Sinterability and Microstructure of Bi-Added SnO₂ Nanomaterials by Precipitation Method

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Abstract

The influence of systematic bismuth addition into SnO₂ ceramics on the sinterability and microstructure was investigated. The general composition is SnCl₄·H₂O + (x)Bi(NO₃)₃·5H₂O, where x = 0.00, 0.0025, 0.005 and 0.01. The nanoscale powders were synthesized by chemical precipitation method and characterized by TGA, FTIR, XRD and TEM. The obtained nanopowders were in the 10 nm range. The sintering characteristics were found to depend tremendously upon the amounts of bismuth addition. SEM revealed improvement in grain growth with increasing bismuth content. Liquid phase formation, with evidence of abnormal grain growth and lower bulk densities, and vaporization as well as inhomogeneous distribution of bismuth, is believed to be mainly responsible for the degradation in the densification rate in these Bi-added samples.

Key words: Sinterability, Varistor, SnO₂, Nanoparticle, Precipitation

Introduction

Metal oxide varistors are electronic ceramic devices with primary functions of sensing and limiting transient voltage surges in electronic devices and energy-related transmission equipments. Among several metal oxides, tin dioxide (SnO₂)-based materials have received much attention recently due to their crucial technological applications. They have been used in electro-optical equipments and glass industry, catalysts, gas sensors and varistors. The SnO₂ varistor-based systems offer electrical characteristics of non-linearity and breakdown voltage often reported to be superior to their ZnO-based counterparts. However, the low densification rate due to SnO₂’s high surface diffusion and high partial pressure at high temperatures have limited its use for varistor application which requires high bulk density for optimal performance. Addition of bismuth has been shown to be effective to densify ZnO-based ceramics and other related oxide systems. However, no systematic investigation of such addition (compositional-wise) has been reported. Besides being compositionally dependent, the processing method also has a great influence on the varistor’s properties whose characteristics are closely related to the sintered microstructure. Chemical precipitation has emerged as one practical, inexpensive synthesis method, capable of producing nanosized powders. In this work, SnO₂ ceramics with systematic Bi addition were synthesized by chemical precipitation. Their sinterability and microstructure were investigated.

Materials and Experimental Procedures

All chemicals used in this study were reagent-grade. The general composition is SnCl₄·H₂O + (x)Bi(NO₃)₃·5H₂O, where x = 0.00, 0.0025, 0.005, 0.01 and 0.02. SnCl₄·H₂O was dissolved in distilled water (1M). Bi(NO₃)₃·5H₂O was slowly added, with varying stoichiometry, to the solution under vigorous stirring. A 1M NaOH solution was slowly added drop-wise to adjust the pH of the system to be 10. After one-hour of stirring, the solutions were oven-dried and washed.

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with distilled water ten times to remove chloride ions. AgNO₃ was used to confirm complete removal of the chloride ions. The precipitates were calcined at 400°C for 6 hours to remove organics; this temperature was determined from Thermogravimetric Analysis (TGA, 7 Perkin-Elemer). The synthesized nanoparticles were characterized for structural properties by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet, Impact 410), X-rays diffractometry (XRD, D/MAX 2000 Rigaku) and Transmission Electron Microscope (TEM, Philips EM201C). The calcined powders (with an averaged particle size of approximately 5 nm as determined by the Scherrer’s formula) were consolidated into pellets of approximately 8 mm in diameter and 2 mm in thickness. These pellets were sintered in air for 6 hours at temperatures ranging from 900°C to 1400°C. The microstructure was examined by Scanning Electron Microscopy (SEM, Hitachi S-3000N). The pellets’ surfaces were ground with alumina polishing powders and thermally etched at 100°C lower than the sintering temperature for 30 minutes. The averaged grain size was measured by the line-intercept method. The relative bulk density was calculated using 6.02 g/cm³ as a theoretical density value of the cassiterite SnO₂ structure.

Results and Discussion

The thermal decomposition profile of the precipitates (x = 0.005) is shown in Figure 1. A continuous decrease in the product weight of approximately 7% was observed with a sharp decomposition rate between 100°C and 200°C. The remaining weight became relatively constant after 400°C, the temperature at which calcination of the precipitates was performed. The weight loss beyond 100°C is likely due to the decomposition of the hydroxides and other organic residues present in the precursors or formed during the precipitation process. Figure 2 shows the FTIR spectra of the (x = 0.005) powder calcined at 400°C for 6 hours. The spectra contain several peaks which could be assigned to different functional groups. The very broad peak at 3420 cm⁻¹ belongs to the OH group whereas those between 1300 cm⁻¹ and 1700 cm⁻¹ are likely associated with several functional groups such as –OH, N-H and H-O-H (bending vibration from the molecular H₂O).¹¹ The N-H peak could be explained by the use of a nitrate precursor. A broad peak between 500°C and 1000°C signifies bonding between tin and oxygen. The presence of stretching vibration bands of O-Sn-O and Sn-O has been reported to be at 663 and 565 cm⁻¹ with an averaged broad peak at 610 cm⁻¹ (11-13). Therefore, these experimental results confirmed the formation of SnO₂ nanoparticles in this study.

Figure 1. Gravimetric thermo-analysis curve of a x = 0.005 powder precipitated at pH = 10.

Figure 2. FTIR spectrum of a x = 0.005 sample calcined at 400°C for 6 hours.

Such phase formation is confirmed in Figure 3(a). The XRD profile of the calcined (x = 0.005) powders contains broad reflections that can be indexed according to JCPDS 41-1445 with a cassiterite structure. There are no observable secondary reflections. Such absence does not imply single phasic nature of the synthesized powders; rather, this could possibly be due to a very large width at the base of the main SnO₂ reflections, overshadowing any small secondary reflections near the baseline. In addition, very low amounts of dopant (x = 0.005) or its resulting impurity might be under the detection limit of XRD. Using the Scherrer’s formula, the averaged crystallite size was determined to be approximately 10 nm. The TEM image in Figure 4 also reaffirms the calculated
crystallite size as well as exposes the effect of extensive agglomeration of these nanoparticles. The tendency to floc together is induced by a very high specific surface area. Nevertheless, the problem of agglomeration is not a major concern in this study since these nanopowders would later be pressed into consolidated ceramic pieces.

Figure 3. XRD patterns of $x = 0.005$ samples. (a) Calcined at 400°C for 6 hours, and (b) Sintered at 1300°C for 6 hours.

Figure 4. TEM viewgraph of a $x = 0.005$ sample calcined at 400°C for 6 hours.

Figure 5 shows bulk densities of the ceramic pellets sintered between 900°C and 1400°C for 6 hours. It can be seen that all four compositions possess conventional sintering behavior; a very sharp rate of sintering is detected after certain temperatures. For example, the onset temperature of sintering was higher than 1000°C for the $x = 0.00$ and $x = 0.0025$ samples. The samples with higher doping levels ($x = 0.005$ and 0.01) never reached relative densities of more than 80%, comparing to 85% achieved in the samples with lower amounts of dopants. The highest obtained density was 87% in the $x = 0.0025$ sample sintered at 1400°C. Low densities have been previously reported in the Bi$_2$O$_3$-SnO$_2$ system.$^{(9)}$ Examining the density data, there appears to be two distinct regimes that occurred during sintering. The first regime can be assigned to the sintering temperature of 1000°C and lower. At 1000°C, increasing amount of bismuth resulted in slightly higher densities. Although the differences are quite small (less than 5%), it could still be significant given a crucial role of bismuth as a sintering aid in ZnO-based compositions. The eutectic temperature was reported to be as low as 750°C in the ZnO-Bi$_2$O$_3$ binary system.$^{(6-7)}$ Thus, it is likely that, within this regime, liquid-phase sintering induced by the presence of Bi$_2$O$_3$ plays a dominant role for densification of the ceramic pieces. The second regime starts at 1100°C and displays an opposite trend to that in the first regime. At higher sintering temperatures, the samples with lower doping amounts ($x = 0.00$ and 0.0025) became denser, signaling that other mechanisms might be dominant in addition to the proposed liquid-phase sintering. This could possibly be explained by vaporization of bismuth at high temperatures, given its low melting temperature.$^{(7, 9)}$ Preliminary investigation on the weight change of the sintered samples indicated a higher loss (up to two weight percent) in the samples with higher amounts of doping. Such mass loss could leave behind pores and voids in the structure, severely retarding the densification process. The sintering temperatures in this study were below the vaporization temperature of SnO$_2$; therefore, the only species prone to vaporize is bismuth.$^{(5)}$

Figure 5. Relative densities from isothermal sintering of 6 hours. All four compositions are included.

Figure 6 displays SEM images of the samples sintered at 1300°C for 6 hours. The microstructures
contain intergranular porosity, a testimony to the low relative densities in the 77% to 84% range these samples possess. The grain shape comprises both isotropic and rod-like characteristics. The latter could be related to the tetragonal crystal structure of the cassiterite phase of SnO$_2$ itself, which could be confirmed by XRD in Figure 3(b). No secondary reflections were detected in the XRD pattern of the sintered (x = 0.005) sample. The averaged grain sizes are summarized in Table 1. Increasing amount of bismuth addition yielded larger grains but with simultaneous slight reduction in bulk density. A large distribution in grain size is clearly observed in the x = 0.005 sample (Figure 6(c)). The movement of the liquid phase along grain boundary, as previously mentioned, has been reported to induce a capillary force and enhance mass transfer rate, resulting in abnormal grain growth. Interestingly, such large grain size distribution, however, was not observed in the x = 0.0025 sample. The amount of the liquid phase from the starting bismuth precursor at this composition might not be sufficient to induce abnormal grain growth. This type of bimodal grain size distribution was also reported by in the SnO$_2$-based system.$^{(10)}$ Therefore, it is likely that the liquid phase formation could be responsible for the deterioration in densification in the samples with higher degrees of bismuth addition.

Table 1. Bulk densities and averaged grain sizes of the samples sintered at 1300°C for 6 hours.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm$^3$)</th>
<th>Grain Size ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.00</td>
<td>4.97</td>
<td>0.85</td>
</tr>
<tr>
<td>x = 0.0025</td>
<td>5.06</td>
<td>1.71</td>
</tr>
<tr>
<td>x = 0.005</td>
<td>4.70</td>
<td>2.55</td>
</tr>
<tr>
<td>x = 0.01</td>
<td>4.76</td>
<td>2.80</td>
</tr>
</tbody>
</table>

It seems, from the previous experimental results, that the nature of a liquid phase in the Bi$_2$O$_3$-SnO$_2$ system plays a crucial role in the microstructural evolution of the ceramics during sintering. Several involved aspects of this liquid-phase effect involved in the sintering process include the phasic type, the quantity, and most importantly, the distribution within the structure.$^{(1)}$ The type of

Figure 6. SEM images for the samples sintered at 1300 °C for 6 hours. (a) x = 0.00, (b) x = 0.0025, (c) x = 0.005 and (d) x = 0.01.
the liquid phase within the microstructure could not be determined in this study. However, it is highly possible that a liquid phase that exists along the grain boundary did not have enough time to crystallize during cooling, resulting in thin layers of amorphous phase which could not be detected by XRD. The quantity of the liquid phase, as determined by the initial amount of bismuth dopant, also affects the densification rate especially in the temperatures lower than 1100°C as shown in Figure 5. The degree of dopant distribution could also be another key factor determining the sinterability in this Bi$_2$O$_3$-SnO$_2$ system. A closer examination of the x = 0.005 sample reveals inhomogeneity in the microstructure (Figure 7). The sample is composed of two different regions; one contains relatively densely-packed grains while the other is clearly porous in nature. Clusters of densifying regions were found distributing throughout the structure surrounded by interconnected macroscopic voids. This low level of structural inhomogeneity could likely be caused by inadequate mixing capability during synthesis of nanoparticles, resulting in non-uniformity in the densified regions. Such structural heterogeneity inevitably leads to low sinterability clearly portrayed in these samples. \(^{(1-2)}\)

![Figure 7. SEM image of a x = 0.005 sample at 1300°C for 6 hours. Larger magnification was employed to demonstrate microstructural inhomogeneity.](image)

**Conclusions**

The sinterability and microstructure of Bi-added SnO$_2$ nanosized powders synthesized by chemical precipitation were reported. The calcined nanopowders were equiaxed in nature and were approximately 10 nm in size. No secondary phases were detected by XRD in both calcined powders and sintered samples. Addition of Bi yielded a slightly higher densification rate at sintering temperatures lower than 1100 °C. The sintering behavior could be characterized into two regimes and was shown to be strongly dependent on the composition of the amount of added bismuth. It is believed that liquid phase formation, with evidence of abnormal grain growth, vaporization of bismuth species and lower bulk densities, is mainly responsible for the lowering in the densification rate in these Bi-added samples. Structural inhomogeneity was also observed and could likely be induced by insufficient amount as well as inhomogeneous distribution of the bismuth liquid phase.

**References**


