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Low-temperature sintering and electrical properties of PGO-doped PNN-PZT ceramics

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Densification, microstructures and electrical properties were investigated in $Pb_5Ge_3O_{11}$ (PGO)-doped $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbZrO_3$-$PbTiO_3$ (PNN-PZT) ceramics sintered at 900 °C and lower. PNN-PZT ceramics with a density of about 7.772 g/cm^3 or higher, could be prepared at a sintering temperature of 800 °C by adding 1-3 wt% PGO. PGO-doping increased effectively the sintered density and the average grain size of PNN-PZT ceramics at a low sintering temperature of around 800 °C. Bulk density, dielectric constant and piezoelectric constant of the 1 wt% PGO doped PNN-PZT ceramic were 8.02 g/cm^3, 2231 and 387 pC/N at a sintering temperature of 850 °C.

Key words: piezoelectric, PNN-PZT ceramics, $Pb_5Ge_3O_{11}$, sintering.

Introduction

$Pb(Zr,Ti)O_3$(PZT)-based piezoelectric ceramics have been applied to ultrasonic vibrators, filters, sensors, actuators, etc. Multilayer-structured PZT ceramics are being used in many applications such as actuators, transformers etc because of their small size and high performance [1-3]. Multilayer-structured PZT ceramics are fabricated by co-firing tape-cast ceramic sheets and noble metal internal electrodes such as Ag/Pd. In order to reduce the amount of the expensive noble metal, many efforts have been made to reduce the sintering temperature of PZT ceramics [3, 4]. If the sintering temperature could be reduced to 900 °C or lower, base metal electrodes such as Ag and Cu could be used as internal electrodes. Recently, piezoelectric microelectromechanical system (MEMS) devices such as microactuators and microsensors have been fabricated by micromachining piezoelectric thin or thick films on silicon substrates [5-8]. A screen printing method has been widely applied to thick film fabrications due to its cost effectiveness and because it is a simple manufacturing process [9, 10]. PZT thick films for MEMS devices should, however, be fired at a low temperature around or below 900 °C for compatibility with silicon micromachining technology.

Undoped PZT ceramics are sintered at a temperature higher than 1200 °C. The most common and effective method to reduce the sintering temperature of PZT ceramics is to add low-temperature melting compounds for liquid phase sintering at a low temperature [3-4, 11-18]. Many researchers have successfully reduced the sintering temperature of PZT ceramics by using various additives such as B_2O_3-Bi_2O_3-CdO, Li_2CO_3-Bi_2O_3-CdO, V_2O_3-PbO, $LiBiO_2$, CuO, CuO+ZnO, $BiFeO_3$, CuO+Bi_2O_3, Li_2CO_3, etc. [3-4, 11-18]. In many cases, these additives facilitate the sintering at a low temperature, but reduce the piezoelectric properties due to the formation of piezoelectrically-inactive phases in the grain boundary regions at the same time and show better dielectric and piezoelectric properties when sintered at a higher temperature than that for the largest sintered density [14, 17, 19, 20]. Most low-temperature PZT compositions show the best piezoelectric properties at a temperature of 900-1100 °C, but a lower sintering temperature gives more advantages for the processing on multilayer and MEMS piezoelectric devices.

There are only a few reports in which PZT ceramics showed excellent piezoelectric properties at a sintering temperature of 900 °C or lower. Zhilun *et al*. have reported that $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbZrO_3$-$PbTiO_3$ (PNN-PZT) ceramics, in which 2 mole% Pb was substituted by Cd, had excellent dielectric and piezoelectric properties at a sintering tem- perature around 900 °C. According to their report, the addition of both SiO_2 and Pb_3O_4 reduced the sintering temperature to 900 °C in PNN-PZT ceramics [11]. They explained that a liquid phase was formed from the eutectic melt of PbO-SiO_2 which promoted densification in the initial and intermediate stages of sintering and then was reabsorbed in the final stage of sintering. This transient liquid phase sintering, in which the undesired inactive glassy phases do not remain in the grain boundary regions, is one of the effective ways for low-temperature sintering of piezoelectric ceramics. Another approach is to use piezoelec- tric materials with a low melting temperature as a sintering additive. $Pb_5Ge_3O_{11}$

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(PGO) has been tried as a sintering aid for piezoelectric ceramics and thick films because PGO is a ferroelectric and melts about 738 °C [20-22] Hayashi *et al*. could reduce the sintering temperature of nano-sized PZT powders from 800 to 750 °C by coating with PGO, prepared from a precursor solution of $Ge(OiPr)_4$ and $Pb(NO_3)_2$ by a sol-gel method [21]. PGO also decreased the sintering temperature of $(Pb,Ba,Sr)(Zr,Ti,Sb)O_3$ (PBSZT) ceramics by more than 200 °C in all solid state process; PBSZT ceramics with 1 wt% PGO showed a high density of 7.5 g/cm^3 at a sintering temperature of 800 °C. But the dielectric and piezoelectric properties showed very low values at a sintering temperature of 800-900 °C due to the formation of a second phase [20].

In this study, $Pb_5Ge_3O_{11}$ (PGO) was selected as a sintering aid in a 2 atomic % Cd-substituted PNN-PZT ceramic which had been reported to show excellent piezoelectric properties at a sintering temperature of 900 °C. The densification, microstructures and electrical properties were investigated in PGO-doped PNN-PZT ceramics sintered at 900 °C and lower.

Experimental Procedure

$0.25Pb(Ni_{1/3}Nb_{2/3})O_3$-$0.35PbZrO_3$-$0.40PbTiO_3$ (PNN-PZT) in which 2 atomic % Pb was substituted by Cd was prepared by a conventional ceramic process. $NiNb_2O_6$ was synthesized by calcining a mixture of NiO and Nb_2O_5 powder at 1300 °C for 1 hour. The $NiNb_2O_6$ phase formation was confirmed by X-ray diffraction analysis. PbO, ZrO_2, TiO_2, CdO and $NiNb_2O_6$ powder were mixed in the desired mol ratio by ball milling for 24 hours, dried on a hot plate and calcined at 800 °C for 3 hours in air. It was confirmed that the perovskite PNN-PZT phase was formed without any second phase after calcination. $Pb_5Ge_3O_{11}$ (PGO) powder was synthesized by calcining a mixture of PbO and GeO_2 powder at 600 °C for 2 hours. The PGO powder was added to the calcined PNN-PZT powder and ball-milled for 12 hours and dried on a hot plate. The dried powder was compacted into disk-shaped samples using a mold with a diameter of 9 mm under a pressure of about 50 MPa. The compacted samples were sintered at 750-900 °C for 1 hour. Phases were identified using an X-ray diffractometer (Shimadzu, XD-D1) and microstructures were observed using a field emission scanning electron microscope (Hitachi, S-4300). Ag paste was printed on the surfaces of the sintered samples and fired at 650 °C for 10 minutes. Capacitances and dielectric losses were measured using an impedance analyzer (HP4192A). The samples were poled in a silicon oil at 120 °C by applying a dc electric field of 2.5 kV/mm for 30 minutes. Piezoelectric constants (d_{33}) of the poled samples were measured using a d_{33} tester (APC International Ltd.).

Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of PGO-doped PNN-PZT ceramics sintered at 850 °C for 1 hour. No second phase was observed in the undoped and PGO-doped PNN-PZT ceramics. This is contrary to the report by Hayashi *et al*. [20] in which a second phase was observed in X-ray diffraction patterns of PBSZT ceramics. This indicates that PGO does not react with the PNN-PZT phase and form a second phase when sintered at 850 °C.

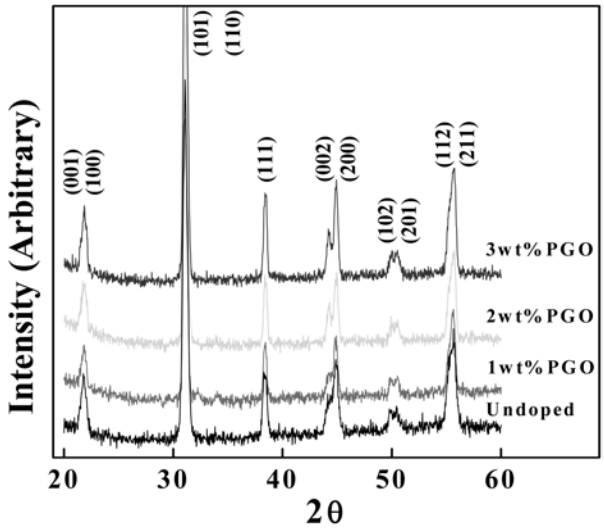

Fig. 1. X-ray diffraction patterns of undoped and PGO-doped PNN-PZT ceramics sintered at 850 °C.

Fig. 2 demonstrates the variation of the bulk density with the sintering temperature. The bulk density of an undoped PNN-PZT ceramic was increased continuously from 5.00 to 6.97 g/cm^3 when the sintering temperature was increased from 750 °C to 900 °C. The bulk densities of PGO-doped PNN-PZT ceramics, however, increased at first when the sintering temperature rose from 750 °C to 800 °C and saturated at a temperature above 800 °C. The 3 wt% PGO-

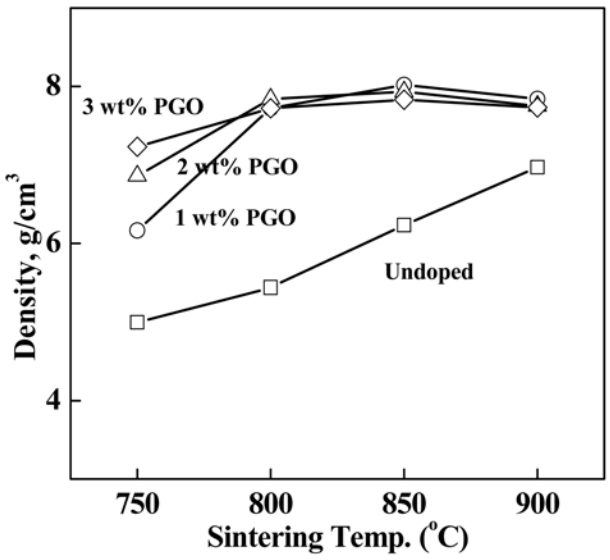

Fig. 2. Variation of the density with the sintering temperature in undoped and PGO-doped PNN-PZT ceramics.

doped PNN-PZT ceramic showed the largest bulk density at a sintering temperature of 750 °C, but the bulk densities of PGO-doped PNN-PZT ceramics were almost saturated at 800 °C, regardless of the PGO content. Fig. 2 illustrates that the sintering temperature of the PNN-PZT ceramics was effectively reduced to 800 °C by adding PGO. The PGO is thought to form a liquid phase when PNN-PZT ceramics were sintered at 750 °C and above because the melting temperature of PGO is about 740 °C. The liquid phase facilitated the densification of PNN-PZT ceramics effectively during the sintering. 1 wt% PGO is thought to form a sufficient amount of liquid phase for the densification of PNN-PZT ceramics at a sintering temperature of 800 °C and above, while 3 wt% PGO or more was needed for the effective densification at a sintering temperature of 750 °C.

Microstructures of the PNN-PZT ceramics sintered at and above 800 °C are shown in Fig. 3. PGO-doped PNN-PZT ceramics show a denser microstructure than the undoped one, which is consistent with the densities in Fig. 2. The grain size increased with the sintering temperature in all samples and was larger in the PGO-doped PNN-PZT ceramics than the undoped one. Fig. 3 also discloses that PGO doping by more than 1 wt% had little effect on the grain size of the PNN-PZT ceramics sintered at and above 800 °C.

The dielectric constants of the PNN-PZT ceramics are shown in Fig. 4. The dielectric constant of the undoped PNN-PZT ceramic increased continuously from 383 to 1478 when the sintering temperature rose from 750 °C to 900 °C. The dielectric constants of the PGO-doped PNN-PZT ceramics increased rapidly when the sintering temperature increased from 750 °C to 800 °C, and then increased gently or were saturated at a sintering temperature above 800 °C.

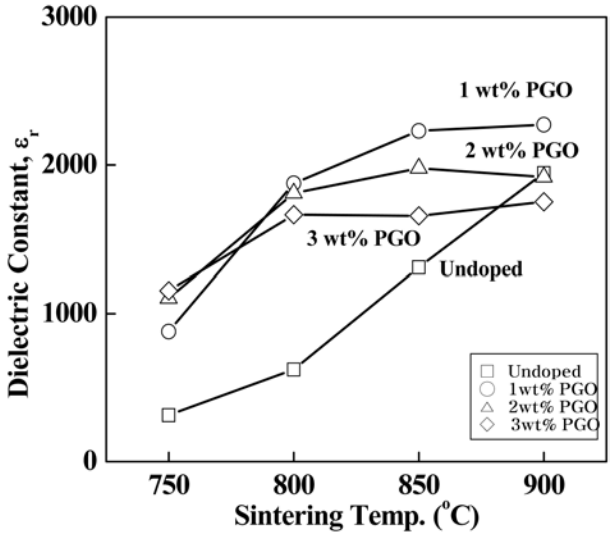

Fig. 4. Variation of the dielectric constant with the sintering temperature in undoped and PGO-doped PNN-PZT ceramics.

This is very similar to the change in the density with the sintering temperature. The dielectric constant showed the largest value in the PNN-PZT ceramic doped with 1 wt% PGO and decreased with an increase of the amount of PGO at a sintering temperature above 800 °C. The addition of more than 1 wt% PGO is thought to result in the formation of a second phase with a low dielectric constant or change the composition of the PNN-PZT ceramics in the grain boundary regions, which deteriorates the dielectric property in PGO-doped PNN-PZT ceramics. Actually, the dielectric constant of pure PGO is less than 40. A small increase of

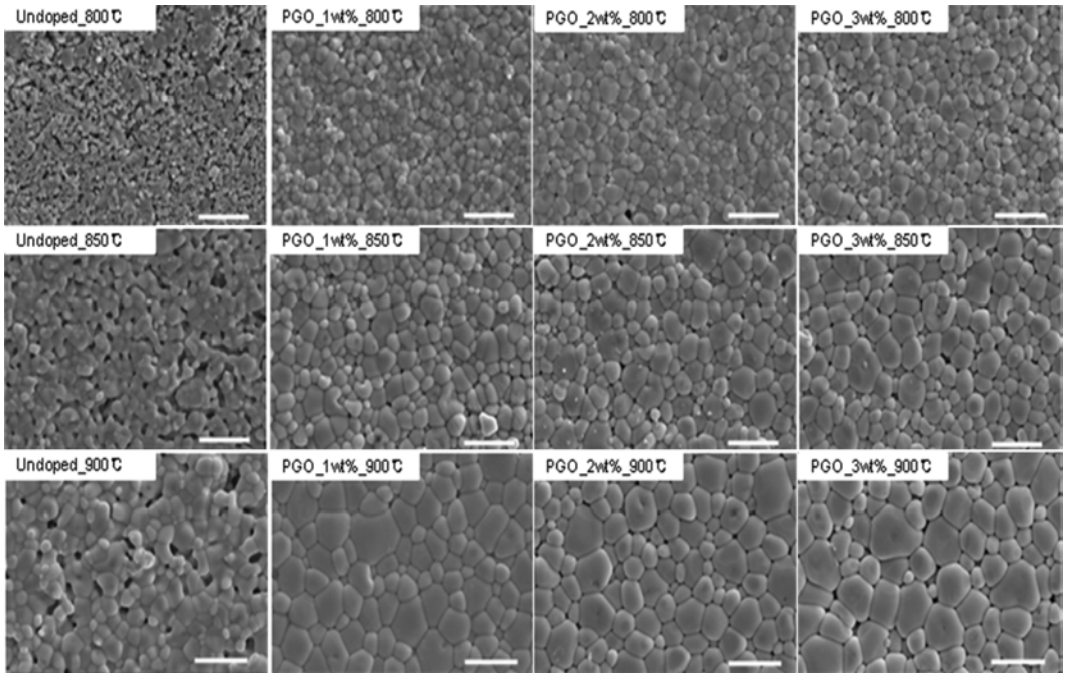

Fig. 3. Microstructures of (a) undoped, (b) 1 wt% PGO-doped, (c) 2 wt% PGO-doped, and (d) 3 wt% PGO-doped PNN-PZT ceramics sintered at various temperatures. (scale bar: 5 m)

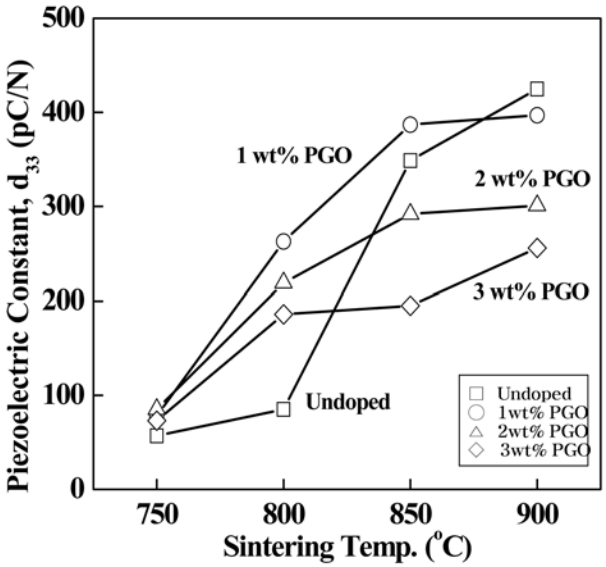

Fig. 5. Variation of the piezoelectric constant (d_{33}) with the sintering temperature in undoped and PGO-doped PNN-PZT ceramics.

the dielectric constant with an increase of the sintering temperature above 800 °C in the 1 wt% PGO-doped PNN-PZT ceramic seems to be caused by the increase of grain size.

Fig. 5 shows the variation of the piezoelectric constant (d_{33}) of the PNN-PZT ceramics with a change of the sintering temperature. The piezoelectric constant changed with the sintering temperature in a very similar manner as the dielectric constant shown in Fig. 4. The piezoelectric constant of the PGO-doped PNN-PZT ceramics increased with the sintering temperature up to 850 °C and then saturated above 850 °C. The PNN-PZT ceramic doped with 1 wt% PGO shows a higher piezoelectric constant over those doped with a larger amount of PGO at a sintering temperature above 800 °C. Fig. 5 also shows that the a undoped PNN-PZT ceramic has a higher piezoelectric constant than the PGO-doped ceramics sintered at 900 °C even though the density of the undoped one was lower than those of the PGO-doped ceramics sintered at 900 °C. This illustrates that a large amount of a liquid phase formed during sintering deteriorates the piezoelectric constant more seriously than the dielectric constant in PGO-doped PNN-PZT ceramics.

From the above results, PGO was confirmed as a very effective sintering aid for PNN-PZT ceramics at a sintering temperature lower than 900 °C. The 1 wt% PGO-doped PNN-PZT ceramic exhibited the best electrical properties at a sintering temperature at and above 800 °C.

Conclusions

$Pb_5Ge_3O_{11}$ (PGO) was added as a sintering aid to the 2 atomic % Cd-substituted $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbZrO_3$-$PbTiO_3$ (PNN-PZT) ceramics. PGO-doping increased effectively the sintered density and the average grain size of PNN-PZT ceramics when sintered at a temperature of 750 °C-900 °C. The PNN-PZT ceramics with a density of about 7.772 g/cm^3 or higher, could be prepared at a sintering temperature of 800 °C by adding 1-3 wt% $Pb_5Ge_3O_{11}$ (PGO). The 1 wt% PGO-doped PNN-PZT ceramic shows the best electrical properties at a sintering temperature of 800 °C or above. The bulk density, dielectric constant and piezoelectric constant of the 1 wt% PGO doped PNN-PZT ceramic were 7.72 g/cm^3, 1877 and 263 pC/N at a sintering temperature of 800 °C and 8.02 g/cm^3, 2231 and 387 pC/N at a sintering temperature of 850 °C.

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