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Thermoelectric characterization of $Na_xM_{x/2}Ti_{1-x/2}O_2$ (M = Co, Ni and Fe) polycrystalline materials

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Abstract

Layered α-titanate materials, $Na_xM_{x/2}Ti_{1-x/2}O_2$ (M = Co, Ni and Fe, $x = 0.2$–0.4), were synthesized by flux reactions, and electrical properties of polycrystalline products were measured at 300–800 °C. After sintering at 1250 °C in Ar, all products show n-type thermoelectric behavior. The values of both d.c. conductivity and Seebeck coefficient of polycrystalline $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ were ca. 7×10^3 S/m and ca. −193 μV/K around 700 °C, respectively. The measured thermal conductivity of layered α-titanate materials has lower value than conductive oxide materials. It was ca. 1.5 Wm^{-1} K^{-1} at 800 °C. The estimated thermoelectric figure-of-merit, Z, of $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ and $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ was about 1.9×10^{-4} and 1.2×10^{-4} K^{-1} around 700 °C, respectively. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Thermoelectric properties; $Na_xM_x/2Ti_{1-x/2}$; Polycrystalline material

1. Introduction

Thermoelectric oxide materials are attractive for the thermoelectric power generation using waste heat energy at high temperature operation. Conventional thermoelectric materials including PbTe, SiGe and alloy and non-oxide semiconductors have some inevitable shortcomings under high temperature conditions. Recently, both high electrical power factor and low thermal conductivity have been investigated in the layer-structural oxide materials such as $NaCo_2O_4$ and $Ca_3Co_4O_9$ being p-type high performance thermoelectric materials [1–4]. On the other hand, development of n-type thermoelectric oxide materials is strongly expecting for fabrication of oxide thermoelectric elements because almost n-type thermoelectric oxide materials are known as low thermoelectric power as comparison with p-type materials.

α-Titanate ($Na_xM_{x/2}Ti_{1-x/2}O_2$, M = Co, Ni and Fe) is well-known as same layered crystal structure such as $NaCo_2O_4$ (Rhombohedral α-$NaFeO_2$-type structure, R3m), which is edge-shared TiO_6-octahedral structure [5,6] (see Fig. 1).

These layered materials are expected to have simultaneous control of both electrical and thermal properties such as layered cobalt oxide materials [2–4]. For the purpose of developing of new n-type thermoelectric materials, we have prepared n-type layered titanate materials, $Na_xM_{x/2}Ti_{1-x/2}O_2$ (M = Co, Ni and Fe, $x = 0.2$–0.8), and have characterized the thermoelectric properties of polycrystalline products under high temperature conditions.

2. Experimental procedure

Layered α-titante, $Na_xM_{x/2}Ti_{1-x/2}O_2$ (M = Fe, Ni, Co, $x = 0.2$–0.4), was prepared by flux reactions using Fe_3O_4, NiO, Co_3O_4, Na_2CO_3 and TiO_2 (anatase 99.99%) at 1100–1300 °C for 12 h in air, and then sintered at 1250 °C for 6 h in Ar [6]. The resulted phases were identified by X-ray diffraction analysis using Cu-K_α radiation and graphite monochrometer (Rigaku Co. Japan). d.c. Conductivity and Seebeck coefficient were measured simultaneously by 4-probe method using a thermoelectric analyzer, ZEM-1 (ULVAC Co., Japan). Thermal conductivity of polycrystalline samples was measured by laser flash method using TC-7000 (ULVAC Co., Japan) at ~800 °C under vacuum conditions.

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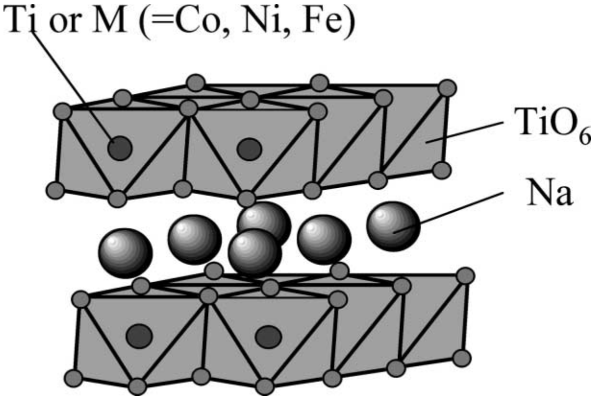

Fig. 1. Scheme of crystal structure of α-titanate, $Na_xM_{x/2}Ti_{1-x/2}O_2$ (R3m).

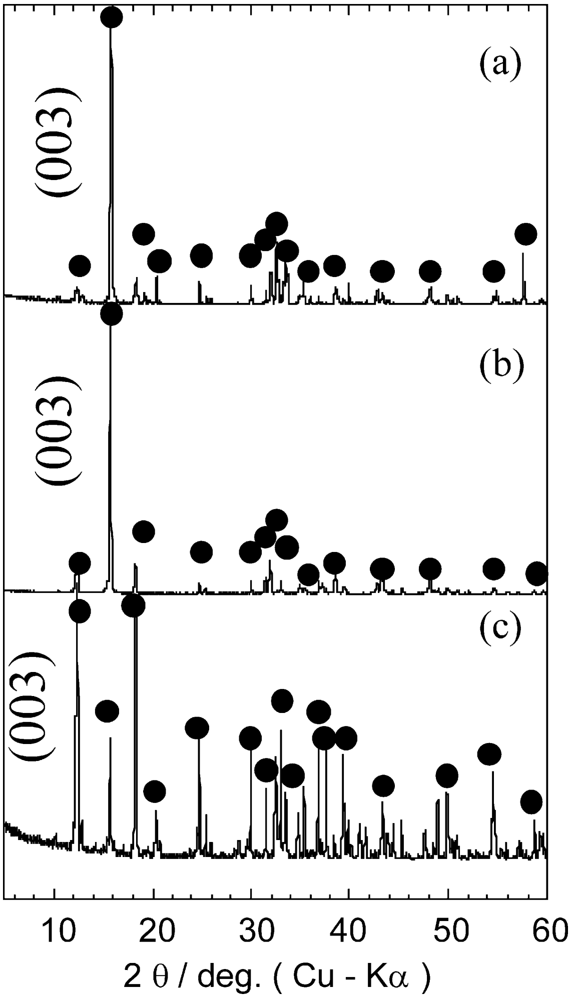

Fig. 2. XRD patterns of α-titanate products, (a) $Na_{0.4}Co_{0.2}Ti_{10.8}O_2$, (b) $Na_{0.4}Ni_{0.2}Ti_{10.8}O_2$, and (c) $Na_{0.4}Fe_{0.2}Ti_{10.8}O_2$ prepared at 1250 °C for 12 h in air.

3. Results and discussion

XRD patterns of the products of $Na_{0.4}M_{0.2}Ti_{0.8}O_2$ (M = Co, Ni and Fe) prepared at 1250 °C in Ar, and the sintered $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ are shown in Figs. 2 and 3.

Single phase α-$NaFeO_3$-type titanate of $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ and $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ forms at 1250 °C in Ar [6]. However, some impurity phases were observed in $Na_{0.4}Fe_{0.2}Ti_{0.8}O_2$ products. Strong peak of XRD at low angle ~16° indicate a formation of the layered crystal materials. The [003] peak intensity in Miller index increased after sintering at 1250 °C in Ar. Same products of layer-type titanate, $Na_xM_{x/2}Ti_{1-x/2}O_2$ were observed at $x = 0.2$–0.4 at 1250 °C for 12 h.

Microstructures of the prepared polycrystalline $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ are shown in Fig. 4. Some pores and plate-like crystal grains of $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ were observed in the products after sintering at 1250 °C in air. When the green body of the prepared α-titanate particles was sintered at <1200 °C in Ar, DC conductivity of polycrystalline α-titanate decreased. The relative density of bulk products is ca. 70%. It was calculated using theoretical density ~2.083 g/cm^3.

Thermal stability of $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ was checked by TG–DTA, and the exothermic peak corresponding to melting of products was observed around 1280 °C. The melting point of the prepared products decreased with the increasing Na contents. When $Na_{0.8}Co_{0.4}Ti_{0.6}O_2$ was annealed at 1250 °C, melting product formed.

d.c. Conductivity, σ, of polycrystalline $Na_{0.4}M_{0.2}Ti_{0.8}O_2$ (M = Co, Ni and Fe) is shown in Fig. 5. The value of DC conductivity of polycrystalline $Na_{0.4}M_{0.2}Ti_{0.8}O_2$ (M = Co, Ni and Fe) increased with increasing temperature, showing a semiconductor behavior. d.c. Conductivity of the prepared polycrystalline α-titanate changed in order $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2 > Na_{0.4}Co_{0.2}Ti_{0.8}O_2 > Na_{0.4}Fe_{0.2}Ti_{0.8}O_2$. The value of d.c. conductivity of $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ and $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ at 700 °C was ca. 7×10^3 and 4×10^3 Sm, respectively. d.c. conductivity of polycrystalline products decreased with x decreasing in $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$. After annealing in air, the prepared products showed an electroconduction in the measured temperature range.

The values of the Seebeck coefficient, S, of the prepared polycrystalline $Na_{0.4}M_{0.2}Ti_{0.8}O_2$ (M = Co, Ni and Fe) are shown in Fig. 6. The Seebeck coefficient showed a negative value, indicating n-type behavior. The values of the Seebeck coefficient of $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ and $Na_{0.4}Fe_{0.2}Ti_{0.8}O_2$ were large. They were ca. −190 μV/K at 700 °C.

The values of the Seebeck coefficient and the calculated thermoelectric power factor, $S^2\,\sigma$, of the prepared α-titanate are shown in Table 1. The values of the Seebeck coefficient and $S^2\,\sigma$ of $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ were higher than appropriate values of the another products. The calculated $S^2\,\sigma$ of $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$, $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$, and $Na_{0.4}\,Fe_{0.2}Ti_{0.8}O_2$ at 780 °C are 2.5×10^{-4}, 1.4×10^{-4}, and 1.4×10^{-4} Wm^{-1} K^{-2}, respectively.

For consideration of the conductive mechanism of the prepared α-titanate, XPS spectra of $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ and TiO_2 (anatase) have been measured as shown in

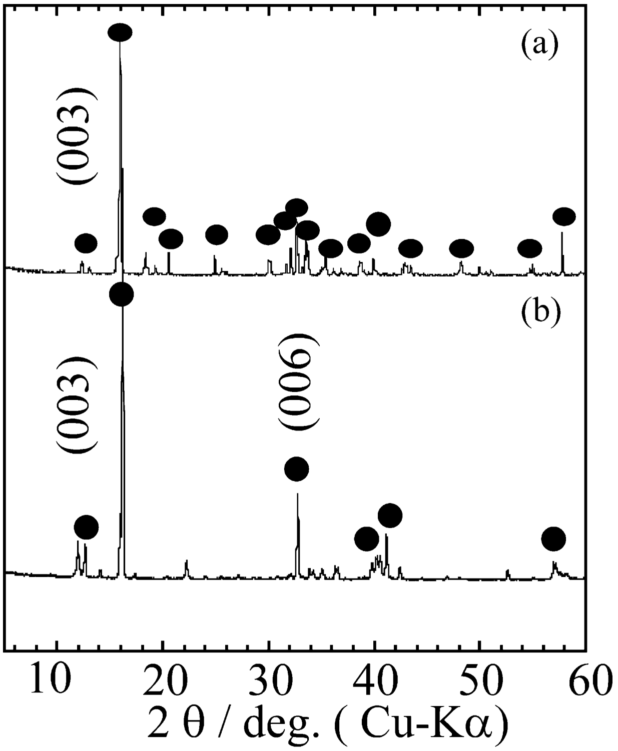

Fig. 3. XRD patterns of (a) particle of $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ prepared at 1250 °C for 12 h in air, and (b) the sintered products at 1250 °C for 6 h in Ar.

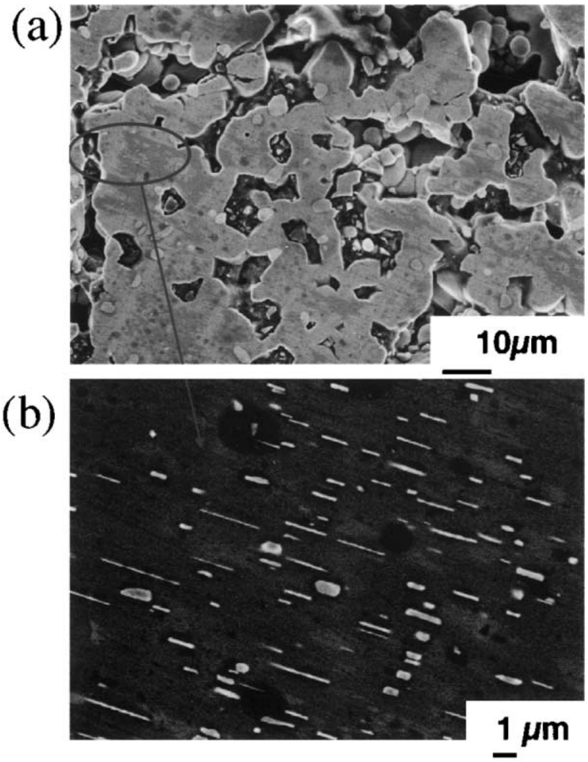

Fig. 4. Microphotographs of polycrystalline $Na_{0.4}Co_{0.2}Ti_{10.8}O_2$ prepared at 1250 °C for 6 h in Ar.

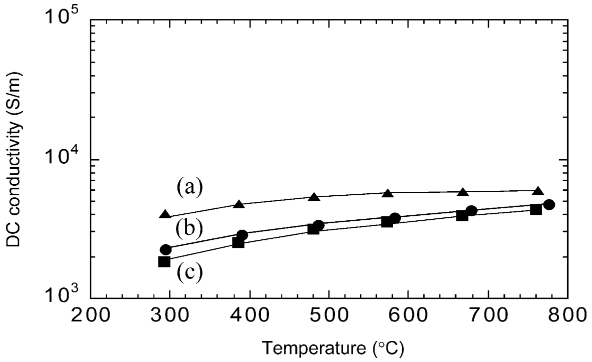

Fig. 5. Temperature dependence of d.c. conductivity, σ, of polycrystalline (a) $Na_{0.4}Ni_{0.2}Ti_{10.8}O_2$, (b) $Na_{0.4}Co_{0.2}Ti_{10.8}O_2$, and (c) $Na_{0.4}Fe_{0.2}Ti_{10.8}O_2$.

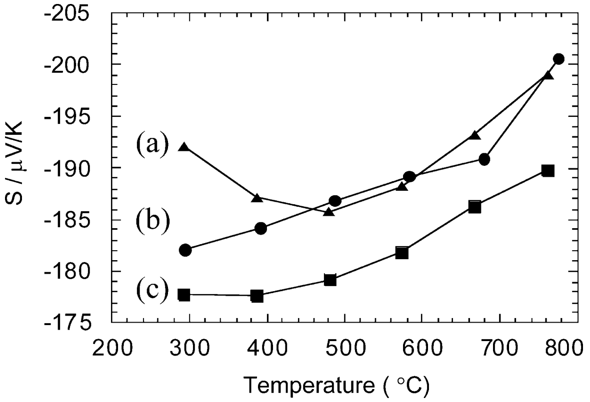

Fig. 6. Temperature dependence of the Seebeck coefficient, S, of (a) $Na_{0.4}Ni_{0.2}Ti_{10.8}O_2$, (b) $Na_{0.4}Fe_{0.2}Ti_{10.8}O_2$,and (c) $Na_{0.4}Co_{0.2}Ti_{10.8}O_2$.

Table 1
Thermoelectric properties of polycrystalline α-titanate materials at 700 °C

Products	S(μV/K)	S^2 (Wm^{-1} K^{-2})	(Wm^{-1} K^{-1})
$Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$	−193	2.5×10^{-4}	1.3
$Na_{0.4}Co_{0.2}Ti_{0.8}O_2$	−185	1.4×10^{-4}	1.2
$Na_{0.4}Fe_{0.2}Ti_{0.8}O_2$	−191	1.4×10^{-4}	1.2

Fig. 7. Besides the contributions from Ti^{4+} species, shoulders were observed on the lower binding energy side of Ti $2p_{1/2}$ and Ti $2P_{3/2}$ peaks in $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$. The shoulders may be attributed to formation of Ti^{3+} [7]. The results suggest that part of Ti sites are reduced to Ti^{3+} by sintering at 1250 °C in Ar.

This reduction of titanium site may contribute to electron carrier as n-type semiconducting behavior. The Co $2P_{3/2}$ spectrum of $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ showed a main peak at 780.1 eV accompanied by a weak satellite peak at ca. 788 eV. The satellite peak indicates the presence of low spin Co^{3+} in the products [8]. The electrical conduction of the prepared α-titanate may be contribute

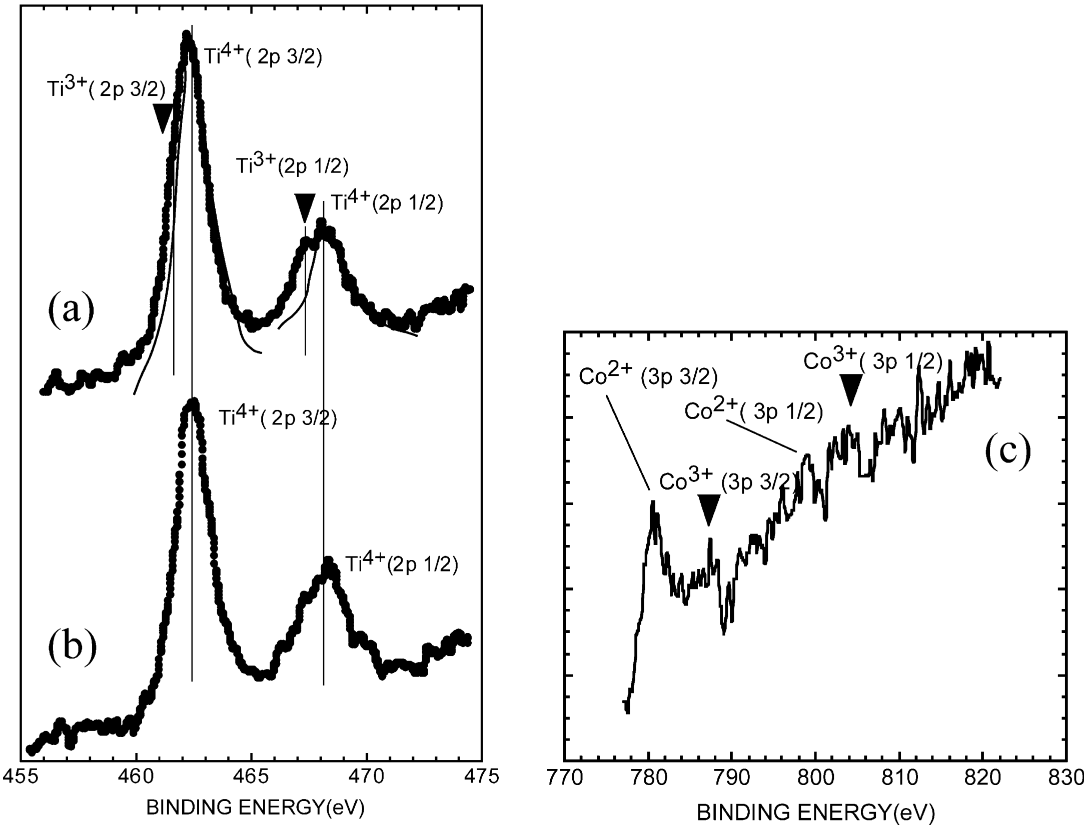

Fig. 7. XPS spectra of (a) $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ and (b) TiO_2 (anatase).

to reduction of Ti^{4+} site and formation of Co^{3+} site in the TiO_6 octahedral layer according to Eq. (1)

$$\mathrm{Co}_{\mathrm{Co}}^{x}(\mathrm{II}) + \mathrm{Ti}_{\mathrm{Ti}}^{X}(\mathrm{IV}) \rightarrow \mathrm{Co}_{\mathrm{Co}}{}^{\bullet}(\mathrm{III}) + \mathrm{Ti}_{\mathrm{Ti}}{}'(\mathrm{II}) + 1/2\ \mathrm{V}_{\mathrm{Co}}{}'' + 1/2\mathrm{V}_{\mathrm{O}}{}^{\bullet\bullet} \quad (1)$$

Thermal conductivity of polycrystalline $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ and $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ is shown in Fig. 8. The values of thermal conductivity of $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ and $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ at 700 °C were ca. 1.3 and 1.2 Wm^{-1} K^{-1}, respectively. The prepared α-titanate showed low thermal conductivity as compared with other n-type thermoelectric materials such as Al-doped ZnO etc. [9,10]. Thermal conductivity of semiconductor materials depends on the morphology and crystal structures of products. One reason of low thermal conductivity for the prepared layered α-titanate may be attributed to lower density of products as shown in Fig. 4. Another effect on thermal properties may be related to low dimensional structure of α-titanate, i.e. incorporating

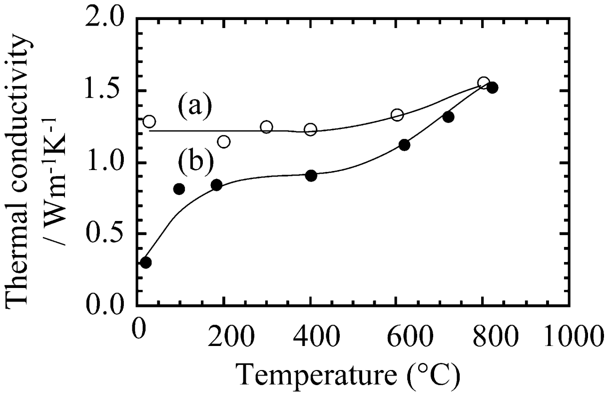

Fig. 8. Temperature dependence of thermal conductivity, κ, of polycrystalline (a) $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$, and (b) $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$.

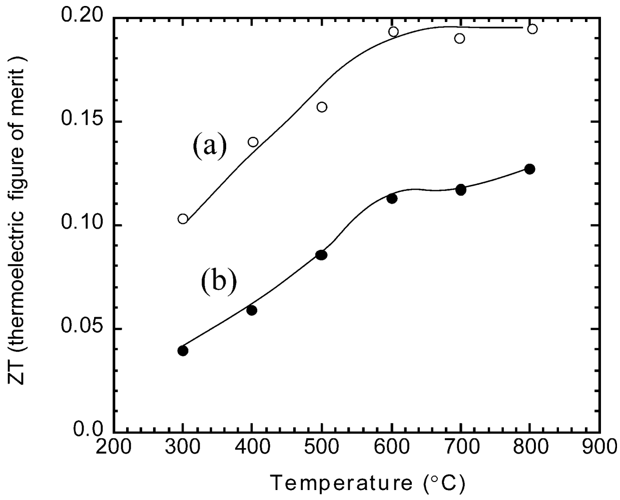

Fig. 9. Temperature dependence of figure-of-merit, ZT, of polycrystalline (a) $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$, and (b) $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$.

sodium ion between interlayers. Structural effect may be contributed to one phonon scattering factor at the interface of two electroconducting (Ti^{4+}, Ti^{3+})O_6 octahedral layers as reported for p-type layer-type oxide materials in [11].

The estimated thermoelectric figure-of-merit, ZT of polycrystalline $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ and $Na_{0.4}Co_{0.2}Ti_{0.8}O_2$ is shown in Fig. 9. The calculated ZT of polycrystalline α-titanate was increased with increasing temperature in the measured temperature range. The value of ZT of $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ is ca. 0.19 at 600–800 °C. The ZT of $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ is higher than that of β-SiC, but lower than that of 2 mol% Al-doped ZnO as n-type oxide materials [10].

4. Conclusions

We have synthesized a new series of n-type oxide ceramics, $Na_{0.4}M_{0.2}Ti_{0.8}O_2$ (M = Co, Ni and Fe) with α-$NaFeO_3$ structure. Polycrsyalline $Na_{0.4}Ni_{0.2}Ti_{0.8}O_2$ reveals not only reasonable value of both d.c. conductivity and the Seebeck coefficient, but also has low thermal conductivity as n-type oxide materials. The calculated ZT is about 0.19 at 600–800 °C.

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