Thermoelectric properties of Nb-doped SrTiO₃ ceramics enhanced by potassium titanate nanowires addition

Ning WANG,^{*,**} Hongcai HE,^{*} Yaoshuai BA,^{**} Chunlei WAN^{**,***} and Kunihito KOUMOTO^{**,***,†}

^{*}State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China

^{**}Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya-shi 464–8603

^{***}CREST, Japan Science and Technology Agency, Honcho, Kawaguchi-shi 332–0012

Nb-doped SrTiO₃ thermoelectric ceramic composites with potassium titanate (KTO) nanowires addition were fabricated by the pressure-less sintering method in an Ar atmosphere. KTO addition significantly reduced the thermal conductivity and enhanced the electrical conductivity. Meanwhile, the Seebeck coefficient was almost independent of KTO addition, thus, enhancing the dimensionless thermoelectric figure of merit, *ZT*. The sample with 3 wt % KTO addition gave the maximum *ZT* of 0.34 at 900 K. The reason for the enhanced thermoelectric properties by KTO addition was also investigated.

©2010 The Ceramic Society of Japan. All rights reserved.

Key-words : Ceramics, Oxide materials, Thermoelectric, Strontium titanate

[Received July 7, 2010; Accepted August 19, 2010]

1. Introduction

In order to improve the performance of thermoelectric materials, thermal conductivity should be reduced, and electrical conductivity should be increased: The two requirements can go together by using certain types of nanocomposites. Thermoelectric bulk materials with nanostructured constituents have been proposed to be promising materials with high thermoelectric performances.¹⁾

Recently, a variety of thermoelectric bulk nanocomposite materials with thermoelectric properties better than bulk materials have been prepared. Zhang et al. prepared Ag_xSb_{2–x}Te_{3–x} thermoelectric materials with nanostructured Ag₂Te embedded in the AgSbTe₂ matrix by in-situ precipitation method, and the maximum dimensionless thermoelectric figure of merit, *ZT*, of 1.53 was obtained at 500 K.²⁾ Ahn et al. prepared PbTe/CdTe thermoelectric bulk alloys with CdTe nanocrystals by melt technique, and the obtained maximum *ZT* was 1.2 at 723 K.³⁾ Fan et al. fabricated Bi_{0.4}Sb_{1.6}Te₃ nanocomposites through mixing nanostructured Bi_{0.4}Sb_{1.6}Te₃ particles with micron-sized particles, and the maximum *ZT* of 1.8 at 316 K was obtained.⁴⁾ Lan et al. prepared bulk nanograined bismuth antimony telluride by a ball milling and hot-pressing method, and the maximum *ZT* reached 1.4 at 373 K.⁵⁾

However, the use of rare or toxic elements in above-mentioned compounds with nanostructured constituents will limit their large-scale commercial applications, even though their *ZT* values were more than 1.0.

Nowadays, ceramic oxide thermoelectric materials are receiving increased interest because they are economical, environmentally friendly, possess various chemical compositions, and consist of naturally abundant elements. Among the *p*-type oxide thermoelectric bulk materials, the layered sodium cobaltite Na_xCoO_{2–δ} single crystal has the highest dimensionless figure

of merit, *ZT* value, higher than 1.0 at 800 K,⁶⁾ which can meet the basic requirements of practical applications. However, among the *n*-type oxide thermoelectric bulk materials, even though Nb-doped SrTiO₃ bulk ceramic (prepared by hot-pressing method) has the highest *ZT* value at 900 K, 0.29,⁷⁾ but it is still very low, compared with *p*-type sodium cobaltite, and thus urgently needs to improve. Very recently, we prepared Nb-doped SrTiO₃ composites by adding nanostructured yttria stabilized zirconia (YSZ)⁸⁾ and mesoporous silica (MS)⁹⁾ by the pressure-less sintering method. These additions could effectively reduce thermal conductivity by enhancing phonon scattering at grain boundaries and increase the electrical conductivity by promoting densification, and then enhanced the *ZT* value, which strongly triggered our interest to investigate other effective nanosized additions to further enhance the thermoelectric properties of Nb-doped SrTiO₃.

Herein, we used potassium titanate (KTO) nanowire for the nanosized addition, and investigated its effects on the thermoelectric properties of Nb-doped SrTiO₃ ceramics.

2. Experimental procedure

Single-phase Nb-doped SrTiO₃ (Sr(Ti_{0.85}Nb_{0.15})O₃, Nb-STO) powders were prepared by solid-state reaction of SrCO₃, TiO₂ and Nb₂O₅ powders at 1400°C for 4 h in an Ar atmosphere. Then, home-made KTO (K₂Ti₆O₁₃) nanowires prepared according to the literature,¹⁰⁾ with the diameter of 20–40 nm and the length of several hundreds, were homogeneously mixed into Nb-doped SrTiO₃ powders. Finally, Nb-doped SrTiO₃ ceramic samples without KTO and with KTO addition, 1 wt % (1.7 vol %), 3 wt % (5 vol %) and 5 wt % (8.3 vol %), were fabricated by conventional pressure-less sintering at 1500°C for 3 h in an Ar atmosphere. The morphologies of the specimens were observed by a scanning electron microscope (SEM, S-3000N, Hitachi). The thermoelectric properties, including the Seebeck coefficient and electrical conductivity, were measured at 300–900 K in an Ar atmosphere using an automatic thermoelectric measuring apparatus (RZ-2001K, Ozawa Scientific). The thermal diffusivity was

[†] Corresponding author: K. Koumoto; E-mail: koumoto@apchem.nagoya-u.ac.jp

Fig. 1. Temperature dependent electric transport properties of KTO/Nb-STO composites: (a) electrical conductivity; (b) Seebeck coefficient.

measured by the common laser flash method (TC-9000V, ULVAC-RIKO). The specific heat capacity was measured by a differential scanning calorimeter system (DSC-2910, TA Instruments).

3. Results and discussion

Figure 1 shows the temperature dependence of electronic transport properties of KTO/Nb-STO composites, namely, electrical conductivity (σ) and Seebeck coefficient (S). KTO addition significantly increased the electrical conductivity (Fig. 1(a)). Meanwhile, KTO addition only had a very small effect on Seebeck coefficient (Fig. 1(b)).

Figure 2(a) shows the temperature dependence of the measured thermal conductivity (κ_{measured}) of KTO/Nb-STO composites. The relative density of these samples drastically differed. Hence, the measured thermal conductivity does not accurately reflect the effect of KTO addition. To exclude the effect of porosity, the extrapolated thermal conductivity (Fig. 2(b)) of a completely dense KTO/Nb-STO composite with zero porosity (κ_0) was calculated using Klemens' equation:¹¹⁾

$$\kappa_{\text{measured}}/\kappa_0 = 1 - 4\phi/3, \quad (1)$$

Fig. 2. Temperature dependent thermal conductivities of KTO/Nb-STO composites: (a) measured values; (b) calculated values with theoretical density of 100%.

Fig. 3. Temperature dependent dimensionless figure of merit ZT of KTO/Nb-STO composites.

where ϕ is the porosity of samples. Fig. 2(b) shows that KTO addition could reduce the thermal conductivity of Nb-STO polycrystalline ceramics significantly.

The temperature dependent dimensionless figure of merit, ZT , of KTO/Nb-STO composites is shown in **Figure 3**. It was found that the ZT value was increased significantly by KTO addition. The sample with 3 wt % KTO gave the highest ZT value at 900 K, 0.34, which was 14 times higher than the sample without KTO addition. The enhancement in ZT value was mainly beneficial from the significantly increased electrical conductivity and reduced thermal conductivity. The maximum ZT value, 0.34 at 900 K, is much higher than our previous ZT values obtained by using nanostructured YSZ addition ($ZT = 0.21$ at 900 K)⁸⁾ and MS addition ($ZT = 0.165$ at 900 K).⁹⁾ It strongly suggests that KTO addition is more effective than YSZ or MS additions to enhance the thermoelectric properties of Nb-STO.

Figure 4 shows the XRD pattern of KTO/Nb-STO composites. In the composites with KTO content of 1 wt %, 3 wt % and 5 wt %, KTO content was very low, thus only diffraction peaks from STO could be detected. To verify whether KTO reacted

Fig. 4. XRD patterns of KTO/Nb-STO composites.

with STO at high temperatures, we increased the KTO content to 30 wt % (50 vol %) (Fig. 4(e)), and a new phase, $K_3Ti_8O_{17}$ was formed, strongly suggesting that $K_3Ti_8O_{17}$ was also formed from starting $K_2Ti_6O_{13}$ in the composites with low KTO content even though it was not detected in the XRD patterns.

Figure 5 shows scanning electron micrographs (SEM) of KTO/Nb-STO composites. It was found that KTO addition promoted the grain growth of Nb-STO markedly. Energy dispersive X-ray (EDX) analysis (Fig. 5(e)) of the sample with 3 wt % KTO addition (Fig. 5(d)) indicated that the titanium content in the grain boundary was much higher than that in the grain, which revealed that KTO addition could be mainly distributed in the grain boundary regions. As with SrTiO₃ ceramic, generally, when the sintering temperature was higher than 1250°C, the volume diffusion is the main sintering mechanism.¹²⁾ Nb-STO composite with KTO addition ($K_2Ti_6O_{13}$) was Ti-rich than SrTiO₃, and Ti excess may create cation vacancies and therefore promoted volume diffusion. It is also speculated that KTO addition and second phase formation may have changed the major sintering mechanism. For example, liquid phase sintering may have enhanced both densification and grain growth. However, sintering mechanism is still unclear and should be subject to the future investigation.

Grain growth of Nb-STO reduced interface scattering of the electrons, enhanced carrier mobility,^{8),13)} and hence increased the

electrical conductivity. KTO with much lower thermal conductivity than STO,¹⁴⁾ located in grain boundaries can scatter phonons more effectively, which might be the main reason for the reduced thermal conductivity of Nb-STO ceramic.

It seems to be peculiar at first sight that Seebeck coefficient did not change very much by KTO addition (Fig. 1(b)) while electrical conductivity and thermal conductivity were significantly affected. It was already reported that heavily Nb-doped STO (more than 10% Nb doping) is a degenerate semiconductor^{15),16)} and the Seebeck coefficient (S) can be expressed, in general, by the following equation:¹⁷⁾

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}, \quad (2)$$

where k_B , h , m^* , and n are Boltzmann constant, Planck constant, the effective mass of the carriers, and the carrier concentration, respectively. Equation (2) indicates the Seebeck coefficient strongly depends on the carrier concentration. For the case of our composite samples, though the added KTO was transformed from $K_2Ti_6O_{13}$ to $K_3Ti_8O_{17}$, and formed the second phase. However, KTO didn't react with Nb-STO, and hence the carrier concentration would not have been affected significantly,⁹⁾ which was the main reason for the independence of the Seebeck coefficient of KTO addition.

4. Conclusions

Addition of potassium titanate (KTO) nanowires enhanced the ZT value of Nb-STO ceramics significantly, and the sample with KTO addition (3 wt %) gave the maximum ZT of 0.34 at 900K. As for the improvement in the thermoelectric properties of Nb-STO, KTO addition was more effective than YSZ and MS additions. Obviously reduced thermal conductivity and increased electrical conductivity contributed to the enhancement in ZT value. Enhancement of the electrical conductivity was mainly caused by promoted grain growth. Reduction of the thermal conductivity was mainly due to the enhanced phonon scattering at grain boundaries. Seebeck coefficient was almost independent of KTO addition, which could be mainly because KTO addition didn't affect the carrier concentration.

Acknowledgment This work was financially supported by Japan Science and Technology Agency (CREST project), International Cooperation MOST-JST Program Fund (No. 2010DFA61410), Western Light Project of Chinese Academy of Sciences (No. LHXZ200902), National Natural Science Foundation of China (No. 50802013), One of the authors (N.W.) was supported by a Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists.

Fig. 5. SEM micrographs of KTO/Nb-STO composites with various KTO contents: (a) 0 wt %; (b) 1 wt %; (c) 5 wt %; (d) 3 wt %; (e) EDX spectra obtained from (d), the grain interior (i) and the grain boundary region (ii).

References

- 1) M. S. Dresselhaus, G. Chen, M. Y. Tang, R. Yang, H. Lee, D. Wang, Z. Ren, J. P. Fleurial and P. Gogna, *Adv. Mater.*, **19**, 1043–1053 (2007).
- 2) S. N. Zhang, T. J. Zhu, S. H. Yang, C. Yu and X. B. Zhao, *J. Alloys Compd.*, **499**, 215–220 (2010).
- 3) K. Ahn, M. K. Han, J. He, J. Androulakis, S. Ballikaya, C. Uher, V. P. Dravid and M. G. Kanatzidis, *J. Am. Chem. Soc.*, **132**, 5227–5235 (2010).
- 4) S. Fan, J. Zhao, J. Guo, Q. Yan, J. Ma and H. H. Hng, *Appl. Phys. Lett.*, **96**, 182104 (2010).
- 5) Y. Lan, B. Poudel, Y. Ma, D. Wang, M. S. Dresselhaus, G. Chen and Z. Ren, *Nano Lett.*, **9**, 1419–1422 (2009).
- 6) K. Fujita, T. Mochida and K. Nakamura, *Jpn. J. Appl. Phys.*, **40**, 4644–4647 (2001).
- 7) S. Ohta, H. Ohta and K. Koumoto, *J. Ceram. Soc. Japan*, **114**, 102–105 (2006).
- 8) N. Wang, L. Han, Y. Ba, Y. Wang, C. Wan, K. Fujinami and K. Koumoto, *J. Electron. Mater.*, **39**, 1777–1781 (2010).
- 9) N. Wang, L. Han, H. He, Y. Ba and K. Koumoto, *J. Alloys Compd.*, **497**, 308–311 (2010).
- 10) X. Meng, D. Wang, J. Liu, B. Lin and Z. Fu, *Solid State Commun.*, **137**, 146–149 (2006).
- 11) P. G. Klemens, *High Temp. - High Pressures*, **45**, 574–588 (1973).
- 12) M. Bäurer, H. Kung and M. J. Hoffmann, *J. Am. Ceram. Soc.*, **92**, 601–606 (2009).
- 13) P. P. Shang, B. P. Zhang, J. F. Li and N. Ma, *Solid State Sci.*, **12**, 1341–1346 (2010).
- 14) H. C. Gullledge, *Ind. Eng. Chem.*, **52**, 117–118 (1960).
- 15) S. Ohta, T. Nomura, H. Ohta and K. Koumoto, *J. Appl. Phys.*, **97**, 034106 (2005).
- 16) S. Ohta, T. Nomura, H. Ohta, M. Hirano, H. Hosono and K. Koumoto, *Appl. Phys. Lett.*, **87**, 092108 (2005).
- 17) M. Cutler, J. F. Leavy and R. L. Fitzpatrick, *Phys. Rev.*, **133**, A1143–A1152 (1964).