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Effect of Na_2O and B_2O_3 Addition on Nonlinear Electrical Properties of WO_3-Based Capacitor–Varistors

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Abstract

WO_3-based varistors with added Na_2O and B_2O_3 were synthesized by the solid-state reaction. The undoped and B_2O_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_2O and more significantly after the addition of Na_2O and B_2O_3. The nonlinearity coefficients α of the WO_3, $Na_{0.005}WO_3$, and $Na_{0.005}WO_3$–5 wt % B_2O_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_2O_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_2O_3 ceramic were ~50–150 and less than 0.3, respectively, for frequencies ranging from 1 to 1000 kHz.

Keywords: WO_3, varistor, nonlineality, 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 & Viegers, 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_2O ((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_2O_3 as a sintering aid (Miyazaki, Ando, Nose, Suzuki, & Ota, 2015). The addition of B_2O_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_2O_3.

In this study, WO_3-based ceramic varistors were synthesized by adding Na_2O and B_2O_3. We evaluated the crystallographic structure and microstructure of the sintered ceramics as well as the effects of Na_2O and B_2O_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_2CO_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_2O_3 powder (Wako Pure Chemical Industries, Ltd., Japan) with B_2O_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_2O_3–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_2O), 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.

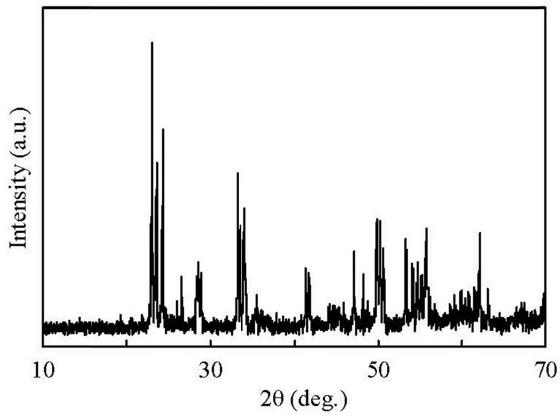

Figure 1. XRD pattern of the $Na_{0.005}WO_3$ ceramic.

WO_3 and B_2O_3 powder mixtures containing 0–20 wt % B_2O_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_2O_3 addition increased the sinterability of the resulting ceramics. Conversely, B_2O_3 reaction residues that resulted from excessive B_2O_3 addition were observed at the grain boundaries for the ceramics with more than 10 wt % B_2O_3 addition. Figure 3 illustrates the *I–V* characteristics of these ceramics. B_2O_3 addition caused the electrical resistance to increase when the B_2O_3 contents were less than 10 wt %, and did not affect the electrical resistance when the B_2O_3 contents were higher than 10 wt %. B_2O_3 addition caused weak nonlinear *I–V* characteristics, and the nonlinearity coefficients α of those were slightly higher than 1. These results (SEM and *I–V* characteristics) suggested that 10 wt % or more B_2O_3 addition was excessive, thus we used B_2O_3 contents of 5 wt % to prepare the WO_3–B_2O_3 (or Na_2O–WO_3–B_2O_3) ceramics.

After the reaction of Na_2CO_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_2O_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_2O_3 sintered ceramics. All the ceramics sintered well, and the sintering characteristics of undoped WO_3 were improved by the addition of Na_2O and B_2O_3. These results revealed that the resulting WO_3, $Na_{0.005}WO_3$, and $Na_{0.005}WO_3$–5 wt % B_2O_3 B_2O_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 α of the ceramics were calculated from the following equation (Wang, Shao, Zhang, Li, & Yu, 2010):

$$\alpha = \frac{\log(I_2 / I_1)}{\log(V_2 / V_1)} \tag{1}$$

where I_2 = 7.0 mA/cm^2, I_1 = 1.0 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_2O_3 addition showed large nonlinear *I–V* characteristics, and the nonlinearity coefficients α of the WO_3, $Na_{0.005}WO_3$, and $Na_{0.005}WO_3$–5 wt% B_2O_3

ceramics were 1.86, 2.03, and 5.22, respectively. Na_2O 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 B_2O_3 to the $Na_{0.005}WO_3$ ceramic increased the nonlinearity coefficient α. From the SEM observation (Figure 2), the large value of α of the $Na_{0.005}WO_3$–5wt % B_2O_3 ceramic assumed to be attributed to the existence of the B_2O_3 at the grain boundaries.

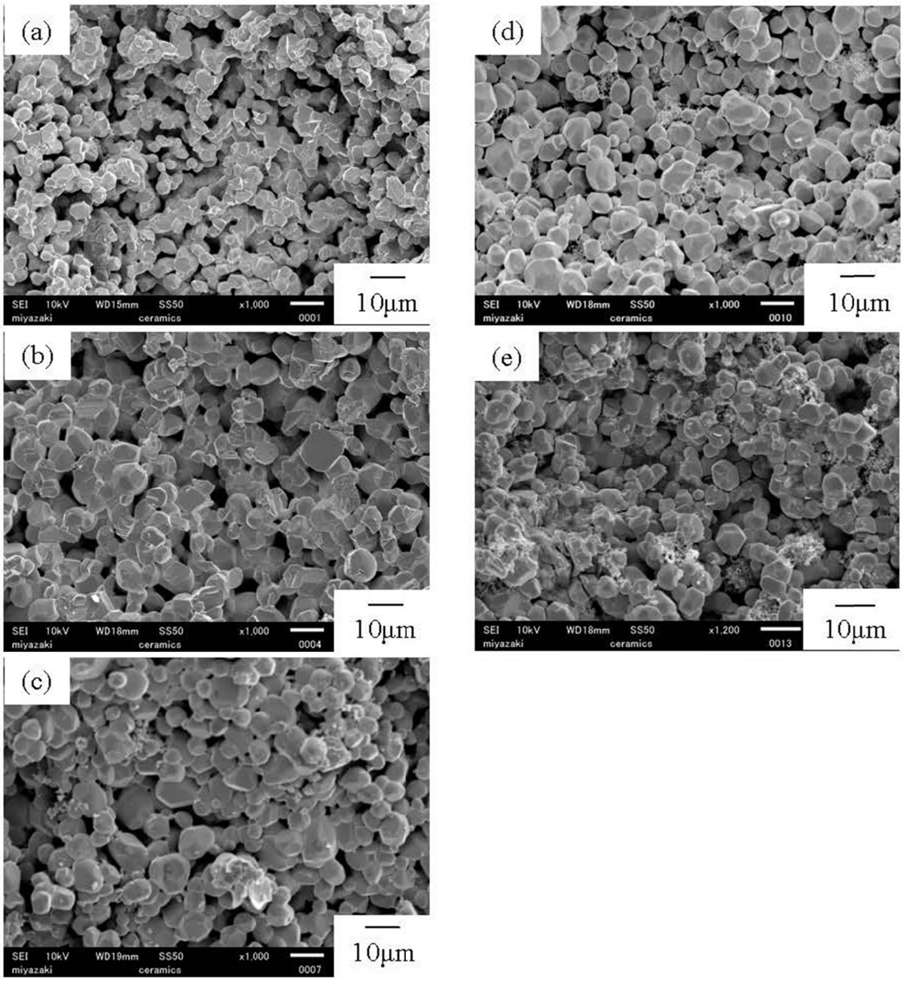

Figure 2. SEM images of the sintered WO_3 ceramics with B_2O_3 contents of (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, (d) 15 wt %, and (e) 20 wt %

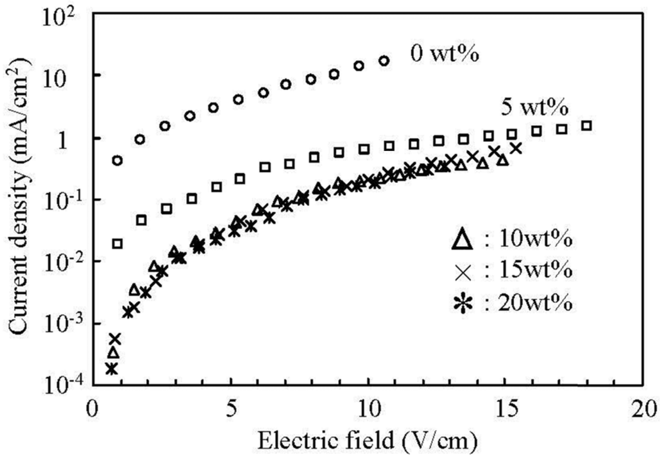

Figure 3. *I–V* characteristics of the sintered WO_3 ceramics with B_2O_3 contents of 0–20 wt %

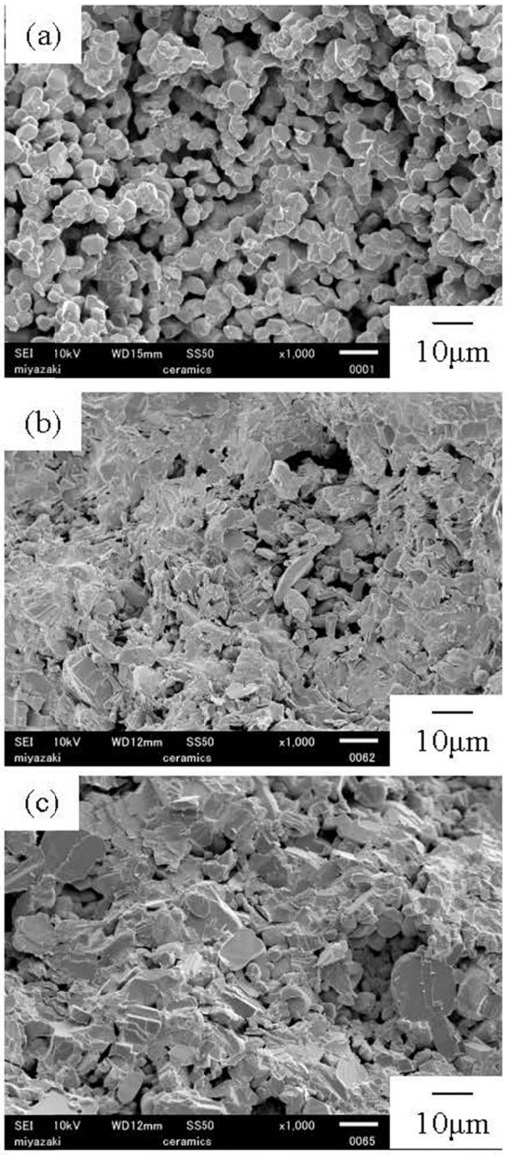

Figure 4. SEM images of the (a) WO_3, (b) $Na_{0.005}WO_3$, and (c) $Na_{0.005}WO_3$–5 wt% B_2O_3 ceramics

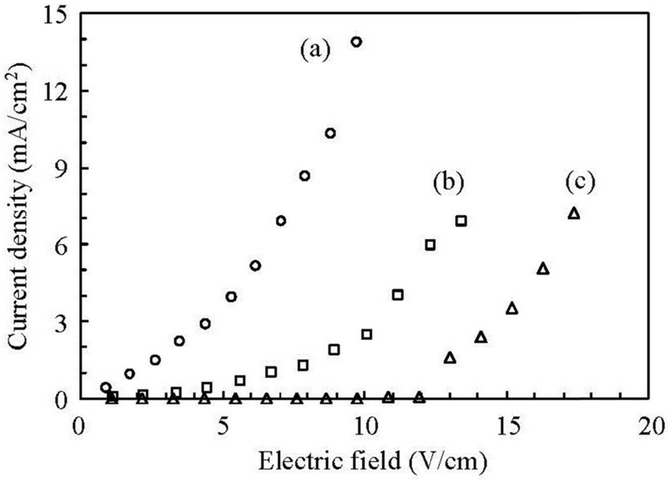

Figure 5. *I*–*V* characteristics of the (a) WO_3, (b) $Na_{0.005}WO_3$, and (c) $Na_{0.005}WO_3$–5 wt% B_2O_3 ceramics

The breakdown voltage is defined as the field density when the current density reaches 1 mA/cm^2 (Wang, Shao, Zhang, Li, & Yu, 2010). The breakdown voltages of the WO_3, $Na_{0.005}WO_3$, and $Na_{0.005}WO_3$–5 wt% B_2O_3 ceramics were 1.56, 6.05, and 12.42 V/cm, respectively. Addition of B_2O_3 increased the breakdown voltage. B_2O_3 existed at the grain boundary in the sintered ceramics; thus, B_2O_3 addition increased the breakdown voltage of the WO_3-based varistor.

The above characterstics reveal that the varistor properties of WO_3 ceramics can be controlled by the addition of Na_2O and B_2O_3. The resistivities of the presented samples were also evaluated at low voltages (less than 5V/cm) and found to display linear, close to ohmic, *I–V* characteristics. The resistivities of the WO_3, $Na_{0.005}WO_3$, and $Na_{0.005}WO_3$–5 wt % B_2O_3 ceramics were 1.3×10^3 Ω·cm, 3.7×10^3 Ω·cm, and 2.0×10^4 Ω·cm, respectively. B_2O_3 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, B_2O_3 addition to Na_2O–WO_3 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 $Na_{0.005}WO_3$–5 wt% B_2O_3 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 WO_3 ceramics (1000–10000) (Miyazaki, Nose, Suzuki, & Ota, 2011). Addition of Na_2O and B_2O_3 to WO_3 ceramics led to a reduction in the dielectric constant compared to that of the undoped WO_3. 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 WO_3 ceramics (Miyazaki, Nose, Suzuki, & Ota, 2011). Na_2O doping increases the electrical conductivity (by polarons), thus the loss is assumed to increase with Na_2O (Na_2CO_3) addition. The $Na_{0.005}WO_3$–5 wt% B_2O_3 ceramic showed relatively large dielectric constant and relatively small dielectric loss. Improvement of dielectric properties of WO_3-based ceramic varistors warrants further investigation in the future.

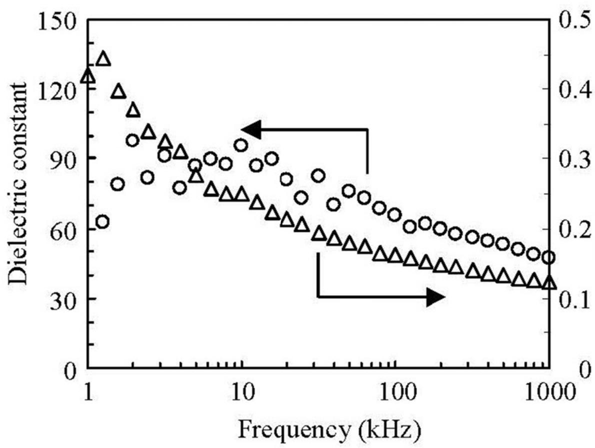

Figure 6. Dielectric properties of the $Na_{0.005}WO_3$–5 wt% B_2O_3 ceramic

4. Conclusion

WO_3-based varistors with additions of Na_2O and B_2O_3 were synthesized by traditional solid-state reaction, and the effects of the addition of Na_2O and B_2O_3 on the electrical properties were evaluated. Co-addition of B_2O_3 and Na_2O in the WO_3 varistor increased the nonlinearity coefficient, resistivity, and breakdown voltage. The resulting $Na_{0.005}WO_3$–5 wt % B_2O_3 ceramic varistor showed a relatively large dielectric constant for frenquencies ranging from 1 to 1000 kHz. These results suggest that B_2O_3–Na_2O–WO_3 ceramics seem promising for their application as materials for capacitor–varistors.

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