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# Design of pyroelectric properties by controlling compositional distribution

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**Abstract**

Sintering of a mixture of different compositions generally causes a change in the compositional distribution in the starting material. Change in the compositional distribution during sintering was examined for normal sintering, hot pressing and spark plasma sintering (SPS). Only SPS method produced a highly sintered material without changing the initial compositional distribution. Combination of pyroelectric properties of different compositions was accomplished by SPS. A mixture of three compositions corresponding to pyroelectric materials having the peak at 0 °C, 25 °C and 50 °C were mixed and sintered by the normal sintering method. The normal sintering resulted in a pyroelectric material having single peak, due to the homogenization process during the sintering. Sintered material by SPS produced a material having pyroelectric peaks corresponding to the initial compositions. Combination of SPS and diffusion-treatment produced a pyroelectric materials having high pyroelectric coefficient in the temperature range between 25 °C and 50 °C.


*Keywords:* Sintering; Electrical properties; PZT; Sensors

## 1. Introduction

Pyroelectric materials can be used for infrared sensors. High pyroelectric coefficient is desirable for such sensors, because infrared sensors having higher pyroelectric coefficient have higher sensitivity. Rhombohedral region in the system of $PbTiO_3$-$PbZrO_3$, has a phase transition between ferroelectric-low-temperature form and ferroelectric-high-temperature form. At the transition point, the material exhibits a peak of pyroelectric coefficient. However, this material cannot be used for infrared sensor, because the peak is too sharp, so that if the temperature changes slightly from the peak temperature, the sensitivity decreases significantly. One way to obtain stable pyroelectric property is to broaden the peak by some additives. Even when the peak is broadened, the area under the peak does not change. Thus, the wider the peak is broadened, the lower the pyroelectric values at each temperature is (Fig. 1, dotted line). If a pyroelectric property which have high value in the operation temperature region and have low value outside the operation temperature as shown in Fig. 1 (trapezoidal *p–T* curve, solid line), the value can be concentrated in the operation temperature region.

Pyroelectric property having trapezoidal *p–T* curve would be attained, if a several properties could be combined (Fig. 2). This would be materialized by mixing several compositions and sintering. However, sintering usually alters the initial compositional distribution. Sintering can be achieved by diffusion. Homogenization process during firing is also achieved by diffusion. Thus, it is natural that the compositional distribution in solid solutions decreases as the sintering proceeds.

Generally, solid solutions tend to have distribution of composition. Method to determine the width of the distribution has been reported.[1–3] This method revealed that ceramics of lead zirconate titanate prepared by solid state reaction has a large compositional distribution.[4] The compositional distribution decreases with firing period as a process of homogenization. The rate of the decrease of

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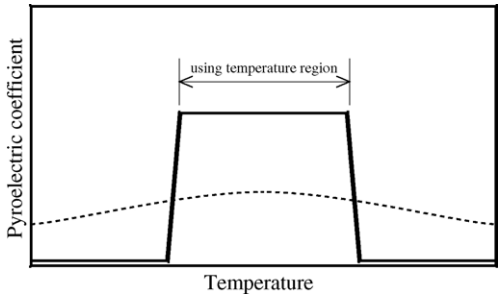


Fig. 1. Ideal pyroelectric property (trapezoid, solid line) and broadened pyroelectric property (dotted line).

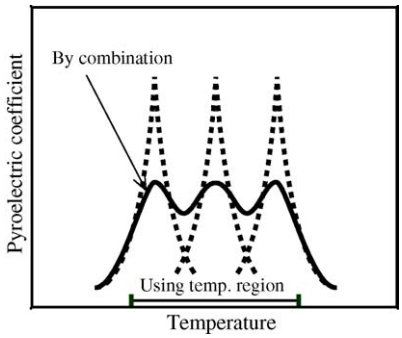


Fig. 2. Combined pyroelectric property (solid line).

the compositional distribution is higher at higher firing temperatures.

Spark plasma sintering (SPS) method[5,6] has received much attention, because it sinters many materials at lower temperatures within few minutes. In the SPS method, powder sample in graphite die is pressed in vacuo, and heated by a pulse current. The die is heated by the joule heat. It is said that the sintering proceeds very quickly because of the spark plasma caused by the large pulse current. This method can be used in metallurgic,[7] ceramics[8,9] and even in plastics.[10] Because SPS sinters many materials at lower temperatures and shorter period, it is expected that the change in the compositional distribution by SPS is small. This means that sintering with almost no change in the compositional distribution can be performed by SPS.

Hotpressing and SPS are similar sintering methods. Only different point is that SPS uses pulse current. In this paper, change in the compositional distribution in lead zirconate titanate solid solution (PZT) during sintering by SPS was examined and compared with that by hotpressing and the normal sintering method. In addition, methods of combination of pyroelectric properties were developed.

## 2. Experimental

Lead oxide (Wako Pure Chemicals, 99.5%), zirconium oxide (Mitsuwa Chemical, 99.5%) and titanium oxide (Kishida Chemical, 99.5%) were blended in the ratio corresponding to a composition of $Pb(Zr_{0.3}Ti_{0.7})O_3$ and mixed thoroughly with agate mortar and pestle. The mixture was put in a small magnesia crucible. An equimolar mixture of lead oxide and zirconium oxide was put in another small crucible. This crucible was stacked on the former crucible. They were put in a larger magnesia crucible and covered with another larger crucible (magnesia double crucible[11]). This was fired at 800 °C for 1 h as a calcination. The sample was ground again. The powder was put in a graphite die. Carbon sheet was inserted between the die and the sample in order to avoid the reaction between the sample and the die during the sintering. The graphite die was put in a SPS apparatus (SPS-515S, SMC). Unidirectional pressure was 29 MPa pressure of the atmosphere was 4–6 Pa. Heating rate was 100 °C/min between room temperature and 700 °C, 33 °C/min between 700 °C and 800 °C. After soaking for prescribed period at 800 °C, the pressure was released and pulse current was cut. Carbon sheet stuck on the sintered body was scraped off.

For comparison, normal sintering was carried out. Calcined powder was pressed into a disk (diameter: 13 mm, thickness: 1.5 mm) put into magnesia double crucible and fired. Hotpressing was also carried out. Unidirectional pressure was 29 MPa. Heating rate was 10 °C/min. Carbon die was used.

Bulk densities of sintered samples were measured by Archimedes method. For the measurements of powder XRD (MXP18VA/HF, MAC Science Inc.), a Cu target was used with a monochromator. As an optical system for the qualitative measurements, a divergence slit of 1°, a scattering slit of 1°, and a receiving slit of 0.15 mm were used. The net peak width ($\beta$) caused from the sample was figured out using MXP System Standard Software (MAC Science Inc.). Widths at half-maximum intensity for Si were used as a standard. These values were used for a calculation of the width of the compositional distribution.

Lead oxide, titanium oxide, zirconium oxide, zinc oxide (Kanto Chemical, grade G) and niobium oxide (Wako Pure Chemicals, 99.9%) were mixed in the ratios corresponding to the composition, $PbTi_{0.1-x}Zr_{0.9}(Zn_{1/3}Nb_{2/3})_xO_3$ and calcined. Calcined powders were mixed and sintered by the normal sintering, SPS and hotpressing. Because SPS and hotpressing use carbon die and they were carried out in vacuo, samples were partially reduced. Thus, sintered bodies were heated again in the magnesia double crucible at 800 °C for 20 min in air as a reoxidation treatment. Silver electrode was applied to the both sides of the sintered pellet and poled at 15 kV/cm for 30 min. Pyroelectric current was measured with heating rate at 1 °C/min and pyroelectric coefficient was calculated.

## 3. Results and discussions

Fig. 3 (close circle) shows a relation between bulk density of sintered body by the normal sintering and soaking time at 1200 °C. Plot at sintering time = 0 indicates a green density. The starting material was calcined at 800 °C for

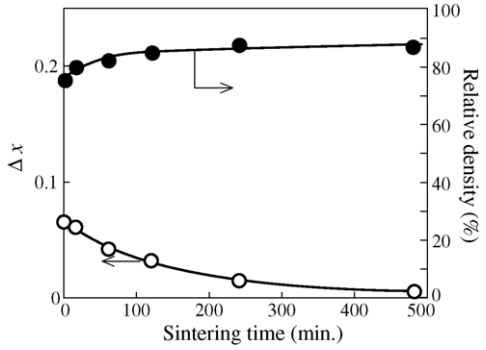


Fig. 3. Change in width of compositional distribution and sintered density with sintering time by normal sintering for $Pb(Zr_{0.3}Ti_{0.7})O_3$. Calcination: 800 °C/2 h. Sintering: 1200 °C.

2 h. The bulk density increased with the soaking time. The change in the bulk density is typical. By the normal sintering, temperature around 1200 °C and several hours is required for such densification rate. The width of the compositional distribution, $\Delta x$ (difference between the compositions of upper limit and lower limit of the compositional distribution in $Pb(Zr_xTi_{1-x})O_3$) was also measured.[12] Relation between width of the compositional distribution and soaking time is shown in Fig. 3 (open circle). The width of the distribution of composition of calcined material is plotted at sintering time = 0. As the sintering period increased, the width of the compositional distribution decreased. This is caused from diffusion during the sintering. Inhomogeneous solid solutions have a tendency toward homogenization. This tendency is achieved by diffusion. Thus, the homogenization process can be considered to be parallel with sintering process.

Fig. 4 (close circle) shows a relation between bulk densities of sintered body and soaking time at 800 °C by SPS method. The starting material calcined was the same as that for the normal sintering. SPS was performed at 800 °C. The higher temperature is not required and is not appropriate in SPS method. SPS is performed in vacuo. The evaporation of PbO from sample becomes serious in vacuo at higher temperatures. At 800 °C, the sintering rate was very high. The density was 98% after soaking for 10 min. Relation between width of the compositional distribution and soaking time for samples sintered by SPS method is shown in Fig. 4 (open circle). From sintering results, data within 15 min were determined, because it reached almost theoretical density by a sintering for 15 min. Change in the width of the compositional distribution was little. The width of the compositional distribution of the calcined powder was $\Delta x = 0.2$. The initial compositional distribution in the starting calcined powder was maintained under those conditions.

Behavior of the change of the compositional distribution during a sintering by hotpressing was also examined, because hotpressing is similar to SPS in the point that both methods use uniaxial pressure. Fig. 5 shows the width of the compositional distribution (open circle) and sintered density (close circle) as a function of sintering temperature by hotpressing. The soaking time was 15 min. Sintered density increases as the sintering temperature increases. The width of the compositional distribution decreases as the sintering temperature increases. In this point, the behavior is similar to the normal sintering, except that hotpressing results higher sintered density.

Considering that the sintering conditions of SPS are at 800 °C for few minutes, it is not strange that the change in the compositional distribution in Fig. 4 was little. However, it is noteworthy that the sample that has high sintered density has still large compositional distribution. It is more important to consider the relation between width of the compositional distribution and sintered density than that between width of the compositional distribution and sintering conditions. Fig. 6 shows the relation between width of the compositional distribution and bulk density. Double circle is a plot for the powder compact before the sintering. By the normal sintering method, the width of the compositional distribution decreases as the bulk density increases. This is a typical phenomenon. Sintering is achieved by diffusion at firing temperatures, and diffusion also plays a role of homogenization, i.e. decrease in the width of the compositional distribution. Although the degree of the decrease in the width of the compositional distribution by hotpressing is smaller than that by normal sintering, the width of the compositional distribution decreased as the

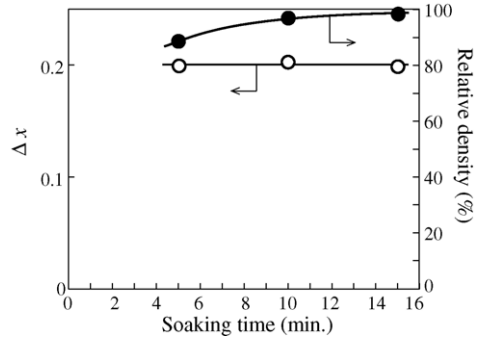


Fig. 4. Change in width of compositional distribution and sintered density with sintering time by SPS for $Pb(Zr_{0.3}Ti_{0.7})O_3$. Calcination: 800 °C/2 h. SPS: 800 °C.

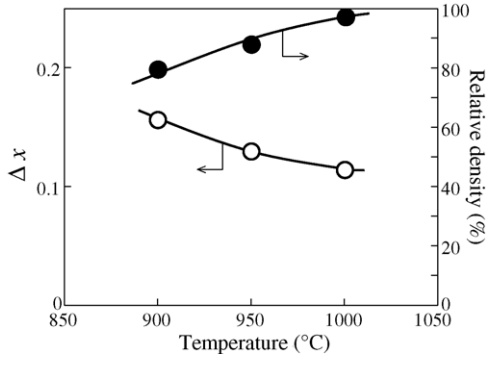


Fig. 5. Change in width of compositional distribution and sintered density with sintering temperature by hotpressing for $Pb(Zr_{0.3}Ti_{0.7})O_3$. Calcination: 800 °C/2 h. Hotpressing: 15 min.

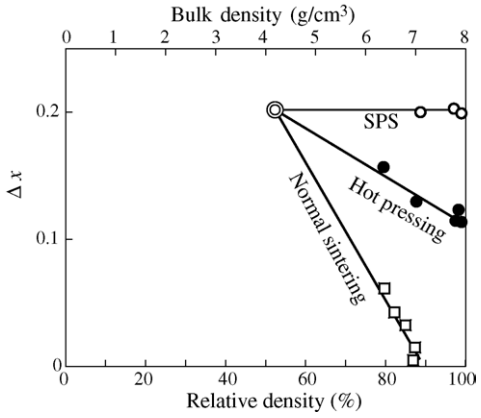


Fig. 6. Relation between width of compositional distribution and sintered density for normal sintering, SPS and hotpressing.

sintered density increased. Compared with these results, it is worth to be focused that by SPS the sintered density reached almost the theoretical value without changing the width of the compositional distribution. Only SPS enables a production of sintered body having compositional distribution that is introduced by design in the starting material.

From the results thus far, it is expected that a combination of properties can be possible by preparing a mixture of compositions having different electric properties and sintering by SPS. Calcined powders of $PbTiO_3$-$PbZrO_3$-$Pb(Zn_{1/3}Nb_{2/3})O_3$ system having compositions, A: $PbZr_{0.9}(Zn_{1/3}Nb_{2/3})_{0.1}O_3$, B: $PbTi_{0.025}Zr_{0.9}(Zn_{1/3}Nb_{2/3})_{0.075}O_3$, C: $PbTi_{0.05}Zr_{0.9}(Zn_{1/3}Nb_{2/3})_{0.05}O_3$, D: $PbTi_{0.012}Zr_{0.9}(Zn_{1/3}Nb_{2/3})_{0.088}O_3$ and E: $PbTi_{0.038}Zr_{0.9}(Zn_{1/3}Nb_{2/3})_{0.062}O_3$ were prepared. Pyroelectric properties of these compositions after sintering by the normal method at 1200 °C are shown in Fig. 7. A, B and C have pyroelectric peaks at 0 °C, 25 °C and 50 °C, respectively, and D and E have peaks at 12.5 °C and 37.5 °C, respectively.

Calcined powders of A, B and C were mixed and sintered by the normal sintering method. The pyroelectric property of this material is shown in Fig. 8. In this case, only a single peak was observed. This was caused from a homogenization during sintering. The sintered material does not have the initial compositional distribution.

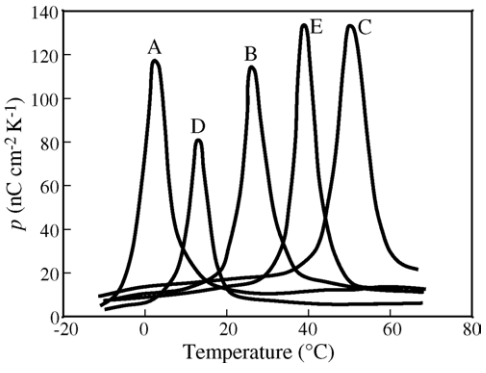


Fig. 7. Pyroelectric coefficient as a function of temperature for A: $PbZr_{0.9}(Zn_{1/3}Nb_{2/3})_{0.1}O_3$, B: $PbTi_{0.025}Zr_{0.9}(Zn_{1/3}Nb_{2/3})_{0.075}O_3$, C: $PbTi_{0.05}Zr_{0.9}(Zn_{1/3}Nb_{2/3})_{0.05}O_3$, D: $PbTi_{0.012}Zr_{0.9}(Zn_{1/3}Nb_{2/3})_{0.088}O_3$ and E: $PbTi_{0.038}Zr_{0.9}(Zn_{1/3}Nb_{2/3})_{0.062}O_3$. Calcination: 900 °C/1 h. Sintering: 1250 °C/1 h (normal sintering).

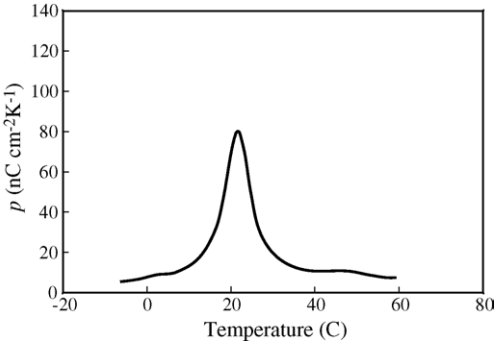


Fig. 8. Pyroelectric coefficient as a function of temperature for a sintered body by normal sintering at 1250 °C for 1 h from a mixture of A, B and C.

Calcined powders of A, B, C, D and E were mixed and sintered by SPS. The pyroelectric property of this material is shown in Fig. 9. Contrary to the result by the normal sintering, pyroelectric peaks corresponding to the initial compositions were remained. Therefore, SPS method enables combinations of properties of different compositions.

Although properties of five compositions can be combined as shown in Fig. 9, the pyroelectric property has still dips in the range between 0 °C and 50 °C. It needs more compositions in the starting mixture in order to eliminate such dips. Then we tried to obtain the property having trapezoidal *p–T* curve by a partial diffusion from two compositions. Sintered material of a mixture of B and C by SPS had pyroelectric peaks at 25 °C and 50 °C. When it was heated, the shape of the peaks changed. When it was heated at 950 °C for 1 h, the trapezoidal *p–T* curve was obtained. The pyroelectric property for the material such prepared is shown in Fig. 10. The heat-treatment allows a partial diffusion in the sintered material. This method has an advantage that only two compo-

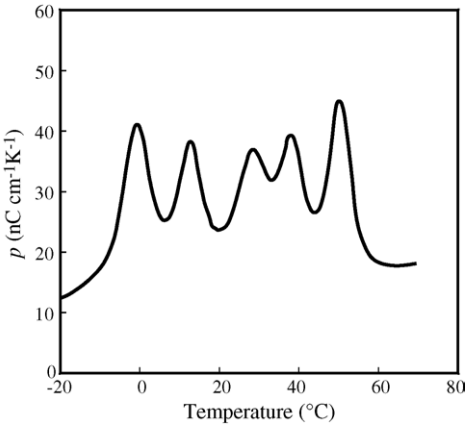


Fig. 9. Pyroelectric coefficient as a function of temperature for sintered body by SPS from a mixture of five compositions. Calcination: 1200 °C/1 h. SPS: 800 °C/10 min. Reoxidation: 800 °C/20 min.

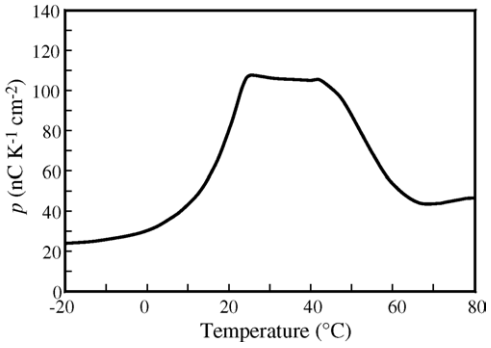


Fig. 10. Pyroelectric coefficient as a function of temperature for a material from a mixture of B and C, which was sintered by SPS and heat-treated. Calcination: B: 1100 °C, C: 1150 °C. SPS: 800 °C/10 min. Heat-treatment: 950 °C/1 h.

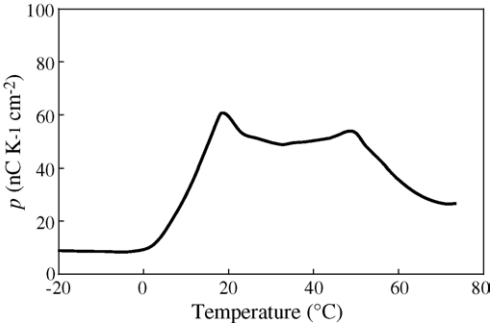


Fig. 11. Pyroelectric coefficient as a function of temperature for an SPS-sintered material from a heat-treated mixture of B and C. Calcination: 1050 °C/1 h. Heat-treatment: 1050 °C/1 h. SPS: 800 °C/10 min. Reoxidation: 800 °C/20 min.

sitions are needed for the starting material, and flat property in the wide temperature range can be obtained.

In the above-mentioned method, partial-diffusion treatment was carried out after sintering. Partial-diffusion treatment was also carried out before sintering. Mixture of calcined powders of B and C was heat-treated under various conditions and sintered at 800 °C for 10 min by SPS. When the mixture was heat-treated at 1050 °C for 1 h the property having trapezoidal *p–T* curve was obtained. The property is shown in Fig. 11. This method has similar advantages to the method that diffusion-treatment is carried out after sintering. The difference of the values of the pyroelectric coefficient between Figs. 10 and 11 may be due to the difference of the sintering temperature.

## 4. Conclusions

It was revealed that only SPS method can sinter materials without changing initial compositional distribution. Using these characteristics, combination of pyroelectric properties of different compositions was enabled. In addition combination of SPS and diffusion-treatment produced pyroelectric material that have high pyroelectric coefficient in the region between 25 °C and 50 °C.

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