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Effect of Al_2O_3 on the microstructure and electrical properties of WO_3-based varistor ceramics

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Abstract

The influence of Al_2O_3 additive on the electrical properties and microstructure of (Na,Mn)-doped WO_3 ceramics was studied. Addition of Al_2O_3 shifts the current–voltage characteristics to higher fields and inhibits the grain growth of the WO_3-based non-Ohmic ceramics. The non-linearity coefficient of the current–voltage characteristics of the Al_2O_3-doped WO_3 ceramics increases with sintering temperature and attains a maximum value at 1250°C.

Keywords: Electrical properties; Grain growth; Microstructure-final; Varistors; WO_3; Al_2O_3

1. Introduction

The WO_3-based ceramic materials are interesting mainly as candidates for low voltage varistors. Tungsten oxide ceramics doped by Na_2O and MnO_2 exhibit non-linear current–voltage characteristics.[1] The addition of Na_2O has been found to be essential for forming non-Ohmic behaviour. The influence of Al_2O_3,MnO_2,Co_3O_4 and Na_2O on the sintering capacity of WO_3 ceramics was investigated in Ref. 2. The effect of the addition of small amounts of Li_2O,V_2O_5,Co_2O_3 and La_2O_3 on the electrical properties of WO_3 ceramics has been studied by Kaneki et al.[3]

In this study we shall present the effect of Al_2O_3 additive on the varistor characteristics and microstructure of (Na,Mn)-doped WO_3 ceramics.

2. Experimental

A series,of specimens, in the WO_3–Na_2O, WO_3–Na_2O-MnO_2, WO_3–Na_2O–Al_2O_3 and WO_3–Na_2O–MnO_2–Al_2O_3 systems were prepared by conventional ceramic techniques. Reagent grade powders of WO_3, Na_2CO_3, MnO_2 and $A1_2O_3$ were mixed in the desired proportion using alcohol as a medium. After drying, the mixture was pressed into disks of 6 mm diameter at a pressure of 200 MPa. The samples were sintered at 1100–1300°C in air for 2 h.

For electrical measurements liquid In–Ga alloy contacts were used as electrode material. Current–voltage (I–V) measurements were made in d.c. mode in the current range up to 1 mA at room temperature. The non-ohmic I–V characteristics were expressed empirically by $I = kV^{\alpha}$, where α is non-linear coefficient and k is a constant. The non-linear coefficient was calculated in the current density ranges of 0.1–1 mA cm^{-2}. The specific conductivity (σ_0) was measured at an electric field of 1 V mm^{-1} in the ohmic region. For breakdown field (E_1) the field at the current density of 1 mA cm^{-2} was taken.

Sintered samples were examined by scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1 shows the I–V characteristics for WO_3 ceramics of different compositions. Electrical parameters and average grain sizes for the obtained samples are listed in Table 1. It can be seen that the Al_2O_3 dopant decreases the leakage current at the ohmic region and increases the breakdown field of the (Na,Mn)-doped samples. From analysis of the obtained data it becomes evident that the breakdown field is closely correlated with the grain size and, therefore, the non-ohmic behavior of the WO_3 ceramics is a grain boundary property. Samples containing 3 mol% MnO_2 have a lower breakdown voltage, probably because of the great amount of a liquid phase, which seems to enhance grain growth in this system.

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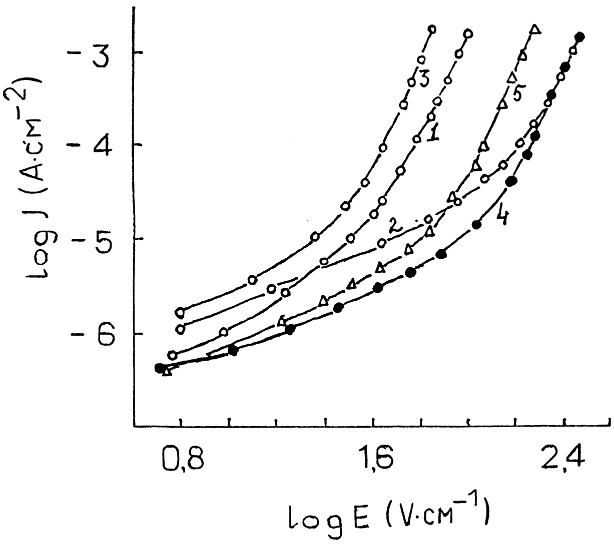


Fig. 1. I–V characteristics of different WO_3 ceramics sintered at 1250°C for 2 h (mol%): (1) WO3–0.5Na_2O; (2) WO_3–0.5Na_2O–0.5Al_2O_3; (3) WO_3–0.5Na_2O–0.5MnO_2; (4) WO_3–0.5Na_2O–0.5MnO_2–O.5Al_2O_3; (5) WO_3–0.5Na_2O–3.0MnO_2–0.5Al_2O_3.

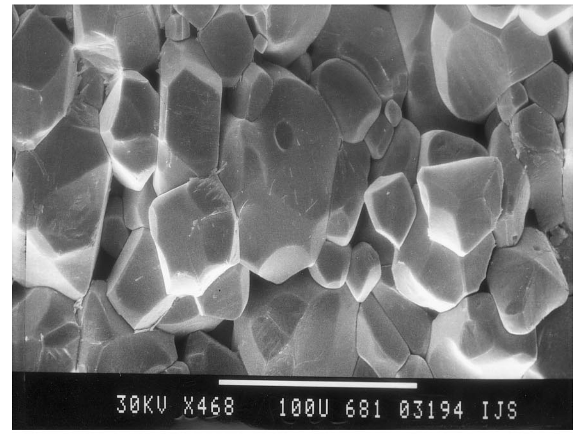
Table 1
Electrical parameters of the WO_3-based varistor ceramics sintered at 1250°C for 2 h

Content mol%	σ_0 Ohm^{-1} cm^{-1}	α	E_1 Vmm^{-1}	Average grain size μm
1. WO_3–0.5Na_2O	1.1×10^{-7}	5.5	9	30
2. WO_3–0.5Na2O–0.5 Al_2O_3	1.8×10^{-7}	5.3	27	6
3. WO_3–0.5Na_2O–0.5 MnO_2	2.6×10^{-7}	5.8	6.5	35
4. WO_3–0.5Na_2O–0.5 MnO_2–0.5Al_2O_3	6.3×10^{-7}	5.3	27	8
5. WO_3–0.5Na_2O–3.0 MnO_2–0.5Al_2O_3	7.1×10^{-7}	6.0	17	15

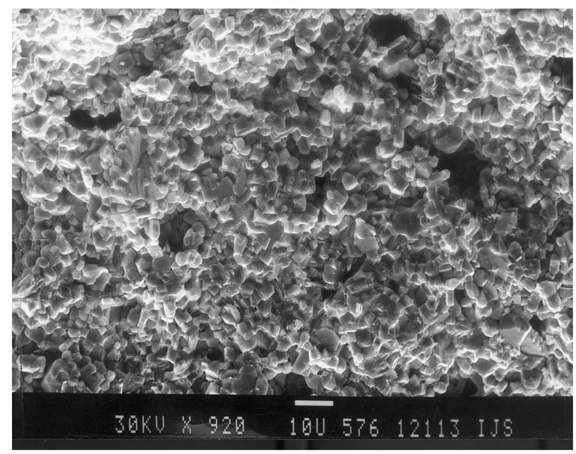
The microstructures of WO_3–Na_2O and Al_2O_3-doped WO_3 ceramic were shown in Fig. 2. Obviously, addition of Al_2O_3 inhibits the grain growth of the WO_3-based ceramics. The average grain size for Al_2O_3-doped samples is 6 μm, compared with 30 μm for the WO_3–Na_2O system.

Variation of the conductivity and nonlinear coefficient as a function of Al_2O_3 content is shown in Fig. 3. It can be seen that the conductivity decreases with increase in concentration of Al_2O_3. But, the non-linear coefficient decreases also with addition of Al_2O_3. The small addition of Al_2O_3 about 0.5 mol% is an optimal.

The effect of sintering temperature on the nonlinearity coefficient and the electrical conductivity was studied for the WO_3–Na_2O–Al_2O_3 ceramics and are summarised in Fig. 4. It can be seen that σ_0 decreases and α increases with increase in the sintering temperature and attains the maximum value at the 1250°C. It was also observed that the breakdown field decreases from 64 to 22 V mm^{-1} on increasing the T_s.



(a)



(b)

Fig. 2. A typical scanning electron micrograph of WO_3–O.5Na_2O, (A) and WO_3–0.5Na_2O–0.5Al_2O_3, (B) ceramics sintered at 1200°C for 2 h.

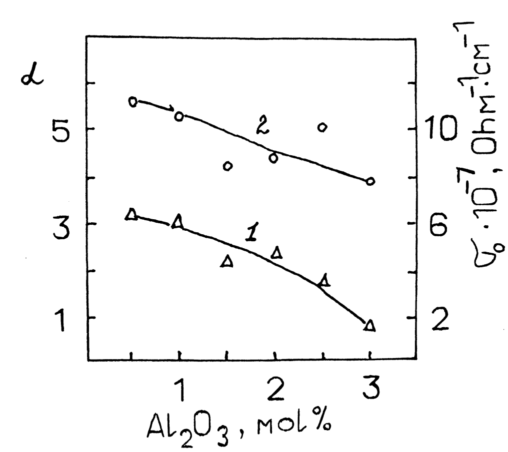


Fig. 3. Conductivity (1) and non-linear coefficient (2) of WO_3 ceramics as function of the Al_2O_3 content.

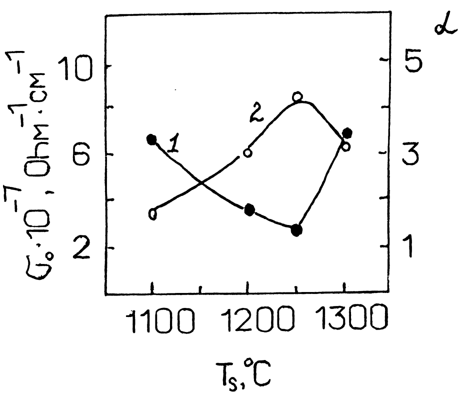


Fig. 4. Conductivity (1) and non-linear coefficient (2) of WO_3–Na_2O–Al_2O_3 ceramics as function of sintering temperature. The sintering time is 2 h.

4. Conclusion

Based on the experimental data, the following conclusions can be drawn:

1. Addition of Al_2O_3 inhibits the grain growth of the WO_3-based ceramics.
2. The Al_2O_3 dopant increases the breakdown field of the WO_3 non-ohmic ceramics.The breakdown field is about inversely proportional to the grain size.
3. The non-linearity coefficient of the current–voltage characteristics of the Al_2O_3-doped WO_3 ceramics increases with sintering temperature and attains a maximum value at 1250°C.

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References

1. Makarov, V. O. and Trontelj, M., Novel varistor material based on tungsten oxide. *J. Mater. Sci. Lett.*, 1994, **13**, 937–939.
2. Makarov, V. O. and Trontelj, M., Sintering and electrical conductivity of doped WO_3. *J. Eur. Ceram. Soc.*, 1996, **16**, 791–794.
3. Kaneki, N., Hara, H. and Shimuzu, T., Effect of atmosphere on resistivity of WO_3 ceramics. *J. Am. Ceram. Soc.*, 1976, **59**, 368–369.