Dielectric and Pyroelectric Properties of Y-modified PSS-PT-PZ Ceramics

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(Received November 25 2004, Accepted April 6 2005)

$0.10Pb(Sb_{1/2}Sn_{1/2})O_3$-$0.25PbTiO_3$-$0.65PbZrO_3$ specimens doped with MnO_2 (0.18 mol%) and Y_2O_3 (0~0.4 wt%) were fabricated by the mixed-oxide method. All specimens showed the typical XRD patterns of a perovskite polycrystalline structure and the lattice constant decreased with increasing amount of Y_2O_3. The relative dielectric constant and the dielectric loss of the specimens doped with 0.2 wt% Y_2O_3 were 704 and 0.0201, respectively. The remanent polarization, the coercive field and the pyroelectric coefficient of the specimen doped with 0.2 wt% Y_2O_3 were $10.88x10^{-2}$ Cm^{-2}, $11.12x10^2$ kVm^{-1} and $5.03x10^{-4}$ $Cm^{-2}K^{-1}$ at 25 °C, respectively. The figures of merit, F_V for the voltage responsivity and F_D for the specific detectivity, of the specimen doped with 0.2 wt% Y_2O_3 were the good values of $3.04x10^{-2}$ m^2C^{-1} and $1.50x10^{-5}$ $Pa^{-1/2}$, respectively.

Keywords : PZT ceramics, Dielectric properties, Pyroelectric properties, Figures of merit

1. INTRODUCTION

Ferroelectric ceramic materials have received much attention for their possible applications to capacitors of dynamic random access memories (DRAMs), gate materials of ferroelectric RAM (FeRAM), piezo micro-actuators, pyroelectric infrared sensors, tunable micro-wave devices, non-linear optical devices and a various kinds of transducers due to their unique properties. Among the various ferroelectrics, $Pb(Zr,Ti)O_3$ (PZT) system ceramics, which exhibit spontaneous polarization and a high dielectric constant, were widely investigated because of their potential for low temperature processing and various electrical properties obtained by varying the composition ratio and the minor modification of dopants.

Generally, a number of studies into different solid solutions of PZT with other ceramic oxides such as $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$ have been focused on piezoelectric properties of compositions in the system, mainly in the region of the morphotropic phase boundary [1]. And only a few works on the pyroelectric properties of these materials have been carried out[2]. Pyroelectric infrared detectors are an important class of thermal transducers which are based on the temperature-induced spontaneous polarization change exhibited by ferro-electric materials. Uncooled infrared detection has become an important technology in field of security, energy-saving, cooking, medical appliances, human environment and others[3].

In a previous paper, we have reported on the good pyroelectric properties of $Pb(Sb_{1/2}Sn_{1/2})O_3$-$Pb(Zr,Ti)O_3$ ceramics for infrared detectors[4]. In this study, Mn and Y ions as dopants in $Pb(Sb_{1/2}Sn_{1/2})O_3$-$Pb(Zr,Ti)O_3$ ceramics were added to improve the figures of merit (FOM) properties for practical use with high performance. And we investigated the structural and pyro-electric properties of the specimens with different amount of Y_2O_3 (0~0.4 wt%) for infrared detectors.

2. EXPERIMENTAL PROCEDURES

The chemical composition of the specimens was given according to the following formula: $0.10Pb(Sb_{1/2}Sn_{1/2})O_3$-$0.25PbTiO_3$-$0.65PbZrO_3$ (PSSTZ) + 0.18 mol% MnO_2 + x wt% Y_2O_3 (x=0~0.4). PSSTZ specimens doped with 0.18 mol% MnO_2 were selected for their basic composition on the basis of previous experiments [8]. PSSTZ powders, starting with a mixture of pure PbO(Aldrich, 99 %), Sb_2O_3(Fluka, 98 %), SnO_2(Aldrich, 99 %), TiO_2(Junsei, 99 %), ZrO_2(Fluka, 99 %), MnO_2 (Aldrich, 99 %) and Y_2O_3(Aldrich, 99 %), were prepared by using the mixed oxide method. The powder mixtures with ZrO_2 grinding media in alcohol solution were

milled in a polyethylene ball jar. After ball-milling and drying, the mixed powders were calcined at 850 °C for 2 h. Disk specimens, 12 mm diameter and about 2 mm thickness, were pressed at 2 ton/cm^2 and sintered at 1230 °C for 2 h under a PbO atmosphere. For the electrode formation, silver paste was coated and fired on both surfaces of the specimens. And the sintered specimens were poled in a silicone oil bath at 120 °C, by using a 3.5 MV/m dc electric field for 20 min.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used, respectively, in order to analyze the crystallinity and the microstructure of the PSSTZ specimens. The variation in the dielectric constant and the dielectric loss of specimens with temperature and the Y_2O_3 content were measured using an impedance/gain analyzer (HP 4194A) at 1 kHz. The pyroelectric current i_p was measured using a pA meter (Keithley 6514) at a constant rate of temperature change of 2.5 °C/min for increasing temperatures in the ranged from -45 °C to 80 °C. After measuring i_p, the pyroelectric coefficient p was derived from

$$p = i_p \cdot (dt/dT)S \quad (Cm^{-2}K^{-1}) \qquad (1)$$

where, i_p is the pyroelectric current (A), S is the electrode area (m^2), T is the absolute temperature (K), t is the time (s) and dt/dT is 24.0 (s/K).

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of the Y_2O_3–doped PSSTZ specimens. All specimens showed the typical XRD patterns of a perovskite polycrystalline structure. The pyrochlore phase due to evaporation of PbO was observed at around 2 θ= 29 ° and 32 °[10].

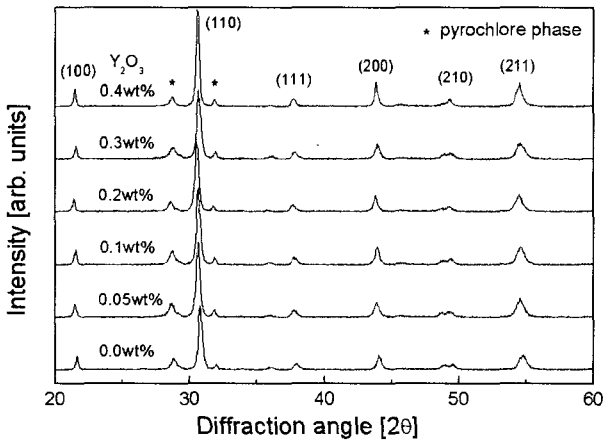

Fig. 1. X-ray diffraction patterns of PSSTZ specimens for various Y_2O_3 contents.

Figure 2 shows the surface SEM micrographs of the PSSTZ specimens for various Y_2O_3 contents. The specimen exhibited a dense and uniform grain structure with increasing Y_2O_3 amount. However, in the specimens doped with more than 0.3 wt% Y_2O_3, the grain size decreased because a portion of the doping Y ions precipitate out of the normal grain and stay at grain boundaries with subsequently retard the grain growth. The average grain size in the PSSTZ specimen doped with 0.2 wt% Y_2O_3 was about 2.2 μm.

Figure 3(a) and 3(b) show the relative dielectric constant and the dielectric loss of PSSTZ specimens as a function of temperature and Y_2O_3 amount at 1 kHz, respectively. The relative dielectric constant increased and the dielectric loss decreased with increasing Y_2O_3 amount. These properties are due to the fact that Pb^{2+} ions with a lower valence are replaced partially by the Y^{3+} ions with a higher valence in PZT ceramics. Therefore, Y ions compensate the cation deficient caused by PbO vapor evaporation during the sintering process [5]. However, when the amount of doping of Y_2O_3 exceeds 0.2 wt%, the relative dielectric constant decreased and the dielectric loss increased with increasing Y_2O_3 content due to the effects of the decreasing grain size and increasing the compositional inhomogeneity at grain boundaries with an excess doping, respectively. The Y_2O_3 addition does not change the Curie temperature of the PSSTZ specimens (T_c = 245 °C). The relative dielectric constant and the dielectric loss of the PSSTZ specimen doped with 0.2 wt% Y_2O_3 were 704 and 0.0201, respectively.

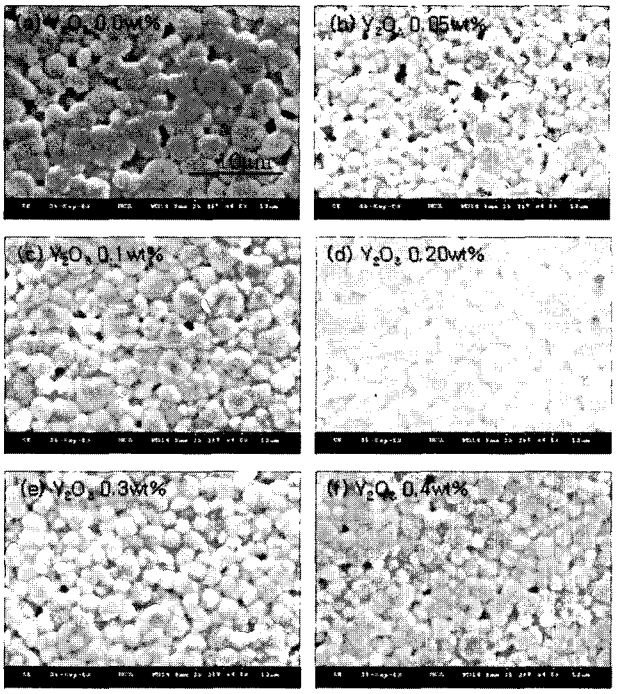

Fig. 2. Surface SEM micrographs of the PSSTZ specimens for various Y_2O_3 contents.

Figure 4(a) shows the hysteresis loops of the PSSTZ specimens with variation of Y_2O_3 amount. Well-saturated hysteresis loops could be obtained for all specimens. Figure 4(b) shows the remanent polarization and the coercive field of the PSSTZ specimens with variation of Y_2O_3 amount. The specimen doped with 0.2 wt% Y_2O_3 showed a maximum remanent polarization of 10.88×10^{-2} Cm^{-2}. When Y^{3+} ions substituted for Pb^{2+} ions in PSSTZ specimen, Y ions compensated the cation deficient caused by Pb vacancies, as shown in Fig. 3. This enhances the electrical neutrality, the remanent polarization increases with increasing Y_2O_3 amount. But, in the specimens doped with more than 0.2 wt% Y_2O_3, the remanent polarization decreased and the coercive field increased due to the creation of the Pb vacancy with an excessive doping[6] and the increasing internal stress with decreasing grain size.

Figure 5 shows the pyroelectric coefficient of PSSTZ specimens as a function of temperature for various Y_2O_3 amount. The specimen doped with 0.2 wt% Y_2O_3 showed a good value of 5.03×10^{-4} $Cm^{-2}K^{-1}$ at 25 °C. This is due to the fact that the specimen had the highest remanent polarization value and satisfied the charge neutrality, as shown in Fig. 6.

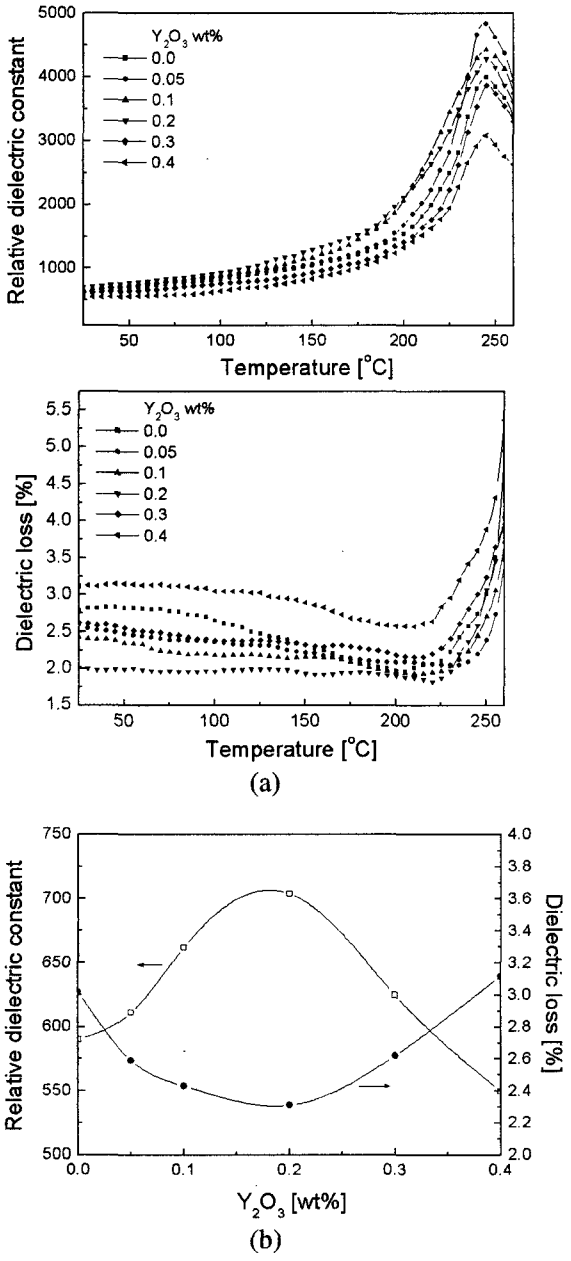

Fig. 3. Relative dielectric constant and dielectric loss of the PSSTZ specimens at 1 kHz as a function of temperature (a) and as a function of Y_2O_3 content (b).

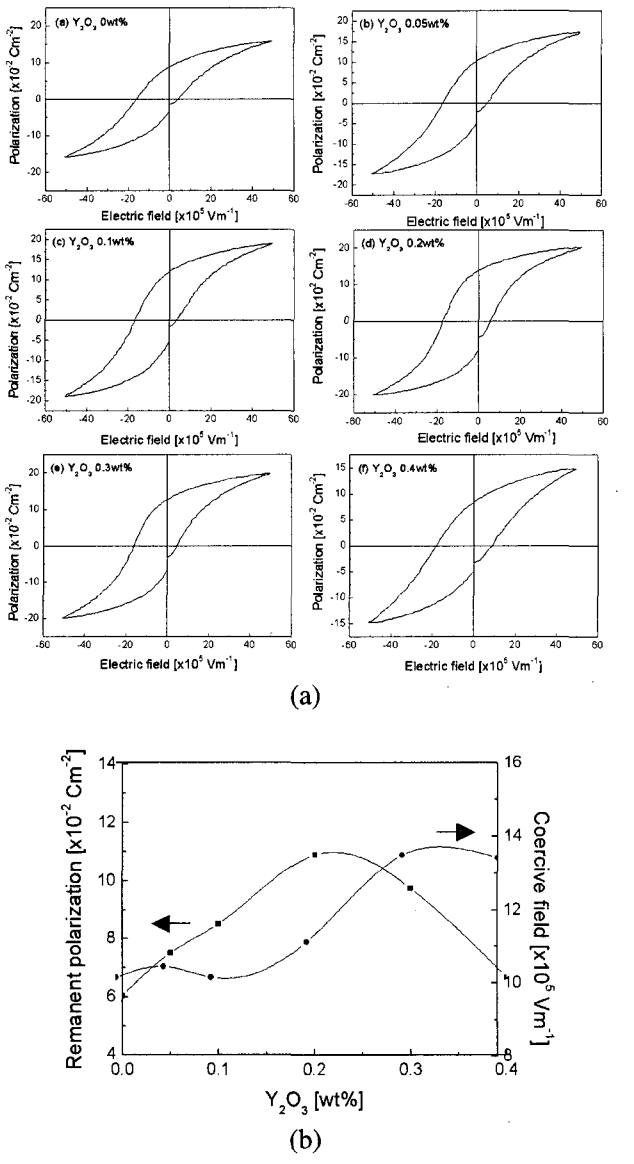

Fig. 4. P-E hysteresis loops (a) and remanent polarization and coercive field (b) of the PSSTZ specimens as a function of Y_2O_3 content.

The effects of the dopants upon pyroelectric performance, independence of geometric parameters, can be measured in terms of the usual figures of merits (FOM), defined[7] as,

$$F_V = p/c_v\varepsilon\varepsilon_o \quad (2)$$

$$F_D = p/c_v(\varepsilon\varepsilon_o\tan\delta)^{1/2} \quad (3)$$

Where, F_V = figure of merit for voltage responsivity, F_D = figure of merit for specific detectivity, p = pyroelectric coefficient, c_v = volume specific heat (= 2.6 $Jcm^{-3}K^{-1}$)[6], ε = dielectric constant, ε_o = permittivity of free space and tanδ = dielectric loss. We used the dielectric properties measured at 33 Hz to calculate the figures of merit characteristics. These are combinations of the electrical properties of the pyroelectric material that are directly related to the performances of the devices for IR detectors. F_V and F_D are proportional to the voltage responsivity and the specific detectivity of the device, respectively[8]. Figure 6 shows the F_V and F_D of PSSTZ specimens as function of Y_2O_3 contents. The F_V and F_D of the specimen doped with 0.2 wt% Y_2O_3 were 3.04×10^{-2} m^2C^{-1} and 1.50×10^{-5} $Pa^{-1/2}$, respectively. Even the specimen doped with 0.3 wt% Y_2O_3 had a maximum F_V value of 3.19×10^{-2} m^2C^{-1} and showed a low F_D value of 1.40×10^{-5} $Pa^{-1/2}$, due to their high dielectric loss. But, these values are slightly smaller than those of the modified PZT ceramics[9], for which values of F_V = 4 to 7×10^{-2} m^2C^{-1} and F_D = 4 to 6×10^{-5} $Pa^{-1/2}$ are typical. This is attributed to the effect of the high dielectric constant and dielectric loss properties.

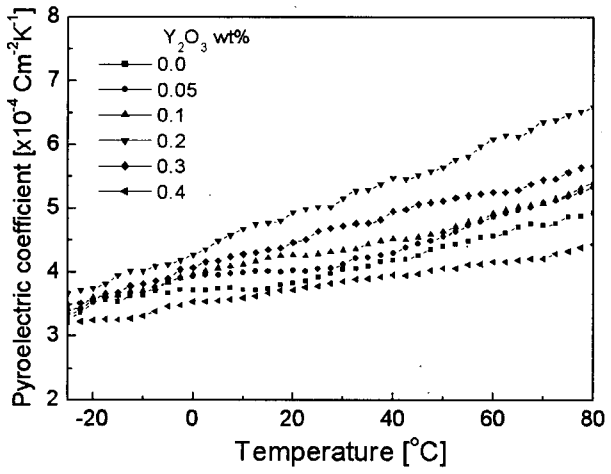

Fig. 5. Pyroelectric coefficient as a function of temperature for PSSTZ specimens for various Y_2O_3 contents.

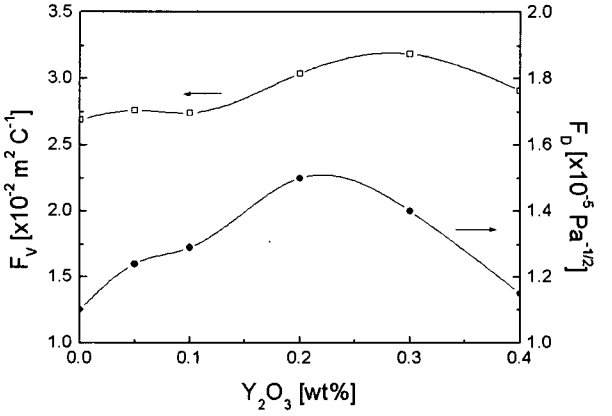

Fig. 6. Pyroelectric figures of merit F_V and F_D of the PSSTZ specimens as function of Y_2O_3 content.

4. CONCLUSION

$Pb(Sb_{1/2}Sn_{1/2})O_3$-$Pb(Zr,Ti)O_3$ ceramics doped with MnO_2 (0.18 mol%) and Y_2O_3 (0~0.4 wt%) have been fabricated by using the mixed-oxide method. The crystal structure of all PSSTZ specimens was rhombohedral and the grain sizes of the specimen doped with more than 0.3 wt% Y_2O_3 decreased because some Y is deposited at grain boundaries which retard grain growth. Y ion act as a donor dopant, having little effect on the Curie temperature (T_c=245 °C). The specimen doped with 0.2 wt% Y_2O_3 showed a maximum remanent polarization and pyroelectric coefficient due to a dense and uniform grain structures and a satisfaction of the charge neutrality. The figure of merit F_D for specific detectivity of the specimen doped with 0.2 wt% Y_2O_3 showed the highest value due to their high pyroelectric coefficient and good dielectric loss properties.

ACKNOWLEDGMENTS

This work has been supported by KESRI (R-2004-B-124), which is funded by the MOCIE(Ministry of Commerce, Industry and Energy).

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