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Influence of Fe_2O_3 doping on microstructural and electrical properties of $ZnO–Pr_6O_{11}$ based varistor ceramic materials

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ABSTRACT

The doping effect of Fe_2O_3 on the microstructural and electrical properties of $ZnO–Pr_6O_{11}$ based varistor ceramic materials was investigated. Fe_2O_3 doping would inhibit the growth of ZnO grains, whose average sizes were found to decrease from 3.0 to 2.7 μm with the doping level of Fe_2O_3 increased from 0 to 1 mol%. When the doping level of Fe_2O_3 was 0.005 mol%, the varistors exhibited the optimum nonlinear electrical characteristics with nonlinear coefficient of about 26, breakdown voltage of approximately 571 V/mm and leakage current of less than 65 μA. With higher doping level of Fe_2O_3, more Fe atoms would segregate at grain boundaries, providing more extra electrical carriers, decreasing the resistances of the grain boundaries, and $PrFeO_3$ would be formed, destroying the construction of grain boundaries. Therefore, the nonlinear electrical properties of the resultant varistor materials were deteriorated.

1. Introduction

ZnO-based varistors are polycrystalline electronic ceramic devices, which are obtained by sintering ZnO powder with small amounts of other metal oxides. The most excellent property of ZnO varistor materials is their nonlinear voltage–current characteristics due to the potential barriers formed at grain boundaries. Their primary function is to protect electronics and electrical circuits from being destroyed by transient voltage surges, and this protection function can be performed promptly and repeatedly. So they are very much useful both in power industry as well as in electronic industry [1–5].

The conducting mechanism of ZnO-based varistors is a double Schottky phenomenon. The key that a ZnO-based varistor functions is the formation of grain boundary layer of high electrical resistivity. According to the different varistor forming oxides in the grain boundary layer, ZnO-based varistor materials are classified into Bi-doped, Pr-doped, V-doped and Ca-doped ZnO varistor materials, and so on [5,6]. Other oxides are doped into varistor ceramics to achieve, hopefully, a larger nonlinear coefficient and higher resistivity [7–12].

Up to now, the majority of commercial ZnO varistor materials are Bi-doped ZnO-based semiconductors [5,6]. However, the most commercially applied Bi-doped ZnO varistor materials have a few drawbacks due to the high volatility and reactivity of Bi_2O_3 during liquid sintering. The former changes varistor characteristics with the deviation of inter-composition ratio of additives, and the latter destroys the multi-layer structure of chip varistors, which generates an insulating spinel phase deteriorating surge-absorption capabilities [5,13,14]. To overcome these problems, various fabrication techniques to reduce the volatility have been continuously developed for Bi-doped ZnO varistor materials [2,13–18], and different varistor forming oxides have been tentatively investigated into ZnO varistor materials [19–24], in which Pr-doped ZnO varistor materials are most promising in application and have been intensively studied [19–22], due to their advantages over Bi-doped ZnO varistor materials in relatively simple two-phase microstructure of ZnO grains and praseodymium oxide intergranular phases, reducing quantity of composition materials and improving the electrical properties of the ceramics, and stable composition at high temperature sintering stemming from the high melting point of Pr_6O_{11} [5,21].

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It is a pity, however, that Pr-doped ZnO varistor materials have not been studied as extensively as done for the Bi-doped ZnO varistor materials. As main dopants, to our knowledge, only the effects of Co-doping and rare-earth doping on the microstructural and electrical properties of Pr-doped ZnO varistor materials have been reported in literature. And several other kinds of metal oxides such as MnO_2, Sb_2O_3, Al_2O_3, NiO, Cr_2O_3, TiO_2 and K_2O which are commonly used in the ZnO–Bi_2O_3 system were tried into Pr-doped ZnO varistor materials [5,19–22]. Their mutual interactions, especially the one between the varistor forming oxide, Pr_6O_{11}, and other electrical property improvers, have been under dimness.

For example, it was reported that Fe_2O_3 would be a fatal additive for ZnO–Bi_2O_3 system [25], but Song and Liu [26] claimed that when the content of Fe_2O_3 was less than 0.1 mol% in ZnO–Bi_2O_3 system, it could improve the electrical properties of ZnO–Bi_2O_3 based varistor materials. However, the influence of Fe_2O_3 doping on ZnO–Pr_6O_{11} based varistor materials has not been reported. So, the aim of this work is to investigate the effect of Fe_2O_3 doping (which is hardly to be avoided during the industrial production of ZnO varistors due to the usage of iron-made equipments) on the microstructural and electrical properties of ZnO–Pr_6O_{11} based varistor materials, and to try to understand the mutual interaction and reaction mechanism between the oxides in the material system.

2. Experimental procedures

2.1. Sample preparation

The samples were fabricated using a conventional ceramic process [27,28] with a nominal composition of $(98.0 - x)$ mol% ZnO + 0.5 mol% Pr_6O_{11} + 1.0 mol% Co_3O_4 + 0.5 mol% Cr_2O_3 + $x$mol% Fe_2O_3 (x = 0.0, 0.001, 0.003, 0.005, 0.01, 0.025, 0.1, 0.5, 1.0). The powder mixtures were ball-milled in water for 24 h with highly wear-resistant ZrO_2 as media, in which the weight ratio of ZrO_2 balls to powder mixture was 2:1. The milled slurries were dried in air at 120 °C for at least 24 h. The dried powder mixtures were then crashed into fine powders, sieved, and pressed into discs of 6.0 mm in diameter and 2.0 mm in thickness. The prepared green bodies have a density between 2.8 and 3.5 g/cm^3. And then the green discs were sintered at 1300 °C in air for 1 h with heating rates of 2 °C/min and cooling naturally. To measure the electrical properties, silver pastes were coated and toasted on both sides of the sintered samples.

2.2. Materials characterization

The sample densities were measured by Archimedes method according to international standard (ISO18754). The phase compositions of the sintered samples were identified by X-ray diffractometer (XRD, D/max2550HB+/PC, Cu Kα and λ = 1.5418 Å) through a continuous scanning mode with speed of 8°/min. The fractural surfaces of the as-prepared samples were observed via SSX-550 scanning electron microscope (SEM), and the polished surfaces of the samples were examined using LEO-1530 scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDX). The average sizes (d) of ZnO grains were determined using linear intercept method from the SEM images of the polished samples.

The electric field to current density (E–J) characteristics of the as-prepared samples was measured at room temperature with a high-voltage source measurement unit (Model: CJ1001). The varistor voltage (V_B) was determined at 1 mA/cm^2 (V_{1mA}) and the nonlinear coefficient (α) was calculated using

$$\alpha = \frac{\log(J_2/J_1)}{\log(E_2/E_1)} = \frac{1}{\log(E_2/E_1)} \tag{1}$$

where E_1 and E_2 are the voltage fields corresponding to J_1 = 1 mA/cm^2 and J_2 = 10 mA/cm^2, respectively. The leakage current (I_L) was determined at 0.75 V_{1mA}.

The applied voltage per grain boundary (V_{gb}) was calculated using

$$V_{gb} = V_B \frac{d}{D} \tag{2}$$

where V_B is the varistor voltage of the ceramic varistors, d is the average size of ZnO grains, and D is the thickness of the sintered samples.

The dependence of impedance (reactance Z'' and resistance Z') of the ceramic varistors on frequency was determined with an Agilent 4294A impedance analyzer in the frequency range of 40 Hz–15 MHz at temperature of 250 °C.

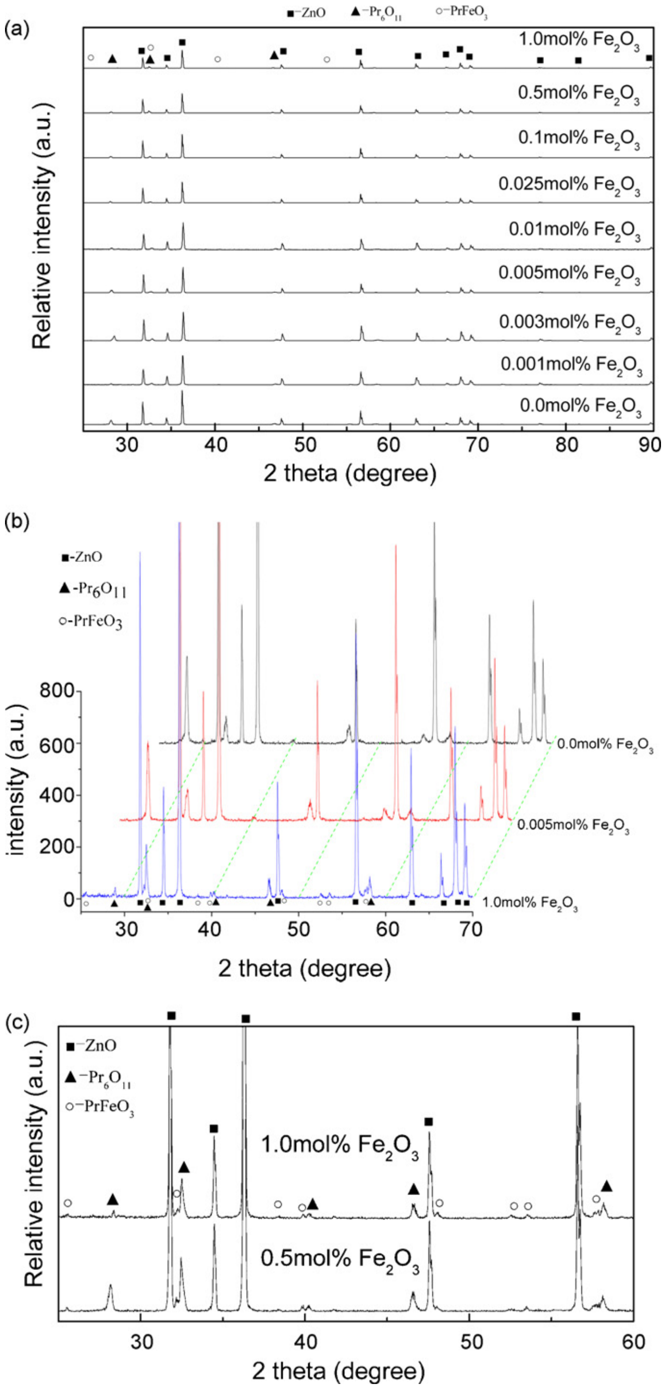

Fig. 1. XRD patterns of typical samples doped with different amounts of Fe_2O_3 (a), in which the samples doped with 0.0 mol%, 0.05 mol% and 1.0 mol% Fe_2O_3 were magnified in (b), and the samples doped with 0.5 mol% and 1.0 mol% Fe_2O_3 were compared in (c).

3. Results and discussion

3.1. Composition and microstructure

Fig. 1a shows the XRD patterns with normalized peak intensities of the as-prepared ZnO–Pr_6O_{11} based varistor ceramic samples doped with different amounts of Fe_2O_3. The experimental results indicate that, when the doping amounts of Fe_2O_3 into the samples are less than 0.10 mol%, the identifiable phases in the samples are almost the same as that in the sample without Fe_2O_3 doped, where excepting the major phase of ZnO, only could praseodymium