



Full Length Article

Effect of mesoporous structure on the Seebeck coefficient and electrical properties of SrTi_{0.8}Nb_{0.2}O₃Chang-Sun Park^a, Min-Hee Hong^a, Hyung Hee Cho^b, Hyung-Ho Park^{a,*}^a Department of Materials Science and Engineering, 50 Yonsei-ro, Yonsei University, Seodaemun-Ku, Seoul 03722, Republic of Korea^b School of Mechanical Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea

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ABSTRACT

The porosity of mesoporous SrTi_{0.8}Nb_{0.2}O₃ (STNO) was controlled by changing the surfactant concentration to investigate the porosity effect on the thermoelectric properties. Mesoporous structure typically induces a large decrease in the carrier mobility and a small increase in the carrier concentration owing to carrier scattering and oxygen vacancies. These changes in the carrier mobility and concentration induce a change in the thermoelectric properties by enhancing the Seebeck coefficient owing to an increase in the electrical resistivity and carrier filtering effect. Brij-S10 surfactant induces a carrier filtering effect in STNO, and so the Seebeck coefficient could be enhanced even with increasing carrier concentration. Because the Seebeck coefficient affects the power factor more strongly than the electrical resistivity does, incorporation of Brij-S10 surfactant into STNO films increases the power factor. The maximum value of the power factor, approximately 2.2×10^{-4} W/mK² at 200 °C, was obtained at a Brij-S10 molar ratio of 0.075. From this result, we can expect the application of STNO as a thermoelectric material with an enhanced power factor through successful adoption of mesoporous structure.

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1. Introduction

Energy conversion techniques are currently among the most critical issues for decreasing reliance on fossil fuels, reducing environmental pollution, and preventing global warming. The need for sources of energy other than fossil fuels, as well as the need to use energy most efficiently, has sparked significant research into various energy conversion technologies. Among them, thermoelectric generators, in which heat is converted directly into electricity using a class of materials known as thermoelectric materials, have received attention recently [1,2]. The efficiency of a thermoelectric material is determined by its figure of merit, $Z = S^2\sigma/\kappa$, where S , σ , and κ are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively [3]. A good thermoelectric material typically has high electrical conductivity, high Seebeck coefficient, and low thermal conductivity. In addition, the fabrication process needs to be cost-effective, stable, and simple. To obtain good thermoelectric materials, various studies have applied techniques such as structure modification, doping, and complexation. Among the resulting materials, doped strontium titanate (SrTiO₃) has received much attention as a good thermoelectric material owing to its high

Seebeck coefficient and thermal stability [4,5]. In addition, SrTiO₃ exhibits metallic conductivity when substitutionally doped with La³⁺ and Nb⁵⁺, among other ions [6,7]. However, doping studies report only limited improvement in the thermoelectric properties. Further, the thermoelectric conversion performance of SrTiO₃ remains low because of its high thermal conductivity compared with other thermoelectric materials. A low thermal conductivity in thermoelectric materials could be achieved using layered structures [8] and nanostructures [9,10]. However, these structures are generally difficult and cost-ineffective to synthesize. Among the reported studies of reduced thermal conductivity, those involving the preparation of ceramics with mesoporous structures are particularly interesting [11]. Mesoporous structures can be synthesized using the evaporation-induced self-assembly process [12], which is simple, easy, and inexpensive [13,14]. In addition, when a material is prepared in mesoporous form, the electrical conductivity is decreased because of electron scattering by pores; however, the thermal conductivity is decreased even more by additional phonon scattering by pores. Thus, the introduction of mesoporous structural features could be more effective in reducing the thermal conductivity than in reducing the electrical conductivity; furthermore, the inelastic mean free path of phonons is longer than that of electrons [15–17]. In addition, as a consequence of carrier filtering or a change in the band structures caused by pore structuring, the Seebeck coefficient is enhanced [18–20]. In this study, we applied

* Corresponding author.

E-mail address: hnpark@yonsei.ac.kr (H.-H. Park).

mesoporous structure to SrTiO₃ to reduce the thermal conductivity and enhance the Seebeck coefficient. In addition, through Nb metal substitution, we attempted to enhance the electrical conductivity, and the material's structural and electrical properties were investigated to determine its suitability as a thermoelectric material. To investigate the role of mesoporous structure, the composition of Nb-doped SrTiO₃ was fixed as SrTi_{0.8}Nb_{0.2}O₃ (STNO) because this composition is widely used in thermoelectric materials [21].

2. Material and methods

Strontium acetate [Sr(CH₃CO₂)₂, Aldrich], niobium ethoxide [Nb(OCH₂CH₃)₅, Aldrich, 99.95%], and titanium tetraisopropoxide [Ti(OPrⁱ)₄, TTIP, Aldrich, 97%] were used as metal propionate powders serving as STNO precursors. The triblock copolymer Brij-S10 [C₁₈H₃₇(OCH₂CH₂)₁₀OH, MW 711, Aldrich] was used as a surfactant. The strontium acetate was dissolved in a large excess of propionic acid (C₃H₆O₂, Duksan), and the liberated acetic acid was distilled to prepare the propionates powder. The excess propionic acid was separated by centrifugation, and the carboxylates were precipitated with acetone (CH₃COCH₃, Duksan) and dried in an oven to produce dry strontium propionates [22]. The strontium propionate powders were dissolved in propionic acid under stirring for 4 h. Next, the Brij-S10 surfactant was dissolved in *n*-butyl alcohol [CH₃(CH₂)₃OH, Duksan] under stirring for 1 h and mixed with the niobium ethoxide and TTIP solution. Finally, the Sr precursors were mixed with a TTIP (niobium ethoxide added) solution and stirred for 15 min. The composition of the final product, the STNO:Brij-S10:propionic acid:*n*-butyl alcohol precursor, was uniform at a molar ratio of 1:*x*:15:20. Here, *x* is the Brij-S10 ratio, which was 0, 0.025, 0.05, 0.075, or 0.1. The as-prepared STNO precursor solutions were spin-coated on clean SiO₂ and Si substrates at room temperature. Spin-coating was performed at 2000 rpm for 20 s to spread the solution uniformly over the substrates. The spin-coated films were thermally treated in a tube furnace under air atmosphere at 850 °C for 4 h to crystallize the films.

To investigate the pore ordering and crystal structure of the mesoporous STNO films, X-ray diffraction (XRD, Ultima IV, Rigaku) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) was performed. Small-angle and wide-angle patterns were recorded in 2θ ranges from 0.5° to 5° and from 20° to 60°, respectively. The refractive indices of the STNO films were obtained using an ellipsometer (Gatan L117C, 632.8 nm He–Ne laser). On the basis of these refractive indices, the porosities were calculated using the Lorentz–Lorenz equation [23]. The chemical states of the films were analyzed using high-resolution photoemission spectroscopy (PES) and O 1s near-edge X-ray absorption fine structure (NEXAFS) measurements in an ultrahigh-vacuum chamber of the 4D and 8A2 beamlines at the Pohang Accelerator Laboratory in Korea. The Seebeck coefficients and electrical resistivities of the films were measured using a commercial thermoelectric property measurement system (Seepel, TEP 800) based on the four-point probe method; the repeatability is within $\pm 3\%$, and the resolution is within $\pm 1\%$.

3. Results and discussion

In this work, we need to crystallize STNO (SrTi_{0.8}Nb_{0.2}O₃) to obtain good, stable thermoelectric properties [24]. Through the previous work, 850 °C was found to be an optimum annealing temperature for crystallization of STO [25]. Therefore, 850 °C was selected as an annealing temperature for crystallization. Brij-S10 was introduced into STNO films to form a mesoporous structure. To confirm the formation of mesoporous structure in the STNO films, small-angle XRD analyses of the films were performed after annealing at 850 °C. As shown in Fig. 1, the intensities of the diffraction

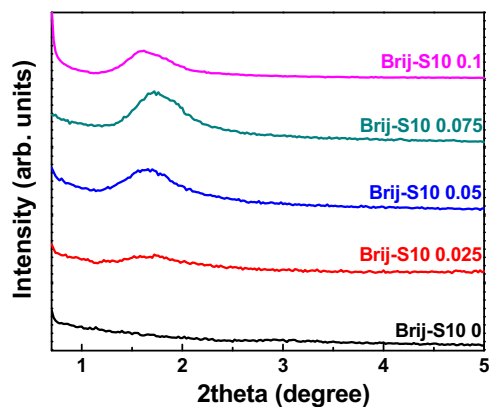


Fig. 1. Small-angle XRD patterns of mesoporous STNO films with various surfactant concentrations annealed at 850 °C.

peaks due to pore ordering in the mesoporous STNO films varied according to the surfactant concentration. Specifically, the diffraction peak intensity increased for surfactant concentrations up to 0.075 but decreased at a surfactant concentration of 0.1. This result indicates that the formation and ordered arrangement of pores are enhanced with increasing surfactant concentration up to 0.075. When the surfactant concentration is as high as 0.1, however, the ordered micelle structure in the film collapses during calcination, and cracks are formed on the surface, so a film is hardly formed [26]. The pore size and interpore distance were calculated using small angle XRD data. It is known that the ratio of the size of pore to wall thickness of pore structure is about 2:1 [27,28]. Inter-pore distance of (100) plane, as supposed that pore structure has HCP, could be calculated by using Bragg equation from Small angle XRD peak. As the concentration of surfactant increases to 0.05, 0.075 and 0.1, it is possible to observe inter-pore distance varies to 5.26, 5.08 and 5.29 nm (when the concentration was 0.025, it was not possible to calculate the inter-pore distance due to low peak intensity). Moreover, lattice constant a_0 could be calculated to be $2d\sqrt{3}$, and the value becomes 6.07, 5.86 and 6.11 nm as the concentration increases. This value is calculated to the summation of wall thickness and pore size, and the converted values of pore size, varying with value of a_0 , are found to be 4.05, 3.91 and 4.07 nm. Using ellipsometry, we obtained the porosity values of STNO with various surfactant molar ratios as 15.4%, 17.3%, 24.1%, 29%, and 19.7% for surfactant concentrations of 0, 0.025, 0.05, 0.075, and 0.1, respectively. All the samples showed broad diffraction peaks, suggesting that a partially ordered pore structure was formed in the films. From these results, we confirmed that a surfactant concentration of 0.075 was optimal for the formation of pores with an ordered arrangement. Owing to the generation of surface cracks and the less-ordered pore structure at higher surfactant concentrations, further analyses were limited to the samples with surfactant concentrations up to 0.075.

To confirm the effect of the surfactant concentration on the crystal structure of STNO, wide-angle XRD analyses were performed, as shown in Fig. 2. The intensity of the diffraction peak decreased slightly with increasing surfactant concentration. Thermal decomposition of a surfactant in a film generally degrades the crystallinity of the film owing to the incorporation of organic impurities into the film [29]. However, there was no significant difference in the grain size of STNO films calculated using the Scherrer equation [30] with increasing surfactant concentration. This was because of the thermal treatment conditions, such as the long time (4 h) at high temperature (850 °C). Generally, for perovskite oxides, surface defects might be confirmed by oxygen and metal photoemission spectra [31]. The O 1s and Ti 2p_{3/2} PES data of the STNO films shown

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