Modification and Pyroelectricity of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ -Based Ceramics Using HIP with Novel Glass Encapsulation

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ガラスカプセル HIP 法による $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ 系セラミックスの改質と焦電特性

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The improvement of the pyroelectric properties of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) ceramics by means of compositional and morphological modification was realized. A compact body consisting mainly of equimolar PbZrO_3 (PZ) and PZT raw powders was encapsulated within a petri dish, followed by Ar-HIP under the conditions of 900°C -98 MPa-2h. The dense body obtained was probably composed of the two raw powders and their serial solid solutions, of which the temperature dependence of the pyroelectric coefficient of $9.4 \times 10^{-4} \text{ C} \cdot \text{m}^{-2} \cdot ^\circ\text{C}^{-1}$ at 25°C was almost flat over a wide temperature range of 15 - 70°C . Furthermore, the figure of merit (FM1) of this dense body was $199 \times 10^{-14} \text{ C} \cdot \text{m} \cdot \text{J}^{-1}$ which was sufficient for practical applications.

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1. Introduction

Pyroelectric materials that generate electrical charge on their surfaces through a temperature change caused by the incidence of infrared rays are expected for practical applications.^{1,2)} Among the many kinds of inorganic and organic materials that show pyroelectricity, PbTiO_3 - and $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ -based ceramics have great advantages compared with LiTaO_3 single crystal and $(\text{Gly})_3\text{H}_2\text{SO}_4$ in terms of cost and stability as practical detectors for the fire and the human body. However, the possibility of their applications with improved pyroelectric potential to highly sensitive infrared sensors remains to be determined. Kobune et al. reported the improvement of the sensitivity of lanthanum-modified PbTiO_3 ceramics by the addition of MgO with the aim of utilizing them for one- or two-dimensional infrared detector arrays.³⁾

It is known that the sensitivity of an infrared sensor increases at around the phase transition temperature between the two ferroelectric phases of rhombohedral PZT,⁴⁾ labeled as $F_{\text{LT}}(\text{R})$ and $F_{\text{HT}}(\text{R})$.⁵⁾ The sensitivity-temperature curve of rhombohedral PZT has a sharp peak at the phase transition temperature. Also, this transition temperature can be lowered to room temperature by means of compositional modification. We intend to apply this phenomenon to the development of a highly sensitive infrared sensor. One of the possible ways of reducing the temperature dependence of the pyroelectric sensitivity is

the hybridization of materials with different temperature dependences, as illustrated in Fig. 1. The pyroelectric sensitivity of raw materials (A) and (B) exhibits a maximum at a particular temperature. This temperature corresponds to the phase transition temperature. A mixture of (A) and (B) is sintered to form serial solid solutions (C) that coexist with (A) and (B) within the densified body. Consequently, the integration of the pyroelectric characteristics of (A), (B) and (C) will result in the reduction of the temperature dependence. However, it is difficult to obtain a target material with such flat characteristics in sensitivity by means of conventional pressureless

Fig. 1. Schematic illustration of the concept for reduction in temperature dependence of the pyroelectric sensitivity by means of hybridization between A and B.

sintering, since the raw materials will form a solid solution perfectly and change to a single phase at a sintering temperature of about 1200°C. Recently, some attempts to realize the above concept have been made by means of the formation of a multilayer structure^{6),7)} or liquid-phase sintering.⁸⁾

The "encapsulation hot isostatic pressing (HIP)" method, in which the sample is entirely covered with a gastight material, is generally used for a sample with low density in order to prevent penetration of the pressing gas. The capsules are mostly made of metal or glass owing to their high plasticity at HIP temperatures. Soda-lime glass is one of the most appropriate capsule materials for HIP of the above-mentioned PZT specimens at temperatures of 800 to 1000°C. In the present work, a compact body including two raw powders of different peak temperatures was subjected to HIP using a petri dish as a capsule,^{9),10)} and the temperature dependence of its pyroelectric sensitivity was examined.

2. Experimental

The nominal compositions of the starting materials were $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})_{0.1}\text{Zr}_{0.9}\text{O}_3 + 0.5 \text{ mass}\% \text{ MnO}_2 + 0.5 \text{ mass}\% \text{ Cr}_2\text{O}_3$ (abbreviated as P1) and $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})_{0.1}\text{Zr}_{0.875}\text{Ti}_{0.025}\text{O}_3 + 0.5 \text{ mass}\% \text{ MnO}_2 + 0.5 \text{ mass}\% \text{ Cr}_2\text{O}_3$ (P2). They were prepared by sintering mixtures consisting of the corresponding metal oxides and carbonates of reagent grade. Both of them were pyroelectric materials; the peak temperatures for P1 and P2 were 30 and 50°C, respectively. They were ground and granulated using an air-jet mill and a spray dryer. The particle size distributions of P1 and P2 after grinding were almost the same. The average particle size was determined to be 2.1 μm and more than 99% of particles have a diameter less than 10 μm from the optical measurement using a laser beam (Seishin Enterprise, PRO-7000S). They were mixed at a molar ratio of 1 : 1, and then the mixture was formed into rods of 45 mm in diameter and 80 mm in length, followed by the evaporation of organic binder from the rod samples at 850°C for 2h in air. Bulk densities of the rod samples ranged from $6.0 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$ to $6.5 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$ (75–80% in relative densities). The rod samples were cut into tablets of 30 mm in diameter and 6 mm in thickness.

Commercially available petri dishes made from soda-lime glass (the inside dimensions were 41 mm ϕ $\times$ 14 mm high) were used as capsule materials. The mechanical processing of the petri dish was carried out for rapid evacuation and gas-tight sealing, as shown in Fig. 2. The tablet was placed in the processed petri dish, and the open space around the tablet was filled with intermediary powder, which was obtained through the calcination of aluminum oxide (Wako Pure Chem. Ind. Ltd., special grade) at 1050°C. This loaded petri dish was embedded in aluminum oxide powder in an alumina porcelain cruci-

Fig. 2. Schematic illustration of mechanical processing of a petri dish.

ble and then evacuated to less than 1.33 hPa, followed by heating at a rate of 5°C/min up to 800°C and holding at that temperature for 2h to induce sealing. A hot isostatic pressing (HIP) apparatus (Kobe Steel, Ltd., SYSTEM20) was used for the densification of the tablet using argon gas (Gastec, 99.99 vol% purity). A "pressing-after-heating" schedule was employed in the HIP treatment, as described in Fig. 3.

The bulk densities of the HIP-treated samples were measured and the microstructure was observed by scanning electron microscopy (JEOL, FE-SEM, JSM-6300F). The samples were cut into tablets of 20 mm in diameter and 0.5 mm in thickness, coated with silver by evaporation, and polarized at 80°C, $2 \times 10^6 \text{ V}\cdot\text{m}^{-1}$ in a silicone oil bath for 1h. The relationship between electric displacement (D) and applied field (E) was measured using a Pepinsky bridge circuit.¹¹⁾ Pyroelectric currents were measured in a thermostatic furnace at a heating rate of 1.0°C/min, and pyroelectric coefficients (P) were calculated from the following equation:¹²⁾

Typical values for P_n , T_n and r_n .

T_1	T_2	T_3	r_1	r_2	r_3	P_1	P_2	P_3
750	800	800	20	1.0	7.0	0.3	98	98
750	800	850	20	1.0	7.0	0.3	93	98
750	800	900	20	1.0	7.0	0.3	91	98
750	800	1000	20	1.0	7.0	0.3	86	98

Fig. 3. A diagram of temperature and pressure schedule for HIP treatment of the petri dish capsules. P_n , T_n and r_n ($n=1, 2, 3$) represent pressure, temperature and heating rate, respectively. The typical values for P_n , T_n and r_n are listed under the diagram.

$$P = \frac{dP_s}{dT} = \frac{i/A}{dT/dt} \quad (1)$$

where P_s is spontaneous polarization, T temperature, i pyroelectric current, A surface area of electrode and t time.

3. Results and discussion

Figure 4 shows the relationship between bulk density and HIP temperature. The increase in bulk density from 800 to 900°C is larger than that from 900 to 1000°C, indicating that densification proceeded rapidly at temperatures above 900°C under a pressure of 98 MPa. The relative densities are 95 and 97% at 900 and 1000°C, respectively. It is known empirically that a relative density of more than 95% is required for attaining sufficient mechanical strength and good electrical properties for pyroelectric use; this density could be obtained at a HIP temperature of 900°C. It was noted that the HIP method could reduce the sintering temperature by approximately 300°C, since a sintering temperature above 1200°C was required to obtain the relative density of 95% by means of conventional pressureless sintering. Figure 5 shows a SEM image of the fracture surface of the sample which was subjected to HIP at 900°C under 98 MPa for 2h. The average grain size was 3 μm, which was slightly different from those of P1 and P2 of 2.1 μm. In contrast, the average grain size for the sample subjected to conventional pressureless sintering at 1200°C for 2h grew up to 10 μm. The HIP sintering

Fig. 4. Relationship between bulk density and HIP temperature.

Fig. 5. SEM micrograph of fracture surface of the hybridized material subjected to HIP at 900°C under 98 MPa for 2h.

at 900°C promoted densification without remarkable grain growth. Also, it is assumed that the solid solution reaction, which mostly involves the grain growth process, occurred only to a slight extent.

Figure 6 shows the result of D - E observation for the hybridized material. The hysteresis loop unique to ferroelectrics is observed, and the remanent polarization and coercive field are $11 \times 10^{-2} \text{ C} \cdot \text{m}^{-2}$ and $10 \times 10^5 \text{ V} \cdot \text{m}^{-1}$, respectively. From considerations of a phase diagram of the PZT-based system, it is possible that the antiferroelectric or nonpyroelectric phase formed in case of an anomalous solid solution reaction at the hybridization stage. In general, a typical D - E relation for antiferroelectrics shows no hysteresis, in which the polarization is reduced to zero at $E=0$. Accordingly, the D - E hysteresis loop of the ferroelectric phase which is accompanied by a large amount of the antiferroelectric phase is expected to be markedly different from a typical ferroelectric pattern. However, no such distortion is seen in Fig. 6; that is, the antiferroelectric phase was hardly formed.

Figure 7 shows the temperature dependences of the pyroelectric coefficients for P1, P2 and their hybridized material subjected to HIP at 900°C under 98 MPa for 2h (P1+P2). While P1 and P2 exhibit extremely high pyroelectric coefficients in a limited temperature range, these disappear and the pyroelec-

Fig. 6. D - E hysteresis loop of the hybridized material subjected to HIP at 900°C under 98 MPa for 2h.

Fig. 7. Temperature dependence of the pyroelectric coefficients of the constituent materials (P1, P2) and the hybridized material subjected to HIP at 900°C under 98 MPa for 2h (P1+P2).

tric coefficient is almost unchanged at around $10 \times 10^{-4} \text{ C} \cdot \text{m}^{-2} \cdot ^\circ\text{C}^{-1}$ from 15 to 70°C for P1+P2, which is more than twice that of a typical practical pyroelectric material.¹³⁾ According to this result, the pyroelectric stability of the hybridized material could be obtained without losing the advantage of the constituent materials, that is, high pyroelectric coefficients. Previous studies have shown that the pyroelectric peaks did not disappear completely.^{6)–8)} The reduction in the temperature dependence must have originated from the integration of the pyroelectric characteristics of P1, P2 and the reformed part, as described in Fig. 1. The broad pyroelectric peak around 40°C , which was probably due to overgrowth of the reformed part, appeared in the case of the sample subjected to HIP at 1000°C under 98 MPa for 2h.

Since the reduction in the temperature dependence of the pyroelectric coefficient is caused by quenching of the solid-state reaction at the initial stage, there is a possibility that a slight deviation from the prescribed HIP conditions will bring about a large difference in pyroelectric properties. As a result of a supplementary experiment to examine this possibility, approximately the same temperature dependence of the pyroelectric coefficient (8×10^{-4} to $11 \times 10^{-4} \text{ C} \cdot \text{m}^{-2} \cdot ^\circ\text{C}^{-1}$ in the temperature range of 15 to 70°C) as P1+P2 in Fig. 7 was obtained with high reproducibility from HIP temperatures of 870 to 950°C and HIP pressures of 78 to 147 MPa.

In general, the pyroelectric sensitivity is evaluated in terms of “figure of merit”, FM1, which is given by

$$\text{FM1} = \frac{P}{(\rho C \epsilon_r)} \quad (2)$$

where P , ρ , C and ϵ_r are the pyroelectric coefficient, the density, the specific heat at constant volume and the relative permittivity, respectively. Table 1 shows a comparison of these values for the PZT ceramics in this study with those in other reports.^{13),14)} $\text{PbTi}_{0.07}\text{Zr}_{0.93}\text{O}_3$ ceramic in Table 1, which was developed for pyroelectric application, shows an extremely high FM1 owing to its low ϵ_r . It can be seen that the hybridized material in this study possesses the highest P , the lowest C , a relatively low ϵ_r , and the highest FM1 among the materials listed in Table 1.

Table 1. Comparison of the Pyroelectric Coefficient (P , $10^{-4} \text{ C} \cdot \text{m}^{-2} \cdot ^\circ\text{C}^{-1}$), the Specific Heat at Constant Volume (C , $10^2 \text{ J} \cdot \text{kg}^{-1} \cdot ^\circ\text{C}^{-1}$), the Density (ρ , $10^3 \text{ kg} \cdot \text{m}^{-3}$), the Relative Permittivity at 1 kHz (ϵ_r), and the Figure of Merit (FM1, $10^{-14} \text{ C} \cdot \text{m} \cdot \text{J}^{-1}$) for PZT-Based Ceramics in This Study and in Literatures

Material	P	C	ρ	ϵ_r	FM1
(this study)	9.4	2.7	7.6	230	199
PZT-4 ¹⁴⁾	3.7	4.0	7.5	1400	8.8
PZT G-1306 ¹⁴⁾	4.6	3.9	7.6	1730	9.0
PZT HST-41 ¹⁴⁾	2.0	3.9	7.6	1800	3.7
$\text{PbTi}_{0.07}\text{Zr}_{0.93}\text{O}_3$ ¹³⁾	3.9	3.6	7.35	180	81.9

These results lead to the conclusion that the pyroelectric sensitivity of the hybridized material is high enough for practical applications.

4. Conclusions

PZT-based pyroelectric ceramic with small temperature dependence of the pyroelectric sensitivity was obtained by densification of a mixture of samples with different peak temperatures, preventing the formation of a single solid solution. Densification was performed through the encapsulation of samples in petri dishes and subsequent hot isostatic press (HIP) using Ar gas. The reduction in the temperature dependence of the pyroelectric sensitivity may be due to the integration of the characteristics of the raw materials and those of their serial solid solutions. The optimum HIP conditions for this purpose were 900°C –98 MPa–2h, which gave a pyroelectric coefficient of about $9.4 \times 10^{-4} \text{ C} \cdot \text{m}^{-2} \cdot ^\circ\text{C}^{-1}$ in the temperature range of 15 to 70°C . Furthermore, the figure of merit (FM1) of the dense body was high enough for practical applications.

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