the successful control of its characteristics through annealing under different atmospheres.