Paper

Preparation of Perovskite-Type $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ Ceramics by an Oxalate Coprecipitation Method and the Thermoelectric PropertiesMasahiro Yasukawa^{☆1} and Toshio Kono^{☆2}^{☆1}Department of Materials Science and Engineering, Kochi National College of Technology, 200-1 Monobe, Nankoku 783-8508, Japan.^{☆2}Kochi Prefectural Industrial Technology Center, 3992-3 Nunoshida, Kochi 781-5101, Japan.

Received January 28, 2008

SYNOPSIS

An oxalate coprecipitation method was applied to prepare dense ceramics of perovskite-type $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ solid solutions with $x = 0.0 \sim 0.5$, and the electrical conductivity and Seebeck coefficient were measured at high temperatures to estimate the thermoelectric power factors. Sr–Ba–Pb oxalates were coprecipitated from starting nitrate solutions with molar ratios of metallic ions controlled to $\text{Pb}/\text{Sr}_{1-x}\text{Ba}_x = 1.05$ and calcined at 700°C to obtain fine oxide powders. The small amount of PbO particles, which were dispersed well in the calcined powders composed mainly of SrPbO_3 and BaPbO_3 , formed liquid phase during the sintering and led to the formation of the dense $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics. The thermoelectric power factors of the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics with $x = 0.0 \sim 0.5$ were estimated to be $1.0 \times 10^{-4} \sim 3.6 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ in the temperature range $373 \sim 1073 \text{ K}$ and the value was maximized for the $\text{Sr}_{0.7}\text{Ba}_{0.3}\text{PbO}_3$ ceramic. This study suggests that the present oxalate coprecipitation method is a simple and useful way to prepare dense $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics showing comparatively high thermoelectric power factors.

KEY WORDS

Ceramics, perovskites, coprecipitation, sintering, thermoelectric properties

1 Introduction

Thermoelectric energy conversion is an important technology for effective utilization of waste heat, and development of thermoelectric materials showing high efficiency of energy conversion is essential for the technology. Oxide ceramics are promising as thermoelectric materials used at high temperatures in air because of their high stability under the conditions, and exploration of thermoelectric oxide ceramics has been a key issue for the last decade^{1–4}. Thermoelectric figure of merit Z of a material is expressed by the equation $Z = S^2 \sigma \kappa^{-1}$, where S , σ , κ are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively, and the dimensionless figure of merit exhibiting $ZT \geq 1$ is the criterion for the practical use of the material, where T is the absolute temperature. The $S^2 \sigma$ is the thermoelectric power factor by which the thermoelectric performance of the material can be roughly estimated.

Perovskite-type $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ($x = 0 \sim 1$) solid solutions were reported to be n -type potential thermoelectric oxides at high temperatures for non-civil applications^{5,6}. Since these oxides had low sinterability due to volatilization of lead oxide component in preparation of the ceramics at

ambient pressure by a solid-state reaction method, a press-sintering method was used to prepare dense $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics. The Z and $S^2 \sigma$ values were estimated to be $2 \times 10^{-4} \text{ K}^{-1}$ at 673 K and $4 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ at 773 K for the $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$ ceramic, respectively^{5,6}. On the other hand, coprecipitation method in aqueous solutions is generally known to be an effective technique to prepare dense oxide ceramics, when the size and composition of the calcined particles are controlled. Kodama *et al.*⁷ prepared dense BaPbO_3 ceramics by an oxalate coprecipitation method. The Ba–Pb oxalate was coprecipitated in the starting nitrate solution with a molar ratio of $\text{Pb}/\text{Ba} = 1.0$. The densification of the ceramics was accomplished by control of the temperature and duration for the sintering of the calcined powders. We reported a modified oxalate coprecipitation method to prepare dense BaPbO_3 ceramics, in which the Pb/Ba molar ratio in the starting solution was controlled to a slight excess of Pb content⁸. The dense ceramics were prepared by liquid phase sintering of the fine particles composed of BaPbO_3 and a small amount of PbO , which were formed by the calcination of the coprecipitated Ba–Pb oxalate. Nagamoto *et al.*⁹ previously prepared $\text{Ba}_{1-x}\text{Sr}_x\text{Pb}_{1+y}\text{O}_{3-\delta}$ ceramics by the similar coprecipitation

method to elucidate the effect of excess Pb content on the positive temperature coefficient of resistivity (PTCR) effect of the ceramics, but the effect on the densification was not addressed.

In this study, the oxalate coprecipitation method was applied to prepare dense $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ($x = 0.0 \sim 0.5$) ceramics and the effect of excess Pb content on the densification of the ceramics was examined. The thermoelectric power factors were also estimated from the electrical conductivity and Seebeck coefficient measured at high temperatures.

2 Experimental

Sr–Ba–Pb oxalates were coprecipitated in aqueous solutions made from $\text{Sr}(\text{NO}_3)_2$ ($\geq 98\%$), $\text{Ba}(\text{NO}_3)_2$ ($\geq 99\%$), and $\text{Pb}(\text{NO}_3)_2$ ($\geq 99.5\%$) (Kishida Chemical Co., Ltd, Japan). The reagents were weighed with molar ratio of $\text{Sr}/\text{Ba}/\text{Pb} = 1 - x/x/1.05$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$), and dissolved in deionized water. The concentration of Pb ions was fixed to 0.105 mol L^{-1} . An excess of ammonium oxalate solution was added to the solution, and a white precipitate of Sr–Ba–Pb oxalate was formed. The pH of the solution was then adjusted to 8.0 with aqueous ammonia to complete the coprecipitation. The coprecipitate was filtered and dried at 80°C in air. The dried powder is hereafter called the precursor. The precursor was calcined at 700°C for 6 h in air flow with intermittent grinding to form fine oxide powder. The calcined powder was ground and molded into a cylinder with 5 mm in diameter and ~ 10 mm in height, followed by pressing at a pressure of 200 MPa using cold isostatic press and sintering at $850 \sim 900^\circ\text{C}$ for 3 h in air flow.

Thermogravimetry (TG) and differential thermal analysis (DTA) of the Sr–Ba–Pb oxalates were performed at a heating rate of $10^\circ\text{C min}^{-1}$ in the temperature range $50 \sim 1000^\circ\text{C}$ with air flow. X-ray powder diffraction (XRD) patterns were measured with $\text{CuK}\alpha$ radiation to identify the phases and determine the lattice parameters using Ge as an internal standard. Relative density of the ceramics was estimated as a percentage ratio of the bulk density to the theoretical one; the former was estimated from the mass and volume of the ceramics and the latter from the lattice parameters assuming the stoichiometric composition of $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$. Microstructures were observed by scanning electron microscopy (SEM). Molar ratio of Sr/Ba/Pb in the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics was analyzed by inductively coupled plasma emission spectroscopy (ICP) using aqueous solutions in nitric acid with added hydrogen peroxide. Electrical conductivity and Seebeck coefficient were

measured at temperatures $373 \sim 1073 \text{ K}$ in air. The former was measured by a direct current four-probe method. The latter was evaluated by correcting the linear gradient of $\Delta V/\Delta T$ for the thermopower of platinum¹⁰, where ΔV and ΔT are the thermoelectromotive force and temperature difference between two ends of the sample measured with Pt wires and Pt/Pt–Rh thermocouples, respectively.

3 Results and discussion

3.1 Thermal decomposition of Sr–Ba–Pb oxalates and formation of $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ solid solutions

The XRD patterns for the precursors with $x = 0.0 \sim 0.5$ showed that each one was not a single phase but a mixture composed of complicated oxalate hydrates. Despite the mixed oxalate hydrates, the thermal decomposition behaviors of the precursors were mainly classified into three steps from the TG-DTA curves. Fig. 1 shows TG-DTA curves of the precursor with $x = 0.5$, and the thermal decomposition behavior is summarized in Table 1. Here, an assumed chemical formula, $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Pb}_{1.05}(\text{C}_2\text{O}_4)_{2.05} \cdot n\text{H}_2\text{O}$, is used as the precursor for the main expression of the thermal decompositions. The first step showing a weight loss of 6.40% with endothermic peaks in the temperature range $115 \sim 200^\circ\text{C}$ is attributed to dehydration of the oxalate hydrates. The n value was estimated to be 1.94 from the weight loss in the temperature range. The second step showing a weight loss of 20.4% with exothermic peaks in the temperature range $330 \sim 460^\circ\text{C}$ is due to decomposition of the anhydrous oxalates to SrCO_3 , BaCO_3 , and PbO . The third step showing a weight loss of

Fig. 1 TG-DTA curves of a coprecipitated oxalate sample with $x = 0.5$. The sample was heated at a rate of $10^\circ\text{C min}^{-1}$ in air flow. $\alpha\text{-Al}_2\text{O}_3$ powder was used as a reference material.

Table 1 Thermal decomposition of oxalate sample with $x=0.5$ and formation of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{PbO}_3$ solid solution.

Temperature (°C)	Δw (%)		ΔT	Reaction
	Experimental	Theoretical		
115 – 200	6.40	–	endo.	$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Pb}_{1.05}(\text{C}_2\text{O}_4)_{2.05} \cdot n\text{H}_2\text{O}$ $\rightarrow \text{Sr}_{0.5}\text{Ba}_{0.5}\text{Pb}_{1.05}(\text{C}_2\text{O}_4)_{2.05} + n\text{H}_2\text{O}$
330 – 460	20.4	20.3	exo.	$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Pb}_{1.05}(\text{C}_2\text{O}_4)_{2.05}$ $\rightarrow 0.5\text{SrCO}_3 + 0.5\text{BaCO}_3 + 1.05\text{PbO} + 1.05\text{CO}_2 + 2.05\text{CO}$
570 – 800	7.01	6.88	endo.	$0.5\text{SrCO}_3 + 0.5\text{BaCO}_3 + 1.05\text{PbO}$ $\rightarrow 0.5\text{SrPbO}_3 + 0.5\text{BaPbO}_3 + 0.05\text{PbO} + \text{CO}$
800 – 950	–	0.00	endo.	$0.5\text{SrPbO}_3 + 0.5\text{BaPbO}_3 + 0.05\text{PbO}$ $\rightarrow \text{Sr}_{0.5}\text{Ba}_{0.5}\text{PbO}_3 + 0.05\text{PbO}$

Fig.2 X-ray powder diffraction patterns for the samples after heating the precursor with $x=0.5$ at several temperatures. The marks indicate the following compounds; ▽ : PbO (massicot), ● : BaPbO₃, □ : SrPbO₃, ⊙ : Sr_{0.5}Ba_{0.5}PbO₃.

7.01% with an endothermic deviation in the temperature range 570~800 °C is due to formation of perovskite-type oxides of SrPbO₃ and BaPbO₃ releasing CO gas. The following endothermic deviation in the temperature range 800 ~ 950 °C is probably due to formation of a solid solution Sr_{0.5}Ba_{0.5}PbO₃. Fig. 2 shows XRD patterns for the samples after heating the precursor with $x=0.5$ at several temperatures for 1 h in air flow. The samples heated

at 800~830 °C were composed of two perovskite phases, SrPbO₃ and BaPbO₃, while those heated at the temperatures ≥ 840 °C became the solid solution Sr_{0.5}Ba_{0.5}PbO₃.

3.2 Preparation of perovskite-type Sr_{1-x}Ba_xPbO₃ ceramics

The samples calcined at 700 °C were found to be mixed fine particles composed of SrPbO₃, BaPbO₃, and a small amount of PbO (massicot), as the XRD result for $x=0.5$ is shown in Fig. 2. The particle size was almost 0.1 ~ 0.3 μm from the SEM observations. The calcined powders were sintered at 850 °C for $x=0.0$ and 0.1 and at 900 °C for $x=0.2, 0.3, 0.4, 0.5$. The lower sintering temperature for the Sr-rich samples suppressed the formation of a secondary phase Sr₂PbO₄, which was caused by volatilization of lead oxide. All the molded cylinders with $x=0.0\sim 0.5$ shrank after the sintering and the dense ceramics were obtained. Fig. 3 shows XRD patterns for the Sr_{1-x}Ba_xPbO₃ ceramics. All the patterns were indexed with an orthorhombic SrPbO₃-type structure¹¹⁾, indicating the formation of the perovskite-type single phase. The molar ratio of Sr/Ba/Pb analyzed by ICP, cell lengths a, b, c , cell volume V , and relative density for the ceramics are listed in Table 2. The analyzed molar ratio of Sr/Ba/Pb was relatively close to the nominal one for all the ceramics, showing excess Pb content of Pb/Sr_{1-x}Ba_x > 1.00. The Ba content dependence of the lattice parameters a, b, c , and V is shown in Fig. 4. The lattice parameters increased with increasing Ba content, indicating the formation of the Sr_{1-x}Ba_xPbO₃ solid solutions. The crystal lattice of the Sr_{1-x}Ba_xPbO₃ with $x=0.3\sim 0.5$ can be regarded as a pseudo-cubic cell satisfying the relation $\sqrt{2}a \cong b \cong \sqrt{2}c$. The relative density of the ceramics was estimated to be 88~93%, the values being comparable to those for the ceramics prepared by the press-sintering

Fig.3 X-ray powder diffraction patterns for the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics with $x = 0.0 \sim 0.5$. The arrows indicate the diffraction peaks of Ge as an internal standard.

method⁶⁾. Fig. 5 shows SEM images for the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics of which the surfaces were polished and thermally etched. All the images exhibited well-densified structures consisting of grains with several microns in size.

The effect of slight excess of Pb content on the densification of the ceramics is described. Fig. 6 shows firing temperature dependence of the bulk density and diameter at room temperature for the cylindrical ceramics with the nominal molar ratios of $\text{Pb}/\text{Sr}_{0.5}\text{Ba}_{0.5} = 1.00$ and 1.05. The firing of the molded cylinders was performed

Fig.4 Ba content dependence of the orthorhombic cell lengths a , b , c , and cell volume V for the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$. The crystal lattice for $x = 0.3 \sim 0.5$ can be regarded as a pseudo-cubic cell with $\sqrt{2}a \equiv b \equiv \sqrt{2}c$.

in the temperature range $800 \sim 900^\circ\text{C}$ for 3 h in air flow. It was found that the samples with $\text{Pb}/\text{Sr}_{0.5}\text{Ba}_{0.5} = 1.00$ were not densified at the firing temperatures up to 900°C , while those with $\text{Pb}/\text{Sr}_{0.5}\text{Ba}_{0.5} = 1.05$ were well densified at the temperatures $\geq 840^\circ\text{C}$ along with the drastic shrinkage of the volume, the relative density being beyond 93% of the theoretical density for the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{PbO}_3$ solid solution. It should be noted that the critical temperature ($\sim 840^\circ\text{C}$) of the densification agreed with the formation temperature of the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{PbO}_3$ solid solution in the case of $\text{Pb}/\text{Sr}_{0.5}\text{Ba}_{0.5} = 1.05$. On the contrary, two perovskite phases

Table 2 Molar ratio, lattice parameters, and relative density for $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics.

Nominal molar ratio			Analyzed molar ratio*			Lattice parameters (orthorhombic)				Relative density / %
Sr	Ba	Pb	Sr	Ba	Pb	a / nm	b / nm	c / nm	V / nm ³	
1.00	0.00	1.05	1.00	0.00	1.04	0.59603(3)	0.83305(7)	0.58614(4)	0.29103(3)	89
0.90	0.10	1.05	0.89	0.11	1.02	0.59626(8)	0.8352(1)	0.58871(9)	0.29317(6)	88
0.80	0.20	1.05	0.79	0.21	1.04	0.5957(2)	0.8381(3)	0.5921(2)	0.2956(1)	89
0.70	0.30	1.05	0.72	0.28	1.02	0.5952(2)	0.8415(2)	0.5947(2)	0.2979(1)	93
0.60	0.40	1.05	0.58	0.42	1.03	0.5963(1)	0.8429(2)	0.5960(1)	0.29959(8)	91
0.50	0.50	1.05	0.47	0.53	1.02	0.59761(5)	0.84503(8)	0.59756(6)	0.30177(4)	93

*Sum of the molar ratio of Sr and Ba was normalized to 1.00.

Fig.5 SEM images for the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics with (a) $x=0.0$, (b) $x=0.1$, (c) $x=0.2$, (d) $x=0.3$, (e) $x=0.4$, (f) $x=0.5$. The surfaces were polished and etched thermally at 800°C for 1 h in air.

Fig.6 Firing temperature dependence of the bulk density and diameter at room temperature for the cylindrical ceramics with the nominal molar ratios of $\text{Pb}/\text{Sr}_{0.5}\text{Ba}_{0.5}=1.00$ and 1.05 . The firing was performed in the temperature range $800 \sim 900^\circ\text{C}$ for 3 h in air flow. The open and closed circles represent the bulk density for $\text{Pb}/\text{Sr}_{0.5}\text{Ba}_{0.5}=1.00$ and 1.05 , respectively, and the open and closed triangles represent the diameter for $\text{Pb}/\text{Sr}_{0.5}\text{Ba}_{0.5}=1.00$ and 1.05 , respectively. The dashed line shows the theoretical density (8.09 g cm^{-3}) at room temperature for the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{PbO}_3$ solid solution.

of SrPbO_3 and BaPbO_3 were observed even after the firing at 840°C in the case of $\text{Pb}/\text{Sr}_{0.5}\text{Ba}_{0.5}=1.00$. This difference suggests that the densification and the formation of the solid solution were promoted by the firing under the coexistence of a small amount of PbO in the calcined

powders, whereas they were suppressed without a small amount of PbO in the calcined powders. The possible reason for the densification is that a small amount of PbO particles dispersed in the surrounding SrPbO_3 and BaPbO_3 particles formed a liquid phase during the firing and closely connected the perovskite-type particles, consequently promoting the formation reaction of the solid solution. It should be noted that the well-mixed fine particles composed of SrPbO_3 , BaPbO_3 , and a small amount of PbO , which were derived from the coprecipitation and calcination, were essential for the densification. The small amount of lead oxide component, which was not detected by the XRD measurements after the sintering, should exist in the grain boundaries connecting the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ grains, as previously reported from the XPS data for the $\text{Ba}_{1-x}\text{Sr}_x\text{Pb}_{1+y}\text{O}_{3-\delta}$ ceramics⁹⁾.

3.3 Thermoelectric properties of perovskite-type $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics ($x=0.0 \sim 0.5$)

Figs. 7 (a) and 7 (b) show reciprocal temperature dependence of the electrical conductivity σ and Seebeck coefficient S for the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics, respectively. The σ values increased with increasing Ba content, and also increased with increasing temperature for all the samples, although the values for the samples with $x=0.3 \sim 0.5$ were less dependent on temperature below $\sim 700 \text{ K}$. The drop in σ observed above 1023 K was probably due to the PTCR effect relating to the grain boundaries of the ceramics, as reported for the $\text{Ba}_{1-x}\text{Sr}_x\text{Pb}_{1+y}\text{O}_{3-\delta}$ ceramics⁹⁾. The S values were negative for all the samples, indicating that the major carriers were electrons. The absolute values of S increased with increasing temperature but decreased at higher temperatures, and also decreased with increasing

Fig.7 Reciprocal temperature dependence of (a) the electrical conductivity σ and (b) the Seebeck coefficient S for the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics.

Ba content. The noticeable change in the temperature dependence of the σ and S was observed around 700 K for the samples with $x = 0.3 \sim 0.5$. Except the σ drop above 1023 K, the observed conduction behaviors were consistent with those for the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics prepared by the press-sintering method, which indicated the change from n -type degenerate semiconductor to n -type semi-metal with increasing Ba content⁶⁾. The increase in the σ and the decrease in the absolute values of S with increasing Ba content were ascribed to the increase in the carrier concentrations of both electrons and holes, which was caused by the increase in the energy overlap between the conduction band bottom and the valence band top with increasing Ba content⁶⁾.

Fig. 8 shows temperature dependence of the power factor $S^2\sigma$. Each power factor curve had a peak, which shifted to lower temperature with increasing Ba content, being also consistent with the result for the press-sintering method⁶⁾. It was found in this study that the $S^2\sigma$ values were maximized in a temperature range 723 ~ 1023 K for the $\text{Sr}_{0.7}\text{Ba}_{0.3}\text{PbO}_3$ ceramic due to optimization of the absolute values of σ and S , which were in a trade-off relation with respect to the Ba content. The highest value was $3.6 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ at 870 K, being comparable to the highest value,

Fig.8 Temperature dependence of the thermoelectric power factor $S^2\sigma$ for the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics.

$4.3 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ at 773 K, for the $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$ ceramic prepared by the press-sintering method⁶⁾. Therefore, the

present oxalate coprecipitation technique is a simple and useful solution method to prepare dense $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics showing comparatively high thermoelectric power factors.

4 Conclusions

The Sr-Ba-Pb oxalates were coprecipitated from nitrate solutions with molar ratios of metallic ions controlled to $\text{Pb}/\text{Sr}_{1-x}\text{Ba}_x = 1.05$ ($x = 0.0 \sim 0.5$) and converted into fine powders composed of SrPbO_3 , BaPbO_3 , and a small amount of PbO by calcinations at 700°C . Dense $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics with relative densities of $\sim 90\%$ were prepared by the sintering at $850 \sim 900^\circ\text{C}$. The small amount of PbO particles dispersed well in the calcined powders formed liquid phase during the sintering and promoted the densification and the formation of the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ solid solutions. The thermoelectric power factors were estimated to be $1.0 \times 10^{-4} \sim 3.6 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ in the temperature range $373 \sim 1073 \text{ K}$ for the $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics and maximized for the $\text{Sr}_{0.7}\text{Ba}_{0.3}\text{PbO}_3$ ceramic by the optimization of the absolute values of the electrical conductivity and the Seebeck coefficient which were in a trade-off relation with respect to the Ba content. The present oxalate coprecipitation method is a simple and useful way to prepare dense $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ ceramics showing comparatively high thermoelectric power factors.

References

- 1) M.Ohtaki, H.Koga, T.Tokunaga, K.Eguchi and H.Arai: "Electrical Transport Properties and High-Temperature Thermoelectric Performance of $(\text{Ca}_{0.9}\text{M}_{0.1})\text{MnO}_3$ ($\text{M} = \text{Y, La, Ce, Sm, In, Sn, Sb, Pb, Bi}$)", *J. Solid State Chem.*, **120**(1995)105-111.
- 2) M.Ohtaki, T.Tsubota, K.Eguchi and H.Arai: "High-Temperature Thermoelectric Properties of $(\text{Zn}_{1-x}\text{Al}_x)\text{O}$ ", *J. Appl. Phys.*, **79**(1996)1816-1818.
- 3) H.Ohta, W.-S.Seo and K.Koumoto: "Thermoelectric Properties of Homologous Compounds in the $\text{ZnO-In}_2\text{O}_3$ System", *J. Am. Ceram. Soc.*, **79**(1996)2193-2196.
- 4) I.Terasaki, Y.Sasago and K.Uchinokura: "Large Thermoelectric Power in NaCo_2O_4 Single Crystals", *Phys. Rev. B*, **56**(1997)R12685-R12687.
- 5) M.Yasukawa and N.Murayama: "High-Temperature Thermoelectric Properties of the Oxide Material: $\text{Ba}_{1-x}\text{Sr}_x\text{PbO}_3$ ($x = 0 - 0.6$)", *J. Mater. Sci. Lett.*, **16**(1997)1731-1734.
- 6) M.Yasukawa and N.Murayama: "A Promising Oxide Material for High-Temperature Thermoelectric Energy Conversion: $\text{Ba}_{1-x}\text{Sr}_x\text{PbO}_3$ Solid Solution System", *Mater. Sci. Eng. B*, **54**(1998)64-69.
- 7) Y.Kodama, N.Murayama, Y.Torii and M.Yasukawa: "Chemical Preparation and Properties of Semi-Metal BaPbO_3 Ceramics", *J. Mater. Sci. Lett.*, **17**(1998)1999-2001.
- 8) M.Yasukawa and T.Kono: "Preparation of Dense BaPbO_3 -Based Ceramics by a Coprecipitation and their Thermoelectric Properties", *J. Alloys Compd.*, **426**(2006)420-425.
- 9) H.Nagamoto, H.Kagotani, T.Okubo and T.Koya: "Positive Temperature Coefficient of Resistivity in $\text{Ba}_{1-x}\text{Sr}_x\text{Pb}_{1+y}\text{O}_{3-\delta}$ Ceramics", *J. Am. Ceram. Soc.*, **76**(1993)2053-2058.
- 10) N.Cusack and P.Kendall: "The Absolute Scale of Thermoelectric Power at High Temperature", *Proc. Phys. Soc. (Lond.)*, **72**(1958)898-901.
- 11) R.D.Shannon: "Unit Cell and Space Group of SrPbO_3 ", *J. Solid State Chem.*, **3**(1971)184-185.