Sintering Behaviour of ZnO:Cu Ceramics Fabricated by Sol–Gel Derived Powders

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Doped zinc(II) oxide (ZnO:Cu) ceramics were prepared from sol–gel derived nanocrystalline powders. Powders were prepared by dissolving zinc and copper acetates in isopropyl alcohol. Ethanolamine was used to enhance the solubility of acetates. Powders were produced by the calcination of the dried gels at 750 °C. The crystal size of the undoped powders were uniform and around 50 nm while grain size of Cu doped powders varied between 0.3 and 2 μm. X-ray mapping of the powders showed that Cu was not homogeneously distributed and some particles had higher Cu content. After pressing of the powders, both doped and undoped ceramics were sintered at 1200 °C for 2 h. Microstructure of the Cu doped ceramics showed that Cu atoms partially dissolved in ZnO matrix and the rest formed a second phase in the grain boundaries. Average grain size of the ZnO:Cu ceramics was around 30 μm. Relative densities of the ceramics increased from 0.695 to 0.857 by Cu doping.

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1. Introduction

Nowadays zinc oxide is one of the most studied materials due to its potential applications such as optoelectronics and spintronics [1]. Single crystal and thin-film ZnO are attracting a great deal of interest for UV and blue light emitter applications. Sintered ZnO ceramics doped with Bi_2O_3 and other oxide additives are quite important as varistors [2, 3].

Different wet chemical methods have been applied to produce ZnO nanopowders [4–9]. Nanoparticles yield a narrow grain size distribution and excellent stability against grain growth. In addition, they can be sintered at lower temperatures than ceramics with larger grain size [6]. When semiconductors are prepared in the form of ultrafine particles, they experience great changes of properties, such as blue shift in absorption edge due to charge carrier confinement resulting in the widening of the band gap [5].

Due to its similar electronic shell structure, Cu has many physical and chemical properties similar to those of Zn [10]. The solubility of Cu in ZnO lattice is estimated to be around 1.0 mol.% Cu [11]. It is well known that Zn^{2+} ions are substituted by Cu^{+} ions in the ZnO lattice. Hall coefficient measurements have shown that number of carriers is reduced by Cu doping at room temperature since some of the n-type ZnO electrons occupies empty lower energy $3d$ Cu states leading to Cu^{+} ions [12]. West et al. [13] proposed a donor–acceptor model for Cu_{zn} where

$$\left[Cu_{zn}^{+}(3d^{10})\right]^{-} + Zn_{i}^{+}(4s^1)$$
$$\to \left\{\left[Cu_{zn}^{+}(3d^{10})\middle|Zn_{i}^{+}(4s^1)\right]\right\}^0. \qquad (1)$$
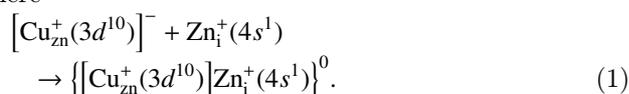
This model can be written in the Kröger and Vink notation as below [14]:

$$Cu_{zn}' + Zn_{i}^{\bullet} \to [Cu_{zn} + Zn_{i}]^{x}. \qquad (2)$$
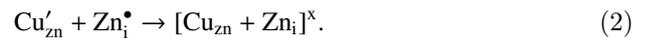
In present work, we report on the solitary effects of Cu doping, possible to be used as a doping element in varistors, on the microstructure and sintering behavior of ZnO ceramics prepared from sol–gel derived nanocrystalline powders. Varistor ceramics contain many doping elements to give a combined effect on microstructure and electrical properties and there have been many studies on the different varistor compositions. However, the separate effects of different doping elements on the microstructure of ZnO ceramics have been less frequently studied.

2. Experimental

The solutions were prepared by dissolving zinc acetate $(Zn(CH_3COO)_2 \cdot 2H_2O)$ in isopropanol $(CH_3CHOHCH_3)$ and ethanolamine (C_2H_7NO). The final solutions, with concentrations of 4 M, were light brown and clear without any suspension of particles. Copper acetate $((CH_3COO)_2 \cdot Cu \cdot H_2O)$ was added to the resulting solution to attain Zn:Cu, 0.95:0.05 in the final ceramics. After mixing the doped solution for 20 min by using a magnetic stirrer, the solution was dried under open atmosphere for one week. Afterwards, the dried gels were calcinated at 750 °C for 2 h. Resulting powders were passed through a 30 μm sieve to separate agglomerated particles during calcination. Then the fine powder was uniaxially pressed under 75 MPa. Finally, resulting ceramics were sintered at 1200 °C for 4 h.

3. Result and discussion

3.1. Analysis of sol–gel derived nanopowders

X-ray diffraction (XRD) patterns of the undoped calcinated powders showed reflections solely belonging to zincite phase (Fig. 1a). Cu doped calcinated powders showed the same peaks, however, there were slight shifts in the peak positions towards the higher angle indicating reduction of the lattice parameters (Fig. 1b, Table). In addition, there were additional low intensity peaks identified to be belonging to tenorite (CuO) phase.
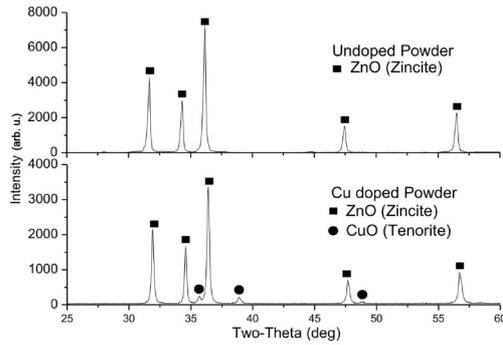
Fig. 1. XRD patterns of the (a) undoped, (b) Cu doped ZnO powders.

Scanning electron microscopy (SEM) micrograph of the powders showed that crystallite size of the undoped powders was around 50 nm and this value considerably increased in Cu doped powders to 0.3–2 μm (Fig. 2). The spherical particles encountered in undoped powder are probably formed by the aggregation of nanosize crystallites (colloids) preexisting in the sol. The crystals in Cu doped powders seemed to have less isotropic shapes compared to undoped powders.
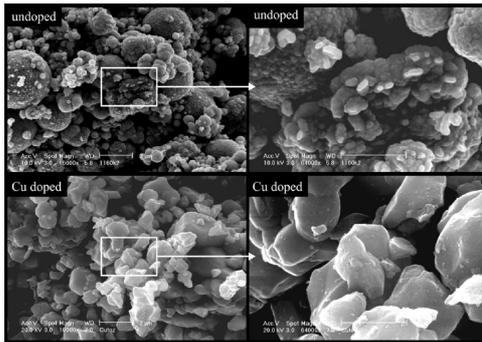
Fig. 2. SEM micrographs of undoped and Cu doped ZnO powders.

Figure 3 shows the X-ray mapping of ZnO:Cu powders. There were some exaggerated grain growth in some of the crystals of ZnO:Cu powders as it can be seen in the secondary electron image of the mapped area to reveal any composition difference between the smaller and

TABLE

Lattice parameters of the undoped and Cu doped ZnO powders and ceramics.

Sample	a [Å]	c [Å]
ZnO (powder)	3.248	5.199
ZnO (ceramic)	3.247	5.198
ZnO:Cu (powder)	3.233	5.179
ZnO:Cu (ceramic)	3.233	5.181
JCPDS 36-1451	3.249	5.206

larger crystals. Mapping was applied to the area of the powder comprising both types of the crystals. Since the amount of the X-rays reaching the detector is also affected by the topological differences in the powders. In addition to composition, the comparison was made by using the intensity difference between all mapped elements (i.e. zinc, oxygen and copper). There was no apparent difference between the zinc and oxygen concentrated areas regardless of the size of the crystals. There were some small of Cu concentrated areas indicating that tenorite phase had a very small crystal size. The rest of the powders had homogeneously distributed Cu among the other crystallites of the powder. Exaggeratedly grown crystals did not display any compositional difference.
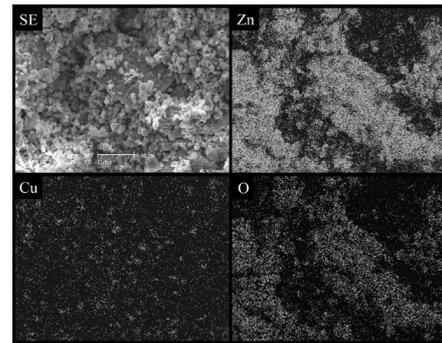
Fig. 3. X-ray mapping of the Cu doped ZnO powder.

3.2. Effects of doping on microstructure and sintering behavior

XRD patterns of the ceramics were similar to XRD patterns of powders (Fig. 4a, b). Accordingly, both lattice parameters (a and c) of the zincite structure decreased after Cu doping which can be an evidence for substitution of some Cu^{++} (ionic radius of Cu^{++} = 0.073 nm) on Zn lattice sites (ionic radius of Zn^{2+} = 0.074 nm) (Table).

Figure 5 shows the SEM micrographs of the ceramics. The results showed that the grain size of the undoped ceramics was distributed in the range 2–10 μm while the grain size of the Cu doped ceramics was considerably larger and was between 10 and 40 μm (Fig. 5). There were pores in both doped and undoped ceramics. However, the number of the pores in the pure ZnO ceramics
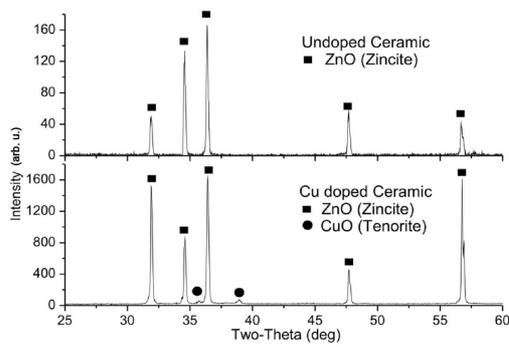
Fig. 4. XRD patterns of the (a) undoped, (b) Cu doped ZnO ceramics.
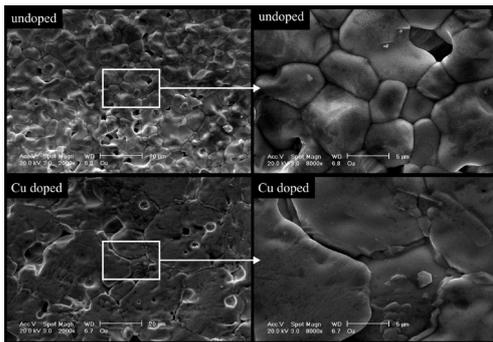
Fig. 5. SEM micrographs of undoped and Cu doped ZnO ceramics.

was higher. In addition, the pores in the pure ceramics were between the grains indicating that sintering had not been completed due to low diffusional mobility. The most of the pores present in the ZnO:Cu ceramics were within the grains which showed that grain growth had began before the completion of pore shrinkage.

X-ray mapping of the Cu doped ceramics showed the presence of second phase (tenorite phase observed in XRD results). Zn and Cu maps showed that tenorite phase was segregated in the grain boundaries (Fig. 6). Oxygen map did not show any difference between the two phases and supported the XRD results (CuO vs. ZnO).
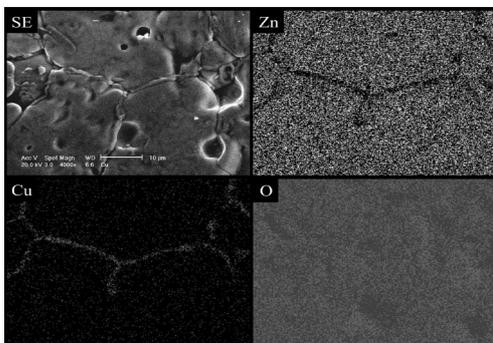
Fig. 6. X-ray mapping of the Cu doped ZnO ceramics.

4. Conclusions

1. ZnO:Cu ceramics (Zn:Cu, 0.95:0.05) have been successfully fabricated from sol–gel derived nanocrystalline powders and relative densities of the ceramics increased from 0.695 to 0.857 by Cu doping after sintering at 1200 °C.

2. Cu doped powders showed increased crystalline size compared to undoped powders.

3. Compared to the undoped ZnO, the lattice parameters of both Cu doped powders and ceramics decreased.

4. Both doped powders and doped ceramics showed the presence of tenorite phase. The second phase was segregated in the grain boundaries in the ceramics while it formed separate tenorite crystals in the powders.

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