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Improvement of Niobium Doped SrTiO₃ by Nanostructuring

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Abstract— The thermoelectric performance and the microstructure of 20%-Nb-doped SrTiO₃ samples at high temperatures (300 – 1200 K) prepared by conventional solid-state reaction in a reduced atmosphere, followed by a Spark Plasma Sintering (SPS) process were investigated. The absolute Seebeck coefficient (S) increased from 65 $\mu\text{V/K}$ to about 180 $\mu\text{V/K}$, while the electrical conductivity (σ) was found to decrease from 220 S/cm to about 150 S/cm with increasing temperature. Notably, the thermal conductivity of these samples was significantly reduced in the high temperature region.

Keywords— Thermoelectric material, n-type semiconductor, Spark Plasma Sintering, Electrical conductivity, Figure of merit

I. INTRODUCTION

With the depletion of natural resources, the exploration of the alternative energy resources is becoming more into focus. Thermoelectric materials are attracting extensive interest because of their potential of converting waste heat into electricity [1].

Typically, the performance of thermoelectric materials is evaluated by the dimensionless thermoelectric figure of merit $ZT = S^2 \sigma T / \kappa$, where S , σ , T , and κ are the Seebeck coefficient, the electrical conductivity, the absolute temperature, and the thermal conductivity, respectively [2]. Good thermoelectric materials require a large Seebeck coefficient for generating a large thermal voltage, a high electrical conductivity for minimizing Joule heating, and a low thermal conductivity for retaining the heat at the junctions to obtain a high ZT . Since Terasaki et al. [3] found a large thermopower and a high conductivity in layered cobaltite NaCo₂O₄ oxides, this system has been investigated intensively as an interesting alternative candidate for high temperature applications. Oxides are thermally stable in the high temperature range, are resistant towards oxidation and furthermore; they are composed of cheap elements.

In recent years, n -type thermoelectric oxides with the perovskite-type structure, especially doped SrTiO₃ [4]–[9], have been intensively studied. Looking through the previous publish data on this system, there seems to be different ways to obtain a single phase of Nb-doped SrTiO₃. Most researchers have synthesized the samples by the solid state reactions where it is feasible to get large amounts of materials, cheap starting materials, as well as cheap processing. Ohta et al. [10] for example have heated the powders at 1573 K for 6 h in Ar atmosphere, while Page et al. [11] have sintered the pellets

twice at 1623K for 20 h in flowing H₂ atmosphere with intermediate grinding and repelletization between the two different sintering sequences. In another report by Wang et al. [12] the mixed powders were sintered at 1673 K only for 4 h in Ar atmosphere. It is obvious that the performance of these materials is strongly dependent on the materials processing, reflecting their microstructure i.e. grains size and grains boundaries, their actual compositions i.e. crystal structure and electronic configuration. As for thermoelectric performance of these materials, only Ohta's group could attain a $ZT = 0.35$ at 1000 K for the 20% Nb-doped SrTiO₃, so far.

When making bulk materials for thermoelectric use the main challenge is how to get a fully dense pellet and still keeping the desire microstructure. In a conventional sintering or hot pressing a high density is often reached but unfortunately at the same time the grain grows. Spark plasma sintering (SPS), also known as pulsed electric current sintering, is a sintering technique which can provide a possible solution to the long sintering time which is often needed in conventional sintering. The main characteristic of SPS is that a pulsed DC current directly passes through a graphite die, as well as the powder compact, in case of conductive samples resulting in heat which is generated internally, in contrast to a conventional hot pressing, where the heat is provided by external heating elements. This facilitates a very high heating or cooling rate (up to 1000 Kmin⁻¹), hence the sintering process generally is very fast (within a few minutes) preventing grain growth. The general short time scale of the process can lead to a rapid densification of the powders without significant grain coarsening which accompanies standard densification routes. This technique is now being widely applied for thermoelectric bulk nanostructured materials.

In this study we have chosen the most promising composition of n -type thermoelectric material, 20 % Niobium doped SrTiO₃ which show the highest thermoelectric effect [10]. The powders were synthesized using the conventional method in a modified reduced atmosphere to obtain nanoparticles followed by SPS technique. Thermoelectric properties were measured from 300 to 1200 K. The microstructures of these samples were investigated with respect to the grains size and grains boundaries effect on the thermoelectric performance.

II. EXPERIMENTAL

Niobium doped SrTi_{0.8}Nb_{0.2}O₃ was prepared by solid-state reaction with stoichiometric quantities of SrCO₃, Ti₃O₅ and Nb₂O₅. The powder was thoroughly mixed by ball-milled with

ethanol for 48 h and then dried and calcined in air at 1572 K for 12 h. The calcined powders were pressed into pellets under a uniaxial pressure of 32 MPa, followed by cold isostatic pressing at 255 MPa. The pellets were then sintered at 1793 K in forming gas of 9 mol% H₂ in N₂ for 24 h. The pellets were then crushed, ball-milled, repelletized and sintered again under the same conditions. A single phase SrTi_{0.8}Nb_{0.2}O₃ could be obtained at this step however the pellet was crushed again and ball-milled to get fine powders. The final processing was carried out using spark plasma sintering (SPS-515S, SPS Syntex Inc). The precursory powders were filled into a graphite die with $\Phi = 12.7$ mm and heated to 1573 K for 1 min under a uniaxial pressure of 50 MPa. Pulsed electric current (2000 A, 4 V) was then passed through the sample under vacuum (10⁻³ bar).

X-ray diffraction patterns were collected at ambient temperature from 18-80° on a Bruker D8 diffractometer with Cu K_α radiation. Particles size before SPS was measured with a LS 13 320 Particle Size Analyser from Beckman Coulter Inc., USA. Electrical resistivity and Seebeck coefficient was measured simultaneously from room temperature to 1200 K in low-pressure He atmosphere on a ZEM3-M10 unit from ULVAC Technologies Inc., Japan. The thermal conductivity (κ) was determined from the density (d), thermal diffusivity (α) and specific heat (C_p) using the equation $\kappa = d \times \alpha \times C_p$. The thermal diffusivity of the pellet was measured on a LFA-457 laser flash apparatus from Netzsch under N₂ flow from room temperature to 1164 K. The specific heat was determined by the ratio method comparing with the reference sample, inconel, during the thermal diffusivity measurement. The bulk density was obtained by the Archimedes' method. Microstructure of samples was observed from the fractured surfaces using a Hitachi scanning electron microscopy (TM-1000) system.

III. RESULTS AND DISCUSSION

Fig. 1 presents the XRD patterns of the sample and of a standard SrTiO₃ (PDF card #01-070-8508). It can be seen from Fig. 1 that all the XRD peaks can be identified as the standard phase of SrTiO₃. They are, however, shifted to a lower scattering angle for the Nb-doped sample, comparing to those for the standard SrTiO₃ without Nb. This probably is a distortion of lattice parameters caused by substitution of Nb⁵⁺ and by formation of Ti³⁺ ions with larger ionic radius (0.64 Å and 0.67 Å) than Ti⁴⁺ ions (0.605 Å) [13].

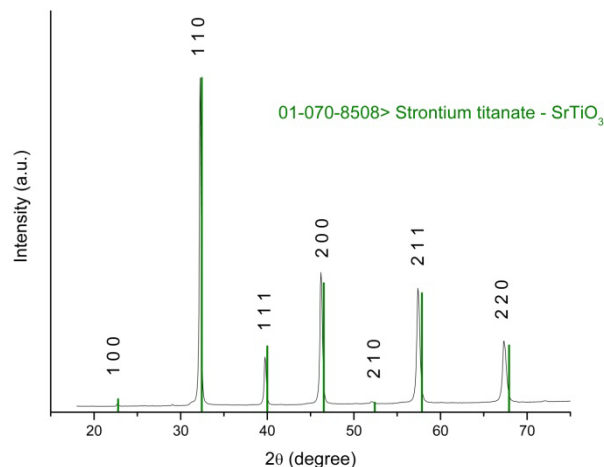


Fig. 1 XRD patterns of sintered SrTi_{0.8}Nb_{0.2}O₃ sample as compared with PDF card #01-070-8508 of SrTiO₃ with a cubic structure.

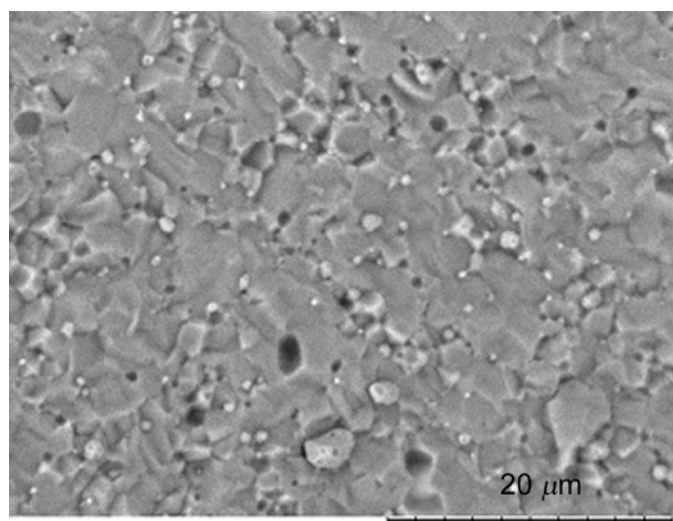


Fig. 2 SEM image of fractured surface of SPS sample SrTi_{0.8}Nb_{0.2}O₃

Fig. 2 shows SEM image taken from the fractured cross-section of SPSed-sample. It is clear that grains are very small varying from nanosize to several microns. This correspond well with the average grains size of the powders after ball-milling of the crushed sintered pellets before SPS which were measured to be around 0.6 μm. The sample is fully dense (4.93 gcm⁻³/94% relative density [9]).

The temperature dependence of the electrical conductivity (upper) and Seebeck coefficient (lower) is shown in Fig. 3. Typically, the electrical conductivity decreases with increasing temperature for the sample with Nb doping, showing a metallic behaviour. However, the electrical conductivity firstly increases with increasing temperature when temperature is below 600 K, reaching a maximum of 222 Scm⁻¹ and then decreases to 150 Scm⁻¹ with further increasing of temperature up to 1138 K. The thermopower of the sample shows a negative value over the measured temperature range, indicating that the majority of charge carriers are electrons as expected. The magnitude of

thermopower increases with increasing temperature from $-64 \mu\text{VK}^{-1}$ at room temperature to a maximum of $-176 \mu\text{VK}^{-1}$ at 1138 K. The values of the Seebeck coefficient given by Ohta et al. [10] for a ceramic is $-50 \mu\text{VK}^{-1}$ at 300 K and $-180 \mu\text{VK}^{-1}$ at 1000 K, so our value is in the same range and follow the same trend.

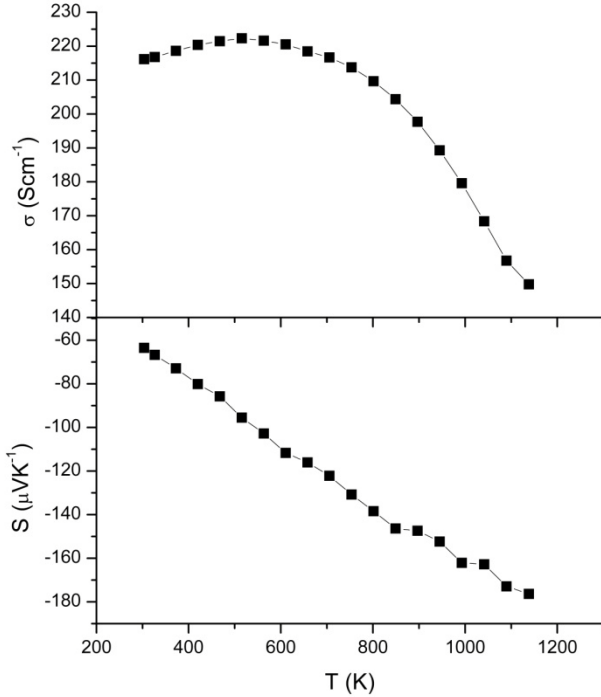


Fig. 3 Temperature dependence of the electrical conductivity and the Seebeck coefficient of the SPS sample.

Fig. 4 shows the temperature dependence of the power factor, which gives a combined impact of the Seebeck coefficient and the electrical conductivity. The power factor increases with increasing temperature from 300 K to about 900 K, it then tends to level-off with further increasing of temperature. The maximum power factor is $4.72 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ attaining at about 993 K.

The thermal conductivity, κ , (upper) and the dimensionless figure of merit, ZT, (lower) as functions of temperature are shown in Fig. 5.

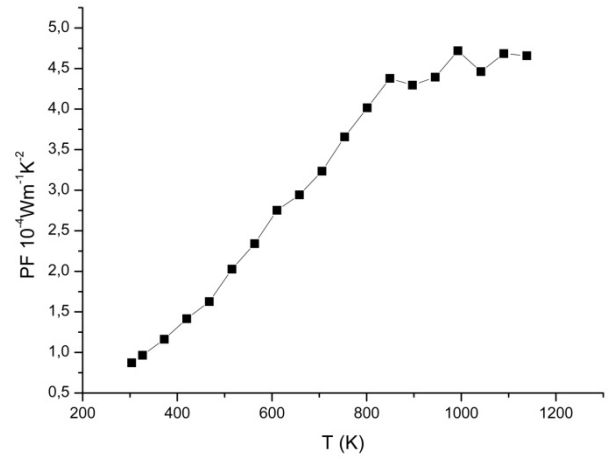


Fig. 4 Temperature dependence of the power factor for the SPS sample.

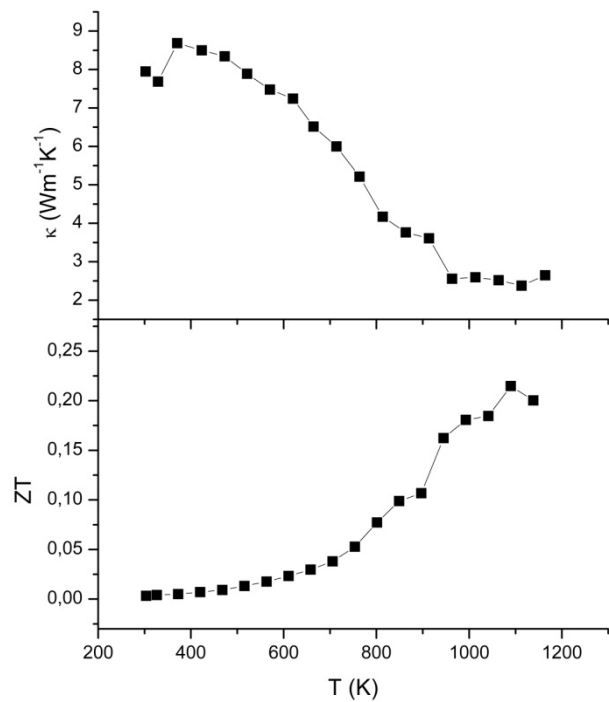


Fig. 5 Temperature dependence of the thermal conductivity and dimensionless figure of merit.

The thermal conductivity value decreases with increasing temperature and reaches a minimum at $2.4 \text{ Wm}^{-1}\text{K}^{-1}$ at 1113 K, which is favorable for high temperature thermoelectric application. For comparison the lowest value for a ceramic obtained by Ohta et al. [10] is $3.1 \text{ Wm}^{-1}\text{K}^{-1}$ at 1000 K for $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ while the value reported by Wang et al. [14] is $4.1 \text{ Wm}^{-1}\text{K}^{-1}$ at 1100 K for $\text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{0.90}\text{Nb}_{0.10}\text{O}_3$. It is noted that our κ shows a lower value, which is associated with nanostructured of the sample as clearly shown in the SEM image (Fig. 2).

As a result of combining the power factor and the thermal conductivity, the ZT increases with increasing temperature

and has a maximum of 0.21 at 1090 K. Unfortunately our low electrical conductivity means that we get a lower ZT than Ohta et al. [10] value of 0.35 at 1000 K but much higher than 0.02 obtained by Wang et al. [12] at 900 K. In addition this value is comparable with reported by Zhang et al. [9] of about 0.22 at 800 K for $\text{Sr}_{0.92}\text{La}_{0.08}\text{TiO}_3$.

IV. CONCLUSIONS

The solid state synthesis route of niobium doped strontium titanate is not trivial. In this work we sintered the powder twice to get a single phase powder. The thermoelectric data obtained are in the range of published data and the thermal conductivity is even lower than the published data. The next step in increasing the ZT of $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ will be to vary the pressure and temperature pattern during spark plasma sintering.

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