Chemical Processing of (Zr, Sn)TiO₄ Dielectrics through Metal Alkoxide Route and Their Microwave Characteristics

Takashi HAYASHI*

1. Introduction

The communication at microwave frequencies has been required with the advances of communication network. Many kinds of dielectric materials have been developed for microwave applications up to date. Among them, a zirconium titanate solid solution, ZrₓTiₙ₋ₓSnₓO₄ (x+y+z=2), is known to have a high dielectric constant, a high Q value, and a low temperature coefficient of resonant frequency. Due to the difficulty of sintering the compound without additives, it has been sintered with additives such as ZnO, NiO, Fe₂O₃, and La₂O₃. These additives, however, led to the degradation of its own dielectric properties. Therefore, the reduction of the amounts of additives, impurities, and oxygen defects has been required for the improvement of the dielectric properties.

The phase transition of ZrTiO₄ at a temperature below 1200°C was noticed by Coughanour et al., and suggested to be an order-disorder transition by Newham. Subsequently, some anomalous features of the transition have been clarified. The transformation from a high-temperature structure with a random distribution of cations to a low-temperature structure occurs sluggishly and is accompanied by a continuous decrease of the c-axis length, probably because of partial ordering of the cations. Substitutional tin in the solid solution can stabilize the high-temperature structure to some extent by interfering with the ordering of metal ions.

Systematic compositional variations of this solid solution afford ceramic dielectrics with a controllable temperature coefficient of their dielectric constants and resonant frequencies, as required for specific device applications. S. Hirano et al. reported the advantages to prepare the controlled sintered microwave dielectrics through the metal-alkoxide method.

This study was focused on the chemical processing of (Zr, Sn)TiO₄ microwave dielectrics without any additives through sol-gel method with metal alkoxides and the evaluation of their microwave characteristics.

2. Experimental Procedure

Zirconium n-propoxide (>99% purity), titanium isopropoxide (>99% purity), and tin
isopropoxide (>99% purity) were used as starting materials. They were weighed in desired amounts according to the formula \((\text{Zr}_x\text{Sn}_y)\text{TiO}_4\) \((x+z=1)\), and were dissolved in absolute n-propanol solvent. A metal alkoxide mixture was refluxed for 24 h, and subsequently hydrolyzed by adding four times the equivalent amount of deionized water \((\text{pH} 7)\) or aq. \(\text{NH}_3\) \((\text{pH} 12)\) required for hydrolysis at room temperature or under refluxing. All procedures mentioned above were carried out under a dry \(\text{N}_2\) atmosphere. After the hydrolysis, the resulting suspension was aged by refluxing further for 24 h. The precipitates were ultrafiltered, washed, and dried at 50°C.

The green compacts were formed by following two processes. In process A, as-precipitated amorphous powders were uniaxially pressed to disks at 100 MPa in a steel die, followed by cold isostatic pressing at 300 MPa, and then preheated at crystallization temperature of 690°C. In process B, as-precipitated powders were first calcined at 650°C for 5 h, and then pressed into the disks, followed by cold isostatic pressing at 300 MPa. Both these disks were sintered at 1600°C for 3 and 24 h in a flow of \(\text{O}_2\). The bodies sintered at 1600°C for 3 h were annealed at 1350 and 1450°C for 15 h to elucidate the effect of the oxygen defects on the dielectric properties. In addition, in order to clarify the effect of the phase transition of \((\text{Zr}_x\text{Sn}_y)\text{TiO}_4\) compound on the dielectric properties, the specimens sintered at 1600°C for 24 h were rapidly quenched to room temperature after the heat-treatment at 1000 to 1600°C for 5 h.

To compare this metal alkoxide method with the conventional solid state reaction method, the mixture of \(\text{ZrO}_2\), \(\text{SnO}_2\), and \(\text{TiO}_2\) powders was ball-milled in deionized water, dried, and then calcined at 1000°C. After milling again, the powders were pressed into disks and sintered at 1600°C for 3 h in a flow of \(\text{O}_2\).

The particle size, particle size distribution, and morphology of as-precipitated particles were characterized by a scanning electron microscope and dynamic laser light scattering analysis. The chemical homogeneity and composition of as-precipitated particles were examined by analytical electron microscopy (AEM) and ICP emission analysis, respectively. The lattice parameters of the sintered bodies were determined from \(\{220\}\), \(\{202\}\), \(\{022\}\) reflections by X-ray powder diffraction. The dielectric properties of dense sintered bodies were measured at microwave frequencies by the resonant cavity method with \(\text{TE}_01\) mode.

### 3. Results and Discussion

#### 1) Preparation of Monosized Spherical Fine Particles

Table 1 shows the effect of hydrolysis conditions on the particle sizes and morphology of as-precipitated particles of \((\text{Zr}_0.8\text{Sn}_0.2)\text{TiO}_4\) compound. As-precipitated powders were amorphous. The particle size and morphology of as-precipitated powders did depend on the hydrolysis temperatures and the metal alkoxides concentration. The higher the hydrolysis temperature, the size of as-precipitated particles tended to become larger. As shown in Fig. 1, spherical fine particles were prepared by the hydrolysis of the alkoxides solution at a refluxing temperature of 150°C for 24 h. As-precipitated powders by the hydrolysis of the metal alkoxides of 0.025 mol/l under was.

<table>
<thead>
<tr>
<th>Conc. (mol/l)</th>
<th>Hydrolysis Temp.</th>
<th>Particle Size (μm)</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>room temp.</td>
<td>&lt;0.1</td>
<td>irregular</td>
</tr>
<tr>
<td>0.05</td>
<td>reflux</td>
<td>0.3–0.4</td>
<td>spherical</td>
</tr>
<tr>
<td>0.025</td>
<td>room temp.</td>
<td>0.1–0.2</td>
<td>spherical</td>
</tr>
<tr>
<td>0.025</td>
<td>reflux</td>
<td>0.3–0.4</td>
<td>spherical</td>
</tr>
</tbody>
</table>

Amount of water: 4 times the equivalent amount required for hydrolysis.

---

NII-Electronic Library Service
refluxing were found to be monosized un-agglomerated particles of about 0.2 μm with narrow particle size distribution. The particle size and the morphology of as-precipitated particles were also influenced by the pH of the solution for the hydrolysis. The higher pH value yielded the larger particle size and the broader distribution of the particle size. The hydrolysis at pH 7 afforded the spherical particles, while the hydrolysis at pH 12 tended to afford the mixture of spherical and spheroidal particles.

The energy dispersive analysis for X-ray by AEM showed the chemical homogeneity of the composition within each as-precipitated particle, suggesting that the hydrolysis and condensation reactions of each metal alkoxide were conducted at the comparable hydrolysis rate under controlled hydrolysis condition. The chemical composition of as-precipitated powders was found to be nearly the same as the nominal composition from the results of ICP emission analysis, as shown in Table 2.

Figure 2 shows the change of zeta potential of as-prepared particles in aqueous solution as a function of pH. They exhibited an isoelectric point at about pH 6 and possessed the largest positive and negative potentials around pH 4.5 and pH 9, respectively, which

---

Fig. 1. SEM micrographs of as-precipitated powders. a) 0.05 mol/l, room temp., b) 0.05 mol/l, reflux, c) 0.025 mol/l, room temp., d) 0.025 mol/l, reflux.
allow to disperse readily the particles in an aqueous solution.

Figure 3 shows DTA-TG curves of the as-precipitated powder by the controlled hy-

tolysis of the metal alkoxides. An endothermic peak due to the evaporation of water and adsorbed solvent was observed below 200°C. A weak and broad exothermic peak and a strong exothermic peak were observed between 300 and 450°C, and at 690°C, which correspond to the oxidation of organic groups and the crystallization of (Zr,Sn)TiO$_4$, respectively.

2. Sintering Behaviors

The densification of (Zr$_{0.85}$Sn$_{0.15}$)TiO$_4$ powders depended strongly on the processing methods, i.e. the process A (as-precipitates$\rightarrow$direct forming$\rightarrow$crystallization$\rightarrow$sintering) and the process B (as-precipitates$\rightarrow$calcination$\rightarrow$forming$\rightarrow$sintering), as shown in Table 3. The densities of the sintered bodies prepared through the process A were found to be higher than those through the process B, though both green densities were nearly the same. The fine particles (0.1–0.2 μm) yielded the sintered bodies with the higher densities, compared to that prepared from the larger particles (0.3–0.4 μm).

Figure 4 shows the relative densities of sintered bodies of (Zr$_{0.85}$Sn$_{0.15}$)TiO$_4$ as a function of sintering temperature. The relative density of the green compacts preheated at 690°C for 5 h was about 57% of theoretical density, and the relative densities of sintered bodies increased from 61% to 98% of theoretical density with the increase of sintering temperatures from 1300 to 1600°C. The as-precipitated powders by the chemical pro-

Table 2. Compositions of as-precipitated particles of (Zr$_{0.85}$Sn$_{0.15}$)TiO$_4$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Measured (mol%)</th>
<th>Calculated (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>39.1±0.6</td>
<td>40.0</td>
</tr>
<tr>
<td>Ti</td>
<td>49.7±0.6</td>
<td>50.0</td>
</tr>
<tr>
<td>Sn</td>
<td>11.1±0.6</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Table 3. Effect of processing on sintering of (Zr$_{0.85}$Sn$_{0.15}$)TiO$_4$.

<table>
<thead>
<tr>
<th>Particle Size (μm)</th>
<th>Process*</th>
<th>Relative Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Green Body</td>
<td>Sintered Body</td>
</tr>
<tr>
<td>0.1–0.2</td>
<td>A</td>
<td>49</td>
</tr>
<tr>
<td>0.3–0.4</td>
<td>A</td>
<td>55</td>
</tr>
<tr>
<td>0.0–0.4</td>
<td>B</td>
<td>55</td>
</tr>
</tbody>
</table>

* Process A: As-precipitated$\rightarrow$Consolidation$\rightarrow$Crystallization(690°C, 5 hrs)$\rightarrow$Sintering(1600°C, 3 hrs).
Process B: As-precipitated$\rightarrow$Calcination (650°C, 5 hrs)$\rightarrow$Forming$\rightarrow$Sintering (1600°C, 3 hrs).
3) Dielectric Properties of Sintered Bodies of (Zr, Sn)TiO$_3$

The dense sintered bodies with the composition of (Zr$_x$Sn$_{1-x}$)TiO$_3$ ($x$+z=1, 0<z<0.4) were successfully prepared through the direct sintering process A without the calcination of as-precipitated powders. The powders with Sn content of $z$>0.3 resulted in the coexistence of (Ti, Sn)O$_2$ solid solution as a second phase as well as (Zr$_{0.80}$Sn$_{0.20}$)TiO$_3$, while the single phase (Zr$_{0.80}$Sn$_{0.20}$)TiO$_3$ solid solution could be prepared from the powders with $z$<0.3. This result was consistent with one reported by Wolfram et al.$^{15}$.

Figure 5 shows the dielectric properties of dense sintered bodies of (Zr$_{0.80}$Sn$_{0.20}$)TiO$_3$ at 10 GHz. The dielectric constant decreased with the increase of $z$ from 0.00 to 0.30, while the $Q$ value increased. On the other hand, the temperature coefficient of resonant frequency decreased with the increase of Sn content and became zero between $z$=0.20 and 0.30. The dielectric constant, $Q$ value, and the temperature coefficient of resonant frequency changed steeply at $z$=0.40, because of the coexistence of (Ti, Sn)O$_2$ solid solution which had a high dielectric constant, a lower $Q$ value, and a higher temperature coefficient of resonant frequency relative to the (Zr$_{0.80}$Sn$_{0.20}$)TiO$_3$ solid solutions in microwave region. The temperature coefficient of resonant frequency of single phase (Zr$_{0.80}$Sn$_{0.20}$)TiO$_3$ was as low as 3 ppm/°C, and the dielectric constant and the $Q$ value were 40 and 5000 at 10 GHz, respectively. The sintered body of (Zr$_{0.80}$Sn$_{0.20}$)TiO$_3$ showed excellent dielectric properties as a microwave dielectric material, compared with that prepared by the conventional solid state reaction$^{17,13}$.

4) Key Factors to Dielectric Properties

The relative densities and average grain sizes of sintered bodies, oxygen defects and phase transition are considered as key factors influential to the dielectric properties of (Zr$_{0.80}$Sn$_{0.20}$)TiO$_3$.

Figure 6 shows the effects of the dielectric
Fig. 6. Changes of $\varepsilon_r$ and $Q$ with relative densities of $(Zr_{0.80}Sn_{0.20})TiO_4$ sintered bodies.

The dielectric constant increased with the increase of the relative densities of sintered bodies, but it was less affective to the average grain sizes of sintered bodies.

The $Q$ values appears not to relate to the relative densities of sintered bodies. Figure 7 shows SEM micrographs of the surfaces of $(Zr_{0.80}Sn_{0.20})TiO_4$ bodies sintered at 1600°C for 3 and 24 h. Though the average grain sizes of sintered bodies increased remarkably from 5 to 10 $\mu$m by increasing the sintering time from 3 to 24 h, the $Q$ value did not change with the sintering times as shown in Table 4. On the other hand, the dielectrics constant increased slightly because of a small increase of the relative densities of sintered bodies.

To elucidate the effect of oxygen defects on the dielectric properties, the sintered bodies were annealed at 1350 and 1450°C in a flow of $O_2$. Table 5 shows the effect of the annealing temperatures in $O_2$ on the dielectric properties of $(Zr_{0.80}Sn_{0.20})TiO_4$ sintered bodies. Both the dielectric constant and the $Q$ value were improved by annealing at 1450°C for 15 h, being unchanged by annealing at 1350°C for 15 h.

Figures 8 and 9 show the change of the lattice parameters of $ZrTiO_4$ and $(Zr_{0.80}Sn_{0.20})TiO_4$ with quenching temperatures.

Table 4. Effect of sintering time on properties of $(Zr_{0.80}Sn_{0.20})TiO_4$.

<table>
<thead>
<tr>
<th></th>
<th>3 hrs</th>
<th>24 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_r$</td>
<td>R.D.* (%)</td>
<td>$Q$</td>
</tr>
<tr>
<td>40.0</td>
<td>98</td>
<td>4800</td>
</tr>
<tr>
<td>39.4</td>
<td>97</td>
<td>4900</td>
</tr>
</tbody>
</table>

* R.D. (Relative Density)

Fig. 7. SEM micrographs of $(Zr_{0.80}Sn_{0.20})TiO_4$ sintered bodies after thermal etching. (a) Body sintered for 3 hrs, (b) Body sintered for 24 hrs.
both specimens, $a$-axis length decreased slightly with the increase of the quenching temperatures, but $b$-axis length did not changed considerably. On the other hand, the drastic change of $c$-axis length was observed in the specimens quenched from temperatures below or at 1400°C. The lattice parameters are, however, almost constant at the quenching temperatures above 1400°C. Figures 10 and 11 show the changes of the dielectric properties of ZrTiO$_4$ and (Zr$_{0.80}$Sn$_{0.20}$)TiO$_4$, with the $c$-axis length. In both specimens, the dielectric constants increased with the increase of the $c$-axis length, while the $Q$ values decreased. The (Zr$_{0.80}$Sn$_{0.20}$)TiO$_4$ specimen quenched from the temperature as high as 1600°C had black color and exhibited the lower $Q$ value because of the formation of the oxygen defects by reduction.

Electron polarization and ionic polarization

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
As-sintered & 1350°C, 15 hrs & 1450°C, 15 hrs \\
\hline
$\varepsilon_r$ & $Q$ & $\varepsilon_r$ & $Q$ & $\varepsilon_r$ & $Q$ \\
\hline
40.1 & 4800 & 40.0 & 4600 & 40.5 & 5100 \\
39.7 & 5000 & 39.9 & 5100 & 40.0 & 5300 \\
\hline
\end{tabular}
\caption{Effect of annealing on properties of (Zr$_{0.80}$Sn$_{0.20}$)TiO$_4$.}
\end{table}

Fig. 9. Changes of lattice parameters of (Zr$_{0.80}$Sn$_{0.20}$)TiO$_4$ sintered bodies for 5 hrs with quenching temperatures.

Fig. 8. Changes of lattice parameters of ZrTiO$_4$ sintered bodies for 5 hrs with quenching temperatures.

Fig. 10. Changes of $\varepsilon_r$ and $Q$ with $c$-axis lengths of ZrTiO$_4$ sintered bodies at 1500°C.
sintering aid, crystallized, and then sintered at 1600°C for 3 h into the bodies with >96.0% of theoretical density. The dense sintered bodies of (Zr,Sn)TiO₄ showed excellent microwave characteristics, compared with those prepared by the conventional solid state method: εᵣ = 40.0, Q = 5000 and τᵣ = 3 ppm/°C at 10 GHz. The dielectric constant was greatly affected by the relative density of sintered body and the lattice parameters, while Q value was mainly affected by the oxygen defects. The enhancement of ionic polarization caused the increase of the dielectric constant with the increase of the c-axis length in the crystal lattice.

4. Conclusions

Chemical processing of (Zr, Sn)TiO₄ microwave dielectrics was investigated through the sol–gel method with metal alkoxides.

The particle size and morphology of as-precipitated particles of (Zr, Sn)TiO₄ did depend strongly on the concentration of metal alkoxides, the hydrolysis temperature and pH of the solution for hydrolysis. The monosized spherical particles of (Zr₀.₈Sn₀.₂)TiO₄ with an average diameter of about 0.3 μm could be synthesized by the controlled hydrolysis of metal alkoxides. The as-prepared amorphous particles were compacted without any

Fig. 11. Changes of εᵣ and Q with c-axis lengths of (Zr₀.₈Sn₀.₂)TiO₄ sintered bodies at 1500°C. *
*: 1600°C, 5 hrs.

References

Chemical Processing of (Zr, Sn)TiO₄ Dielectrics through Metal Alkoxide Route