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Non-Linearity in Rare Earth Doped Zinc Oxide Varistor Prepared by Flash Combustion Method

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Abstract

A novel processing technique involving flash combustion of nitrate–urea mixtures has been reported for praseodymium doped zinc oxide containing K_2O *in the range 0·0–0·5 mol%. The starting average powder particle size was 2 μm with a tap density of 1250 kg/m*^{3}*. The non-linear behaviour of the prepared zinc oxide varistor was examined in the field range 200–650 V/mm. The breakdown voltage was seen to attain a maximum value of about 600 V/mm in compositions containing 0·3 mol%* K_2O*. The variation of breakdown voltage is explained on the basis of the microstructure and* K_2O *content.*

Der Artikel beschreibt eine neue Herstellungstechnik für praseodymdoteirtes Zinkoxid, das zwischen 0·0 und 0·5 Mol-% K_2O *enthält. Das Verfahren nutzt eine sehr schnelle Zersetzungsreaktion von Nitrat-Harnstoffmischungen. Die mittlere Korngröße des Ausgangspulvers beträgt 2 μm und die Klopfdichte 1250 kg/m*^{3}*. Das nichtlineare Verhalten der hergestellten Zinkoxidvaristoren im elektrischen Feld wurde im Bereich von 200–650 V/mm untersucht. Die Durchbruchspannung hat ein Maximum von c. 600 V/mm für Zusammensetzungen, die 0·3 Mol-%* K_2O *enthalten, wobei die Änderung der Durchbruchspannung durch die Mikrostruktur und den* K_2O*-Gehalt erklärt wird.*

Un nouveau procédé d'obtention d'oxyde de zinc dopé au praséodymium contenant de 0·0 à 0·5% molaires de K_2O *a été décrit, qui fait intervenir la combustion éclair de mélanges de nitrate et d'urée. La granulométrie moyenne de la poudre de départ était de 2 μm, et la densité tapée de 1250 kg/m*^{3}*. Le comportement non-linéaire du varistor d'oxyde de zinc préparé a été examiné pour des champs allant de 200 à 650 V/mm. On a observé que la tension de rupture atteignait un maximum d'environ 600 V/mm pour des compositions contenant 0·3% molaires de* K_2O*. On explique la variation de la tension de rupture sur la base de la microstructure et de la teneur en* K_2O*.*

1 Introduction

The non-linear electrical characteristics of zinc oxide varistors has been a subject of many investigations due to their application as excellent surge protective devices.[1] The grain–grain interfaces formed during sintering and subsequent grain growth in doped zinc oxide give rise to electrical barriers, Schottky barriers, which are believed to be responsible for this large non-linearity.[2] The most commonly used dopant to introduce non-linear characteristic is bismuth oxide[3] and more recently the rare earth doped oxides, praseodymium oxide in particular.[4] The current voltage characteristics of zinc oxide based varistors are dependent as a whole on the grain size of zinc oxide[5] and also on the distribution of dopants. Zinc oxide, however, is reported to undergo grain growth during sintering[6] and recent studies have analysed the effect of doping of K_2O on the grain growth.[7] Most of the methods for the preparation of the doped zinc oxide are based on the usual ceramic mixing route and sometimes on chemical methods.[8–10] The former method requires several heating and grinding steps to ensure homogeneous mixing of the various oxides, while the latter methods demand great care in drying and decomposition of precursors. Solid state decompositions of salts at enhanced reaction rates, reported recently by Kingsley and Patil[11] for fine alumina and zirconia powders, have shown that

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submicron ceramic oxides and composite powders can be made with a high extent of uniformity in distribution and composition.

In the present investigation a novel combustion method involving a mixture of zinc nitrate, dopant metal nitrates and urea to obtain a homogeneous, doped zinc oxide containing different K_2O concentration is reported. The method is similar to the one reported by Sonder *et al.*,[9] but differs in one important aspect in that it is very fast and does not allow the mixture to form melamines with a slow decomposition procedure. The powders are then characterised by particle size distribution, as well as bulk density and surface morphology. The non-linear behaviour in sintered disc samples is also reported.

2 Experimental Details

All metal nitrates were of 99·9% purity; urea was AR (BDH). In a typical experiment 15 g of nitrates corresponding to 97·5 mol% ZnO, 2 mol% Pr_6O_{11}, 0·25 mol% each of Cr_2O_3 and CoO, and 18 g of urea were thoroughly mixed in an agate mortar, taken in a glass dish 100 mm in diameter and 50 mm high, and introduced into a furnace kept at 500°C. The mixture melts and burns into a white flame, and during burning a fluffy powder is formed within about 5 min. Similar experiments were conducted with batches containing 0·3 and 0·5 mol% of K_2O introduced as nitrate. The composite powder thus prepared was then pressed to pellets 10 mm in diameter and 2 mm thick at a pressure of 240 MPa and sintered at 1200°C with a soaking time of 2 h. Particle size analysis of the powder was carried out in a Micromeritics Sedigraph 5000D particle size analyser. I–V characteristics were measured on polished and electroded pellets with a short duration pulse in a Tektronix curve tracer. Powder morphology as well as microstructural features were observed in a JEOL-35C SEM.

3 Results and Discussion

The results are presented and discussed for the flash decomposed composite powder and the non-linearity properties separately.

3.1 The composite powder

The doped zinc oxide powder prepared in the present process of flash decomposition is very fine with an average particle size of 2 μm, as seen from Fig. 1. Further, the powder is seen to possess a well-distributed pattern. The tap density of the powder is 1250 kg/m^3. The colour of the powder can be said to be light pink. The whole reaction time could be mentioned as less than 5 min or so. The mixture of nitrates and urea in the glass dish when kept at a temperature of 500°C first melts into a liquid. This ensures the high extent of homogeneity of the powder. Nitrate to oxide conversion takes place within a very short time and hence avoids any chance of segregation. Metal nitrate–urea reactions are reported to be self-propagating in nature, urea

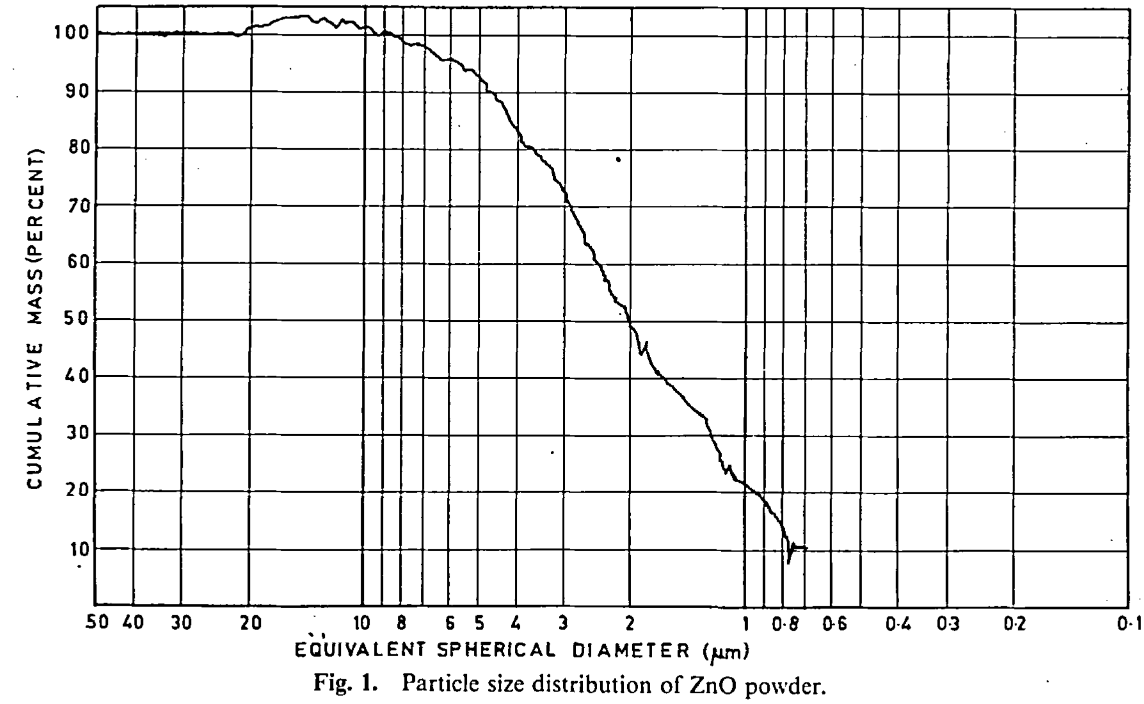

Fig. 1. Particle size distribution of ZnO powder.

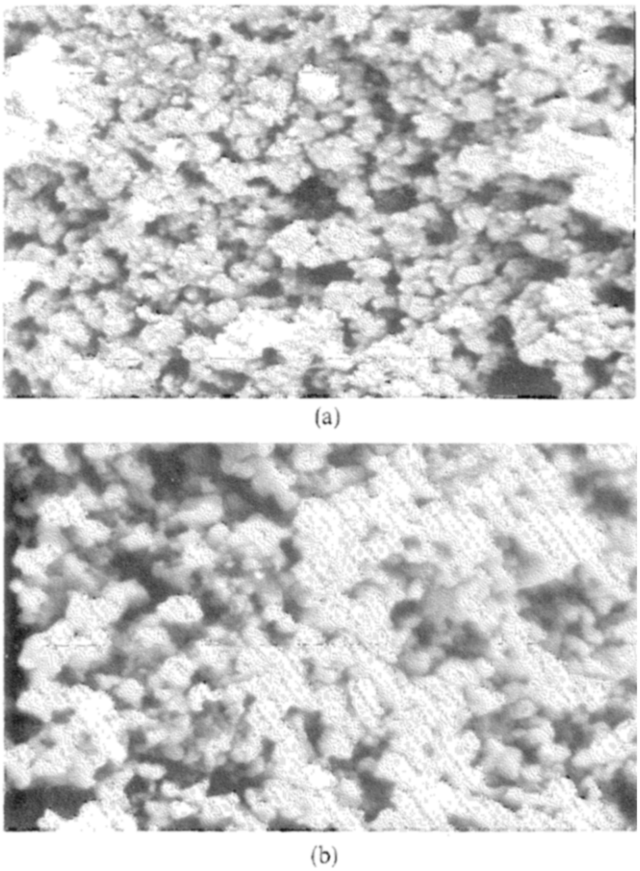

Fig. 2. Morphology of zinc oxide composite powder: (a) as flashed (original magnification ×2000); (b) after grinding (original magnification ×4000).

decomposing to biuret and ammonia at lower temperatures, then to $(HNCO)_3$ trimer[12] at still higher temperatures. The urea is known to act as the fuel and nitrate as the oxidiser.[11] The flame temperature has been measured in aluminium nitrate–urea decomposition reaction to be around 1350°C. Figure 2(a) presents the morphology of the flash-decomposed composite powder and Fig. 2(b) the particles after grinding in a mortar. Although the average particle size is about 3 μm, near to the value obtained from the particle size analysis curve, the basic powder particle is still finer, mostly less than 1 μm (Fig. 2(b)).

3.2 Microstructural features of the doped ZnO

Figure 3(a) represents the micrograph of doped ZnO with no K_2O content heated to 1200°C for 2 h where the grain size is around 3–4 μm. Obviously considerable grain growth, as already known,[6] has taken place since the starting grain size was in the range of 1 μm. Figure 3(b) shows the effect of 0·3 mol% K_2O on the grain growth of zinc oxide heated at 1200°C where the average grain size is only 1–2 μm. K_2O acts as grain growth inhibitor in accordance with the earlier study.[7] Further, the sample seems to have sintered with a low extent of porosity. However, as

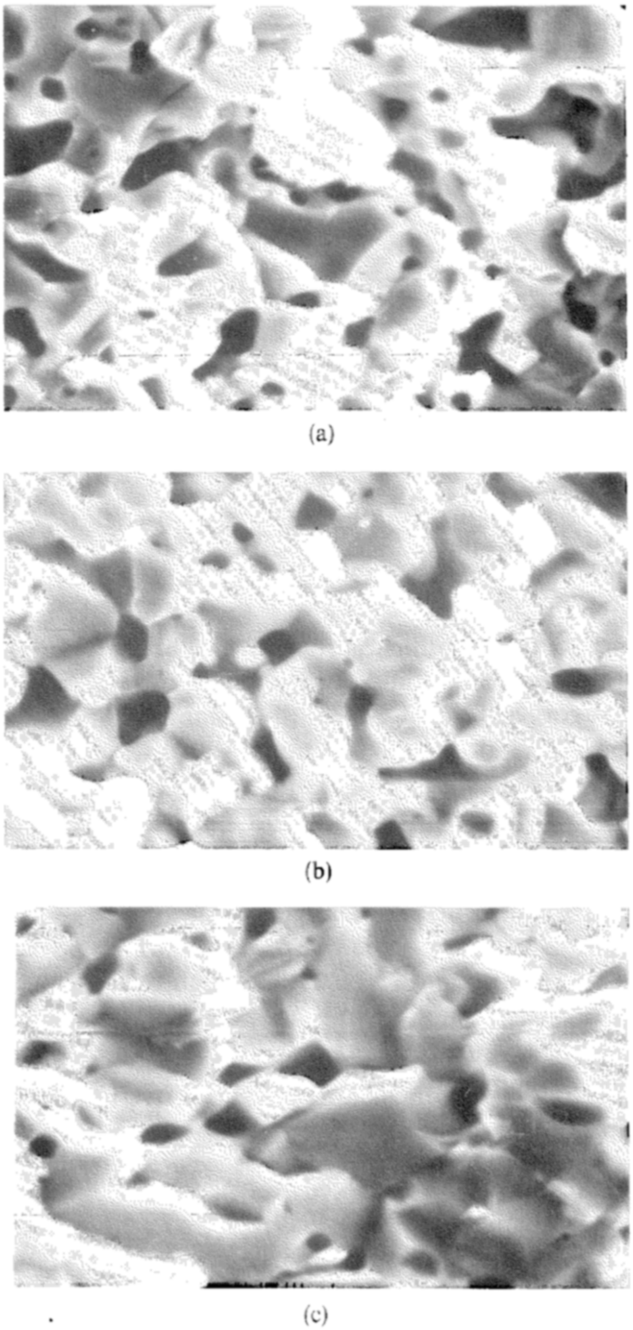

Fig. 3. Fractograph of doped zinc oxide sintered at 1200°C: (a) 0·0 mol%; (b) 0·3 mol%; (c) 0·5 mol% K_2O. (Original magnifications ×4000).

the K_2O content is increased to 0·5 mol%, although the sintered microstructure is more compact, the grain size has started showing a slight increase, as seen in Fig. 3(c). Possibly, K_2O interaction may be taking place in a range near 0·5 mol% only.

3.3 *J–E* characteristics of the varistor

The measurements were limited to field and current densities in the range 200–650 V/mm and $2{\cdot}5 \times 10^{-2}$ to 4×10^{-1} mA/mm^2 respectively. Results are shown in Fig. 4, where log *J* vs log *E* graphs are plotted for different compositions. Within the region of study,

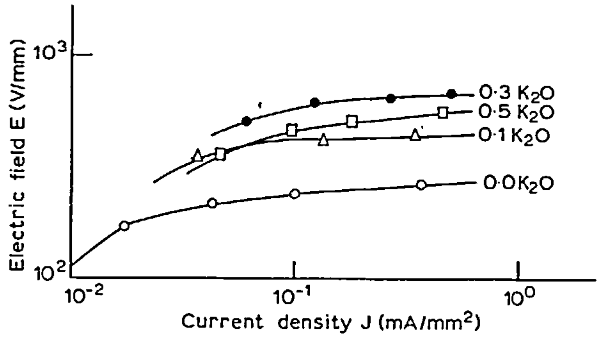

Fig. 4. Current density vs electric field of Pr doped ZnO varistor prepared by flash decomposition method.

the following points may be noted. The breakdown field (E_b, $2{\cdot}5 \times 10^{-2}$ mA/mm^2) of the varistor is observed to increase in all the samples with 0·0–0·3 mol% compared to those without any K_2O. However, the breakdown field is seen to decrease slightly around 0·3–0·5 mol% K_2O. This fact is in accordance with the microstructural observation of grain growth inhibition of K_2O. The increase in the breakdown field of ZnO still containing 0·5 mol% compared to the composition without K_2O is not very clear and probably cannot be fully explained based on grain size alone. As far as the non-linearity coefficient is concerned, the maximum value occurs at a current density around 10 mA/cm^2, which agrees with the ZnO–Pr doped systems with K_2O.[7]

4 Conclusion

The following conclusions can be arrived at from this study:

(1) A novel one-step process based on solid state decomposition of metal salts–urea mixtures has been carried out successfully to prepare highly homogeneous and fine, doped zinc oxide composite powders.
(2) Sintered discs made from the above powder have shown good non-linearity.
(3) K_2O as one of the additives around 0·3 mol% has resulted in considerable increase in the breakdown field as well as decrease in grain size.

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