

Microstructure and seebeck voltage of NaTaO₃ composite ceramics with additions of Mn, Cr, Fe or Ti

Wilfried Wunderlich* and Susumu Soga

Tokai University, Graduate School of Engineering, Material Science Department, 259-1292 Kanagawa-ken, Hiratsuka-shi, Kitakaname 1117, Japan

This paper reports about Seebeck measurements of the perovskite phase NaTaO₃. To increase the carrier concentration, specimens including metallic transition metals such as Mn, Cr, Fe, Ti were sintered at 1273 K and 1473 K. Microstructural characterization by SEM and XRD showed that besides the perovskite phase, transition metal oxides are present. The solubility limit of NaTaO₃ increases with the sintering temperature and is about 17% in the case of Fe after sintering at 1473 K for 10 h. For NaTaO₃ with 50 mol% Fe₂O₃ at a temperature difference of 800 K a Seebeck voltage of –320 mV was measured. This is the highest Seebeck voltage among all the specimens and leads to a Seebeck coefficient of –0.45 mV/K. The specific electric resistivity decreases with an increase in the temperature from 50 MΩm at room temperature to 5 Ωm at 1273 K. The power factor of this new n-type thermoelectric candidate material is estimated.

Key words: n-type thermoelectric materials, Seebeck coefficient, perovskite, microstructure.

Introduction

Successful thermoelectric ceramic materials such as Nb-doped SrTiO₃ have a high effective electron mass ($m/m_0 = 4.8$) [1]. The search for other perovskites leads to NaTaO₃, which has an even higher effective mass ($m/m_0 = 9$) [2]. Pure NaTaO₃ is an insulator and doping in order to increase the carrier concentration has not yet been reported. N-doping requires substitution by an element with more electrons than the host on the A-site of the perovskite lattice [2]. Transition elements with a large density of states near the band gap are usually considered as suitable for this purpose. Thermoelectric materials require a large Seebeck coefficient S , a large electric conductivity σ and a small thermal conductivity k , in order to achieve a large power factor $Z = S^2\sigma/k$. Present research on NaTaO₃ mainly focuses on the photocatalytic properties after the discovery of its large photo-degradation [3, 4], but also the high Seebeck voltage of NaTaO₃ has recently been published [5].

This research has three goals, first to find dopants for NaTaO₃, their solubility limits in the perovskite structure, and finally to characterize their thermoelectric properties.

Experimental

Specimens were produced by mixing well-defined weight ratios of fine powders of NaTaO₃ (Fine Chemicals

Ltd.) and each of the pure metals Mn, Cr, Ti and Fe in a mortar for more than 10 minutes. The specimens were pressed at 100 MPa into pellets 10 mm in diameter and 3 mm in height and sintered in air first at 1273 K for 5 h, then three times at 1473 K for 3 h with slow heating and cooling rates (50 K/h). During sintering the white color of NaTaO₃ specimens turns dark in the case of iron and manganese additions, into dark-green in the case of chromium, and into light orange in the case of titanium additions. Between each annealing step the specimens were characterized by SEM (Hitachi 3200-N) at 30 kV equipped with EDS (Noran) and electric resistivity measurements (Sanwa PC510).

The X-ray diffraction (XRD) analysis was performed using a Rigaku Miniflex device with Co-source with 1.7889 nm wavelength. Simulation of the XRD-patterns was performed with the Carine V3 software (Cristmet). Ab-initio simulations using the LDA-GGA method were performed using the Vasp-software [2, 6].

The thermoelectric measurements were performed with a self-manufactured device as shown in Fig. 1. The specimen was attached to the device, so that its left side lies on a copper block as a heat sink and its right side on a micro-ceramic heater (Sakaguchi Ltd. MS1000) with a power of 1 kW, which was heated up to 1273 K within 3 minutes. Hence, the bottom part of the specimen experienced the large temperature difference, while the upper part was heated through the heat conductivity of the specimen. The temperature distribution as measured by thermocouples is shown in Fig. 1c. Seebeck voltages were measured on both, the bottom and top part of the specimen by Ni-wires which were connected to Sanwa PC510 voltmeters, marked as V1 and V2 in Fig. 1a. The temperature was

*Corresponding author:
Tel : +81-90-7436-0253
Fax: +81-463-50-2096
E-mail: wi-wunder@rocketmail.com

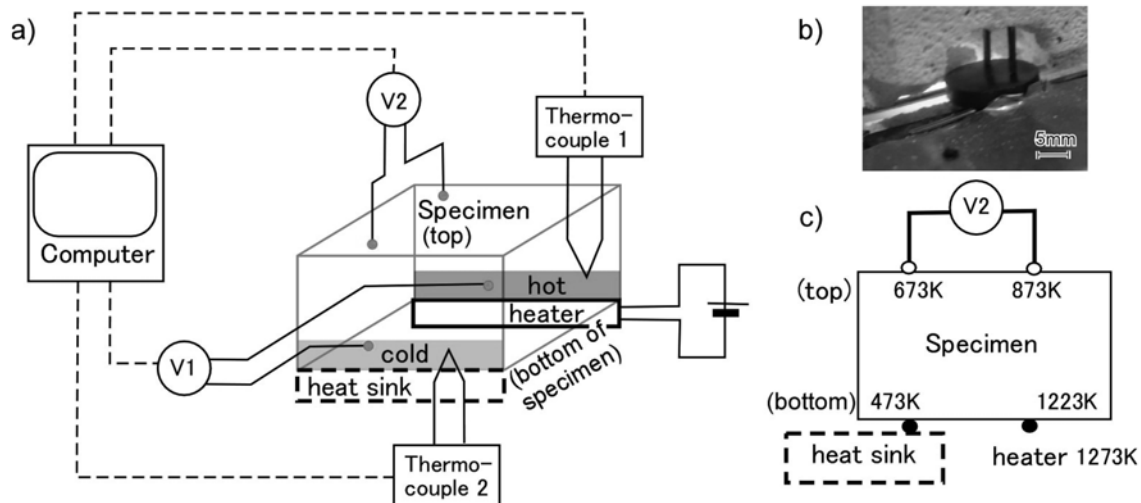


Fig. 1. a) Schematic drawing, b) photograph of the device to measure the temperature and the Seebeck voltage below and above the specimen. V1 and V2 are voltmeters. c) Cross section of the specimen and the temperature distribution in the steady-state condition. The dark dots refer to the wires at the bottom the specimens connected to voltmeter V1. Wires at top and bottom of the specimens have a separation of 5 mm.

measured with thermocouples also attached to Sanwa PC510 devices. The data were recorded online by a personal computer. When shifting the specimen position, so that it lay completely on the heater, the temperature dependence of the electric resistivity was measured using the same device. From the time dependence of the Seebeck voltage the temperature dependence of the Seebeck voltage U_{See} was calculated, and the slope in the graph versus the temperature difference between heated and cold parts of the specimen leads to the Seebeck coefficient $S = \Delta U_{See} / \Delta T$. In the same way the temperature dependence of the resistivity ρ was measured and from the Drude equation $1/\rho = e n \mu$ with μ the mobility. The activation energy E_A for thermal activation of the charge carriers n_e in this n-doped semiconductors was estimated according to $n_e = N \exp(-E_A/2 kT)$ by a suitable data fit.

Results and Discussion

As the specimens were sintered from NaTaO_3 with pure metal additions, both, the weight and the volume of the specimens, increased during the first sintering step due to the oxidation of the metals. Fig. 2 shows the XRD-results for specimens after annealing at 1273 K 5 h and 1473 K 10 h. All peaks in the experimentally-obtained pattern could be identified as follows. The main phase is the perovskite NaTaO_3 phase with a slightly smaller lattice constants (0.3850 nm) than literature data [7]. The high temperature phase with tilted octahedron and space group $Cmcm$ shows peaks on the same positions, but with different intensities and does not match the experimental data. The specimen with Ti additions (Fig. 2a) shows almost identical peaks of the two rutile phases TaO_2 (space group $I41/a$, $a = 1.2654$ nm, $c = 0.5.814$ nm) or TaTiO_4 (space group $P42mm$, $a = 0.4473$ nm, $c = 0.2913$ nm). In both cases the lattice

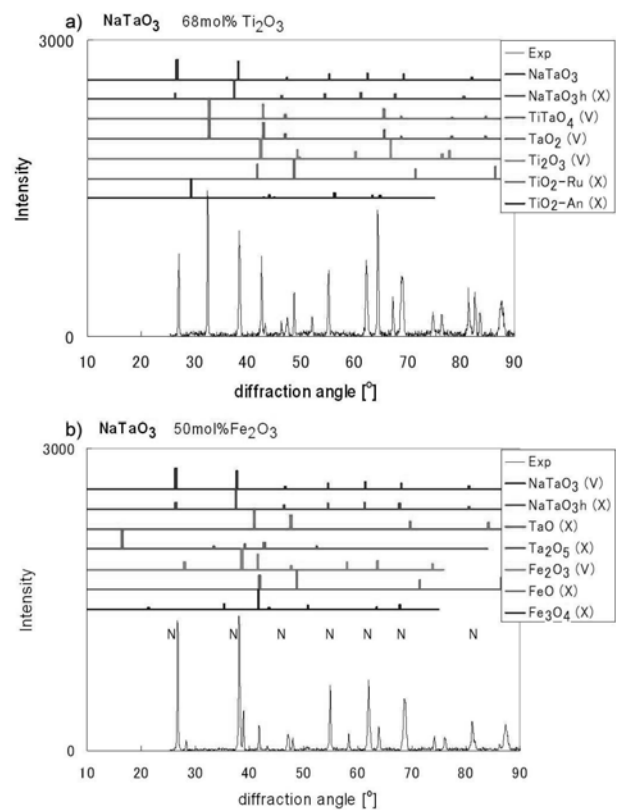


Fig. 2. XRD results of NaTaO_3 with a) 68 mol% Ti_2O_3 b) 50 mol% Fe_2O_3 additions. N marks the peaks of NaTaO_3 .

constants are 5% smaller than the literature values [8, 9]. According to the position and height of the XRD peaks, TiO_2 neither as the anatase nor as rutile phases was present, but they correspond well to Ti_2O_3 (corundum structure $R-3cH$, $a = 0.4926$ nm, $c = 1.2930$ nm). The specimen with Fe additions (Fig. 2b) shows only peaks identified as NaTaO_3 and Fe_2O_3 phases, respectively.

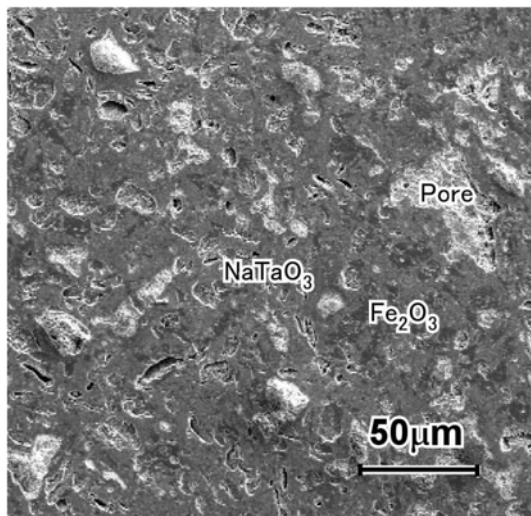


Fig. 3. Microstructure of NaTaO₃ – 50 mol%Fe₂O₃ composite after sintering at 1473 K for 3 h: 1 mm large Fe₂O₃ dark particles are embedded in the grey NaTaO₃ matrix. The white areas are pores due to insufficient sintering.

The microstructure of the 50 mol% NaTaO₃ – 50 mol% Fe₂O₃ composite (in the following referred as NaTaO₃ – 50 mol% Fe₂O₃) as shown in Fig. 3 consists of on average 1 mm sized Fe₂O₃ dark particles embedded in the NaTaO₃ matrix which appears grey in Fig. 3. The particles have a volume fraction of about 30% which correspond well to the intensity ratios of the XRD-pattern. The white areas, which are pores remaining from insufficient compaction, have the same composition as the matrix. Table 1 shows the composition as measured with SEM-EDX. About 8 at% Fe gets dissolved in the NaTaO₃ matrix after sintering at 1273 K for 5 h, and 17 at% Fe gets dissolved after sintering at 1473 K for 10 h leading to an atomic ratio of the three metallic atoms close to about 1 : 1 : 1 (table 1) in SEM-EDS measurements, in which oxygen is undetectable. The Fe₂O₃ phase dissolves about 4% Na and 4% Ta after the first sintering and up to 6% Na and 6% Ta after the fourth sintering step. Ab-initio calculations showed that the Fe is substituting the Ta-atoms on the *B*-sites but not the Na-atoms on the *A*-sites of the perovskite lattice ABO₃ [5] and that the lattice constants remain unchanged. In the case of the other three elements added to NaTaO₃ the results are similar. After four sintering steps, the metal oxide Mn₂O₃ dissolves

Table. 1. Chemical composition of each of the phases in Fig. 3 as measured with SEM-EDX. The white areas are pores with almost the same composition as the grey NaTaO₃-matrix, and the black phase was identified as Fe₂O₃ by XRD

Phase	Composition [at%]		
	Na	Ta	Fe
black	8	4	87
white	36	33	37
grey	30	34	34

about 6% Na, and 8%Ta; Ti₂O₃ about 6% Na, 6% Ta; Cr₂O₃ only 1 %Na and 2% Ta, respectively.

The electric resistivity at room temperature for the specimens after each sintering step was measured under the same conditions with a separation of the Ni-wires of 5 mm. The results are shown in Fig. 4. For the Fe₂O₃ a remarkable decrease was observed after each sintering step at 1473 K, while for Mn and Cr a moderate decrease and for Ti₂O₃ no change was observed. The results can be explained by the reduction of lattice defects due to sintering, which improves the electric conductivity. The temperature dependence of the specific resistivity is shown in the logarithmic plot of Fig. 5 for the specimen NaTaO₃ – 50 mol% Fe₂O₃. Above 500 K the resistivity decreases rapidly and reaches less than 5 Ωm at 1273 K, or a conductivity of 0.2 S/m.

The negative Seebeck voltage increases linearly with the temperature and reaches –320 mV at a temperature difference of 710 K as shown in Fig. 6 for the NaTaO₃ – 50 mol% Fe₂O₃ specimen. From the slope of the Seebeck voltage with temperature a Seebeck coefficient of

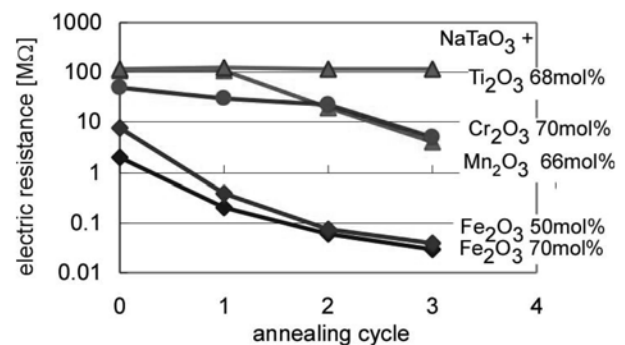


Fig. 4. Resistivity of NaTaO₃ - metal oxide composites after sintering at 1273 K for 5 h and different annealing cycles at 1473 K for 3 h. The numbers refer to mol% parts of the composite.

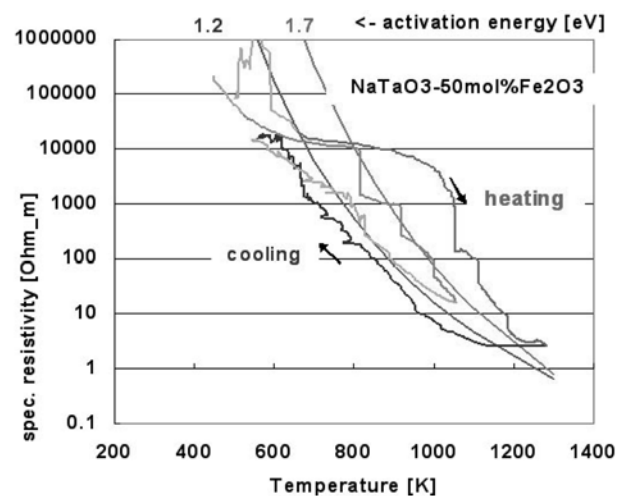


Fig. 5. Temperature dependence of the specific resistivity for NaTaO₃ – 50 mol% Fe₂O₃. Data shown in dark colors were measured from the bottom attached to the heater, those in bright color from the top of the specimen (for details of the geometry see Fig. 1).

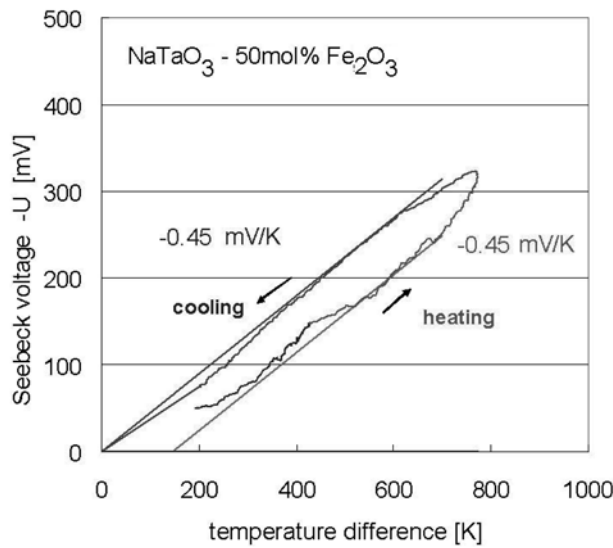


Fig. 6. Negative Seebeck voltage as a function of the applied temperature difference of the NaTaO₃- 50mol% Fe₂O₃ specimen.

−0.45 mV/K was estimated. Specimens in the range of 20 mol to 70 mol% Fe₂O₃ all showed a Seebeck coefficient larger than −0.45 mV/K, while an amount of 10 mol% and more than 70 mol% Fe₂O₃ show lower Seebeck coefficients. From these data the figure of merit can be deduced. For the thermal conductivity the worst case of a high value of 10 W/(mK) was assumed, while usual ceramics lie in the range of 5 W/(mK) or less. This leads to:

$$Z = \frac{S^2 \cdot \sigma}{\kappa} = \frac{(0.45 \text{ mV/K})^2 \cdot 0.2 \text{ S/m}}{10 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}} = 4.05 \times 10^{-9} \text{ K}^{-1},$$

$$ZT_{800\text{K}} = 3.2 \times 10^{-6}.$$

These thermoelectric properties are still not so good as other thermoelectric materials such as Nb-doped SrTiO₃ but improvements of conductivity and microstructure could make the NaTaO₃-Fe₂O₃ composite applicable for many thermoelectric devices for example gas burners

for direct electric power generation or Peltier coolers operating at 1000 K. The Seebeck effect in these composites cannot be explained only by the solid-solution of Fe-atoms in NaTaO₃, but it must be a synergetic effect between NaTaO₃ and Fe₂O₃, as Fe₂O₃ itself also shows a low, but remarkable Seebeck coefficient [10].

Conclusions

1. While pure NaTaO₃ is an insulator, doping with Fe decreases the resistivity remarkably, especially when the sintering is optimized. Addition of Ti does not show such an effect, and Cr and Mn reduce the resistivity less effectively.
2. The solubility limit of Fe in NaTaO₃ was determined to be 17at% Fe.
3. NaTaO₃-Fe₂O₃ composites in the range of 20 to 60 mol% Fe₂O₃ showed a sufficiently low resistivity above 700 K and a large negative Seebeck coefficient of −0.45 mV/K (n-doped semiconductor), which leads to a Seebeck voltage of −320 mV at a temperature difference of 710 K.

References

1. S. Ohta, T. Nomura, H. Ohta and K. Koumoto, *J. Appl. Phys.* 97 (2005) 034106.
2. W. Wunderlich and Kunihiro Koumoto, *International Journal of Materials Research* 97[5] (2006) 657-662.
3. H. Kato and A. Kudo, *Chem. Phys. Lett.* 295[5-6] (1998) 487-492.
4. A. Kudo and H. Kato, *Chem. Phys. Lett.* 331[5-6] (2000) 373-377.
5. W. Wunderlich, *J. Nucl. Mat.* 389[1] (2009) 57-61.
6. G. Kresse and J. Hafner, *Phys. Rev. B* 47 (1993) 558-561.
7. C.N. Darlington and K.S. Knight, *Acta Crystallographica B* 55[1] (1999) 24-30.
8. E. Peters and H. Mueller-Buschbaum, *Zeitschrift fuer Naturforschung, Teil B. Anorg. Chemie* 50 (1995) 1167-1170.
9. V.I. Khitrova, V.V. Klechkovskaya and Z.G. Pinsker, *Kristallografiya* 12 (1967) 1044-1050.
10. F.J. Morin, *Phys. Rev.* 93[6] (1954) 1195-1199.