SHORT REPORTS

0955-2219(95)00204-9

Journal of the European Ceramic Society 16 (1996) 791–794

0955-2219/96/$15.00

Sintering and Electrical Conductivity of Doped WO_3

V. O. Makarov[a] & M. Trontelj[b]

[a]University of Dnepropetrovsk, Gagarina 72, 320625 Dnepropetrovsk, Ukraine
[b]J. Stefan Institute, University of Ljubljana, Jamova 39, 61000 Ljubljana, Slovenia

(Received 30 March 1995; accepted 22 June 1995)

Abstract

The influence of a series of oxide additives, namely Al_2O_3, Co_3O_4, MnO_2 and Na_2O, on the sintering capacity and electrical conductivity of WO_3-based binary ceramic systems was studied. The densification behaviour and the microstructures obtained after firing were dependent on the additive oxide type. A small addition of Na_2O shifts the onset of sintering to lower temperatures, whereas the addition of Al_2O_3 shifts the onset of sintering to higher temperatures compared with undoped WO_3. The inhibition of grain growth was observed in Al_2O_3-doped WO_3. The electrical conductivity of these WO_3 ceramics depends on the additive oxide type and varies in the range from 2×10^{-2} to 9×10^{-7} Ω^{-1} cm^{-1}.

The WO_3–Na_2O system was found to exhibit non-linear current–voltage characteristics and a low breakdown voltage. The non-linearity coefficient of the current–voltage characteristics of the Na_2O-doped WO_3 ceramics increases with sintering temperature and attains a maximum value of around 5.

1 Introduction

Tungsten oxide (WO_3) is a nonstoichiometric n–type semiconductor and even a very small decrease in its oxygen content gives rise to an increase in the electrical conductivity.[1] The electrical conductivity of WO_3 single crystals ranges from 10 to 10^{-4} Ω^{-1} cm^{-1}, depending on the stoichiometry.[1–3] Studies on the electrical conductivity of WO_3-based ceramic materials have been reported.[4,5] The conductivity of doped WO_3 ceramics is claimed to be increased by the addition of La_2O_3, Co_2O_3 and Li_2O.[5] Although several authors have reported sintering studies of WO_3,[6–8] the influence of various additives on the sintering properties and the electrical conductivity has not been systematically investigated.

The present work describes new data on the influence of Al_2O_3, MnO_2, Co_3O_4 and Na_2O on the sintering capacity and electrical conductivity of WO_3-based binary systems.

2 Experimental

Tungsten trioxide powder and 0.5 mol% of additive oxide, either Al_2O_3, MnO_2, Co_3O_4 or Na_2O, were mixed using alcohol as a medium. Sodium oxide was added as Na_2CO_3. After drying, the mixture was then pressed into pellets of 6 mm diameter at a pressure of 200 MPa. Samples were sintered at 1200°C in air for 2 h. The samples doped with Na_2O were sintered at temperatures of 1050 to 1250°C. For investigation of the sintering behaviour of the WO_3-based composites, the pellets were heated to 1300°C at a rate of 10°C min^{-1}. Apparent densities of sintered pellets were determined using Archimedes' method.

For electrical measurements, liquid In–Ga alloy was used as the electrode material. Current–voltage (I–V) measurements were made in the 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 a non-linear coefficient and k is a constant. The non-linear coefficient was calculated in the current density range from 0.1 to 1 mA cm^{-2}. The specific conductivity (σ_0) was measured at an electric field of 1 V mm^{-1} in the ohmic region.

Sintered samples were examined by scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX).

3 Results and Discussion

The shrinkage curves of pure and doped WO_3 are shown in Fig. 1. The addition of Na_2O shifts the onset of sintering to lower temperatures, compared with the undoped WO_3. On the other hand, for the WO_3–Al_2O_3 system shrinkage begins at a higher temperature. For the WO_3–MnO_2 and WO_3–CO_3O_4 systems two different types of shrinkage can be noticed: a slow stage and then a rapid stage when a liquid phase appears. The second stage starts at around 1050°C for both compositions. The appearance of a liquid phase at ~1100°C for

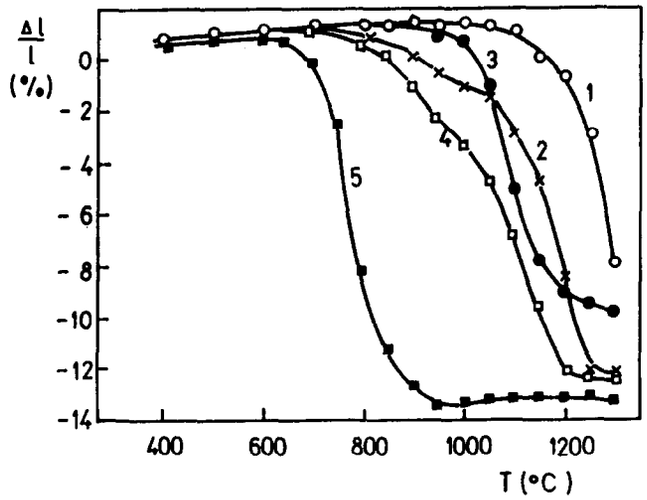

Fig. 1. Dimensional changes as a function of sintering temperature for pure WO_3 (3) and WO_3 doped by 0.5 mol% of Al_2O_3 (1), Co_3O_4 (2), MnO_2 (4) and Na_2O (5).

MnO_2-doped and at ~1050°C for Co_3O_4-doped WO_3 was confirmed by differential thermal analysis (DTA), and is responsible for the sudden rise of the shrinkage rate. The DTA curves for all compositions also showed two endothermic peaks at 760 and 910°C associated with phase transitions in the WO_3.[4]

Fig. 2 shows the microstructure of pure and doped WO_3 ceramics sintered at 1200°C for 2 h. A microstructural comparison showed that all the additives studied except Al_2O_3 enhance grain growth in WO_3. The grain sizes in the WO_3–Al_2O_3 system are smaller than those in the other binary systems, and therefore the addition of Al_2O_3 inhibits grain growth in WO_3. According to phase diagrams of the WO_3–Na_2O system, the liquid phase appears at 665°C whereas for the WO_3–Al_2O_3 system it appears at 1190°C.[9] Microstructural analysis of the polished ceramic surface showed a second intergranular phase for all the binary systems studied. Obviously, the sintering of these systems takes place in the presence of a liquid phase. All compositions have a porous microstructure.

Data on the apparent density, final shrinkage and average grain size of the WO_3-based systems studied, after sintering at 1200°C for 2 h, are listed in Table 1. The bulk density of the samples varied from 80% (pure WO_3) to 93% of the theoretical density, depending upon the composition. The data show an increase in the final shrinkage of doped samples for all compositions compared with undoped WO_3.

The specific electrical conductivity of tungsten oxide ceramics depends on the dopant oxide type and varies in the wide range from 2×10^{-2} to

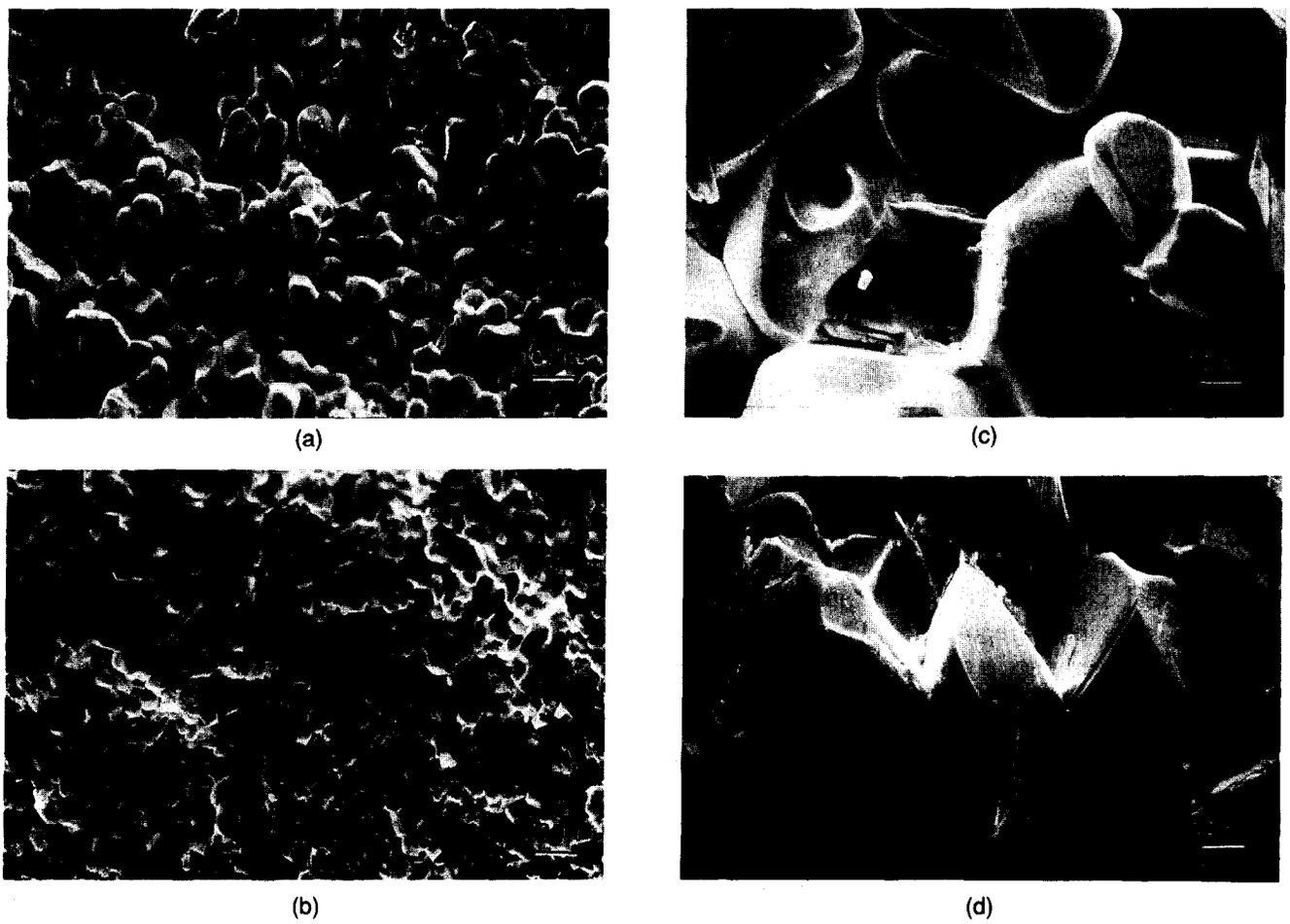

Fig 2. Microstructures of pure (a) and 0.5 mol% doped WO_3 samples after firing at 1200°C for 2 h: (b) WO_3 + Co_3O_4, (c) WO_3 + Al_2O_3 and (d) WO_3 + Na_2O.

Table 1. Apparent density, final shrinkage, average grain size and electrical parameters of various WO_3-based binary ceramic systems, sintered at 1200°C for 2 h

System	*Apparent density* ($g\ cm^{-3}$)	$\Delta l/l$ (%)	*Average grain size* (μm)	*Electrical conductivity* ($\Omega^{-1}\ cm^{-1}$)	*Non-linearity coefficient,* α
WO_3	5.8	11	10	8×10^{-6}	1
WO_3–Al_2O_3	6.7	14	6	2×10^{-2}	1
WO_3–Co_3O_4	6.7	14	65	5×10^{-5}	1
WO_3–MnO_2	6.5	13	150	1×10^{-6}	3
WO_3–Na_2O	6.8	14	30	9×10^{-7}	4

$9 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ (Table 1). It is well known that for polycrystalline materials the conductivity depends on the specific conductivity of the grain, the grain size and the grain boundary resistance. From Table 1 it can be seen that high conductivity WO_3–Al_2O_3 samples have linear *I–V* characteristics. It is believed that there are no barriers at the grain boundaries and the measured conductivity is close to the specific conductivity of WO_3 crystallites.[1–3] The *I–V* characteristics of WO_3 ceramics doped with MnO_2 and Na_2O are non-linear. It is assumed that the conductivity of the WO_3–MnO_2 and WO_3–Na_2O systems is controlled by the grain boundaries. The electrical conduction within the WO_3 grain is believed to be ohmic and non-linearity arises due to the boundaries between the WO_3 grains.

The Na_2O-doped WO_3 ceramic is interesting because of its high non-linear coefficient. The *I–V* characteristics of WO_3–Na_2O samples as a function of sintering temperature are shown in Fig. 3. The effect of the sintering temperature on the non-linearity coefficient α and the electrical conductivity σ_0 are summarized in Fig. 4. It can be seen that α increases and σ_0 decreases with increase in the sintering temperature. It seems that a high temperature increases the grain boundary resistance of Na_2O-doped WO_3 ceramics. Further increase of the sintering temperature does not improve the non-linear characteristics due to partial sublimation of WO_3.

It was also observed that the average grain size for the WO_3–Na_2O system increases from 15 to 40 μm on increasing the sintering temperature from 1050 to 1250°C.

The presence of a second phase between the matrix grains is clearly visible in Fig. 5. This phase is located at multiple grain junctions and probably originates from solidification during cooling of the liquid phase. EDX analysis revealed that this phase is rich in Na and W. Semiquantitative EDX analysis allowed

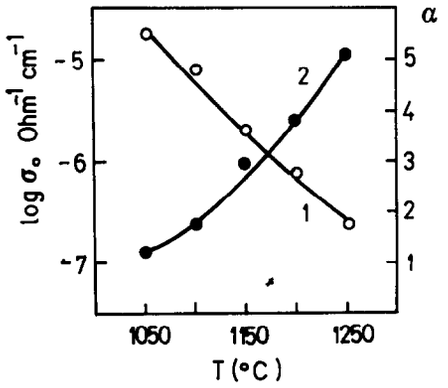

Fig. 4 Variation of conductivity (1) and non-linearity coefficient (2) with sintering temperature for the WO_3–Na_2O ceramics.

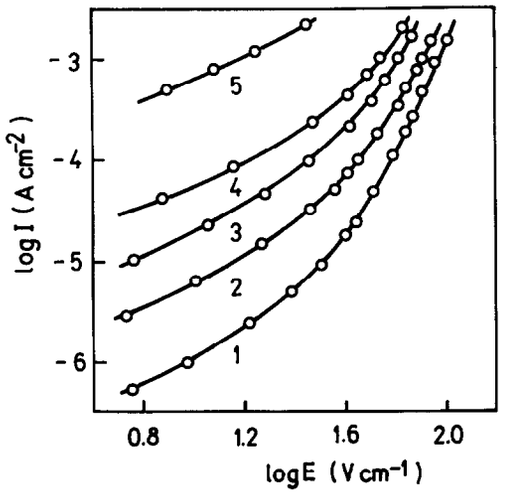

Fig. 3. *I–V* characteristics of WO_3–Na_2O ceramics sintered at different temperatures, 1250°C (1), 1200°C (2), 1150°C (3), 1100°C (4) and 1050°C (5), for 2 h.

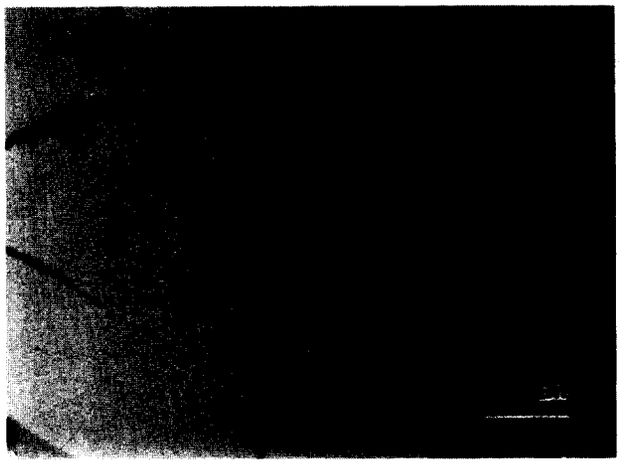

Fig. 5 SEM micrograph of a polished cross-section of a WO_3–Na_2O ceramic showing the presence of the intergranular phase at the corners of the matrix WO_3 grains.

its identification as sodium tungstate Na_xWO_3, where $x = 0.4$–0.5. According to the EDX analysis no dopant was found within the WO_3 grains.

It is important to note that the Na_2O-doped WO_3 ceramic is characterized by a low breakdown voltage. Since the non-linearity coefficient of about 3 to 4 obtained for the WO_3–Na_2O binary systems is inadequate from the practical point of view, it might be possible to improve it by adding other oxides.

4 Conclusions

Based on experimental data, the following conclusions can be drawn on the influence of oxide additives on the sintering capacity and electrical conductivity of WO_3-based ceramics.

(1) Doping of WO_3 by Al_2O_3, Co_3O_4, MnO_2 and Na_2O promotes better densification. The addition of Na_2O shifts the onset of sintering to lower temperatures, whereas the addition of Al_2O_3 shifts the onset of sintering to higher temperatures, compared with pure WO_3. The addition of Al_2O_3 inhibits the grain growth in WO_3. All the other additives studied enhance grain growth. Sintering of the doped WO_3 takes place in the presence of a liquid phase.

(2) The electrical conductivity of tungsten oxide ceramics strongly depends on the oxide additives. It reaches a maximum value of 2×10^{-2} Ω^{-1} cm^{-1} for the WO_3–Al_2O_3 system and a minimum value of 9×10^{-7} Ω^{-1} cm^{-1} for the WO_3–Na_2O system. It was found that the Na_2O-doped WO_3 ceramics exhibit non-linear current–voltage characteristics.

References

1. Sahle, W. & Nygren, M., Electrical conductivity and high resolution electron microscopy studies of WO_{3-x} crystals with $0 \leq x \leq 0{,}28$. *J. Solid State Chem.*, **48** (1983) 154–60.
2. Berak, J. M. & Sienko, M. J., Effect of oxygen-deficiency on electrical transport properties of tungsten trioxide crystals. *J. Solid State Chem.*, **2** (1970) 109–33.
3. Grunin, V. S., Makarov, V. L., Patrina, I. B. & Razumienko, M. V., Defects of nonstoichiometry and electrical conductivity of WO_3 crystals. *Sov. Phys. Solid State*, **30** (1988) 3091–5.
4. Sawada, S. & Danielson, G. C., Electrical conduction in crystals and ceramics of WO_3. *Phys. Rev.*, **113** (1959) 803–5.
5. Kaneki, N., Hara, H., Shimada, K. & Shimuzu, T., Effect of atmosphere on resistivity of WO_3 ceramics. *J. Am. Ceram. Soc.*, **59** (1976) 368–9.
6. Hanafi, Z. & Khilla, M. A., The colour problem of tungsten trioxide electrical conductivity. *Z Physik C. Chem. Neue Folge*, **82** (1972) 209–16.
7. Lefkowitz, I., Dowell, M. B. & Shields, M. A., Phase transitions in tungsten trioxide at low temperatures. *J. Solid State Chem.*, **15** (1975) 24–39.
8. Gehlig, R. & Salje, E., Dielectric properties and polaronic conductivity of WO_3 and $W_xMo_{1-x}O_3$. *Phil. Mag. B*, **47** (1983) 229–45.
9. *Phase Diagrams for Ceramists, Vol. 2, 1969 Supplement*, ed. M. K. Reser. The American Ceramic Society, Westerville, OH, 1969, p. 82 & 97 (after Mokhosoev, M. V. & Fedorov, P. I.) *Russ. J. Inorg. Chem.* (Engl. Transl.), **124** (1961); and Waring J. L., *J. Am. Ceram. Soc.*, **48**(9) (1965) 494.