Effects of a B$_2$O$_3$ additive on the sintering properties of WO$_3$ ceramics

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Abstract

WO₃ ceramics were sintered at various temperatures with a B₂O₃ additive, and WO₃ sintering was observed at temperatures above the heat-treatment temperature of 900 °C. For the WO₃ ceramic with B₂O₃ (heat-treated for 20 h), a dense microstructure with crystal facets was formed, while the numbers of pores decreased. The dielectric constant of the sintered WO₃ ceramic with B₂O₃ additive was twice as large as that without B₂O₃.

KEYWORDS: A. ceramics, B. microstructure C. electron microscopy, D. dielectric properties
1. Introduction

Monoclinic tungsten trioxide (WO$_3$) has a high dielectric constant [1–4], thus WO$_3$ ceramic is a promising candidate compound for use in ceramic capacitors. Previously, we fabricated non-doped (WO$_3$) or phosphorus-doped (P$_x$W$_{1-x}$O$_3$) tungsten trioxide ceramics and evaluated their dielectric properties [5, 6]. In these reports, WO$_3$ ceramics were sintered at 1000 °C for 24 h. Figure 1 shows a cross-sectional SEM image of a sample heat-treated at these conditions. Though slight grain growth was observed for this sample, several pores were also observed.

In order to improve sinterability, many sintering additives were tested in previous investigations, including CuO [7], MgO [8], and B$_2$O$_3$ [9]. Cu and Mg form a complex oxide with WO$_3$. Thus, in the present report, we examined the effects of B$_2$O$_3$ additive on sintering WO$_3$ ceramics, and evaluated the electrical properties of the resulting samples.

2. Experimental procedure

The starting materials were WO$_3$ (Wako Pure Chemical Industries, Ltd., Japan) and B$_2$O$_3$ (Wako Pure Chemical Industries, Ltd., Japan) powders. These powders were mixed with a B$_2$O$_3$ content of 5 wt%. A binder solution of aqueous PVA was added to
the mixture, which was then die-pressed at 15 MPa to produce a pellet. The precursor pellet was sintered at 850~950 °C for 2~20 h, and WO₃ ceramics were fabricated. For comparison with previous investigations, a WO₃ pellet was also sintered at 1000 °C for 24 h without B₂O₃ addition.

The microstructure of the resulting specimens was observed using scanning electron microscopy (SEM, S-3200N; Hitachi Ltd., Japan). The crystal structure of the specimens was determined using X-ray diffraction (XRD, Miniflex; Rigaku Corp., Japan) at room temperature with CuKα. Dielectric measurements were performed at room temperature using an LCR meter (HP 4284A; Hewlett-Packard Inc., USA).

3. Results and discussion

A WO₃ and B₂O₃ powder mixture was made into pellets by die-pressing, and the pellets were sintered at 850~950 °C for 2 h. Figure 2 presents the cross-sectional SEM images of the resulting specimens. Grain growth and sintering were not observed for the specimen heat-treated at 850 °C, but were observed for the specimens heat-treated above 900 °C. Inhomogeneous grain growth was observed for the specimen heat-treated at 950 °C. These results suggested that the suitable sintering temperature of WO₃-B₂O₃ pellets was 900 °C.
Thus, for further study, WO$_3$-B$_2$O$_3$ mixture pellets were sintered at 900 °C for 2~20 h, and Figure 3 shows cross-sectional SEM images of the resulting specimens. Increased sintering time resulted in grain growth of the WO$_3$ ceramic. For the specimen heat-treated for 20 h, a dense microstructure with crystal facets was observed and the numbers of pores decreased. Thus, the ideal sintering time for WO$_3$ with B$_2$O$_3$ additive at 900 °C was taken as 20 h.

Figure 4 illustrates XRD patterns for these WO$_3$-B$_2$O$_3$ pellets and the source WO$_3$ powder. The XRD peaks for both specimens indicated monoclinic WO$_3$, single phase (JCPDS 72-1465), which suggests that the WO$_3$ did not react with the B$_2$O$_3$.

Dielectric constants were then measured for these WO$_3$-B$_2$O$_3$ ceramics. For comparison, dielectric constants of the WO$_3$ ceramic heat-treated at 1000 °C for 24 h without B$_2$O$_3$ additive were also measured. Figure 5 presents the dielectric properties of both specimens. This measurement was carried out at room temperature, and both samples exhibited remarkably large dielectric constants because the temperature of the sample (20 °C) was near the dielectric anomaly temperature for non-doped WO$_3$ [6]. Compared to the non-B$_2$O$_3$ specimen, the specimen heat-treated with B$_2$O$_3$ showed larger dielectric constants for all measured frequencies. Additionally, from the SEM images (Fig.1 and Fig. 4(c)), the specimen sintered with B$_2$O$_3$ showed high sinterability.
compared with the non-B$_2$O$_3$ specimen, which explains the increased dielectric constants observed in the former. The dielectric loss was comparable to the dielectric constant for both samples, so the B$_2$O$_3$ additive was assumed to affect the dielectric loss, which affects electrical conductivity, in sintered WO$_3$ ceramics.

4. Conclusion

WO$_3$ ceramics were sintered with a B$_2$O$_3$ additive, with optimal results for samples prepared at 900 °C for 20 h. Here, the WO$_3$ did not react to the B$_2$O$_3$ additive, and was highly dense compared to its non-B$_2$O$_3$ counterpart. Similarly, the dielectric constant of the WO$_3$-B$_2$O$_3$ ceramic was larger than that of the specimen without B$_2$O$_3$. In conclusion, using B$_2$O$_3$ as an additive not only lowers the sintering temperature for WO$_3$ but also improves the sinterability and electrical performance of WO$_3$. 
References


Figure captions

Fig. 1. An SEM image of the WO₃ ceramic sintered at 1000 °C for 24 h.

Fig. 2. SEM images of the WO₃ ceramics with B₂O₃ additives sintered at (a) 850 °C, (b) 900 °C and (c) 950 °C for 2 h.

Fig. 3. SEM images of the WO₃ ceramics with B₂O₃ additives sintered at 900 °C for (a) 5h, (b) 10 h and (c) 20 h.

Fig. 4. XRD patterns for the WO₃ ceramics with B₂O₃ additives sintered (a) at 1000 °C for 24 h and (b) 900 °C for 20 h.

Fig. 5. Dielectric constant and loss of the WO₃ ceramics sintered at (a) 1000 °C for 24 h without B₂O₃ additive and (b) 900 °C for 20 h with B₂O₃ additives sintered.
Fig. 1.
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An SEM image of the WO$_3$ ceramic sintered at 1000$^\circ$ C for 24 h.
Fig. 2.
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SEM images of the WO$_3$ ceramics with B$_2$O$_3$ additives sintered at (a) 850 $^\circ$ C, (b) 900 $^\circ$ C, and (c) 950 $^\circ$ C for 2 h.
Fig. 3.
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SEM images of the WO$_3$ ceramics with B$_2$O$_3$ additives sintered at 900° C for (a) 5h, (b) 10 h and (c) 20 h.
Fig. 4.
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XRD patterns for the WO$_3$ ceramics with B$_2$O$_3$ additives sintered (a) at 1000 °C for 24 h and (b) 900 °C for 20 h.
Fig. 5.
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Dielectric constant and loss of the WO$_3$ ceramics sintered at (a) 1000 °C for 24 h without B$_2$O$_3$ additive and (b) 900 °C for 20 h with B$_2$O$_3$ additives.