Preparation of Mn-Modified Tetragonal PZT Ceramics and Their Pyroelectric Properties

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マンガンを添加した正方晶 PZT セラミックスの作製とその焦電的性質

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High density tetragonal PZT ceramics with compositions of $\{\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 + 0.5 \text{ mass\% MnO}_2\}$, where $x=0.10-0.50$, were synthesized by hot isostatic pressing (HIP). Pressed samples with $x=0.20$ had the highest bulk density of 7.82 g/cm^3 , which is 98.2% of the theoretical density. The pyroelectric properties of poled PZT ceramics with $x=0.10-0.50$ were evaluated. The Curie temperature T_C decreased linearly with increasing Zr content. The rate of linear decrease m calculated from the slope of the linear plot of T_C with x was approximately $3.0^\circ\text{C/mol\% Zr}$. The PZT sample with $x=0.20$ exhibited the highest figure of merit F.M. of around $2.1 \times 10^{-11} \text{ C}\cdot\text{cm/J}$. Assuming that the volume specific heat C_v of the present sample with $x=0.20$ and that of $\{\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 + 2 \text{ mass\% ZnBi}_{2/3}\text{Mn}_{1/3}\text{O}_3\}$ (PZT-ZBM) ceramic with $x=0.30$ that has already been reported are the same ($3.1 \text{ J/cm}^3\cdot\text{K}$), the F.M. for voltage responsivity of pyroelectric IR sensors fabricated using these ceramics which have the same tetragonal structure should be nearly equal.

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1. Introduction

Lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, (PZT) in which Zr^{4+} ions are partially substituted at the B-sites (Ti^{4+} ions) in PbTiO_3 , is an excellent piezoceramic currently used in devices such as ignition elements, piezoelectric speakers and actuators.¹⁾ PZT has a high relative dielectric constant and excellent polarization properties and has been investigated recently as a potential material for small nonvolatile memory elements²⁾ which can be used in place of magnetic disks. On the other hand, the pyroelectric properties of PZT ceramics have been investigated by adding small amounts of various additives such as 0.3 mass% U_3O_8 at $x=0.74-0.98$,³⁾ 1 mass% Nb_2O_5 at $x=0.52$,⁴⁾ 2 mass% $\text{ZnBi}_{2/3}\text{Mn}_{1/3}\text{O}_3$ at $x=0.30-0.70$ (PZT-ZBM)⁵⁾ and 0-10 mol% $\text{Pb}(\text{Sn}, \text{Sb})\text{O}_3$ (PZT-PSS).⁶⁾ Thus the many studies on the pyroelectric properties have focused on PZT with a rhombohedral structure ($x \geq 0.535$; morphotropic phase boundary). In the case of tetragonal PZT ceramics there are few reports on the figure of merit F.M. for voltage responsivity of pyroelectric IR sensors and its variation with Zr content, except for some on PZT-ZBM ($x=0.30-0.52$).

In this study, we attempted to synthesize high density tetragonal PZT ceramics with composition $\{\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 + 0.5 \text{ mass\% MnO}_2\}$ where $x=0.10-0.50$, by hot isostatic pressing (HIP). The pyroelectric properties of these ceramics are compared with

those of PZT-ZBM ($x=0.30-0.50$) ceramics.

2. Experimental procedures

2.1 Sample preparation

The guaranteed reagents of PbO (massicot type), ZrO_2 , TiO_2 (anatase type) and MnO_2 additive were used as the starting materials. Powders in proportions appropriate to obtain the composition $\{\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 + 0.5 \text{ mass\% MnO}_2, x=0.10-0.50\}$ were uniformly mixed and ground for 30 min in ethanol in an agate mortar. After drying the mixture at 120°C for 6h, it was calcined in a high-purity magnesia crucible of volume 100 cm^3 in air at 850°C for 1h. After the calcines were finely pulverized in ethanol in the agate mortar, mixtures in the ratio of 5 cm^3 of 1.0 mass% PVA solution to 10 g of calcined PZT powders were mixed and ground for around 2h in a planetary zirconia wet-ball mill. The wet powders were dried at about 105°C for 1.5h and then sieved using a 32-mesh screen. The granules obtained were pressed at around 100 MPa into discs 12.7 mm in diameter and 1-2 mm thick. After the discs were placed in a high-purity MgO crucible, they were perfectly inlaid with calcined powders having the same composition as the discs. The crucible was placed in a vertical electric furnace and then fired at 1280°C for 2h in air. Next, the sintered discs were HIPed by the capsule-free method under the following conditions: after the samples prepared by the normal sin-

Fig. 1. Schematic diagram of hot isostatic pressing equipment used for synthesizing PZT ceramics.

1: Introducing gate, 2: Upper lid, 3: High-pressure vessel, 4: Adiabatic material, 5: Al_2O_3 lid, 6: High-purity Al_2O_3 crucible, 7: PZT powder, 8: Pt leaf, 9: PZT ceramics previously fired at 1280°C for 2h, 10: ZrO_2 powder, 11: Pt heating element, 12: Support, 13: Lower lid.

tering were set into the HIP equipment indicated in Fig. 1, they were HIPed under mixed gas ($\text{Ar}/\text{O}_2 = 80/20$) pressure of around 100 MPa at 1280°C for 1h. The samples obtained were then polished to a thickness of around 0.35 mm. After drying, silver electrodes were attached to their surfaces by firing coated silver paste (SS24386, Nippon Acheson) on the surfaces of the discs at 600°C for 30 min in air.

2.2 Measurement of physical properties

The crystalline phase, lattice constant and tetragonality c/a in each sample were analyzed using an X-ray diffractometer (XRD; Rigaku, RINT1500). The lattice constants were determined by applying the least squares method to the X-ray diffraction results obtained using the 111, 200, 112, 211, 123, 312 and 321 reflections of Cu $K\alpha$ radiation with high-purity silicon powder (NIST-640b) as the external standard. The apparent porosity and bulk density of each HIPed sample were measured in accordance with the method for magnesia clinker, which is regulated in Gakushin Method-3. The relative density was then obtained by dividing the bulk density by the theoretical density. After a dried sample had been kept in white kerosene for 4h at reduced pressure, the physical constants were calculated from the weight of white kerosene absorbed into the sample and that of the dried sample. Additionally, the samples were poled at 150°C for 20 min under a constant d.c. electric field of around 40 kV/cm in silicone oil (Shin-Etsu Chemical, KF54). The poled samples were measured according to the system for measuring static pyroelectric properties^{7,8)} which is shown in Fig. 2. The relative dielectric constant ϵ_r of samples in the temperature range 30 – 500°C was measured using a multifrequency LCR meter (Yokogawa Hewlett-Packard, 4274A) at 1 kHz under a constant a.c. electric field of 25 V/cm (the practical effective value). The resistivity ρ at room temperature was measured by the d.c. three-terminal method using a d.c. voltage source (Yokogawa Hewlett-Packard, 4140B). The pyroelectric current i_p was measured

Fig. 2. Schematic diagram for automatic measurement of static pyroelectric properties.

1: Cooling unit, 2: Electric furnace, 3: Heating element, 4: Test piece, 5: Rotary pump, 6: Thermocouple, 7: Quartz tube.

repeatedly using a pA meter (Yokogawa Hewlett-Packard, 4140B) at a constant rate of temperature change of $1.6^\circ\text{C}/\text{min}$ for increasing and decreasing temperature in the range 30 – 200°C in order to eliminate effects due to the induced current. The temperature of the sample was controlled in the range of -30 to 200°C under vacuum by a programmed temperature control system, a cooling unit using liquid N_2 (77 K) as a refrigerant and a rotary pump. After measuring i_p , the pyroelectric coefficient P was derived from

$$P = i_p \cdot (dt/dT) / S \quad (\text{C}/\text{cm}^2 \cdot \text{K}) \quad (1)$$

where i_p is the pyroelectric current (A), S is the electrode area (cm^2), T is the absolute temperature (K), t is the time (s) and dt/dT is 38.0 (s/K). The figure of merit F.M. for voltage responsivity of a pyroelectric infrared (IR) sensor can be expressed by

$$\text{F.M.} = P / (C_v \cdot \epsilon_r) \quad (\text{C} \cdot \text{cm}/\text{J}) \quad (2)$$

where C_v is the volume specific heat which is $3.1\text{ J}/\text{cm}^3 \cdot \text{K}$.⁹⁾ The temperature dependence of ϵ_r was examined in the 30 – 500°C temperature range. From these results, the Curie temperature T_C was determined from the position of the maximum ϵ_r . The rate of linear decrease m was calculated from the slope of the linear plot of T_C against Zr content to evaluate the effects of Zr added.

3. Results and discussion

3.1 Crystalline phase and lattice constant

The X-ray diffraction patterns obtained for $x=0.30$ PZT powder calcined at 850°C for 1h in air, $x=0.30$ PZT ceramic fired at 1280°C for 2h in air and $x=0.30$ PZT ceramic HIPed under 100 MPa at 1280°C for 1h are shown in Figs. 3(a)–(c), respectively. The patterns shown in Figs. 3(a) and 3(b) indicate the formation of the PZT phase in this study occurred to obey the reaction mechanism previously reported by Matsuo and Sasaki,¹⁰⁾ that is, after PbTiO_3 was formed at the initial low-temperature stage, it reacted chemically with PbO and ZrO_2 at temperatures above 1200°C , resulting in the formation of the PZT phase. It can be seen from Figs. 3(b) and 3(c) that PZT ceramics both with and without HIP treatment synthesized at 1280°C exhibit almost

Fig. 3. X-ray diffraction patterns of (a) $x=0.30$ PZT powder calcined at 850°C for 1h in air, (b) $x=0.30$ PZT ceramic fired at 1280°C for 2h in air and (c) $x=0.30$ PZT ceramic HIPed under 100 MPa at 1280°C for 1h.

Fig. 4. Lattice constants and tetragonality c/a as a function of the composition x .

□ a , ○ c , ● c/a .

single-phase PZT tetragonal structure. The lattice constants and tetragonality c/a for all samples after HIP treatment are shown in Fig. 4. The lattice constants of the PZT samples increase gradually along the a -axis but there is little variation along the c -axis with increasing Zr content. The tetragonality c/a of PZT samples with $x=0.10$ – 0.45 showed a tendency to decrease with increasing x . The results obtained are very similar to the lattice constants and tetragonality of PZT ceramics synthesized by the solid-state reaction, which were previously reported by Kakegawa et al.¹¹⁾ The fact that only the value of a -axis varies with increasing x may be attributable to fluctuations in the composition.

3.2 Apparent porosity, bulk density and relative density

The apparent porosity, bulk density, theoretical density and relative density for all samples in this study are shown in Table 1. All samples were sintered bodies with low porosity and high bulk density. In particular, samples with $x=0.20$ had the highest bulk density of 7.82 g/cm^3 , which is 98.2% of the theoretical density.

Table 1. Composition x , Apparent Porosity, Bulk Density, Theoretical Density and Relative Density of the Synthesized PZT Ceramics

Composition x in PZT*	Apparent Porosity (%)	Bulk Density ($\text{g}\cdot\text{cm}^{-3}$)	Theoretical Density ($\text{g}\cdot\text{cm}^{-3}$)	Relative Density** (%)
0.10	0.04	7.75	7.97	97.2
0.20	0.06	7.82	7.97	98.2
0.30	0.07	7.56	8.00	94.5
0.40	0.12	7.69	8.02	96.0
0.45	0.04	7.53	8.05	93.6
0.50	0.11	7.47	7.94	94.1

*PZT; $\{\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3+0.5\text{ mass\% MnO}_2\}$

**Relative Density (%)=(Bulk Density/Theoretical Density) $\times 100$

3.3 Pyroelectric properties

3.3.1 Relative dielectric constant

Figure 5 shows the temperature dependence of the relative dielectric constant ϵ_r with increasing temperature for three typical samples. The temperature at which ϵ_r is a maximum, that is, the Curie temperature T_C apparently shifts toward the lower temperature side with increasing Zr content. Furthermore, the value of ϵ_r at T_C in each sample increased significantly with increasing Zr content. It can be seen from Fig. 6 that ϵ_r at room temperature increases from 196 ($x=0.10$) to 861 ($x=0.50$) with increasing Zr content according to the shifting effect of Zr at the concentration considered in this study. These results nearly agree with the ϵ_r values for PZT-ZBM ($x=0.30$ – 0.50) ceramics, which were reported by Chechkin et al.⁵⁾

3.3.2 Curie temperature

Figure 7 shows the Curie temperature T_C as a function of the composition x for PZT-system ceramics with $x=0.10$ – 0.50 . The Curie temperature, determined from the positions of the ϵ_r maxima decreases linearly with increasing the Zr content. The rate of linear decrease m calculated from the linear plot of T_C with x is approximately $3.0^\circ\text{C/mol\% Zr}$. This result almost coincides with that (approximately $4.0^\circ\text{C/mol\% Zr}$) estimated from previously reported data on PZT-ZBM ceramics with $x=0.30$ – 0.52 .⁵⁾ Based on these results, the Zr shifting effect on the PbTiO_3 was found to be approximately 3.0 – $4.0^\circ\text{C/mol\% Zr}$ regardless of the sintering agent.

3.3.3 Pyroelectric coefficient

The temperature dependence of the pyroelectric coefficient P for three poled samples in the range 30 – 200°C is shown in Fig. 8. The values of P , determined by measuring the actual i_p at various temperatures, vary in proportion to i_p as seen from Eq. (1). P for all samples increased gradually with increasing temperature, and decreased with decreasing temperature. The behavior of P during the heating process for all samples was in good agreement with that during the cooling process within the accuracy of measurement. Therefore, the values of P shown in Fig. 8 are calculated by taking the average of the measured values for increasing and decreasing temperature. The pyroelectric coefficient P at room temperature

Fig. 5.

Fig. 6

Fig. 7

Fig. 5. Temperature dependence of relative dielectric constant at increasing temperature for three samples.
○ $x=0.30$, △ $x=0.40$, ● $x=0.50$.
Fig. 6. Relative dielectric constant at room temperature for all samples as a function of the composition x .
Fig. 7. Curie temperature for all samples as a function of the composition x .
 m : the rate of linear decrease estimated from the slope of the linear plot of T_C with x obtained by the least squares method in the range of $x=0.10\text{--}0.50$.

Fig. 8. Temperature dependence of pyroelectric coefficient for three poled samples in the range 30–200°C.
○ $x=0.20$, □ $x=0.30$, ● $x=0.45$.

increases slightly with increasing Zr content, as shown in the insert in Fig. 8. Thus it was proved that an improvement in P at room temperature could be accomplished due to the shifting effect caused by the substitution of Zr^{4+} ions for Ti in $PbTiO_3$. The values of P for all samples with $x=0.10\text{--}0.50$ were in

the range of $0.9\text{--}2.0 \times 10^{-8} \text{ C/cm}^2 \cdot \text{K}$. In contrast, those for PZT–ZBM ceramics with $x=0.30\text{--}0.50$ are in the range of $2.0\text{--}3.1 \times 10^{-8} \text{ C/cm}^2 \cdot \text{K}$,⁵⁾ which is 1.2–1.7 times larger than those of the present samples when samples with the same composition x are compared. It has been reported that tetragonal PZT ceramics modified with 3 mol% $Pb(\text{Sn}, \text{Sb})\text{O}_3$ ⁶⁾ have a large P ($\cong 1.0\text{--}6.0 \times 10^{-8} \text{ C/cm}^2 \cdot \text{K}$) compared with the above two ceramics. Our results indicate the possibility that larger values of P can be obtained when different plural atoms are incorporated substitutionally into the Ti^{4+} ion sites in $PbTiO_3$ perovskite structure, adjusting their valence in the B-site.

3.3.4 Figure of merit for pyroelectric IR sensors

A comparison of figures of merit F.M. for the present samples with $x=0.10\text{--}0.50$ and PZT–ZBM ceramics with $x=0.30$ is shown in Table 2. The PZT sample with $x=0.20$ exhibited the highest F.M. among the six samples studied here, of around $2.1 \times 10^{-11} \text{ C} \cdot \text{cm/J}$. Assuming that the volume specific heat C_V of the present sample with $x=0.20$ and that of PZT–ZBM ceramic with $x=0.30$ ⁵⁾ are the same

Table 2. Comparison of Figures of Merit for Voltage Responsivity of Pyroelectric IR Sensors Fabricated Using PZT Ceramics and a PZT–ZBM Ceramic with $x=0.30$

Sample	Composition x in PZT	T_C (°C)	ϵ_r	ρ ($\Omega \text{ cm}$)	P ($10^{-8} \text{ Ccm}^{-2} \cdot ^\circ\text{C}^{-1}$)	C_V ($\text{Jcm}^{-3} \cdot ^\circ\text{C}^{-1}$)	F.M. ($10^{-11} \text{ CcmJ}^{-1}$)
PZT ceramics*	0.10	472	196	0.4×10^{11}	0.9	3.1	1.5
	0.20	458	214	3.4×10^{11}	1.4	3.1	2.1
	0.30	435	326	5.3×10^{11}	1.7	3.1	1.7
	0.40	404	500	2.0×10^{11}	1.8	3.1	1.2
	0.45	400	647	1.8×10^{11}	2.0	3.1	1.0
	0.50	350	861	5.2×10^{11}	1.8	3.1	0.7
PZT-ZBM ceramic**	0.30	430	290	—	2.0	—	—

* PZT ; { $Pb(Zr_xTi_{1-x})O_3 + 0.5 \text{ mass\% MnO}_2$, $x=0.10\sim0.50$ }
** PZT-ZBM ; { $Pb(Zr_xTi_{1-x})O_3 + 2 \text{ mass\% ZnBi}_{2/3}\text{Mn}_{1/3}O_3$ }

($3.1 \text{ J/cm}^3 \cdot \text{K}$),⁹⁾ the figures of merit F.M. for voltage responsivity of pyroelectric IR sensors fabricated using these ceramics which have the same tetragonal structure should be nearly equal. Based on these results, it is concluded that PZT ceramics with $x=0.20$ show excellent pyroelectric properties in the tetragonal (PZT+0.5 mass% MnO_2) system.

4. Summary

The results of this study are summarized as follows:

(1) High density tetragonal PZT ceramics with compositions of $\{\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 + 0.5 \text{ mass\% MnO}_2\}$, where $x=0.10\text{--}0.50$, were successfully synthesized by hot isostatic pressing.

(2) HIPed samples with $x=0.20$ had the highest bulk density of 7.82 g/cm^3 , which is 98.2% of the theoretical density.

(3) The Curie temperature T_C for PZT ceramics with $x=0.10\text{--}0.50$ decreased linearly with an increase in Zr content. The rate of linear decrease m calculated from the linear plot of T_C with x was approximately $3.0^\circ\text{C/mol\% Zr}$.

(4) The PZT sample with $x=0.20$ exhibited the highest figure of merit F.M. of around $2.1 \times 10^{-11} \text{ C} \cdot \text{cm/J}$. Assuming that the volume specific heat C_v of the present sample with $x=0.20$ and that of PZT-ZBM ceramic with $x=0.30$ are the same ($3.1 \text{ J/cm}^3 \cdot \text{K}$), the F.M. for voltage responsivity of pyroelectric

IR sensors fabricated using these ceramics which have the same tetragonal structure should be nearly equal.

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