Effect of Na$_2$O and B$_2$O$_3$ Addition on Nonlinear Electrical Properties of WO$_3$-Based Capacitor–Varistors

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Abstract
WO$_3$-based varistors with added Na$_2$O and B$_2$O$_3$ were synthesized by the solid-state reaction. The undoped and B$_2$O$_3$-doped WO$_3$ ceramics exhibited weak nonlinear $I$–$V$ characteristics. The nonlinear $I$–$V$ characteristics of the ceramics increased slightly after the addition of Na$_2$O and more significantly after the addition of Na$_2$O and B$_2$O$_3$. The nonlinearity coefficients $\alpha$ of the WO$_3$, Na$_{0.005}$WO$_3$, and Na$_{0.005}$WO$_3$–5 wt % B$_2$O$_3$ ceramics were 1.86, 2.03, and 5.22, respectively. The breakdown voltages of the WO$_3$, Na$_{0.005}$WO$_3$, and Na$_{0.005}$WO$_3$–5 wt % B$_2$O$_3$ ceramics were 1.56, 6.05, and 12.42 V/cm, respectively. The dielectric constant and the dielectric loss of the Na$_{0.005}$WO$_3$–5 wt % B$_2$O$_3$ ceramic were ~50–150 and less than 0.3, respectively, for frequencies ranging from 1 to 1000 kHz.

Keywords: WO$_3$, varistor, nonlinearity, breakdown voltage

1. Introduction
As varistors exhibit nonlinear $I$–$V$ characteristics, they can be used to protect electrical devices and circuits against voltage surges. ZnO-based varistors exhibit large nonlinear coefficients and high energy handling capabilities (Li, Li, Liu, Alim, & Chen, 2002). SrTiO$_3$-based varistors (Franken & Vieg e rs, 1981; Li, Li, & Alim, 2006) and WO$_3$-based varistors (Makarov & Trontelj, 1994; Wang, Aburas, Yao, & Liu, 1999; Yang, Wang, & Dong, 2004; Zang et al., 2004; Wang, Shao, Zhang, Li, & Yu, 2010) have also been investigated. To improve the nonlinear $I$–$V$ properties of a WO$_3$-based varistor, Na$_2$O ((Makarov & Trontelj, 1994; Wang, Aburas, Yao, & Liu, 1999; Yang, Wang, & Dong, 2004; Zang et al., 2004) or a rare-earth metal oxide (Wang, Shao, Zhang, Li, & Yu, 2010; Yang et al., 2004) has been doped in WO$_3$ ceramics. Furthermore, WO$_3$ has a large dielectric constant (Hirose & Furukawa, 2006; Miyazaki, Nose, Suzuki, & Ota, 2011); thus, WO$_3$ ceramics may be suitable to create capacitor–varistors (Yang, Wang, & Dong, 2004).

Previously, we fabricated a WO$_3$ ceramic capacitor by adding B$_2$O$_3$ as a sintering aid (Miyazaki, Ando, Nose, Suzuki, & Ota, 2015). The addition of B$_2$O$_3$ to WO$_3$ affected the dielectric constants and loss of sintered WO$_3$ ceramics. Therefore, it became evident that the electrical properties of WO$_3$ varistors could be controlled by the addition of B$_2$O$_3$.

In this study, WO$_3$-based ceramic varistors were synthesized by adding Na$_2$O and B$_2$O$_3$. We evaluated the crystallographic structure and microstructure of the sintered ceramics as well as the effects of Na$_2$O and B$_2$O$_3$ addition on the electrical and dielectric properties. These properties were nonlinear and thus a characteristic of varistors.

2. Experimental Procedure
A mixture of powdered WO$_3$ (Wako Pure Chemical Industries, Ltd., Japan) and Na$_2$CO$_3$ (Wako Pure Chemical Industries, Ltd., Japan) was die-pressed at 15 MPa to form a pellet. The pellet was calcined at 1100 °C for 1 h in air, then cooled and ground. The undoped or Na-doped WO$_3$ powders were mixed with B$_2$O$_3$ powder (Wako Pure Chemical Industries, Ltd., Japan) with B$_2$O$_3$ content ranging from 0 to 20 wt%. A PVA aqueous solution was added to the mixture that was then die-pressed at 15 MPa to produce a pellet. The precursor pellet was finally sintered at 1000 °C for 20 h in air to yield the final product.
The crystallographic structures of the specimens were determined using X-ray diffraction (XRD, Miniflex; Rigaku Corp.) with CuKα radiation. The microstructures of the sintered ceramics were observed using scanning electron microscopy (SEM, S-3200N, Hitachi Ltd.). The \( I-V \) characteristics of the sintered ceramics were evaluated using a two-probe method with a digital voltmeter (34405A, Agilent Technologies Inc.) and a power supply (3640A, Agilent Technologies Inc.). Dielectric measurements were performed at room temperature using an LCR meter (HP 4284A, Hewlett-Packard Inc.).

3. Results and Discussion

Na\(_2\)O–WO\(_3\) powders containing 0.5 mol % Na were heat-treated at 1100 °C for 1 h to react according to the methods referred to in a previous report (Wang, Aburas, Yao, & Liu, 1999). Figure 1 illustrates the XRD patterns of the resulting specimens. The specimens showed a single phase WO\(_3\) indicating that the resulting specimens were Na-doped WO\(_3\) ceramics. Whereas, for the heat-treated ceramic doped with 1 mol % Na (Na\(_2\)O), the ceramic surface was slightly white, presumably due to the presence of excess Na. Therefore, Na\(_{0.005}\)WO\(_3\) achieved the optimal doping concentration.

![Figure 1. XRD pattern of the Na\(_{0.005}\)WO\(_3\) ceramic.](Image)

WO\(_3\) and B\(_2\)O\(_3\) powder mixtures containing 0–20 wt % B\(_2\)O\(_3\) were mixed and sintered at 1000 °C for 20 h. The microstructures of the resulting ceramics were evaluated using SEM. Figure 2 shows the SEM images of the ceramics. B\(_2\)O\(_3\) addition increased the sinterability of the resulting ceramics. Conversely, B\(_2\)O\(_3\) reaction residues that resulted from excessive B\(_2\)O\(_3\) addition were observed at the grain boundaries for the ceramics with more than 10 wt % B\(_2\)O\(_3\) addition. Figure 3 illustrates the \( I-V \) characteristics of these ceramics. B\(_2\)O\(_3\) addition caused the electrical resistance to increase when the B\(_2\)O\(_3\) contents were less than 10 wt %, and did not affect the electrical resistance when the B\(_2\)O\(_3\) contents were higher than 10 wt %. B\(_2\)O\(_3\) addition caused weak nonlinear \( I-V \) characteristics, and the nonlinearity coefficients \( \alpha \) of those were slightly higher than 1. These results (SEM and \( I-V \) characteristics) suggested that 10 wt % or more B\(_2\)O\(_3\) addition was excessive, thus we used B\(_2\)O\(_3\) contents of 5 wt % to prepare the WO\(_3\)–B\(_2\)O\(_3\) (or Na\(_2\)O–WO\(_3\)–B\(_2\)O\(_3\)) ceramics.

After the reaction of Na\(_2\)CO\(_3\) and WO\(_3\) powders with Na contents of 0.5 mol % at 1100 °C for 1 h, Na\(_{0.005}\)WO\(_3\) and Na\(_{0.005}\)WO\(_3\)–5 wt % B\(_2\)O\(_3\) powders were sintered to produce ceramic pellets under 1000 °C for 20 h. An undoped WO\(_3\) ceramic was also sintered under the same conditions. Figure 4 depicts the SEM images of the WO\(_3\), Na\(_{0.005}\)WO\(_3\), and Na\(_{0.005}\)WO\(_3\)–5 wt% B\(_2\)O\(_3\) sintered ceramics. All the ceramics sintered well, and the sintering characteristics of undoped WO\(_3\) were improved by the addition of Na\(_2\)O and B\(_2\)O\(_3\). These results revealed that the resulting WO\(_3\), Na\(_{0.005}\)WO\(_3\), and Na\(_{0.005}\)WO\(_3\)–5 wt % B\(_2\)O\(_3\) B\(_2\)O\(_3\) ceramics were sintered sufficiently to measure its electrical properties.

The \( I-V \) characteristics of the three types of ceramics mentioned above are displayed in Figure 5. Nonlinearity coefficients \( \alpha \) of the ceramics were calculated from the following equation (Wang, Shao, Zhang, Li, & Yu, 2010):

\[
\alpha = \frac{\log(I_2 / I_1)}{\log(V_2 / V_1)}
\]

where \( I_2 = 7.0 \text{ mA/cm}^2, I_1 = 1.0 \text{ mA/cm}^2, V_2 \) and \( V_1 \) were the voltages corresponding to the current density of \( I_2 \) and \( I_1 \), respectively. Both of the Na\(_{0.005}\)WO\(_3\)-based ceramics with or without B\(_2\)O\(_3\) addition showed large nonlinear \( I-V \) characteristics, and the nonlinearity coefficients \( \alpha \) of the WO\(_3\), Na\(_{0.005}\)WO\(_3\), and Na\(_{0.005}\)WO\(_3\)–5 wt % B\(_2\)O\(_3\)
ceramics were 1.86, 2.03, and 5.22, respectively. Na2O addition increased the nonlinear $I-V$ characteristics of the ceramics, and the result was consistent with that of previous studies (Makarov & Trontelj, 1994; Zang et al., 2004). Addition of B2O3 to the Na$_{0.005}$WO$_3$ ceramic increased the nonlinearity coefficient $\alpha$. From the SEM observation (Figure 2), the large value of $\alpha$ of the Na$_{0.005}$WO$_3$–5wt % B$_2$O$_3$ ceramic assumed to be attributed to the existence of the B$_2$O$_3$ at the grain boundaries.

Figure 2. SEM images of the sintered WO$_3$ ceramics with B$_2$O$_3$ contents of (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, (d) 15 wt %, and (e) 20 wt %

Figure 3. $I-V$ characteristics of the sintered WO$_3$ ceramics with B$_2$O$_3$ contents of 0–20 wt %
Figure 4. SEM images of the (a) WO$_3$, (b) Na$_{0.005}$WO$_3$, and (c) Na$_{0.005}$WO$_3$–5 wt% B$_2$O$_3$ ceramics

Figure 5. $I$–$V$ characteristics of the (a) WO$_3$, (b) Na$_{0.005}$WO$_3$, and (c) Na$_{0.005}$WO$_3$–5 wt% B$_2$O$_3$ ceramics
The breakdown voltage is defined as the field density when the current density reaches 1 mA/cm² (Wang, Shao, Zhang, Li, & Yu, 2010). The breakdown voltages of the WO₃, Na₀.₀₀₅WO₃ and Na₀.₀₀₅WO₃–5 wt% B₂O₃ ceramics were 1.56, 6.05, and 12.42 V/cm, respectively. Addition of B₂O₃ increased the breakdown voltage. B₂O₃ existed at the grain boundary in the sintered ceramics; thus, B₂O₃ addition increased the breakdown voltage of the WO₃-based varistor.

The above characteristics reveal that the varistor properties of WO₃ ceramics can be controlled by the addition of Na₂O and B₂O₃. The resistivities of the presented samples were also evaluated at low voltages (less than 5 V/cm) and found to display linear, close to ohmic, I–V characteristics. The resistivities of the WO₃, Na₀.₀₀₅WO₃ and Na₀.₀₀₅WO₃–5 wt% B₂O₃ ceramics were 1.3 × 10³ Ω cm, 3.7 × 10³ Ω cm, and 2.0 × 10⁶ Ω cm, respectively. B₂O₃ addition caused the resistivity to increase by an order of magnitude. This is ideal for varistor applications as leakage currents in circuits can be suppressed by varistor devices with high electrical resistances. Thus, B₂O₃ addition to Na₂O–WO₃ varistor ceramics leads to an improvement of the electrical properties, including the nonlinearity coefficient, resistivity, and breakdown voltage.

Figure 6 illustrates the dielectric properties of the Na₀.₀₀₅WO₃–5 wt% B₂O₃ ceramic at room temperature. The dielectric constant was ~50–150 for frequencies ranging from 1 to 1000 kHz, and the value was smaller than for the undoped WO₃ ceramics (1000–10000) (Miyaśaki, Nose, Suzuki, & Ota, 2011). Addition of Na₂O and B₂O₃ to WO₃ ceramics led to a reduction in the dielectric constant compared to that of the undoped WO₃. The dielectric loss was less than 0.3 at frequencies ranging from 1 to 1000 kHz; this was a slightly large value than that of the undoped WO₃ ceramics (Miyaśaki, Nose, Suzuki, & Ota, 2011). Na₂O doping increases the electrical conductivity (by polarons), thus the loss is assumed to increase with Na₂O (Na₂CO₃) addition. The Na₀.₀₀₅WO₃–5 wt% B₂O₃ ceramic showed relatively large dielectric constant and relatively small dielectric loss. Improvement of dielectric properties of WO₃-based ceramic varistors warrants further investigation in the future.

![Figure 6. Dielectric properties of the Na₀.₀₀₅WO₃–5 wt% B₂O₃ ceramic](image)

**4. Conclusion**

WO₃-based varistors with additions of Na₂O and B₂O₃ were synthesized by traditional solid-state reaction, and the effects of the addition of Na₂O and B₂O₃ on the electrical properties were evaluated. Co-addition of B₂O₃ and Na₂O in the WO₃ varistor increased the nonlinearity coefficient, resistivity, and breakdown voltage. The resulting Na₀.₀₀₅WO₃–5 wt % B₂O₃ ceramic varistor showed a relatively large dielectric constant for frequencies ranging from 1 to 1000 kHz. These results suggest that B₂O₃–Na₂O–WO₃ ceramics seem promising for their application as materials for capacitor–varistors.

**References**


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