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# Enhancement of Seebeck coefficient of mesoporous SrTiO<sub>3</sub> with V-group elements V, Nb, and Ta substituted for Ti

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## ABSTRACT

The carrier concentration and effective mass of mesoporous SrTiO<sub>3</sub> films were controlled by the substitution of Ti with V-group elements (V, Nb, and Ta) to enhance the thermoelectric properties. We calculated the effect of the substitution on the effective mass of SrTiO<sub>3</sub> by analyzing its structural and electrical properties. When V was used as a substitute, the effective mass increased slightly due to a small change in the V–O bond distance. Moreover, when Nb and Ta were used as substitutes, the effective mass increased owing to an increase in the electronic density of states near the fermi level due to the increased bond length of Nb(or Ta)–O. Consequently, the use of Nb and Ta as substitutes in the SrTiO<sub>3</sub> film induced an increase in the figure of merit value, which was due to increases in both the effective mass and carrier concentration.

## 1. Introduction

Currently, thermoelectric-energy conversion techniques are urgently required to reduce reliance on fossil fuels, decrease environmental pollution, and prevent global warming [1]. In general, good thermoelectric materials offer high electrical conductivity values, high Seebeck coefficients, and low thermal conductivity [2]. In addition, these materials should be cost-effective, stable, and fabricated in a simple manner [3]. To produce improved thermoelectric materials, various studies have been performed, which involved structure modification, doping, and complexation [4,5]. Among these studies, a study involving the doping of strontium titanate (SrTiO<sub>3</sub>) gained much attention; it achieved the production of a good thermoelectric material with a high Seebeck coefficient and good thermal stability [6,7]. However, the thermoelectric conversion performance of SrTiO<sub>3</sub> still remains low because of its high thermal conductivity compared with that of other thermoelectric materials [8]. To enhance the thermoelectric properties of such materials, several groups have developed methods involving the use of strain [9], low-dimensional structures [10], and pore structures [2], as well as the formation of secondary phases [11], and modification of the electronic structure via dopant substitution [5]. Among the methods developed to enhance the thermoelectric properties of such materials, the adoption of dopant substitution is generating significant interest with regard to the power factor (PF = S<sup>2</sup>σ, where S is the Seebeck coefficient and σ is the electrical conductivity) [12]. This is because the doping method can be

used to increase the electrical conductivity of SrTiO<sub>3</sub> via changes in the carrier supply and electronic structure [13], while the Seebeck coefficient is maintained. The adoption of a mesoporous structure is particularly interesting because mesoporous materials exhibit greater reduction in thermal conductivity compared with that of electrical conductivity. This is because an inelastic mean free path of phonons is longer than that of electrons [14]. Therefore, in our study, we applied a mesoporous structure to SrTiO<sub>3</sub> to reduce its thermal conductivity. In addition, through substitution with V-group metals (V, Nb, and Ta), we aimed to achieve significant enhancement of the power factor. Moreover, to confirm the role of each V-group metal, the dopant-induced changes, with regard to the electronic structure and effective mass, were systematically studied. Using the calculated effective mass, the Seebeck coefficient was calculated and compared with the experimentally measured value. In this study, mesoporous SrTi<sub>1-x</sub>(V, Nb, and Ta)<sub>x</sub>O<sub>3</sub> films were prepared using a surfactant. Here, x represents a substitution ratio of 0.2. Mesoporous-structured SrTiO<sub>3</sub> can be synthesized using the evaporation-induced self-assembly (EISA) process [15]. The EISA process is simple and inexpensive. In this study, the structural and electrical properties of the mesoporous SrTi<sub>1-x</sub>(V, Nb, and Ta)<sub>x</sub>O<sub>3</sub> films were investigated to determine the role of the various V-group metals and the suitability of the resultant thermoelectric materials.

## 2. Material and methods

Strontium acetate (Sr(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, Aldrich) was used as strontium

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propionate powder. Strontium propionate powder and titanium tetraisopropoxide ( $\text{Ti}(\text{OPr})_4$ , TTIP, Aldrich, 97%) were used as  $\text{SrTiO}_3$  precursors. Vanadium oxytriethoxide ( $\text{OV}(\text{OC}_2\text{H}_5)_3$ , Aldrich, 99.5%), niobium ethoxide ( $\text{Nb}(\text{OCH}_2\text{CH}_3)_5$ , Aldrich, 99.95%), and tantalum ethoxide ( $\text{Ta}(\text{OCH}_2\text{H}_5)_5$ , Aldrich, 99.98%) were used as V-group metal precursors. A triblock copolymer, Brij-S10 ( $\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$ , MW 711, Aldrich), was used as a surfactant. The strontium acetate was dissolved in a large excess of propionic acid ( $\text{C}_3\text{H}_6\text{O}_2$ , Duksan), and the liberated acetic acid was distilled to prepare the strontium propionate powders. The excess propionic acid was separated using centrifugation, and the carboxylates were then precipitated with acetone ( $\text{CH}_3\text{COCH}_3$ , Duksan) and oven-dried to produce dried strontium propionate powder [16]. The strontium propionate powders were dissolved in propionic acid under stirring for 4 h. Subsequently, the Brij-S10 surfactant was dissolved in *n*-butyl alcohol ( $\text{CH}_3(\text{CH}_2)_3\text{OH}$ , Duksan) under stirring for 1 h. The resultant Brij-S10 solution was mixed with a V-group metal precursor and/or TTIP. Finally, the Sr precursors were mixed with a TTIP (V-group metal) surfactant solution and stirred for 15 min. The composition of the final product, a  $(\text{SrTi}_{1-x}(\text{V}, \text{Nb}, \text{and Ta})_x\text{O}_3)$ :Brij-S10:propionic acid:*n*-butyl alcohol precursor, was uniform at a molar ratio of 1:0.075:15:20. Here, *x* represents the substitution ratio, 0.2. The as-prepared  $\text{SrTi}_{1-x}(\text{V}, \text{Nb}, \text{and Ta})_x\text{O}_3$  precursor solutions were spin-coated onto clean  $\text{SiO}_2$  and Si substrates at 25 °C. To uniformly coat the solution on the substrates, spin-coating was performed at 2000 rpm for 20 s. The as-prepared films were thermally treated in a tube furnace at 800 °C for 4 h, for crystallization to occur. The final thickness of the samples was around 150 nm. The resultant  $\text{SrTiO}_3$ ,  $\text{SrTi}_{0.8}\text{V}_{0.2}\text{O}_3$ ,  $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ , and  $\text{SrTi}_{0.8}\text{Ta}_{0.2}\text{O}_3$  samples were denoted STO, SVO, SNO, and SAO, respectively. To investigate the pore ordering of the mesoporous films, small-angle X-ray diffraction (SAXRD, Ultima IV, Rigaku), with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), was performed (2 $\theta$  ranged from 0.5° to 5°). Grazing incident wide-angle X-ray diffraction (GIWAXD) measurements were conducted at the PLS-II 9A U-SAX beamline of the Pohang Accelerator Laboratory (PAL) in Korea. The chemical states of the films were analyzed using a high-resolution photoemission spectroscopy (HRPES) system as well as O 1s near edge X-ray absorption fine structure spectroscopy (NEXAFS), conducted in an ultrahigh vacuum chamber of the 4D beamline at the PAL in Korea. X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo VG, UK), with a monochromated Al K $\alpha$  source (1486.6 eV), was used to analyze the elemental composition. A Hall-effect measurement system (Ecopia HMS3000) was used to measure the electrical resistivity of the films. The Seebeck coefficients and electrical resistivity values of the films were measured using a commercial system (Seepel, TEP 800) used to determine thermoelectric properties, based on 4-point probe method. The repeatability was within  $\pm 3\%$  and the resolution was within  $\pm 1\%$ . The thermal conductivity was measured via the 3-omega method using a gold electrode with a width of 50  $\mu\text{m}$ . The 3-omega method is a 1-dimensional, heat-conduction-based thermal conductivity measurement technique that has been widely applied to thin films [17].

### 3. Results and discussion

Owing to their mesoporous structure, formed by a surfactant (Brij-S10), our films exhibit low thermal conductivity. To verify the formation of the mesoporous structure of the films, we analyzed the films using SAXRD; the results are presented in Fig. 1(a). The presence of the diffraction peaks at 0.93–1.11° verify that the films have a mesoporous structure. The intensities and positions of the diffraction peaks varied according to the substitute metal. These results indicate that the inter-pore distances and the ordered arrangement of the pores were related to the substitute metal. To clarify the dependence of the pore structure modification of the films on the substitute metal, we calculated the inter-pore distances of the films; the results are presented in Fig. 1(b). The inter-pore distance values of the films increase in the following order: SNO, SAO, and SVO/STO. It is known that the

substitution of Ti causes changes in the lattice parameters [18]. Therefore, we determined that the changes in the inter-pore distance were owed to the varying ionic sizes of the substitute metals. To clarify the dependence of the crystal structure modification of the films on the substitute metal, we performed GIWAXD analyses following annealing at 800 °C; the results are given in Fig. 1(c). Despite the use of various substitute metals, all the films exhibited similar crystalline states. However, depending on the substitute metal, a shift could be clearly observed with regard to the 110 diffraction peaks, as shown in the inset figure. As shown in the figure, the peak position of the SVO film was similar to that of the STO film. Moreover, in the case of the SNO and SAO samples, there were similar shifts towards lower *q*-values ( $\text{\AA}^{-1}$ ). We determined that the shift in the diffraction peak was due to increases in the lattice parameters owed to expansion of the lattice. The calculated inter-planar spacing and lattice parameters are given in Fig. 1(d). It is known that the ionic radii of  $\text{Ti}^{4+}$ ,  $\text{V}^{4+}$ ,  $\text{V}^{5+}$ ,  $\text{Nb}^{5+}$ , and  $\text{Ta}^{5+}$  are 0.61  $\text{\AA}$ , 0.58  $\text{\AA}$ , 0.54  $\text{\AA}$ , 0.64  $\text{\AA}$ , and 0.64  $\text{\AA}$ , respectively [19]. Therefore, the SNO and SAO films have greater lattice parameters than that of the STO film. In the case of the SVO film, if the oxidation state of V is 5+, the lattice parameter should be lower than that of the STO film; however, it was observed to be similar to that of STO. Normally, vanadium (III) exhibits well-defined coordination chemistry, retaining octahedral complexes in most systems, while the coordination chemistries of vanadium (IV) and vanadium (V) are much more flexible, with several configurations and coordination numbers reported [20].

In the oxidation system, several compounds, with known V-oxidation states and coordination numbers, were used as standards:  $\text{VO}_2$  (4+ : octahedron) and  $\text{V}_2\text{O}_5$  (5+ : trigonal bipyramid). The metal–oxide (M–O) bond distances and ionic radii of the films differ; these are given in Table 1. The main oxidation state of V is 4+; therefore, there was a small difference between the lattice parameters of the STO and SVO films, as shown by the results of the XRD observation.

Considering the chemical bonding state, we monitored the V 2p, Nb 3d, and Ta 4f photoelectron spectra using XPS to confirm the state of the substitution metal. Fig. 2(a) shows the constitutional bonding peaks obtained from the deconvolution of the V 2p, Nb 3d, and Ta 4f peaks of the films. With regard to V-cation substitution, as shown in Fig. 2(a), SVO contained a greater amount of V in the  $\text{V}^{4+}$  oxidation state compared with that in the  $\text{V}^{5+}$  oxidation state. As mentioned above, there is a larger difference between the ionic radii of  $\text{V}^{5+}$  and  $\text{Ti}^{4+}$  ions compared with that of  $\text{V}^{4+}$  and  $\text{Ti}^{4+}$ . This explains the above results. Furthermore, the ionic radii and M–O bond distances of  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  are similar to those of  $\text{Ti}^{4+}$ . Therefore, the SNO and SAO films stably exhibited the valence state of pentavalent cations. To confirm the change in the valence of the Ti metal due to the substitute metal, we investigated the Ti 2p chemical states of the films using XPS. As shown in Fig. 2(b), the Ti 2p $_{3/2}$  spectra of all the films showed a tiny  $\text{Ti}^{3+}$  peak at  $\sim 2 \text{ eV}$  below the main  $\text{Ti}^{4+}$  peak at 459 eV. However, by observing a magnified region at 457 eV, shown in the inset, it could be confirmed that the spectra of the SVO, SNO, and SAO films exhibit a greater  $\text{Ti}^{3+}$  peak than that of the STO film, owing to electronic compensation due to the presence of the pentavalent substitutional cations.

As expected, amongst the SVO, SNO, and SAO films, the spectrum of the SVO film showed the lowest  $\text{Ti}^{3+}$  peak intensity. Based on the above results, all the substitution metals played a role in the doping of the STO material. In the case of the SVO sample, the substitution of  $\text{Ti}^{4+}$  with  $\text{V}^{4+}$  and  $\text{V}^{5+}$  induced little change in the lattice parameters of the STO sample. Furthermore, in the case of the SNO and SAO films, the substitution of  $\text{Ti}^{4+}$  with  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  resulted in an expansion of the lattice parameters compared with those of STO. This change in the lattice parameters could induce a change in the band structure of the films and consequently, the thermoelectric properties of the films could also change. The band structure, valence band, and 1st derivative of the O 1s absorption of the films were investigated using HRPES; the results are shown in Figs. 2(c and d). As shown in Fig. 2(c), the valence bands 'A', 'B', and 'C' are associated with contributions from the

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