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ScienceDirect
Journal of the European Ceramic Society 27 (2007) 3931–3933
www.elsevier.com/locate/jeurceramsoc

Current–voltage characteristic behaviour of dense Zn_2SnO_4-ZnO ceramics

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Available online 7 May 2007

Abstract

The present work deals with the electrical characterization of undoped Zn_2SnO_4 (ZTO) and SnO_2-doped ZnO bulk ceramics in order to clarify the role played by the ZTO spinel type phase in the electrical response of these materials. For this purpose, SnO_2-doped ZnO materials with SnO_2 concentrations of 0.1, 1 and 10 mol% have been prepared by co-precipitation and undoped ZTO powders have been prepared by a classical mixing oxide procedure. ZTO materials with 90–92% of the theoretical density have been obtained and non-linear behaviour is observed for ZTO- and SnO_2-doped ZnO materials. For SnO_2-doped ZnO the appearance of non-linear *I–V* behaviour is mainly dominated by the formation of the ZTO phase and the interfaces associated to its presence. ZTO shows a NTC behaviour that is in disagreement with the PTC behaviour previously reported in the literature.

Keywords: ZnO; Zn_2SnO_4; Electrical conductivity

1. Introduction

ZnO-based materials find a wide spectrum of applications both as bulk polycrystalline ceramics and films. The interest on these materials has been renewed because of their potential for obtaining transparent conductors, magnetic semiconductors and improved gas sensing elements.[1] For this purpose much research is being focused on the control of the ZnO electrical response by doping with different ions. Undoped ZnO crystallizes in the wurtzite structure and due to its native defects exhibits n-type conduction, however p-type conductivity can also be rendered by proper doping. Reported results on the role played by several dopants on the material microstructure and electrical response are often contradictory, actually basic issues as, for instance, the solid solubility limit of certain cations into the ZnO lattice are still unclear.[2,3] Data scattering in the literature is also favoured by the impact on the material reliability of the different processing used either for bulk materials or films.

Recently, the electrical behaviour of Sn-doped ZnO thin films grown by pulsed laser deposition (PLD) has been reported.[4] ZnO films with a nominal 0.1 mol% SnO_2 show lower resistivity than undoped ZnO ones, this is in agreement with the incorporation of Sn^{4+} at Zn^{2+} lattice sites. However if SnO_2 concentration is increased the electrical resistivity also increases and the cubic Zn_2SnO_4 spinel type phase appears as a second phase. This secondary phase has also been observed in Sn-doped ZnO bulk ceramics but it appears even for the 0.1 mol% SnO_2 concentration[5] which indicates that for polycrystalline materials, solid solubility limit of SnO_2 into the ZnO lattice is below 0.1 mol%. The Zn_2SnO_4 (ZTO) spinel phase has been synthesized as nanosized particles with different shapes[6–9] however few data have been found regarding the electrical behaviour of this pure phase. Reported data on ZTO thin films[10] show that their electrical resistivity is in the order of $10^{-2}\ \Omega$ cm as is also reported for ZnO films.[1] Therefore the formation of the ZTO phase itself cannot explain the electrical resistivity increase observed in Sn-doped ZnO films, however it seems plausible that the appearance of interfaces related to the formation of ZTO could play a significant role.

Current–voltage curves and electrical response of layered structures like Zn_2SnO_4/ZnO/Pt have been reported in the literature related to gas sensing applications.[11,12] ZTO samples with very fine grains show electrical resistivity values in the order of $10^7\ \Omega$ cm,[11] that is 9 orders of magnitude higher than reported for ZTO thin films. Nevertheless, these samples are very porous (40% of porosity in the sintered sample) and cannot be easily compared to the films or dense ceramic samples.

The present work deals with the electrical characterization of undoped Zn_2SnO_4 and Sn-doped ZnO bulk ceramics in order to clarify the role played by the ZTO spinel type phase

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0955-2219/$ – see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2007.02.065

in controlling the microstructure and therefore the electrical response of these materials.

2. Experimental procedure

SnO_2-doped ZnO materials with SnO_2 concentrations of 0.1, 1 and 10 mol% were prepared by co-precipitation. Both Zn^{2+} and Sn^{4+} precursors ($Zn(CH_3COO)_2{\cdot}2H_2O$ and $SnCl_4{\cdot}5H_2O$) were dissolved in de-ionized water and mixed together to form a transparent solution. Concentrated NaOH (1 M) was added dropwise to the stirred solution to reach pH 10 and promote a complete precipitation of both cations. Precipitated powders were washed, filtered and treated at 450 °C. Zn_2SnO_4 powders were prepared by a classical mixing oxide procedure. Stoichiometric amounts of high purity ZnO and SnO_2 were mixed and homogeneized by ball milling in ethyl alcohol. Synthesis treatment was carried out at 1000 °C for 4 h. After this treatment only Zn_2SnO_4 is detected by X-ray diffraction. Subsequent milling was performed to re-activate the particles and measured mean particle diameter gave a $d_{50} = 2.8$ μm.

Green pellets of 5 mm radius and 6 mm thickness were obtained by uniaxial pressing (120 MPa) and sintered in air between 1200 and 1300 °C for 2 h to reach apparent density values higher than 90% of the theoretical density. For subsequent characterization the outer surface of the samples was removed by grinding since evidence of Sn^{4+} reduction was observed at this surface.

Crystalline phases present in the samples were characterized by X-ray diffraction (XRD) in a D-5000 Siemens Diffractometer using Cu Kα1 radiation. Microstructure analysis was carried out by Scanning Electron Microscopy (SEM) on both fracture and polished surfaces by using a field emission microscope Hitachi S-4700 and a Noran EDS detector.

For electrical characterization, sintered samples were lapped to 3 mm thick discs and Au electroded. Current–voltage measurements were done by using a DC power multimeter Keithley 2410.

3. Results and discussion

For the ZTO spinel phase, sintered pellets with 90–92% of the theoretical density were only obtained when sintered at 1250–1300 °C in a ZnO powder bed. After sintering, ZTO was the only phase detected by DRX. SEM micrograph of the fractured surface (Fig. 1) reveals different features. Very large grains are generally present in the sample, at localized regions between these large grains, much finer grains are observed forming small colonies. This gives a heterogeneous grain size distribution ranging around 3–70 μm. Within the large ZTO grains appears closed residual porosity which is very difficult to remove and points out to the difficulty for sample densification. As it is known for SnO_2, Sn^{4+} reduction to Sn^{2+} with the consequent oxygen loose may be the origin of this porosity. Microstructure characterization of the SnO_2-doped ZnO materials studied in the present work reveals the characteristics mentioned above and recently discussed in the literature[5]: always two phases are observed and, increasing the SnO_2 obviously increases the ZTO amount but also ZnO grain size strongly decreases. According to reported data[4,5] solid solution limit must be even smaller than 0.1% SnO_2 and therefore ZnO grains might not be actually Sn-doped.

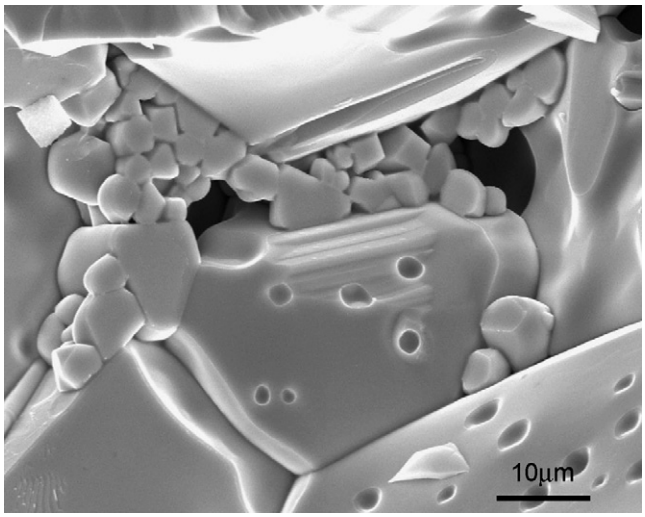

Fig. 1. SEM micrograph of fracture surface of a Zn_2SnO_4 sample sintered at 1250 °C/2 h.

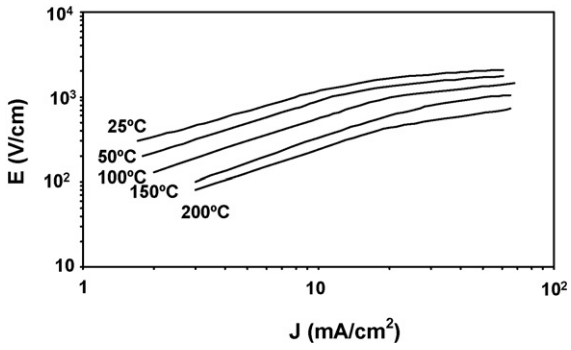

Fig. 2. *I–V* curves for dense Zn_2SnO_4 samples measured at different temperatures.

Fig. 2 shows the current–voltage behaviour observed for the ZTO materials at different temperatures. *I–V* non-linear behaviour is observed for ZTO materials up to 200 °C. This non-linear behaviour is also common for all the SnO_2-doped ZnO materials (Fig. 3). As it is well described for ZnO- and

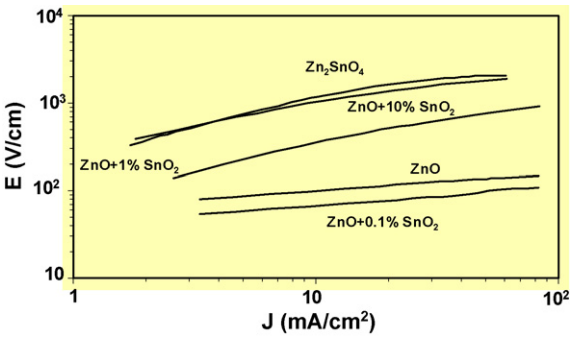

Fig. 3. *I–V* curves measured at room temperature for Zn_2SnO_4 and SnO_2-doped ZnO dense samples.

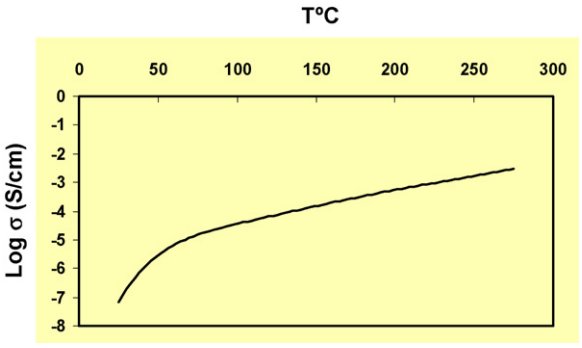

Fig. 4. DC conductivity against temperature for dense Zn_2SnO_4.

SnO_2-based varistors, the formation of potential barriers at the grain boundaries is the origin of the *I–V* non-linearity. Individual barrier characteristics depend on the specific nature of the grain boundary, i.e., ZnO–ZTO interphase or ZnO–ZnO and ZTO–ZTO homo-junctions. Moreover, since the macroscopic behaviour can be described as a series connection of the individual barriers, *I–V* curve will be strongly dependant on both the ZnO/ZTO ratio and grain size since both features change the number and nature of grain boundaries. Comparing the *I–V* curves of Fig. 3 obtained for the different materials it is clearly shown that the highest breakdown field and strongest non-linearity belongs to the ZTO sample. From the microstructure point of view, ZTO material grain size is very heterogeneous and the largest when compared to the SnO_2-doped ZnO and undoped ZnO samples. Both features work against the ZTO *I–V* curve since large and heterogeneous grain sizes decreases the number of interfaces and lead to current localization decreasing the field and non-linearity of the curve. Therefore, ZTO non-linearity must be originated directly on a higher intrinsic potential barrier height at the ZTO/ZTO grain boundaries. For SnO_2-doped ZnO the appearance of non-linear *I–V* behaviour is mainly dominated by the formation of the ZTO phase and the interfaces associated to its presence.

Fig. 4 shows the DC conductivity against temperature for a dense ZTO sample. The curve reflects a continuous increase of the conductivity with temperature. This result is in disagreement with Yu and Choi.[11] These authors reported the existence of PTC behaviour for porous ZTO samples below 150 °C, however our results on dense ZTO do not show this effect. The reasons for such discrepancies might be related to two different points. First, the authors did not take into account the non-linearity of the current–voltage curve for such temperatures and second, it has been shown that in porous materials with this level of conductivity relative humidity can control the electrical response.[13] If this second hypothesis is true, then the increase of the resistivity attributed to PTC behaviour is only related to a "drying" effect at temperatures above 100 °C.

4. Conclusions

ZTO materials with 90–92% of the theoretical density have been obtained sintering at 1250–1300 °C in a ZnO powder bed. Microstructure shows a heterogeneous grain size distribution ranging around 3–70 μm. *I–V* non-linear behaviour is observed for ZTO materials up to 200 °C. This non-linear behaviour is also common for the Sn-doped ZnO materials. ZTO non-linearity is originated directly on a higher intrinsic potential barrier height at the ZTO/ZTO grain boundaries. For SnO_2-doped ZnO the appearance of non-linear *I–V* behaviour is mainly dominated by the formation of the ZTO phase and the interfaces associated to its presence. ZTO shows a NTC behaviour that is in disagreement with the PTC behaviour previously reported in the literature.

References

1. Pearton, S. J., Norton, D. P., Ip, K., Heo, Y. W. and Steiner, T., Recent progress in processing and properties of ZnO. *Prog. Mater. Sci.*, 2005, **50**, 293–340.
2. Costa-Kramer, J. L., Briones, F., Fernández, J. F., Caballero, A. C., Villegas, M., Díaz, M. *et al.*, Nanostructure and magnetic properties of the MnZnO system, a room temperature magnetic semiconductor? *Nanotechnology*, 2005, **16**(2), 214–218.
3. Peiteado, M., Iglesias, Y., de Frutos, J., Fernández, J. F. and Caballero, A. C., Preparation of ZnO-SnO_2 ceramic materials by a co-precipitation method. *Bol. Soc. Esp. Ceram. V*, 2006, **45**(3), 158–162.
4. López-Ponce, E., Costa-Krämer, J. L., Martín-González, M. S., Briones, F., Fernández, J. F., Caballero, A. C. *et al.*, Growth and characterization of Sn doped ZnO thin films by pulsed laser deposition. *Phys. Stat. Sol. (a)*, 2006, **203**(6), 1383–1389.
5. Peiteado, M., Iglesias, Y., Fernández, J. F., de Frutos, J. and Caballero, A. C., Microstructural development of tin doped ZnO bulk ceramics. *Mater. Chem. Phys.*, 2007, **101**, 1–6.
6. Fang, J., Huang, A., Zhu, P., Xu, N., Xie, J., Chi, J. *et al.*, Hydrothermal preparation and characterization of Zn_2SnO_4 particles. *Mater. Res. Bull.*, 2001, **36**, 1391–1397.
7. Wang, C., Wang, X., Zhao, J., Mai, B., Sheng, G., Peng, P. *et al.*, Synthesis, characterization and photocatalytic property of nano-sized Zn_2SnO_4. *J. Mater. Sci.*, 2002, **37**, 2989–2996.
8. Wang, J. X., Xie, S. S., Yuan, H. J., Yan, X. Q., Liu, D. F., Gao, Y. *et al.*, Synthesis, structure, and photoluminescence of Zn_2SnO_4 single-crystal nanobelts and nanorings. *Solid State Commun.*, 2004, **131**, 435–440.
9. Wang, J. X., Xie, S. S., Gao, Y., Yan, X. Q., Liu, D. F., Yuan, H. J. *et al.*, Growth and characterization of axially periodic Zn_2SnO_4 (ZTO) nanostructures. *J. Cryst. Growth*, 2004, **267**, 177–183.
10. Young, D. L., Moutinho, H., Yan, Y. and Coutts, T. J., Growth and characterization of radio frequency magnetron sputter-deposited zinc stannate, Zn_2SnO_4, thin films. *J. Appl. Phys.*, 2002, **92**(1), 310–319.
11. Yu, J. H. and Choi, G. M., Current–voltage characteristics and selective CO detection of Zn_2SnO_4 and ZnO/Zn_2SnO_4 SnO_2/Zn_2SnO_4 layered-type sensors. *Sens. Actuators B Chem.*, 2001, **72**, 141–148.
12. Wagh, M. S., Patil, L. A., Seth, T. and Amalnerkar, D. P., Surface cupricated SnO_2–ZnO thick films as H_2S gas sensors. *Mater. Chem. Phys.*, 2004, **84**, 228–233.
13. Caballero, A. C., Villegas, M., Fernández, J. F., Viviani, M., Buscaglia, M. T. and Leoni, M., Effect of humidity on the electrical response of porous $BaTiO_3$ ceramics. *J. Mater. Sci. Lett.*, 1999, **18**, 1297–1299.