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Quenching Effects and Conduction Characteristics of Al doped ZnO ceramics

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This study, quenching effects and conductive properties of ZnO ceramics doped with Al were examined. Specimens with composition of (1-x) ZnO + x Al_2O_3, where x varied from 0, 0.3, 1, 2, 3, 4, 6, 8 and 10 mol % were prepared by a conventional mixed oxide method and sintered at a temperature of 1200 °C for 2 hours. The samples were divided into two groups; the first group was quenched to room temperature in normal air while the other was slow cooled in the furnace. Current - voltage characteristics of all specimens were investigated. It was found that the specimens with doping level less than 2 mol % showed a good conductive characteristic. The conductivity of 10-20 S/m was found in the undoped specimens and it increased to about 80-120 S/m in specimens doped with Al up to 2 mol %. At higher doping level of more than 2 mol %, the conductivity trended to decrease to 0.1- 0.001 S/m. In addition, the various conductivity due to the Al - doping concentration in all ranges of both groups was similar but the quenched group was slightly higher because of fast freezing of the ionic defects during quenching.
Key words: Al doped ZnO ceramic, quenching, conductivity

1. INTRODUCTION

Zinc oxide has attracted attention because of their interesting applications such as in photocopying industry, antireflection coating in solar cells and gas sensors. Many different applications are due to its photoconductive, electrical and optical properties. Zinc oxide with a hexagonal wurtzite structure is an n - type semiconductor due to oxygen vacancies and zinc interstitial [1]. At room temperature, the electrical resistivity is quite high but many attempts have been made in order to get low resistivity by doping with trivalent cation such as aluminum, which can decrease the resistivity down about 10 times [2]. The effects of small Al doping on the electrical properties, thermoelectric properties, densification and grain growth of ZnO were investigated by several researcher [3-6]. It has been observed that Al increased the electrical conductivity of ZnO resulting in a manifestation of a metallic electrical conduction behavior [3], however, Al doping significantly inhibited the grain growth and reduced the driving force for sintering by forming a second phase [5]. In addition, it has been reported about oxygen diffusion in Al doped ZnO by means of an interstitial mechanism [7,8]. To escape oxygen diffusion while the specimen is cooled down to room temperature, quenching method is applied. The goal of the present work is to investigate the effect of quenching on electrical conductivity, crystal structures and microstructures of zinc oxide ceramics doped with various aluminum concentrations.

2. EXPERIMENTAL PROCEDURE

Reagent grades ZnO and Al_2O_3 powder were used. Specimens with composition of (1-x) ZnO + x Al_2O_3, where x varied from 0, 0.3, 1, 2, 3, 4, 6, 8 and 10 mol % were prepared by a conventional mixed oxide method. The mixtures were ground in ethanol by ball milling for over 24 h and dried, then calcined at 700 °C for 2 h, after that pressed into pellets using a 15 mm diameter die. The samples were sintered at 1200 °C for 2 h in air, then divided into two groups; the first group was quenched to room temperature in normal air while the other was slow cooled from the sintering temperature to 300 °C in a step of 5 °C/min. Sintered samples were polished with 1200 - grit SiC on both sides, ultrasonically cleaned, then painted with In-Ga electrodes. Current - voltage characteristics of all specimens were investigated with a multimeter (Model 34401A, Agilent) and a DC power supply (HP 6553A). The crystal phases were identified by X-ray diffraction (XRD). The microstructures evolutions were observed by scanning electron microscope (SEM) and densities of sintered pellets were measured using Archimedes method with water.

3. RESULTS AND DISCUSSION

3.1 Crystal phase and microstructure

The density of sintered samples with various Al contents is quite different. The relative density over 90 % can be found in specimens doped with Al up to 2 mol %. However, the higher doping content of more than 2 mol % give rise to the lower density. It is believed that the higher sintering temperatures is required. Results from the different cooling processes, quenched and slow cooled in step, is found that the specimen cooling rate does not affect the densification. Moreover, effects due to Al doping can be clearly seen that the grain structures with lower content of Al are much smaller than those of the undoped specimens as shown in Fig.1a and 1b. This may be attributed to the effect of high melting point of aluminum which produce the number of grain refinement resulting in the smaller grain size. In addition, higher Al content up to 10 mol % significantly reduce the driving force for sintering as shown in Fig. 1c.

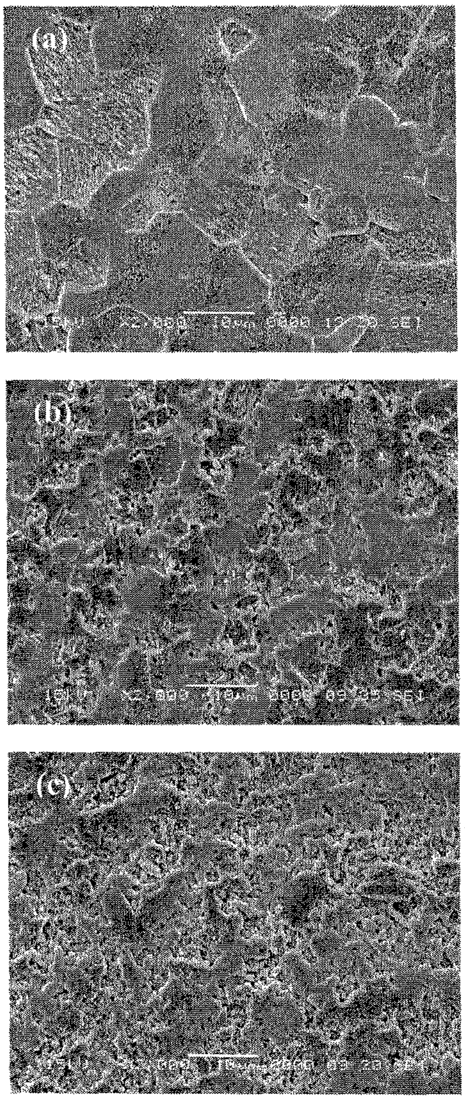

Fig. 1. SEM micrograph of samples with slow cooled in step sintered at 1200 °C for 2 hours ; (a) x=0, (b) x=1 and (c) x=10

For XRD investigation, all specimens are matched with the hexagonal and wurtzite structure (JCPDS file no.05-0664). However, a new phase of $ZnAl_2O_4$ with its (220), (311), (422), (511) and (440) peaks is detected for the samples with Al content greater than 2 mol %, as shown in Fig. 2. K.F. Cai et al [4] have reported similar results for 0-5 mol% Al doped ZnO by sol-gel processing.

3.2 Electrical conductivity

The effect of Al doping on the current-voltage characteristics of quenched specimens is shown in Fig 3. The specimens with Al doping up to 2 mol % show a clearly good conductive characteristic with linear current - voltage behavior while the others are rather good insulators and also show nonlinear behavior.

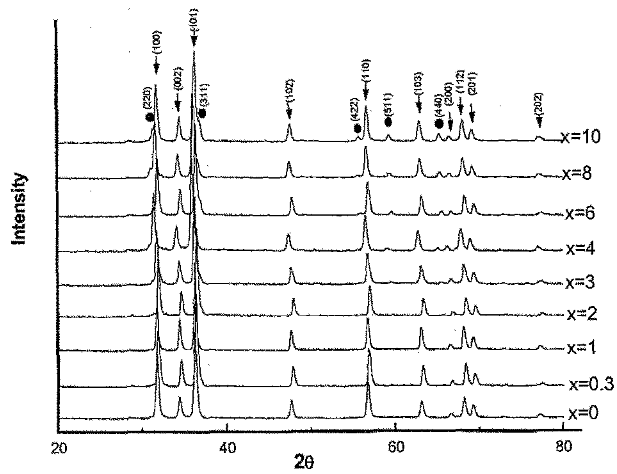

Fig 2. X-ray diffraction spectra of slow cooled specimens with composition of (1-x) ZnO + xAl_2O_3, sintered at 1200 °C

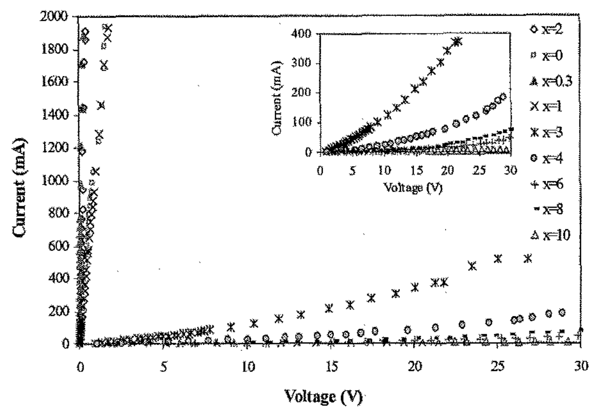

Fig. 3.The current-voltage characteristics of the quenched specimens in various Al doping.

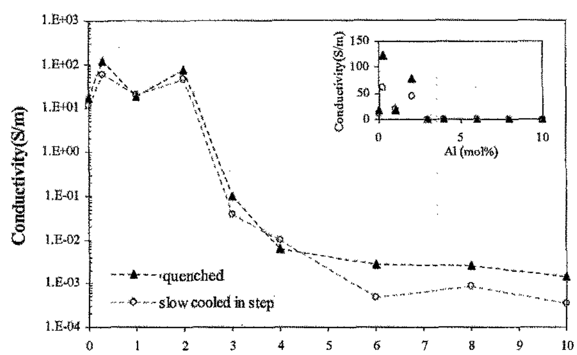

Fig. 4. Room temperature electrical conductivity of the samples as a function of the Al concentration.

Fig.4. shows the room temperature electrical conductivity of quenched and slow cooled specimens with various Al content. The conductivity of 10-20 S/m is found in the undoped specimens of both groups and it increases with the increase in small amount of Al ranging from 0.3 % to 2 mol %. The conductivity up to 120 S/m is obtained in quenched sample of 0.3 mol % Al doping. Moreover, it is higher than that of the slow cooled one. The solid solutions of aluminum in zinc oxide can be

obtained due to the substitution of aluminum atoms in zinc locations and one electron is given up to contribute to the number of charge carrier. However, this figure obviously shows that the conductivity of higher doping level of more than 2 mol % is smaller than that in the undoped specimens, with trend decreased to 0.1- 0.001 S/m. These results agree well with their electron micrographs and XRD investigation. It can be ascribed that higher Al content decrease the sintering driving force by forming a second phase of $ZnAl_2O_4$. In addition, the various conductivity due to the Al doping concentration in all ranges of both groups is similar but the quenched group is slightly higher. This may be attributed to the fast freezing of the ionic defect during quenching. There are 3 factors that cause the ionic defects, oxygen vacancy due to heating up to high temperature, the formation of zinc atoms on interstitial sites and the solid solutions of aluminum in zinc oxide. These ionic defects create electrons into the conduction band. It can be maintained by quenching to avoid the oxygen diffusion in specimens. Therefore, the conductivity of the quenched group trend higher than the slow cooled one.

4. CONCLUSION

The effects of quenching and Al doping on the electrical conductivity of ZnO were investigated. It was found that high conductivity of specimens can be obtained by doping with small amount of Al content and quenching from sintering temperatures to room temperatures that has no effects to their crystal phase. The substitution of aluminum atoms in zinc oxide crystals, the interstitial zinc atom and the oxygen vacancy cause the defect of non-stoichiometry thus promoting electrons into the conduction band. The defects can be preserved by quenching. However, Al doping acts as a grain growth inhibitor that reduce the grain size. In addition, large Al content decline driving force for sintering and also forms the second phase that causes to a reduction in the electrical conductivity.

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