PREPARATION OF LANTHANUM- AND MAGNESIUM-MODIFIED LEAD TITANATE CERAMICS AND THIN FILMS, AND THEIR PYROELECTRIC PROPERTIES

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Abstract: Lanthanum- and magnesium-modified PbTiO$_3$ \{(1-x). Pb$_0.9$La$_{0.1}$Ti$_{0.975}$O$_3$+x Mgo, x=0-0.025, (PLMT)} ceramics and thin films were prepared by normal sintering method and rf-magnetron sputtering method, respectively. The pyroelectric properties of PLMT ceramics and thin films were investigated in detail. The Curie temperature for all samples of both ceramics and films decreased linearly with increasing Mg. The highest figures of merit F.M. for the PLMT ceramics and films were around 0.18~10^{-10} \text{C} \cdot \text{cm/J} at x=0.005 and 1.05~10^{-10} \text{C} \cdot \text{cm/J} at x=0.010, reaching around 2.8 times and 1.5 times as large as those of PL10 (x=0 in PLT) ceramics and films, respectively. The highest F.M. in PLMT films attained to around 5.8 times that in PLMT ceramics. This is principally attributed to substantial differences in pyroelectric properties ($\varepsilon_r$ and $P$) between ceramics and thin films.

Key words: Ferroelectrics, Pyroelectric infrared sensor, Ceramics, Thin film, Curie temperature, Element material, Rf-magnetron sputtering method

1 INTRODUCTION

Pure PbTiO$_3$ is a perovskite-type ferroelectric with a large spontaneous polarization $P_s$ of 75 \mu C/cm$^2$ [1], high Curie temperature $T_c$ of 763K [2] and large tetragonality $c/a$ of 1.063 [3]. On the basis of these excellent physical properties, PbTiO$_3$-system ceramics [4] and thin films [5-7], in recent years, have attracted much attention as element materials for pyroelectric infrared (hereafter "IR") sensors.

A thin film with composition of PL10 (x=0.1) in Pb$_{1-x}$La$_x$Ti$_{1-y/4}$O$_3$, where $x=0.05-0.15$ (hereafter "PLT") [5-7], has already been applied to the element of pyroelectric linear array IR sensor consisting of 512 picture elements with high sensitivity and resolution which has been used in the newest type of air conditioner [8]. To satisfy all demands in the applications to various fields, such as security, domestic electrical appliances, medical appliances and aerospace industries, it is extremely important to improve the figure of merit F.M. ($=P/C_v \cdot \varepsilon_r$; $P$: pyroelectric coefficient, $C_v$: volume specific heat, $\varepsilon_r$: relative dielectric constant) on an element material for pyroelectric IR sensors.

On the other hand, many studies on the synthesis, dielectric properties [9] and piezoelectric properties [10-12] in \{(Pb, La)TiO$_3$+MnO$_2$\}-system ceramics have also been reported so far, but their pyroelectric properties are not clear. Moreover, the pyroelectric properties of simultaneous lanthanum- and magnesium-modified PbTiO$_3$ ceramics and films have not been reported yet.

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obtained were then polished to around 0.3 mm thickness. After drying, their surfaces were electroded with vacuum-evaporated platinum-palladium alloy.

2.1.2 PLMT films

Next, the preparation process of PLMT films with \(x=0.025\) for the measurement of electrical properties was as follows: PLMT thin films were prepared by the rf-magnetron sputtering method. The substrates used in this experiment were (100)-cleaved, polished and surface-treated MgO single crystals (products of Tateho Chemical Ind., Dimensions: \(7.0 \times 7.0 \times 0.5\) mm\(^3\)) by the combination of chemical etching method and oxygen-annealing method [13]. First, (100)-oriented Pt thin-film electrodes with 4 mm diameter and around 0.1 \(\mu\)m thickness were deposited on the MgO substrates by the rf-magnetron sputtering method. The sputtering conditions were the substrate temperature of 873K, atmosphere of Ar 50% and O\(_2\) 50%, and gas pressure of 0.5 Pa [14]. The sputtering targets used were mixtures of calcined PLMT powders and PbO powder. The compositions are represented by the formula \(0.8[(1-x)Pb_{0.9}La_{0.1}Ti_{0.975}O_3+x\cdot MgO]+0.2PbO\), where \(x=0, 0.0025, 0.005, 0.0075, 0.01, 0.015, 0.02, 0.025, \) and denoted as follows: PL10, PLM2.5, PLM5, PLM7.5, PLM10, PLM15, PLM20 and PLM25, respectively. Excess PbO powder of 20 mol% was added to these targets to compensate for loss of Pb from the sputtered films [14]. In addition, the PLMT powders described above were prepared according to the procedure shown below; the starting raw materials were guaranteed reagents of PbO, La\(_2\)O\(_3\), MgCO\(_3\) and TiO\(_2\). The components weighted in appropriate proportions were sufficiently mixed in ethanol in an agate mortar. After the mixtures were dried at 353K for 6h, they were calcined in 99.5% MgO crucible in air at 1023K for 3h. After the calcines were again ground in the same mortar, they were employed as PLMT powders. These powders were filled and pressed at around 25 MPa in shallow Cu dishes of 4 in. diameter. The substrates were fixed on a heating block with a stainless steel (SUS 304) mask of 0.5 mm thickness. The deposition area of PLMT films prepared on the [100]-oriented Pt films is 5 mm in diameter. The sputtering conditions for the synthesis of PLMT films are summarized in Table 1.

Table 1. Sputtering conditions for preparation of PLMT thin films.

<table>
<thead>
<tr>
<th>Input power density</th>
<th>2.0 [W/cm(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering gas</td>
<td>Ar/O(_2) = 90/10</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>0.50 [Pa]</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>917 [K]</td>
</tr>
<tr>
<td>Target-substrate distance</td>
<td>64 [mm]</td>
</tr>
<tr>
<td>Film thickness</td>
<td>1~2 [(\mu)m]</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>4.0 [mm/min]</td>
</tr>
<tr>
<td>Cooling rate</td>
<td>30 [K/min]</td>
</tr>
</tbody>
</table>

2.2 Evaluation of chemical composition

The inductively coupled plasma emission spectroscope (ICP-ES; ICPV-1000W, Shimazu) and electron probe microanalyzer (EPMA; JXA-8900R, JEOL) were used for chemical analysis in the PLMT ceramics and thin films, respectively.

2.3 Evaluation of physical properties

The apparent density and porosity of the obtained ceramic samples were measured using Archimedes method with white kerosene (0.791g/ml at 293K) as the immersion liquid. The crystalline phase and lattice constants in each sample were analyzed at room temperature using an X-ray diffractometer (XRD; RINT1500, Rigaku). The lattice constants, in particular, were determined by applying least squares procedures to the X-ray diffraction method with high-purity silicon powder (NIST-640b) as an external standard, using (101), (111), (002), (200), (112), (211) and (220) reflections of Cu K\(_\alpha\) radiation in ceramics, and (002), (003), (200) and (300) ones in films, respectively. The degrees of c-axis orientation \(\alpha\) for PLMT films with the tetragonal structure were also measured. In addition, \(\alpha\) is defined by

\[
\alpha = I(001)/(I(001)+I(100)), \tag{1}
\]

where \(I(001)\) and \(I(100)\) represent the X-ray diffraction intensities of (001) and (100) reflections, respectively.
2.4 Measuring procedure on pyroelectric properties

The schematic diagram for the measurement of static pyroelectric properties is shown in Fig.2; the relative dielectric constant $\varepsilon_r$ and the dielectric loss $\tan \delta$ in both samples were measured at 1kHz under a constant a.c. field of 25 V/cm (the practical effective value) using a multi-frequency LCR meter (4274A, Yokogawa Hewlett Packard). The measurement of the static pyroelectric properties [15, 16] was carried out after poling treatment in PLMT ceramics that samples were cooled at the rate of 10K/h from high temperature of 2K above the Curie temperature $T_c$ to room temperature under a constant d.c. electric field of around 2.5 kV/cm, and without poling treatment in PLMT films. The pyroelectric current $i_p$ was repeatedly measured by a pA meter (4140B, Yokogawa Hewlett Packard) 1.3K/min during rise and fall in temperature in the 298-523K region, to eliminate effects due to the induced current.

On the basis of the temperature gradient of the measured $i_p$, the pyroelectric coefficient $P$ was derived from

$$P = \frac{i_p \cdot (dT/dT)/S}{\text{C/cm}^2 \cdot \text{K}} \quad [\text{C/cm}^2 \cdot \text{K}] \quad (2)$$

where $i_p$ is the pyroelectric current (A), $S$ is the electrode area (cm²), $T$ is the absolute temperature (K), $t$ is the time (s) and $dT/dT$ is in the 38-46 s/K region. Based on the results, the Curie temperature $T_c$ that is, the phase transition temperature in ceramic samples was determined from the position of maximum of $\varepsilon_r$ in each sample with different composition of $x=0-0.025$ in PLMT, while in film samples, it was determined from the position of maximum of $P$ in each sample, similarly. The figure of merit F.M. for voltage responsivity of the pyroelectric IR sensor can be expressed by the following equation:

$$F.M. = \frac{P}{(C_v \cdot \varepsilon_r)} \quad [\text{C} \cdot \text{cm}/\text{J}] \quad (3)$$

where $C_v$ is volume specific heat and $C_v=3.2 \,(\text{J/cm}^3 \cdot \text{K})$ [17].

3 RESULTS AND DISCUSSION

3.1 Chemical analysis

The ICP-ES results obtained for PLMT ceramics indicated that the chemical composition designed in the preparation was extremely close to the real one in the synthesized samples. Similarly, the EPMA results obtained for PLMT films also indicated that the chemical composition designed in preparation almost corresponded to the real one in the synthesized samples, as shown in Table 2. On the basis of this result, it is considered that the compensation for loss of Pb from the sputtered films was performed by excess 20 mol% PbO in the targets in the preparation process of films.

3.2 Physical properties

From the measurements of X-ray diffraction patterns on the obtained PLMT ceramics and films, all peaks of both samples almost corresponded with those of pure PbTiO$_3$ having the tetragonal perovskite structure listed in JCPDS Card No.6-0452. The apparent porosity, apparent density, lattice constants, tetragonality c/a, theoretical density and relative density of PLMT ceramics in this study are shown in Table 3. All samples were sintered bodies with low porosity and high density. In particular, samples of $x=0.005$ had the highest apparent density of 7.78 g/cm$^3$, reaching 99.8% of theoretical density. Furthermore, the tetragonality estimated from XRD measurement showed nearly a constant value of 1.033 in the range of $x=0-0.020$. This value corresponded to the reduction of around 2.8% compared with that of pure PbTiO$_3$ [3]. On the contrary, the sample of $x=0.025$ had a rather small tetragonality of 1.009. We presume that the principal Mg-solubility at the turning point in the vicinity of 2.5 mol% changes from substitutional solubility to interstitial solubility, based on the variation in lattice constants. On the other hand, lattice constants and tetragonality c/a in PLMT films indicated the behavior...
similar to those in ceramics in the region of x=0.025.

Table 3. Composition x, apparent porosity, apparent density, lattice constant, tetragonality, theoretical density and relative density of various PLMT ceramics.

<table>
<thead>
<tr>
<th>Comp. x (mol%)</th>
<th>Apparent porosity (%)</th>
<th>Apparent density (g/cm³)</th>
<th>Lattice constant a (nm)</th>
<th>Tetragonality c/a</th>
<th>Theoretical density (g/cm³)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.11</td>
<td>7.39</td>
<td>0.3917</td>
<td>0.4046</td>
<td>1.033</td>
<td>7.80</td>
</tr>
<tr>
<td>0.005</td>
<td>0.15</td>
<td>7.78</td>
<td>0.3917</td>
<td>0.4047</td>
<td>1.033</td>
<td>7.79</td>
</tr>
<tr>
<td>0.010</td>
<td>0.12</td>
<td>7.64</td>
<td>0.3917</td>
<td>0.4048</td>
<td>1.033</td>
<td>7.79</td>
</tr>
<tr>
<td>0.015</td>
<td>0.18</td>
<td>7.72</td>
<td>0.3917</td>
<td>0.4050</td>
<td>1.034</td>
<td>7.79</td>
</tr>
<tr>
<td>0.020</td>
<td>0.16</td>
<td>7.70</td>
<td>0.3917</td>
<td>0.4042</td>
<td>1.032</td>
<td>7.79</td>
</tr>
<tr>
<td>0.025</td>
<td>0.15</td>
<td>7.71</td>
<td>0.3953</td>
<td>0.3987</td>
<td>1.009</td>
<td>7.78</td>
</tr>
</tbody>
</table>

*Relative density = (Apparent density/Theoretical density) × 100 [%]

Figure 3. The degree of c-axis orientation α on PLMT films as a function of composition x in PLMT films. The degree of c-axis orientation α decreases linearly with an increase of Mg content. The rate of decrease is estimated to be 0.012/mol% (Mg) from the slope of a straight line obtained by the method of least squares. This linear decrease of α is presumably due to the substantial increase of Mg-solubility into the a-axial direction of the crystal structure with increasing Mg content.

3.3 Relative dielectric constant \( \varepsilon_r \) and pyroelectric coefficient \( P \)

Figure 4 shows the composition dependence of relative dielectric constant \( \varepsilon_r \) at room temperature on PLMT ceramics and films. \( \varepsilon_r \) of PLMT ceramics exhibits a negligibly slight increase, but that of thin films decreases gently with an increase of Mg content. This difference in \( \varepsilon_r \)'s behaviors between ceramics and thin films may be attributed to the structural factors, such as thermal distortions and internal stress present only in PLMT films. Furthermore, as the ratio of thin films/ceramics with the same compositions are, e.g. around 0.65 at x=0 and 0.41 at x=0.025, the figures of merit F.M. at room temperature of PLMT films with x=0 and 0.025 should be improved to around 1.5 times and 2.4 times those of the corresponding PLMT ceramics, as easily seen from Eq. (3), assuming that \( P \) and \( C_v \) for both samples with the same compositions are the same values, respectively.

\[
\varepsilon_r = \frac{\text{Apparent density}}{\text{Theoretical density}} \times 100 \%
\]

The composition dependence of pyroelectric coefficient \( P \) at room temperature on PLMT ceramics and films are shown in Fig.5. The poled PLMT ceramics with x=0.005-0.025 had relatively large \( P \) of \((0.9-1.8) \times 10^{-8} \text{C/cm}^2 \cdot \text{K}\), 1.5-3.0 times as large as that of PL10 (x=0) ceramics. On the other hand, the significant pyroelectric currents \( i_p \) along the direction perpendicular to the film surface were detected on all as-sputtered PLMT films even without poling treatment in the preliminary experiment. Consequently, the PLMT films with x=0.005-0.025 had significantly large \( P \) of \((4.3-5.6) \times 10^{-8} \text{C/cm}^2 \cdot \text{K}\), around 1.0-1.2 times that of PL10 (x=0) films. In addition, the largest \( P \) observed at x=0.010 in films corresponded to around 3.1 times that at x=0.005 in ceramics.

3.4 Curie temperature \( T_c \)

The composition dependence of Curie temperature \( T_c \) on PLMT ceramics and films are shown in Fig.6. The Curie temperature \( T_c \) in PLMT ceramics and films decrease linearly with an increase of Mg content. From the slope of two straight lines obtained by the method of least squares, the rates of decrease are estimated to be around 9.3K/mol% (Mg) in ceramics and 6.4K/mol% (Mg) in films, respectively. Therefore, taking the accuracy of the measurement into account, the Mg-shifter effect to the PL10-composition was found to be
3.5 Figure of merit F.M. for pyroelectric IR sensors

Figure 7 indicates the composition dependence of the figure of merit F.M. at room temperature on PLMT ceramics and films. The PLMT ceramic of \( x=0.005 \) showed the highest F.M. of \( 0.18 \times 10^{-10} \text{C} \cdot \text{cm}^{-2} \cdot \text{J}^{-1} \), corresponding to around 2.8 times that of PL10 \( (x=0) \) ceramic. On the other hand, the PLMT film of \( x=0.010 \) exhibited the highest F.M. of \( 1.05 \times 10^{-10} \text{C} \cdot \text{cm}^{-2} \cdot \text{J}^{-1} \) at room temperature, reaching around 1.5 times as large as those of PL10 ceramics and films, respectively. The highest figure of merit F.M. in PLMT films attained to around 5.8 times that in PLMT ceramics. In conclusion, thin films with the composition of \( \{(1-x) \cdot \text{Pb}_{0.9} \cdot \text{La}_{0.1} \cdot \text{Ti}_{0.975} \cdot \text{O}_3 + x \cdot \text{MgO} \} \), where \( x=0.010 \), show great promise as element materials for pyroelectric IR sensors.
REFERENCES