



La and Nd Co-doped Effect on Thermoelectric Properties of SrTiO₃ Ceramics

Yangyang Li [a], Wei Wei [a], Lianhong Yang [a], Meng Su [a], Yi Sun* [a,b],
Guanghui Min [a,c]

[a] Department of Physics, Changji University, Xinjiang 831100, P. R. China.

[b] Key Laboratory of Phase Transitions and Microstructures of Condensed Matters in Xinjiang,
Yining 835000, P. R. China.

[c] School of Materials Science and Engineering, Shandong University, Shandong 250061, P. R. China.

*Author for correspondence; e-mail: gghels@gmail.com

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ABSTRACT

Ceramic samples of Sr_{1-x-y}La_xNd_yTiO₃ with different La and Nd concentration have been synthesized by conventional solid state reaction technique, and their thermoelectric properties have been investigated. X-ray diffraction characterization confirms that the main crystal structure is of perovskite. SEM images indicate all ceramic samples are dense and compact, and the grain size increase with the doping content increasing. Electrical conductivity and Seebeck coefficient of samples have been measured in the temperature range between 300 K and 1100 K. With increasing of doping concentration, electrical resistivity decreases, and reaches 3.8 mΩ·cm for sample x=0.10 at 1045 K. The absolute Seebeck coefficients increase monotonically with increasing temperature in the whole temperature range. Sample with x=y=0.05 exhibits the highest absolute Seebeck coefficient. The sample with x=y=0.10 exhibits the maximum power factor 14 μWcm⁻¹K⁻² at 456 K.

Keywords: thermoelectric, ceramics, oxide materials, power factor, perovskite

1. INTRODUCTION

Thermoelectric (TE) device could convert heat to electricity and vice versa. Their conversion efficiency depends on the dimensionless TE figure of merit ZT of their materials components. The figure of merit is defined as $ZT = S^2T / \rho\kappa$, where T , S , ρ and κ represent absolute temperature, Seebeck coefficient, electrical resistivity and thermal conductivity, respectively. To increase the thermoelectric performance, materials should have lower κ , and high power factor which

is defined as S^2/ρ [1]. Since the report of high thermoelectric performance in NaCo₂O₄, which shows a large Seebeck coefficient (about 100 μVK⁻¹ at 300 K) and a relatively high conductivity around 2×10⁴ Scm⁻¹ at room temperature [2], oxides thermoelectric materials have received much attention such as Ca₃Co₄O₉ [3], ZnO [4], CaMnO₃ [5] and SrTiO₃ [6-8], etc. Different elements doped SrTiO₃ has been reported as a potential candidate for n-type thermoelectric oxides

with a high power factor. Okuda et al. [8] reported that La-doped SrTiO₃ single crystal shows high power factor at room temperature, 28-36 μWcm⁻¹K⁻², which is comparable to Bi₂Te₃ alloys. Ohta et al. [7] reported that properties of Nb-doped SrTiO₃ epitaxial film. A relatively high power factor about 1.5×10⁻³ Wm⁻¹K⁻² has been obtained, which is approximately half of practically used SiGe alloys, and the figure of merit ZT for SrTi_{0.8}Nb_{0.2}O₃ can reach 0.37 at 1000 K. Most recently, La-doped SrTiO₃ thin film grown by molecular beam epitaxy has been investigated by Jalan et al. [9], a maximum power factor 39 μWcm⁻¹K⁻² which is comparable to that of the single crystalline bulk SrTiO₃ was reported. Liu et al. [10] reported that Nd doping can remarkably enhance the figure of merit of SrTiO₃ ceramics, the maximum ZT reached 0.28 at 873K for the Sr_{0.9}Nd_{0.1}TiO₃ sample. Also, it is reported by wang et al.[11] that double element dope can remarkably enhance the figure of merit ZT, ZT of 0.36 has been obtained at 1045 K for Sr_{0.83}La_{0.1}Dy_{0.07}TiO₃. Encouraged by these results of above studies, influence of La and Nd co-doping on the thermoelectric properties of SrTiO₃ ceramic is investigated in this work. Ceramic samples of Sr_{1-x-y}La_xNd_yTiO₃ with x=y=0.05, 0.08 and 0.10 have been prepared by the solid state reaction method. Their thermoelectric properties have been measured in temperature range between 300 K and 1100 K, and the effects of La and Nd co-doping on thermoelectric properties of SrTiO₃ ceramic have been discussed.

2. MATERIALS AND METHODS

Ceramic samples of Sr_{1-x-y}La_xNd_yTiO₃ with x=y=0.05, 0.08 and 0.10 were prepared by conventional solid state reaction techniques. The starting materials were

SrCO₃ with a purity of 99%, TiO₂ with a purity of 99.8%, La₂O₃ with a purity of 99.99%, and Nd₂O₃ with a purity of 99.99%. These raw materials were weighed in stoichiometric proportions, and mixed by ball-milling in ethanol with zirconia balls for 12 h. After the wet mixtures dried, they were pressed into pellets, and calcined at 1300 °C for 6 h in air. The pellets were smashed and ball-milled for 12 h to obtain a fine powder. Then the powder was repressed into pellets. These pellets were sintered at 1450 °C for 4 h to forming gas with 5 mol% hydrogen in argon. The sintered pellets were cut into rectangular columns with dimensions of 20×1.8×1.8 mm³ to measure the thermoelectric properties. These columns were coated with four electrodes, two on each ends and two on sides, with silver paint annealed at 850 °C for 30 min. For electric measurements, four-probe method was used in the measurement of electrical resistivity ρ. A direct current I of 100 mA was set to pass through the two end electrodes and the potential difference V across the two side electrodes was read. For measurement of Seebeck coefficient S, two NiCr-NiSi thermal couples were attached on each side electrodes of the column with a separation of 8.0 mm. A temperature difference ΔT=T₂-T₁ about 3 °C was built up between the two thermal couples using an auxiliary heater during thermoelectric measurement. Seebeck coefficient S was determined from the slope of ΔV versus ΔT relation by the least-square method, where ΔV is the thermoelectromotive force produced by ΔT between the two electrodes. The crystal structure and lattice parameter were characterized by powder X-ray diffraction with Cu Kα radiation (λ= 0.154056 nm) utilizing a Bruker AXS D8 ADVANCE diffractometer. The surface morphology was obtained on a Hitachi S-4800 scanning

electronic microscope (SEM).

3. RESULTS AND DISCUSSION

XRD patterns of $\text{Sr}_{1-x-y}\text{La}_x\text{Nd}_y\text{TiO}_3$ powders are shown in Figure 1. The major diffraction peaks can be indexed with the

cubic perovskite structure belonging to the $Pm\bar{3}m$ space group. All samples are of single phase in cubic structure. The lattice parameters and theoretical densities were calculated using the lattice constants from XRD, and listed in Table 1.

Table 1. Calculated lattice parameters, theoretical density and relative density for $\text{Sr}_{1-x-y}\text{La}_x\text{Nd}_y\text{TiO}_3$ ($x=0.05, 0.08, \text{ and } 0.10$)

x	a (Å)	V (Å ³)	Theoretical density (g/cm ³)	Relative density
0.05	3.9085	59.71	5.255	92%
0.08	3.9039	59.50	5.364	94%
0.10	3.9048	59.54	5.420	96%

The variation of the lattice constants is very small and could be within the resolution limit of powder XRD. The theoretical density of the sintered samples is calculated from the lattice constants. The relative density is defined as measured density over the theoretical density. The relative density of sample for 92%, 94% and 96% for $x=y=0.05, 0.08$ and 0.10 , respectively.

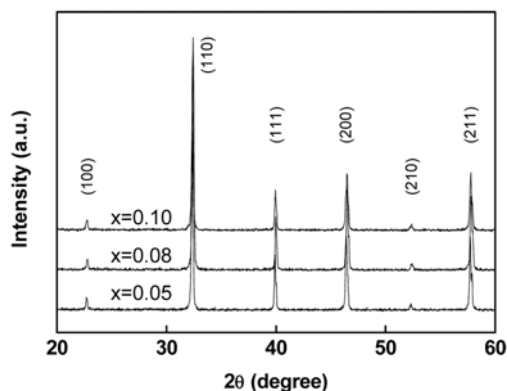


Figure 1. X-ray diffraction patterns of $\text{Sr}_{1-x-y}\text{La}_x\text{Nd}_y\text{TiO}_3$ ($x=0.05, 0.08, \text{ and } 0.10$) powders.

Scanning electronic microscope (SEM) images of surface microstructures for $\text{Sr}_{1-x-y}\text{La}_x\text{Nd}_y\text{TiO}_3$ ceramics are shown in Figure 2(a-c), with Figure 2(a), (b) and (c) for sample of $x=0.05, 0.08$ and 0.10 , respectively.

All patterns show polygon morphology and compact. With the increasing doping concentration, average grain size increase.

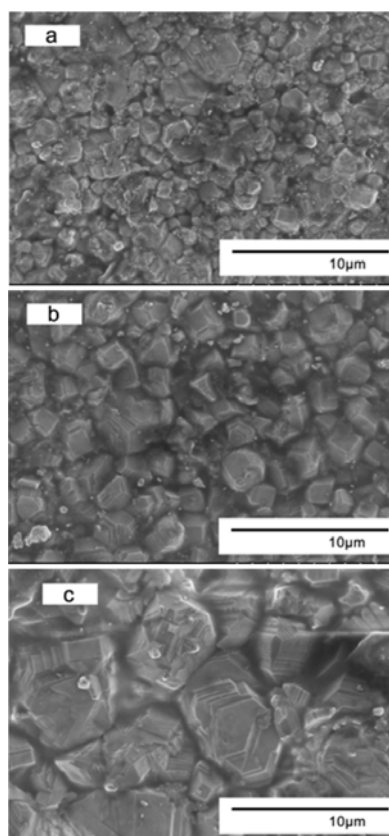


Figure 2. SEM images of $\text{Sr}_{1-x-y}\text{La}_x\text{Nd}_y\text{TiO}_3$ ceramics (a, b, and c represents $x=0.05, 0.08$ and 0.10 , respectively).

Figure 3. shows the temperature dependence of electrical resistivity of $\text{Sr}_{1-x-y}\text{La}_x\text{Nd}_y\text{TiO}_3$ ceramics in temperature range between 300K and 1100K. With increasing doping content, the electrical resistivity decrease, indicating that more electrons are introduced by La and Nd substitution. The electrical resistivity for all samples decrease with temperature increasing when temperature is below about 440 K, then increase with further increasing of temperature. The reduction of electrical conductivities near room temperature coincides with the previous reports on polycrystalline samples [6, 10], which indicates scattering by grain boundaries. The electrical resistivity decrease from 7.4 $\text{m}\Omega\cdot\text{cm}$ for sample $x=0.05$ at 1051 K to 3.8 $\text{m}\Omega\cdot\text{cm}$ for sample $x=0.10$ at 1045 K.

The temperature dependence of the Seebeck coefficient is shown in Figure 4. All samples are showing negative Seebeck coefficients in the temperature range between 300 K and 1100 K, indicating n-type conduction mechanism, or the main carriers are electrons. Generally, the absolute Seebeck coefficients of all samples increase monotonically with increasing temperature. The absolute Seebeck coefficient decreases with the increasing doping concentration. This can be attributed to the carrier concentration increase with increasing of La and Nd content.

Temperature dependence of the power factors, which is calculated from S^2/ρ , is presented in Figure 5. With the increase of temperature, the power factor firstly increases and reaches a maximum around 550 K, then decrease with further increasing of temperature. The general trend of temperature dependence of the power factor does not changed by the doping concentration. The maximum values of power factor for $x=0.05$, 0.08 and 0.10

samples are 13 $\mu\text{Wcm}^{-1}\text{K}^{-2}$ at 500 K, 12 $\mu\text{Wcm}^{-1}\text{K}^{-2}$ at 556 K and 14 $\mu\text{Wcm}^{-1}\text{K}^{-2}$ at 456 K, respectively. Ceramic sample of $\text{Sr}_{0.8}\text{La}_{0.1}\text{Nd}_{0.1}\text{TiO}_3$ exhibits the highest value of power factor in the measured temperature range.

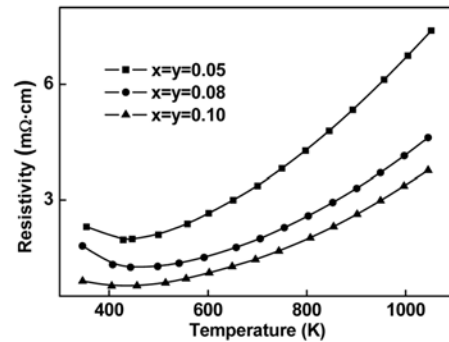


Figure 3. Temperature dependence of electrical resistivity of $\text{Sr}_{1-x-y}\text{La}_x\text{Nd}_y\text{TiO}_3$ ($x=0.05$, 0.08, and 0.10) ceramics.

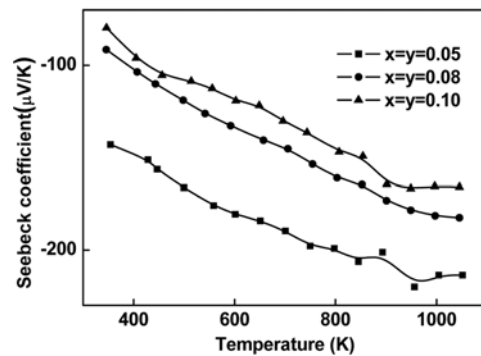


Figure 4. Temperature dependence of the Seebeck coefficients of $\text{Sr}_{1-x-y}\text{La}_x\text{Nd}_y\text{TiO}_3$ ($x=0.05$, 0.08, and 0.10) ceramics.

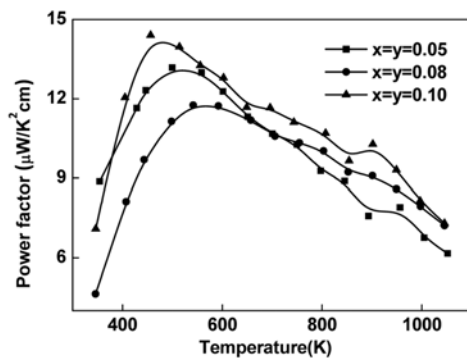


Figure 5. Temperature dependence of the Power Factor of $\text{Sr}_{1-x-y}\text{La}_x\text{Nd}_y\text{TiO}_3$ ($x=0.05$, 0.08, and 0.10) ceramics.

4. CONCLUSIONS

Influence of La and Nd co-doped effect on $\text{La}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$ has been studied from samples prepared by the conventional solid state reaction method. The major phase of all samples is cubic perovskite structure, The electrical resistivity decreases with increasing of doping concentration, The sample of $x=0.10$ possesses the lowest electrical resistivity as well as the highest absolute Seebeck coefficient in temperature range between 300 K to 1000K, and exhibits the highest power factor as $14 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 624 K.

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