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Effect of $ZnAl_2O_4$ content on the microstructure and electrical properties of ZnO-based compound conductive ceramics

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ABSTRACT

ZnO-$ZnAl_2O_4$-SiO_2-Y_2O_3-MgO conductive ceramics were fabricated with different amount of $ZnAl_2O_4$ content. The effects of $ZnAl_2O_4$ on the microstructures and electrical properties of ZnO-based compound conductive ceramics were investigated. Results showed that the continuously adjustable resistivity could be obtained under the percolation threshold through increasing $ZnAl_2O_4$ content and improving the preparing technology. It was found that $ZnAl_2O_4$ grain would be encased in the major ZnO grains, with less than 5.0 mol%. When more $ZnAl_2O_4$ doping in the samples, it acted as a barrier blocking ZnO grain growth. Interestingly, the dielectric properties indicate that the Maxwell-Wagner interfacial polarization and the threshold effect exists in the matrixes. At the same time, the resistance-temperature (*R-T*) characteristics verify that the conduction mechanism of ZnO-based conductive compound ceramics is a thermally activated progress and the grain-boundary effect is negligible. The improvement of the microstructures and electrical properties has a potential application in the high frequency electrical fields.

1. Introduction

ZnO-based conductive ceramics have broad applications in the power industry also in energy technologies due to their nonlinear voltage-current properties, adjustable resistivity, surge protection and low residual voltage, small leakage and so on [1–3]. Conventional ZnO-based conductive ceramics are fabricated through sintering mixtures of ZnO powder with small amounts of additives such as MgO, Al_2O_3, TiO_2, etc [1,4–6]. Some complex secondary phases such as $ZnAl_2O_4$, $MgAl_2O_4$ and $TiAl_2O_4$ are formed during the sintering procedure, then affect the electrical properties significantly. Some studies have been focused on changing the multi-component systems and employing the additives to improve the microstructure and electrical properties [5,7–9]. Unlike varistor, non-ohmic grain boundary layer and active grain boundary have not been detected in the ZnO conductive ceramics, and the conductive process followed percolation conduction and the thermally activated progress [10].

In recent years, many efforts have been attempted on the optimization and upgrading of the additives to improve the composition and performance of ZnO conductive ceramics [5–7]. However, unevenly microstructure, poor repeatability and complex other phases generated by in-situ solid phase reaction have not been solved. Few studies have reported on obtaining the continuously adjustable resistivity and the interfacial effect.

Based on the above, we firstly synthesize the $ZnAl_2O_4$, combine with the conductive percolation model and employ the compound method to obtain a novel ZnO compound conductive ceramics. The pre-synthesized $ZnAl_2O_4$ would distribute evenly in the matrix and then form the embedded structure, affecting the conductive network and interfacial polarization. It has been reported that $ZnAl_2O_4$ existing in the samples could regulate the resistivity and nonlinear coefficient [6,7]. What's more, the particle blocking effect related to $ZnAl_2O_4$ phase may decrease the size of ZnO grains and improve the microstructure [11]. These possibilities remain to be explored, so the aim of this work is to investigate the effects of varying the concentration of $ZnAl_2O_4$ dopant, at a given 5.0 mol% MgO dopant, on the electrical properties of the ternary ZnO-$ZnAl_2O_4$-MgO compound conductive ceramics. Specifically, we focus on the characteristics of continuous adjustable resistivity and the interfacial polarization.

2. Experimental procedures

The raw mixed powder of ZnO and Al_2O_3 was homogenized and

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heated at 1300 °C for 12 h to produce the $ZnAl_2O_4$ dopant. Then the dopant was crushed and mixed with ZnO, SiO_2, Y_2O_3 and MgO with the following molar compositions: (93-x) mol% ZnO-x mol% $ZnAl_2O_4$-1.5 mol% SiO_2-0.5 mol% Y_2O_3-5 mol% MgO (x = 3.0, 5.0, 7.0, 11.0, 13.0, and 15.0). The powder mixtures were mixed firstly and homogenized in a polyethylene battle with ZrO_2 balls in deionized water for 4 h by planetary high-energy ball milling. The slurry was dried at 1050 °C for 2 h, and then pulverized by an agate mortar/pestle. After added 5 wt% polyvinyl alcohol (PVA) binder, the powders were granulated by sieving between 40-mesh and 120-mesh screen to produce starting powders. After that, the powders were uniaxially pressed into discs which were 20 mm in diameter and 5 mm in thickness. Then the pressed discs were sintered in air at 100 °C/h to 1320 °C for 3 h and then cooled to room temperature in the furnace.

The crystalline phases of the samples were analyzed by X-ray diffraction (XRD, Model Rigaku-D/Max-2200 P C, Japan) using Cu-K_α radiation. The sintered samples were grinded and polished with diamond polishing paste as medium, then thermal etched at 1200 °C for 10min to observe the microstructure and distribution of elements by environment scanning electron microscope (ESEM, FEIQ45, American) equipped with energy-dispersive spectroscopy (EDS). The average grain sizes were determined by Mendelson's approach using a computer aided system and the sample densities were measured by the Archimedean method according to international standard (ISO18754).

For measuring the electrical characteristics of the as-prepared samples, aluminum electrodes were painted on both surfaces of the samples and then annealed at 650 °C for 5 min. The dc *I-V* characteristics were characterized by the nonlinear coefficient $[\alpha = 1/lg(V_{1A}/V_{0.01A})]$ using the dc voltage-stabilized source where V_{1A} and $V_{0.01A}$ are the breakdown voltage at 1 and 0.01 A, respectively. The permittivity of each sample was measured using Agilent 4980 A analyzer in the frequency range of 100 Hz to 2 M Hz. The temperature dependence of the resistivity was measured in the 3 V dc low-field using the *R-T* characteristic test system (ZWX-B) in the range of 303.15 and 423.15 K, respectively.

3. Result and discussion

3.1. e composition and microstructure analysis

Fig. 1 shows the XRD patterns of the as-prepared samples sintered at 1320 °C with different amounts of $ZnAl_2O_4$ ($3.0 \le x \le 15.0$ mol%). It was found that the main hexagonal structure ZnO phase and the cubic structure $ZnAl_2O_4$ phase are detectable. Interestingly, there are no apparent impurity peaks that indicate atomic diffusion and solid-phase reaction are not significant. The characteristic peaks are continuously strengthened with the increase of $ZnAl_2O_4$ content, indicating ZnO and $ZnAl_2O_4$ can coexist steadily that coincided with previous reports [11,12]. In sintering progress, internal stress and solid impurities would cause lattice distortion [13], So the characteristic peaks shift to lower angles slightly. Compared with the previous technology, the compound process is a better method for optimizing the composites [14,15].

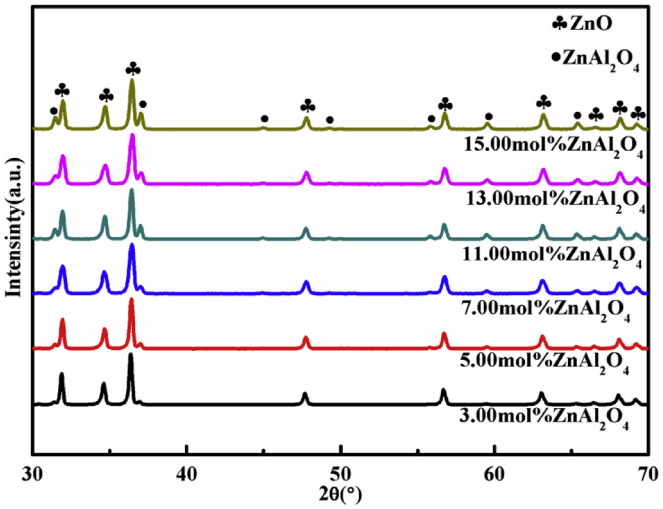

Fig. 1. XRD patterns of as-prepared samples with different content of $ZnAl_2O_4$.

Fig. 2 shows the ESEM micrographs of the sintered ZnO-based compound conductive ceramics with x = 3.0–15.0 mol%. In order to distinguish the different phases and its distributions, the back scattered-electron analysis is adopted, in which off-white grains represent ZnO, black grey grains represent $ZnAl_2O_4$, and grey grains represent MgAlZnO alloy phase. Mendelson's approach is used to compute the change of the average grain size that is listed in Table 1 [16]. From the morphology and distribution, particle blocking effect could inhabit the growth of ZnO grain significantly but have little impact on $ZnAl_2O_4$ grain, with increasing of $ZnAl_2O_4$ content. When the content of $ZnAl_2O_4$ is less than 7 mol%, ZnO grain would encase $ZnAl_2O_4$ grain and causes the decrease in density of as-prepared samples. As the micrographs shown, $ZnAl_2O_4$ grains disperse around the ZnO grains with granular morphology, which could control the movement of ZnO grain boundaries and then refine ZnO grains. On the whole, each phase of the ZnO-based compound

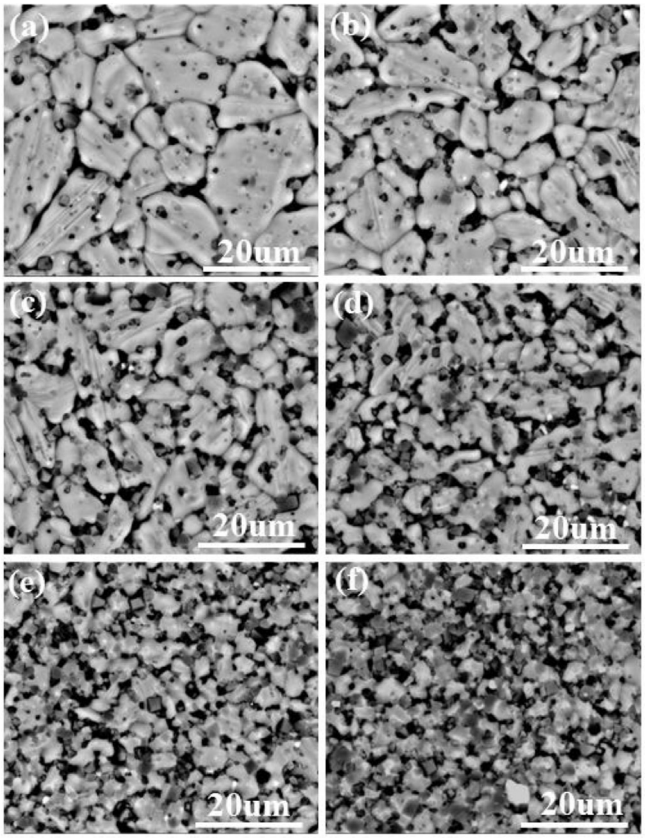

Fig. 2. ESEM micrographs of as-prepared samples with various amounts of $ZnAl_2O_4$: (a) 3.0 mol% $ZnAl_2O_4$; (b) 5.0 mol% $ZnAl_2O_4$; (c) 7.0 mol% $ZnAl_2O_4$; (d) 11.0mol% $ZnAl_2O_4$; (e) 13.0 mol% $ZnAl_2O_4$; (f) 15.0 mol% $ZnAl_2O_4$.