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

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0.10Pb(Sb1/2Sn1/2)O3-0.25PbTiO3-0.65PbZrO3 specimens doped with MnO2 (0.18 mol%) and Y2O3 (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 Y2O3. The relative dielectric constant and the dielectric loss of the specimens doped with 0.2 wt% Y2O3 were 704 and 0.0201, respectively. The remanent polarization, the coercive field and the pyroelectric coefficient of the specimen doped with 0.2 wt% Y2O3 were 10.88×10^{-2} Cm^{-2}, 11.12×10^{2} kVm^{-1} and 5.03×10^{4} Cm^{-2}K^{-1} at 25 °C, respectively. The figures of merit, FV for the voltage responsivity and FD for the specific detectivity, of the specimen doped with 0.2 wt% Y2O3 were the good values of 3.04×10^{-2} m^{2}C^{-1} and 1.50×10^{3} 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 microwave devices, non-linear optical devices and a various kinds of transducers due to their unique properties. Among the various ferroelectrics, Pb(Zr,Ti)O3 (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(Mg1/3Nb2/3)O3, Pb(Zn1/2Nb1/2)O3 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 ferroelectric 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(Sb1/2Sn1/2)O3-Pb(Zr,Ti)O3 ceramics for infrared detectors[4]. In this study, Mn and Y ions as dopants in Pb(Sb1/2Sn1/2)O3-Pb(Zr,Ti)O3 ceramics were added to improve the figures of merit (FOM) properties for practical use with high performance. And we investigated the structural and pyroelectric properties of the specimens with different amount of Y2O3 (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(Sb1/2Sn1/2)O3-0.25PbTiO3-0.65PbZrO3 (PSSTZ) + 0.18 mol% MnO2 + x wt% Y2O3 (x=0-0.4). PSSTZ specimens doped with 0.18 mol% MnO2 were selected for their basic composition on the basis of previous experiments [8]. PSSTZ powders, starting with a mixture of pure PbO (Aldrich, 99 %), Sb2O3 (Fluka, 98 %), SnO2 (Aldrich, 99 %), TiO2 (Junsei, 99 %), ZrO2 (Fluka, 99 %), MnO2 (Aldrich, 99 %) and Y2O3 (Aldrich, 99 %), were prepared by using the mixed oxide method. The powder mixtures with ZrO2 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/cm² 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 Y₂O₃ 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

\[
p = i_p \cdot (\frac{dt}{dT})S \quad (\text{Cm}^2\text{K}^{-1})
\]

where, \(i_p\) is the pyroelectric current (A), \(S\) is the electrode area (m²), \(T\) is the absolute temperature (K), \(t\) is the time (s) and \(\frac{dt}{dT}\) is 24.0 (s/K).

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of the Y₂O₃–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 \(\theta\) = 29° and 32° [10].

Figure 2 shows the surface SEM micrographs of the PSSTZ specimens for various Y₂O₃ contents. The specimen exhibited a dense and uniform grain structure with increasing Y₂O₃ amount. However, in the specimens doped with more than 0.3 wt% Y₂O₃, 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% Y₂O₃ 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 Y₂O₃ amount at 1 kHz, respectively. The relative dielectric constant increased and the dielectric loss decreased with increasing Y₂O₃ amount. These properties are due to the fact that Pb²⁺ ions with a lower valence are replaced partially by the Y³⁺ 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 Y₂O₃ exceeds 0.2 wt%, the relative dielectric constant decreased and the dielectric loss increased with increasing Y₂O₃ content due to the effects of the decreasing grain size and increasing the compositional inhomogeneity at grain boundaries with an excess doping, respectively. The Y₂O₃ 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% Y₂O₃ were 704 and 0.0201, respectively.
Figure 4(a) shows the hysteresis loops of the PSSTZ specimens with variation of Y$_2$O$_3$ 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$_2$O$_3$ amount. The specimen doped with 0.2 wt% Y$_2$O$_3$ showed a maximum remanent polarization of 10.88x10$^{-2}$ 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$_2$O$_3$ amount. But, in the specimens doped with more than 0.2 wt% Y$_2$O$_3$, 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$_2$O$_3$ amount. The specimen doped with 0.2 wt% Y$_2$O$_3$ showed a good value of 5.03x10$^{-4}$ 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$_2$O$_3$ 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$_2$O$_3$ 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,

\[ F_V = \frac{p}{c_v \varepsilon \varepsilon_0} \]  
\[ F_D = \frac{p}{c_v (\varepsilon \varepsilon_0 \tan \delta)^{1/2}} \]

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], \( \varepsilon \) = dielectric constant, \( \varepsilon_0 \) = permittivity of free space and \( \tan \delta \) = 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 3.04x10\(^{-2}\) m\(^2\)C\(^{-1}\) and 1.50x10\(^{-5}\) Pa\(^{-1/2}\), respectively. Even the specimen doped with 0.3 wt% \( Y_2O_3 \) had a maximum \( F_V \) value of 3.19x10\(^{-2}\) m\(^2\)C\(^{-1}\) and showed a low \( F_D \) value of 1.40x10\(^{-5}\) 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 \( 7\times10^{-2}\) m\(^2\)C\(^{-1}\) and \( F_D = 4 \) to \( 6\times10^{-5}\) Pa\(^{-1/2}\) are typical. This is attributed to the effect of the high dielectric constant and dielectric loss properties.

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.

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REFERENCES


