Dielectric properties of SrTiO₃ ceramics synthesis by hybrid method

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Abstract. The SrTiO₃ ceramics were fabricated by sol–gel and solid-state reaction hybrid method. The powders synthesized at the SG:SR molar ratio of 0.1:1 calcined at 950°C for 2 hours were used to prepare the ceramics which were after sintered at 1050, 1150, 1250, and 1350°C. The crystal structures, morphologies and dielectric properties of the ceramics were subsequently characterized. The pure cubic perovskite phase of SrTiO₃ corresponding to JCPDS number 35-0734, was revealed by X-ray diffraction (XRD) in every studied sintering condition. Scanning electron microscope showed the increase in average grain sizes when raising sintering temperature. The grains were approximately spherical with the sizes ranging from 0.20 to 1.07 µm. The highest dielectric constant, found in the ceramic sintered at 1350°C for 2 hours was 441 (at 1 kHz).

1. Introduction
Strontium titanate (SrTiO₃) has a perovskite structure with many interesting properties, for instance, large dielectric constant, low dielectric loss, and high thermal and chemical stability. Consequently, it is one of important ceramic materials which have been widely used in sensors, actuators, electro-optical devices, random access memory devices and multilayer capacitors [1-7]. Because of the fact that synthesis methods have an important role to ceramic performances, for several years, great effort has been devoted to the development and modification of the methods since they differently influence the phase, morphology, particle size, crystal defect and surface property of powders as well as ceramics. SrTiO₃ was typically fabricated by the solid-state reaction and other chemical solution methods. Recently, the sol–gel method is popular for preparing nanomaterials with high purity, homogeneity, small grain size and low calcination temperature; however, the product quantity is relatively low in contrast to the conventional solid-state reaction method which provides high product quantity with large grain size but needs high calcination temperatures [8, 9]. The aims of this research are to propose a novel hybrid method between sol-gel and solid-state reaction and to study the influence of the different sintering temperatures on the crystal structures, microstructures and dielectric properties of SrTiO₃ ceramics.
2. Materials and method
In this study, analytic grade chemicals were used without further purification. The SrTiO\textsubscript{3} powders were prepared by the sol-gel and solid-state reaction hybrid method. In sol-gel precursor (SG) preparation process, citric monohydrate (C\textsubscript{6}H\textsubscript{8}O\textsubscript{7}•H\textsubscript{2}O) was dissolved by continuous stirring in deionized water and then ammonium hydroxide (NH\textsubscript{4}OH) was dropped into the previous solution until its pH is equal to 9. Next, titanium butoxide (C\textsubscript{16}H\textsubscript{36}O\textsubscript{4}Ti) and strontium nitrate (Sr(NO\textsubscript{3})\textsubscript{2}) were added to the pH-adjusted citric solution and follow by heating at 80°C for 4 hours until the gel was formed which we obtain a sol-gel precursor (SG). For solid-state reaction precursor (SR) preparation, strontium carbonate (SrCO\textsubscript{3}) and titanium dioxide (TiO\textsubscript{2}) powders were weighed according to the stoichiometric composition and then mixed with ethanol by ball-milling for 24 hours. The solid-state reaction precursor (SR) was obtained from the mixed powder slurry dried overnight at 100°C. The crystalline powders were prepared by the mixture at the SG:SR molar ratio of 0.1:1 which were after calcined at 950°C for 2 hours. Accordingly, the calcined powders were mixed with PVA and uniaxially pressed at 80 MPa for 1 minute into green body pellets of 15 mm. in diameter, followed by sintering at 1050–1350°C for 2 hours. XRD (PhilipX’Pert mode) was used to investigate the crystal structures of the as-sintered pellets. The pellet surfaces were characterized by SEM (JOEL Leo1455VP model). Silver paste was then therefore coated on both sides of the pellet surfaces and were heated at temperature of 500°C for 30 minutes to form electrodes for the electrical properties measured by precision impedance analyzer (Agilent 4263B) controlled by a computer at 1 kHz measuring from room temperature to 200°C.

3. Results and discussion

![Figure 1. XRD patterns of SrTiO\textsubscript{3} ceramics at different sintering temperatures.](image)

As can be seen from the XRD patterns of SrTiO\textsubscript{3} ceramics sintered at different temperatures depicted in figure 1, only pure cubic perovskite structure of SrTiO\textsubscript{3}, according to JCPDS No. 35-0734, was observed.
Figure 2. SEM micrographs of SrTiO$_3$ ceramics at various sintering temperatures: (a) 1050°C, (b) 1150°C, (c) 1250°C and (d) 1350°C.

The SEM micrographs of SrTiO$_3$ ceramics were shown in figure 2. The hard-agglomerated grains were found in every sintering temperature. In addition, the average grain sizes at various sintering temperatures were shown in table 1. When increasing sintering temperatures, the grains became interconnected and develop their sizes. This possibly attributed to thermal energy influencing the mass transport mechanism in the material affecting to the grain neck growth [10, 11].

Figure 3. Temperature dependence of dielectric constant (solid lines) and loss (dash lines) of SrTiO$_3$ ceramics at various sintering temperatures.

The temperature dependent dielectric properties of SrTiO$_3$ ceramics at 1 kHz with in a temperature range of 25 to 100°C were exhibited in figure 3. The dielectric constants at room temperature increased
when the sintering temperatures increased. Besides, the dielectric loss at room temperature show the decrease whilst the sintering temperatures were raised. The maximum dielectric constant, 441, was found in the ceramic sintered at 1350°C.

Illustrated in table 1, The average grain size increased when temperature increasing which reached 1.07 µm for the ceramic sintered at 1350°C. In the same way, the dielectric increased according to temperature raising. Dielectric constant of ST ceramics increased with higher sintering temperature used in contrast to dielectric loss while dielectric loss was approximately 0.02.

Table 1. The average grain size, dielectric constant and dielectric loss of ceramics sintered at different temperatures.

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Average grain size (µm)</th>
<th>Dielectric constant (at 1 kHz)</th>
<th>Dielectric loss (at 1 kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1050</td>
<td>0.20</td>
<td>195</td>
<td>0.39</td>
</tr>
<tr>
<td>1150</td>
<td>0.21</td>
<td>345</td>
<td>1.26</td>
</tr>
<tr>
<td>1250</td>
<td>0.80</td>
<td>315</td>
<td>0.12</td>
</tr>
<tr>
<td>1350</td>
<td>1.07</td>
<td>441</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Illustrated in table 2, annealing conditions, average grain sizes and dielectric properties of SrTiO$_3$ ceramics prepared by different methods showed that the sol-gel and solid-state reaction hybrid method is comparatively effective to fabricate SrTiO$_3$ ceramics with good dielectric properties and low temperature consumed in the synthesis processing.

Table 2. The SrTiO$_3$ ceramics prepared by various methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Calcination temperature</th>
<th>Sintering temperature</th>
<th>Dielectric constant (at RT)</th>
<th>Dielectric loss (at RT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid-state reaction method [8]</td>
<td>1150°C</td>
<td>1440°C</td>
<td>295 (1 kHz)</td>
<td>0.002 (1 kHz)</td>
</tr>
<tr>
<td>sol-gel method [9]</td>
<td>700°C</td>
<td>1450°C</td>
<td>397 (10 kHz)</td>
<td>0.01 (10 kHz)</td>
</tr>
<tr>
<td>sol-gel and solid-state reaction Hybrid method (This work)</td>
<td>950°C</td>
<td>1350°C</td>
<td>441 (1 kHz)</td>
<td>0.02 (1 kHz)</td>
</tr>
</tbody>
</table>

4. Conclusion
The SrTiO$_3$ ceramics were successfully prepared by sol–gel and solid-state reaction hybrid method. The cubic perovskite structure of SrTiO$_3$ was found with no pyrochlores detected in every studied sintering temperature, 1050-1350°C. The grain sizes increased when raising sintering temperatures. The highest dielectric constant was found in the ceramic sintered at 1350°C for 2 hours.

References


