Effects of a B_2O_3 additive on the sintering properties of WO_3 ceramics

Hidetoshi Miyazaki[1,*], Jun Ando[1], Atsushi Nose[1], Hisao Suzuki[2], Toshitaka Ota[3]

[1]Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060, Nishikawatsu, Matsue, Shimane 690-8504, Japan

*E-mail: miya@riko.shimane-u.ac.jp, Tel: +81-852-32-8893

[2]Graduate School of Science and Technology, Shizuoka University, 3-5-1, Johoku, Hamamatsu, Shizuoka 432-8561, Japan

[3]Ceramic Research Laboratory, Nagoya Institute of Technology, 10-6-29, Asahigaoka, Tajimi, Gifu 507-0071, Japan

Abstract

WO_3 ceramics were sintered at various temperatures with a B_2O_3 additive, and WO_3 sintering was observed at temperatures above the heat-treatment temperature of 900 °C. For the WO_3 ceramic with B_2O_3 (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 WO_3 ceramic with B_2O_3 additive was twice as large as that without B_2O_3.

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 ($P_xW_{1-x}O_3$) 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_2O_3 [9]. Cu and Mg form a complex oxide with WO_3. Thus, in the present report, we examined the effects of B_2O_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_2O_3 (Wako Pure Chemical Industries, Ltd., Japan) powders. These powders were mixed with a B_2O_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 WO_3 ceramics were fabricated. For comparison with previous investigations, a WO_3 pellet was also sintered at 1000 °C for 24 h without B_2O_3 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 WO_3 and B_2O_3 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 WO_3-B_2O_3 pellets was 900 °C.

Thus, for further study, WO_3-B_2O_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_2O_3 additive at 900 °C was taken as 20 h.

Figure 4 illustrates XRD patterns for these WO_3-B_2O_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_2O_3.

Dielectric constants were then measured for these WO_3-B_2O_3 ceramics. For comparison, dielectric constants of the WO_3 ceramic heat-treated at 1000 °C for 24 h without B_2O_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_2O_3 specimen, the specimen heat-treated with B_2O_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_2O_3 showed high sinterability compared with the non-B_2O_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_2O_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_2O_3 additive, with optimal results for samples prepared at 900 °C for 20 h. Here, the WO_3 did not react to the B_2O_3 additive, and was highly dense compared to its non-B_2O_3 counterpart. Similarly, the dielectric constant of the WO_3-B_2O_3 ceramic was larger than that of the specimen without B_2O_3. In conclusion, using B_2O_3 as an additive not only lowers the sintering temperature for WO_3 but also improves the sinterability and electrical performance of WO_3.

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Figure captions

Fig. 1. An SEM image of the WO_3 ceramic sintered at 1000 °C for 24 h.

Fig. 2. SEM images of the WO_3 ceramics with B_2O_3 additives sintered at (a) 850 °C, (b) 900 °C and (c) 950 °C for 2 h.

Fig. 3. SEM images of the WO_3 ceramics with B_2O_3 additives sintered at 900 °C for (a) 5h, (b) 10 h and (c) 20 h.

Fig. 4. XRD patterns for the WO_3 ceramics with B_2O_3 additives sintered (a) at 1000 °C for 24 h and (b) 900 °C for 20 h.

Fig. 5. Dielectric constant and loss of the WO_3 ceramics sintered at (a) 1000 °C for 24 h without B_2O_3 additive and (b) 900 °C for 20 h with B_2O_3 additives sintered.

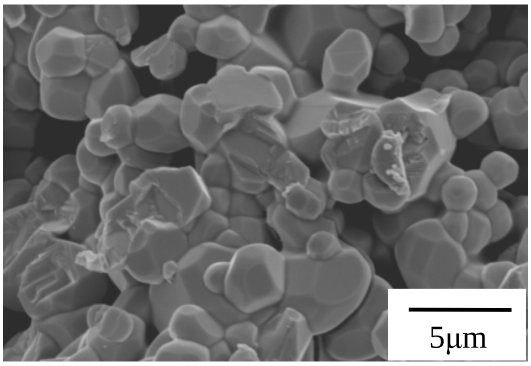

Fig.1.
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An SEM image of the WO_3 ceramic sintered at 1000 ° C for 24 h.

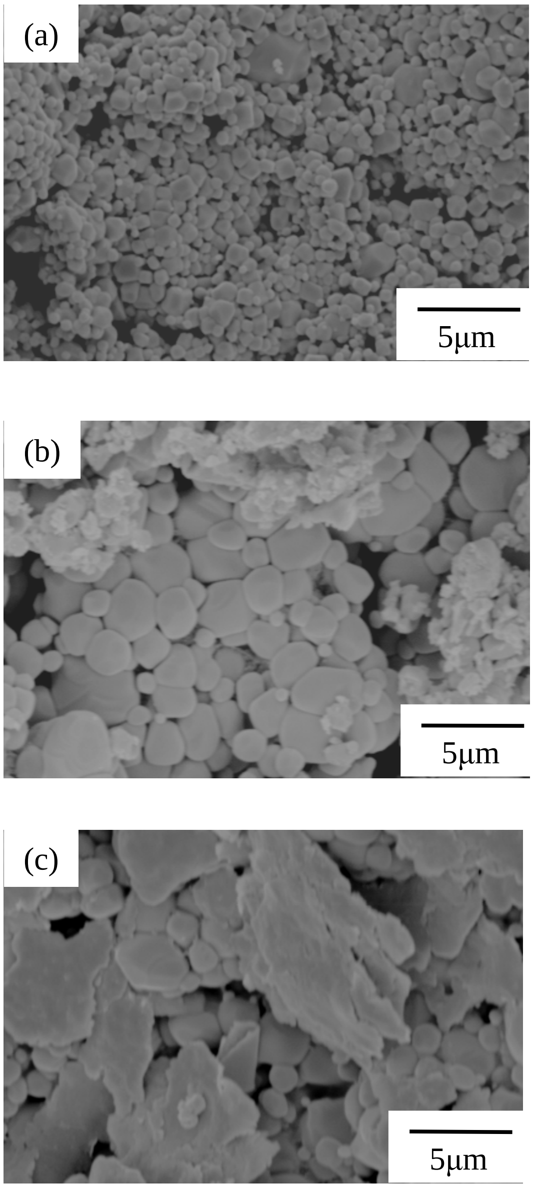

Fig. 2.
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SEM images of the WO_3 ceramics with B_2O_3 additives sintered at (a) 850 °C, (b) 900 °C and (c) 950 °C for 2 h.

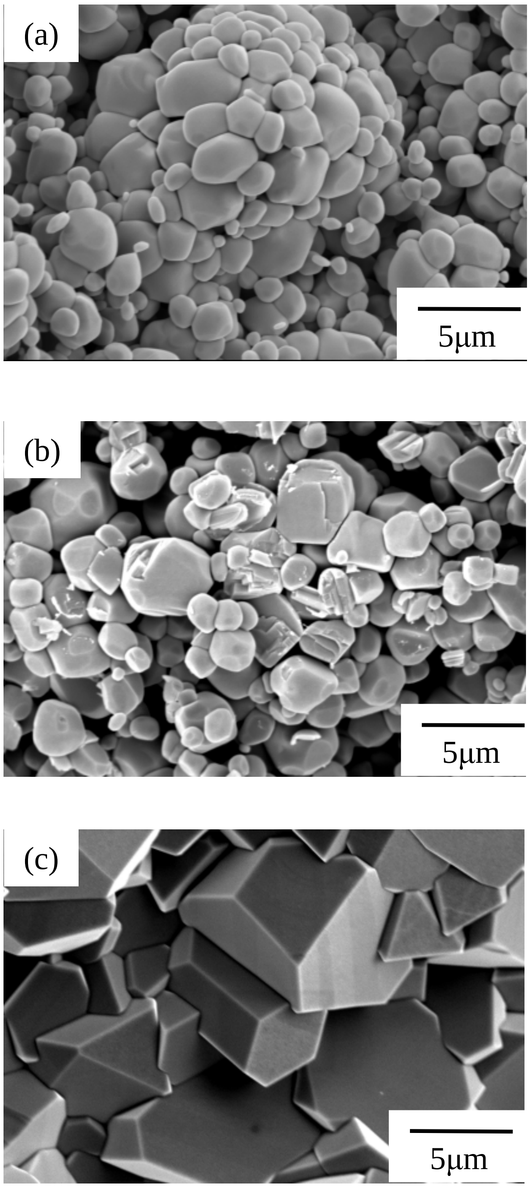

Fig. 3.
H. Miyazaki
SEM images of the WO_3 ceramics with B_2O_3 additives sintered at 900 °C for (a) 5h, (b) 10 h and (c) 20 h.

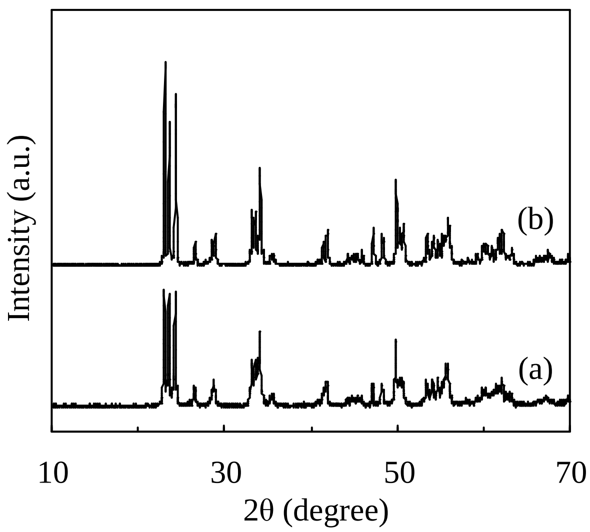

Fig. 4.
H. Miyazaki
XRD patterns for the WO_3 ceramics with B_2O_3 additives sintered (a) at 1000 °C for 24 h and (b) 900 °C for 20 h.

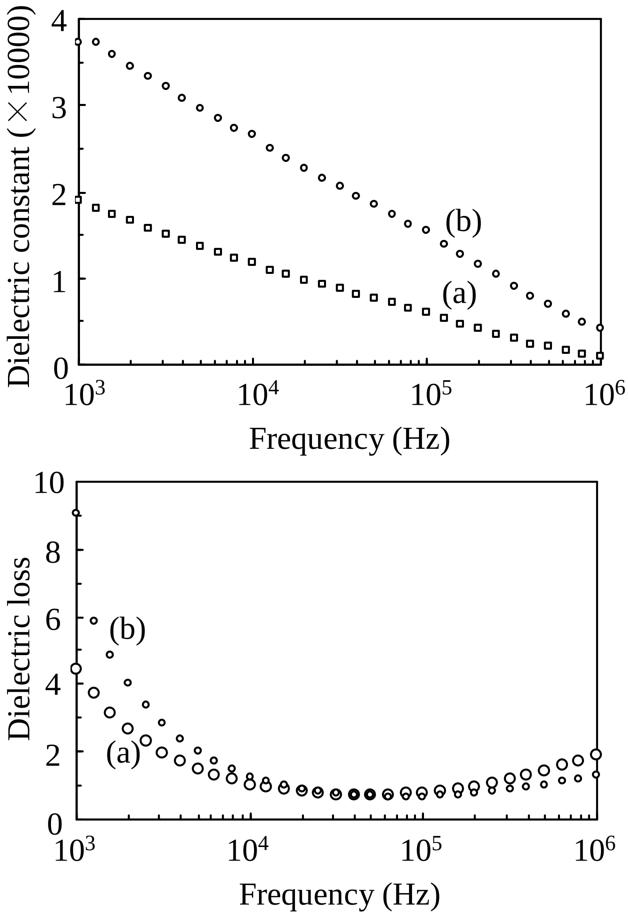

Fig. 5.
H. Miyazaki
Dielectric constant and loss of the WO_3 ceramics sintered at (a) 1000 °C for 24 h without B_2O_3 additive and (b) 900 °C for 20 h with B_2O_3 additives.