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Low Temperature Sintering of PZT Powders Coated with $Pb_5Ge_3O_{11}$ by Sol–Gel Method

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Abstract

Low temperature sintering of PZT powders was investigated using $Pb_5Ge_3O_{11}$(PGO) as a sintering aid. PZT powders with 150 nm particle size were coated with PGO which was prepared from precursor solutions of $Ge(OiPr)_4$ and $Pb(NO_3)_2$ by sol–gel method. 1 wt% PGO-added PZT powders were densified at 750°C for 2 h to sintered bodies with the relative density of approximately 95%. An addition of PGO improved the sinterability of PZT powders with a reduction of sintering temperature by about 300°C. Dielectric and piezoelectric properties of PGO-added PZT ceramics sintered at ≦950°C were superior to those without PGO additives. However, a higher sintering temperature above 1000°C deteriorated the dielectric and piezoelectric properties of PGO-added PZT ceramics. This may be attributed to the change of microstructure involving the formation of solid solution between PZT and PGO. The 1 wt% PGO-added PZT bodies sintered at 750°C exhibited an electromechanical coupling factor, Kp, of about 56%. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: low temperature sintering, sol–gel processes, piezoelectric properties, PZT.

1 Introduction

It is known that the sintering temperature of lead zirconate titanate (PZT) ceramics is above 1200°C. The compositional control and environmental pollution become a serious problem owing to the volatility of lead oxide at such a high temperature. Low sintering process will afford the advantages of improving the reproducibility, reducing the energy consumption and decreasing the pollution. In general, the sintering temperature of ceramics can be reduced by doping with low melting additives. However, some research results indicated that electrical properties of sintered ceramics with sintering aids are degraded. Thus, lead germanium oxide($Pb_5Ge_3O_{11}$:PGO)[1] is expected to be effective as a sintering aid for PZT, because it is a ferroelectric material with the melting point as low as 738°C. It is very important to disperse homogeneously a small amount of sintering aids in the matrix and to control the microstructure of these materials in order to improve their electrical properties and reliability. Hayashi *et al.*[2–5] demonstrated that chemical processing of Nb_2O_5-coated oxides with surface modification through the hydrolysis of metal alkoxides was very promising for the preparation of functional composite materials.

This paper describes the preparation of PGO-added PZT ceramics using sol-gel process. Dielectric, ferroelectric and piezoelectric properties of these samples are also described.

2 Experimental Procedures

PZT powders were prepared using a solid state reaction at 700°C for 2 h between lead oxide(PbO) and zirconium titanium oxide ($Zr_{0.52}Ti_{0.48}O_2$) synthesized by the hydrothermal technique.[6] The purity of raw materials was greater than 99·9%. PZT powders obtained thus were ground by ball milling in ethanol for 48 h. The particle size was about 150 nm.

Figure 1 shows the flow diagram for preparation of PGO-coated PZT composite powders. Ge(O-i-Pr)$_4$ and $Pb(NO_3)_2$ were mixed together in ethyleneglycol and heated at 80°C for 1 h, and then the resulting PGO precusor solutions were added to PZT aqueous suspensions, followed by heating at 80°C for 1 h. PGO-coated PZT powders were ultrafiltered and washed with propanol, and then dried. The content of PGO was varied with 1 to 4 wt%. These powders were pressed, and sintered at 700–1000°C for 2 h. After the sintered disc

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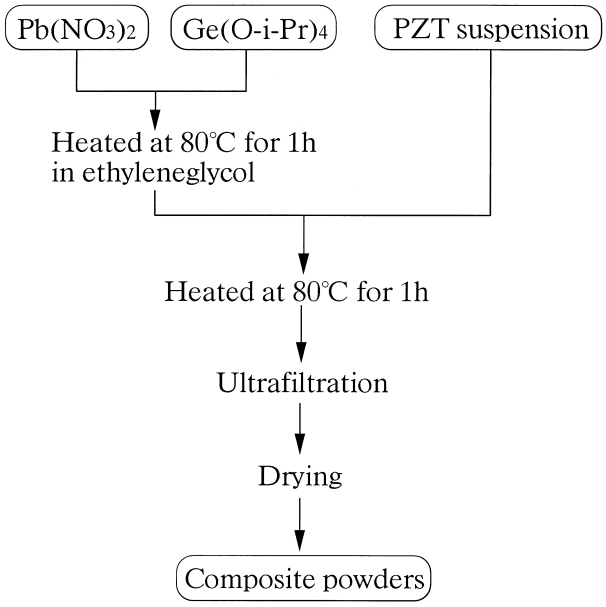

Fig. 1. Flow diagram for preparation of PZT with PGO additive.

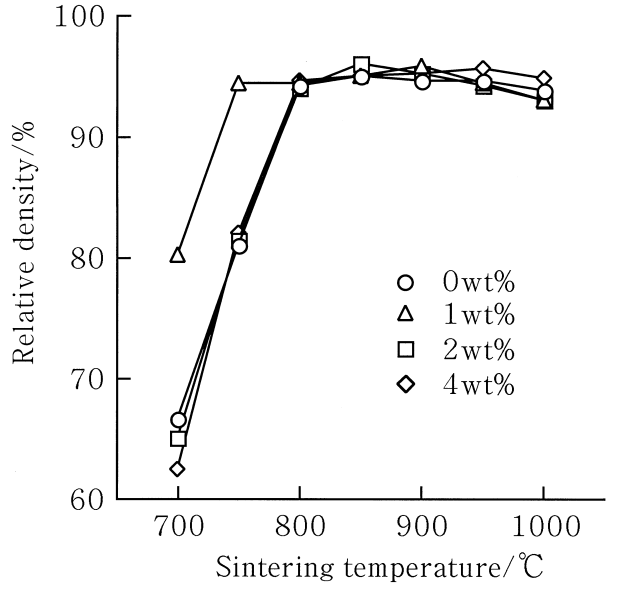

Fig. 2. Relative density of PGO-added PZT sintered bodies as a function of sintering temperature.

samples were polished, fired-on silver paste was applied on both surfaces of the samples as electrodes. The samples were poled at 120°C for 1 h under an electric field of 20 kV/cm in silicone oil. The microstructure and the chemical composition of sintered bodies were observed by a field-emission scanning electron microscope (FE-SEM) and electron probe X-ray microanalyzer (EPMA). The dielectric and piezoelectric properties were measured by an impedance analyzer (YHP-4192A). The polarization-electric field (P-E) hysteresis loops were measured by a Sawyer-Tower circuit at 50 Hz.

3 Results and Discussion

3.1 Physical properties and surface morphology

Figure 2 shows the relative density of PZT sintered bodies with various amounts of PGO additive as a function of sintering temperature. An addition of 1 wt% PGO improved remarkably the sinterability of PZT powders. The 1 wt% PGO-added PZT bodies sintered at 750°C showed a high relative density of 95%. However, an addition of more than 2 wt% PGO deteriorated the sinterability of PZT.

Figure 3 shows the grain size of PGO-added PZT sintered bodies as a function of sintering temperature. An addition of PGO promoted considerable grain growth. This may be due to the liquid phase sintering with addition of PGO.

Figures 4 and 5 show FE-SEM micrographs and EPMA image of surfaces of PGO-added PZT bodies sintered at 950°C and 1000°C. Secondary phase existed along the PZT grain boundary at

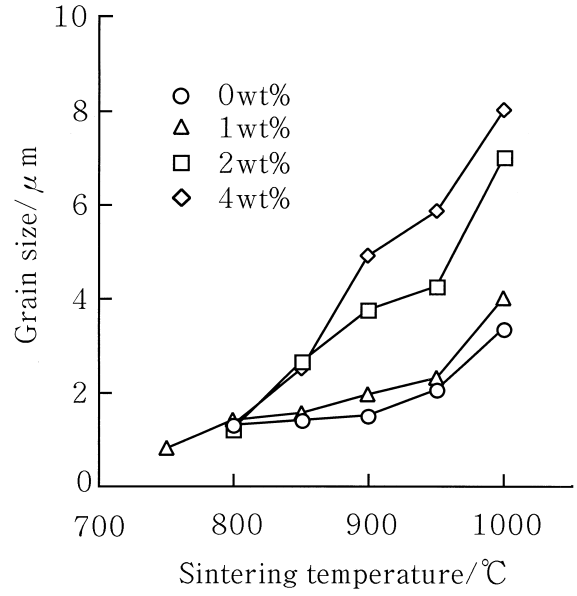

Fig. 3. Grain size of PGO-added PZT sintered bodies as a function of sintering temperature.

sintering temperatures of ≦950°C, as shown in Fig. 4(a). From results of EPMA, it was clarified that germanium was contained in the grain boundary of PZT bodies sintered at 950°C, as shown in Fig. 5. In contrast, the secondary phase could not be observed at the grain boundary of bodies sintered at 1000°C, as shown in Fig. 4(b). This result suggests the formation of solid solution between PZT and PGO at a higher sintering temperature.

3.2 Dielectric and piezoelectric properties

Figure 6 shows dielectric constants of PZT sintered bodies as a function of sintering temperature. The dielectric constants of PGO-added PZT bodies

sintered at ≦950°C were much higher than those of PZT sintered bodies without PGO additive. However, the dielectric constants of PZT sintered bodies without PGO additive increased with increase of sintering temperature from 800 to 1000°C, while in the PGO-added PZT sintered bodies the dielectric constants decreased rapidly from 1500 to 1000 at sintering temperatures above 900°C.

Figure 7 shows the electromechanical coupling factor, Kp, of PZT sintered bodies as a function of sintering temperature. One weight percent PGO-added PZT bodies sintered at 750 and 800°C showed a Kp of 56%. However, the values of Kp of PGO-added PZT sintered bodies decreased rapidly with increase of sintering temperature from 850 to 1000°C. This may be related to the formation of solid solution between PZT and PGO involved with the disappearance of secondary phase, as shown in Fig. 4.

Figure 8 shows P-E hysteresis loops of PZT bodies sintered at 750 and 800°C. The well-saturated

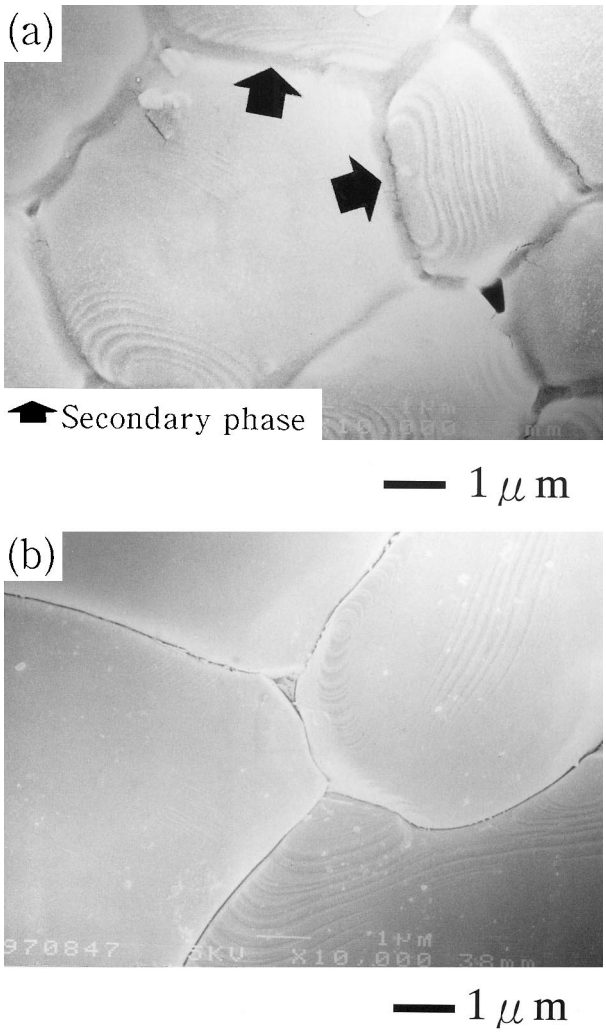

Fig. 4. FE-SEM micrographs of surfaces of PGO-added PZT bodies sintered at (a) 950°C and (b) 1000°C.

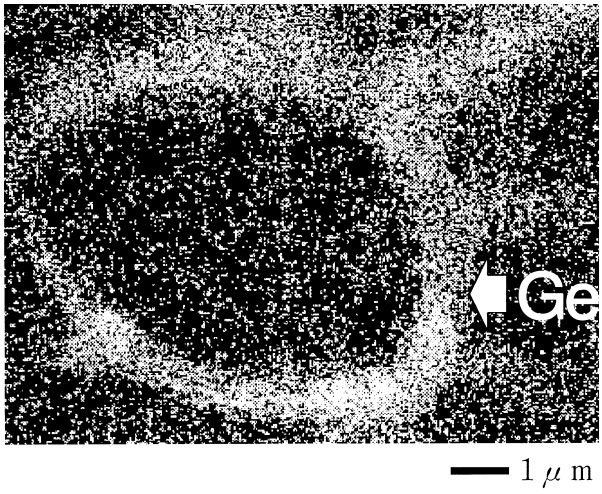

Fig. 5. EPMA image of PGO-added PZT bodies sintered at 950°C.

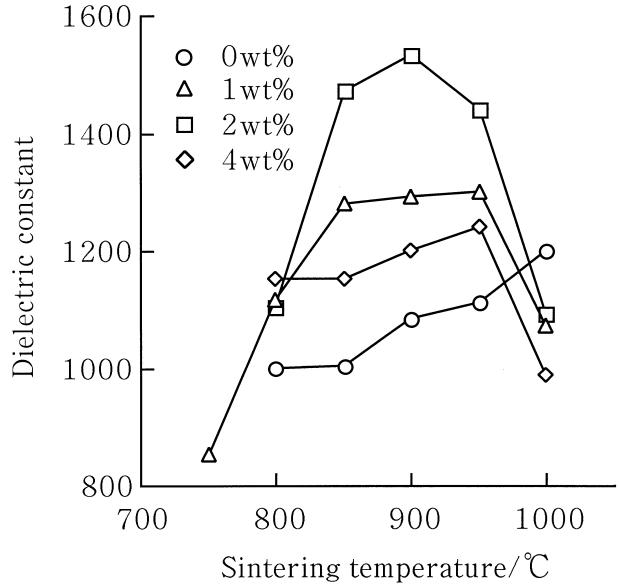

Fig. 6. Dielectric constant of PGO-added PZT sintered bodies as a function of sintering temperature.

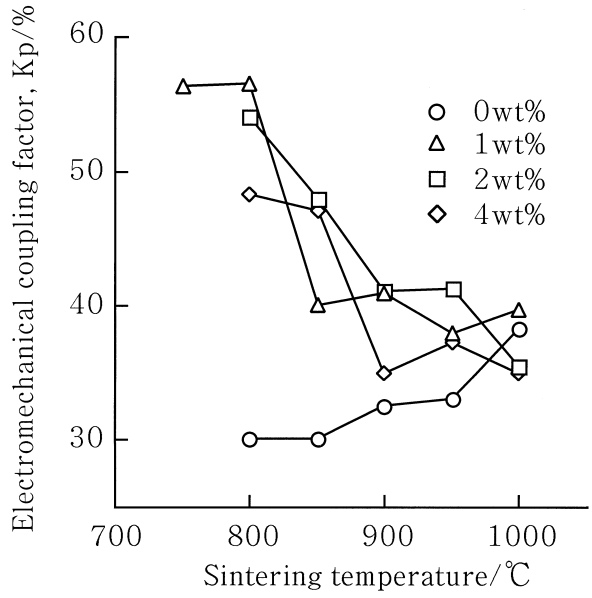

Fig. 7. Electromechanical coupling factor, Kp, of PGO-added PZT sintered bodies as a function of sintering temperature.

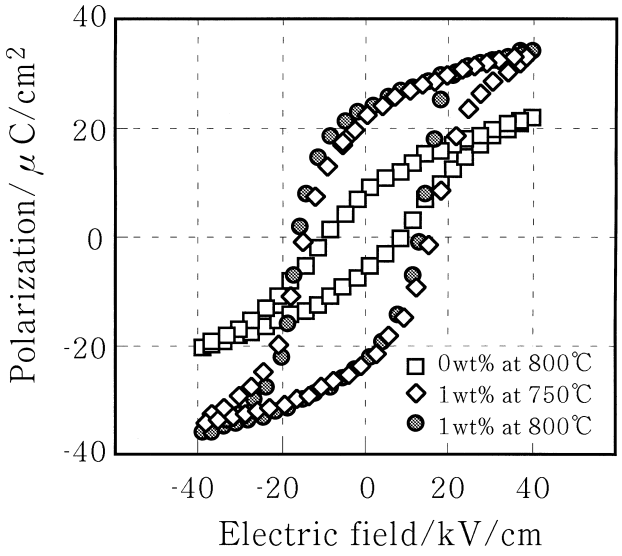

Fig. 8. P–E hysteresis loops of PGO-added PZT sintered bodies.

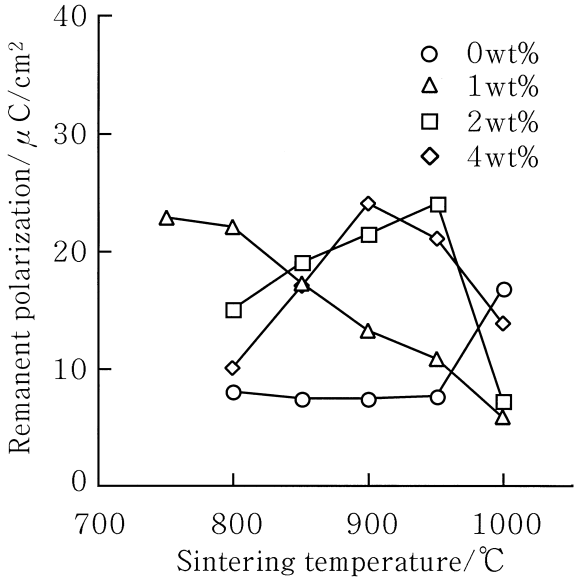

Fig. 9. Remanent polarization, Pr, of PGO-added PZT sintered bodies as a function of sintering temperature.

hysteresis loops were obtained for 1 wt% PGO-added PZT bodies sintered at 750°C. The P-E hysteresis loops of 1 wt% PGO added PZT bodies sintered at 750 and 800°C were superior to those with no addition of PGO. The values of remanent polarization, Pr, and coercive field, Ec, were 22(μC cm^{-2}) and 15(kVcm^{-1}), respectively.

Figure 9 shows the value of Pr as a function of sintering temperature. The 1 wt% PGO-added PZT sintered bodies exhibited a higher Pr value, compared to PZT sintered bodies without PGO additive. But, the dielectric and piezoelectric properties of PGO-added PZT sintered bodies were degraded at a higher sintering temperature above 800°C.

4 Conclusions

Low temperature sintering, microstructural development and dielectric properties of PGO-added PZT ceramics were investigated. The grain boundary phase containing germanium was observed in PGO-added PZT bodies sintered at ≦950°C. An addition of PGO improved dielectric and piezoelectric properties of PZT ceramics at sintering temperatures from 800 to 950°C. However, the properties were deteriorated at a higher sintering temperature because of the formation of solid solution between PZT and PGO. The best piezoelectric properties were found for 1wt% PGO-added PZT bodies sintered at the temperatures of 750 to 800°C. The value of Kp is approximately 56%.

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