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Journal of the European Ceramic Society 26 (2006) 613–617

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Design of pyroelectric properties by controlling compositional distribution

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Available online 10 August 2005

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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doi:10.1016/j.jeurceramsoc.2005.07.013

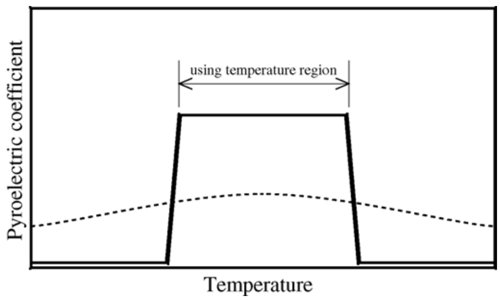

Fig. 1. Ideal pyroelectric property (trapezoid, solid line) and broadened pyroelectric property (dotted line).

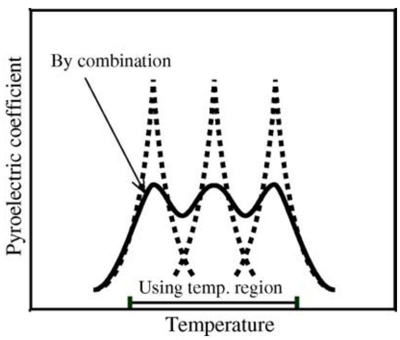

Fig. 2. Combined pyroelectric property (solid line).

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 (β) 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