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Characteristics of Zinc Oxide Powders Precipitated in the Presence of Alcohols and Amines*

M. E. V. Costa & J. L. Baptista

Departamento de Engenharia Cerâmica e do Vidro/INESC, Universidade de Aveiro, 3800 Aveiro, Portugal

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Abstract

Zinc oxide powders have been prepared by adding acidic $ZnCl_2$ solutions to NaOH solutions containing alcohol or amines. The physical characteristics of the powders (particle size and morphology) are conditioned by the presence of the organic molecules. These effects are related to particular growth mechanisms involving an active role of the organic additives. The presence of agglomeration in the powders obtained allows the obtention of low density samples with open porosity suitable for use as atmospheric sensors.

Zinkoxid-Pulver wurde durch die Zugabe saurer $ZnCl_2$-Lösungen zu Alkohol- oder Amine-haltigen NaOH-Lösungen gewonnen. Die physikalischen Eigenschaften der ausgefällten Pulver (Teilchengröße und -morphologie) hängen von der Präsenz organischer Moleküle ab. Ihre Auswirkung ist mit besonderen Wachstumsmechanismen verknüpft, bei denen den organischen Additiven eine aktive Rolle zukommt. Die Präsenz von Agglomeraten in den hergestellten Pulvern ermöglicht die Herstellung von Proben mit geringer Dichte, deren offene Porosität sich gut für die Anwendung als atmosphärische Sensoren eignet.

Des poudres d'oxyde de zinc ont été synthétisées par ajouts de solutions acides de $ZnCl_2$ dans des solutions de soude contenant des alcools ou amines. Les caractéristiques physiques des poudres (morphologie et taille des particules) sont conditionnées par la présence de molécules organiques. Ces effets dépendent de mécanismes de croissance particuliers impliquant un rôle actif des additifs organiques. La présence d'agglomérats dans les poudres obtenues permet l'obtention d'échantillons de faible densité avec une porosité ouverte, adaptée à leur utilisation en tant que capteurs de gaz.

1 Introduction

Zinc oxide has found applications in a wide variety of domains.[1] Some of the most demanding applications are based on some specific properties presented by zinc oxide, which led to its use in the production of devices in such diversified fields as gas sensors,[2,3] varistors[4,5] and transducers.[6]

The quality of the ZnO powders used for producing the components of such devices is usually of great importance to the performance of the final product. While for the production of an electrooptic device a transparent ceramic film with closely controlled porosity, grain size and even crystal orientation is necessary, for a varistor is more important that, during the processing, a proper distribution of dopants between the bulk of the grains and the grain boundaries has been achieved. While in both cases a ceramic with an end-point porosity close to nil is a goal to be pursued, for a zinc oxide disk or a zinc oxide film to be used as a humidity sensor, the requirement is a different one. In this latter case, easy access of the atmosphere to the highest amount of available surface in the device requires open, porous microstructures, with close control of pore size. Both the sensitivity and the response times of ZnO humidity sensors can be optimized by controlling the type of open porosity.[7] Usually a good mechanical strength is also required for several applications of such sensors. These two requirements for a humidity sensor are somewhat contradictory, since they demand a zinc oxide powder that can sinter at a low enough temperature to maintain a high surface area, with energetically favourable surface sites for easy adsorption/desorption of water molecules from the atmosphere and, at the same time, form a rigid and dense continuous skeleton with the necessary mechanical strength.

The sintering behaviour of a ceramic compact is strongly dependent on the packing characteristics of

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its powder particles, which determine the pore size distribution in the green compact. The densification rate at any temperature and time is related to the size of the initial pores that are shrinking.[8–10] Regions with finer pores sinter easily, while nearby large pores can be preserved, since, depending on the pore size and dihedral angle, there is a critical grain size below which the pore is thermodynamically stable. An interconnected pore structure can therefore be created. Since the packing characteristics of a powder depend on the shape, size and size distribution of the powder particles, it can be altered by controlling the characteristics of the powders used.

ZnO powders can be obtained by different methods, either using gas phase[11–13] or liquid-phase reactions.[14–17] Zinc oxide has three atomic arrangements of surface planes, namely the (0001), the $(000\bar{1})$ and the $(10\bar{1}0)$. The first two, the so-called polar planes, have unsaturated coordination of the most outwardly pointing ions, Zn ions and O ions respectively. On the $(10\bar{1}0)$ face, a non-polar one with Zn ions and O ions occupying lattice positions in the same plane, both have saturated coordination.[18] Such differences determine alterations in the type of interaction between the surface and adsorbed molecules[19] and have been shown to be able to control the growth of the crystal planes in particular directions, where adsorbed molecules compete with the lattice ions for the surface sites.[20]

In the present work the authors have evaluated how the presence of selected organic molecules (ethanol and ethanolamines) within the precipitating medium affected the particle size and shape of the ZnO precipitates. The packing and sintering characteristics of the precipitated powders were also evaluated, namely in what concerns the pore size structure of the green and fired samples.

2 Experimental

Zinc oxide powders were precipitated in aqueous media by spraying acidic solutions of $ZnCl_2$ (Merck, Darmstadt, Germany) over continuously stirred solutions of NaOH (BDH, Poole, UK) (powders A), or NaOH solutions containing one of the following organic compounds: ethanol (Merck, Darmstadt, Germany)—(powders B), MEA (monoethanolamine) (Merck, Darmstadt, Germany)—(powders C), and TEA (triethanolamine) (Merck, Darmstadt, Germany)—(powders D). A glass nozzle fed with air at a pressure of $1{\cdot}16 \times 10^5$ Pa assured a very fine spray of the cation solution at a constant adding rate of $0{\cdot}54\,cm^3\,s^{-1}$. All starting solutions were freshly prepared from analytical grade reagents; cation solutions consisted of distilled water solutions 0·5M in $ZnCl_2$ acidified pH = 2·5 with HCl (BDH, Poole, UK); organic solutions were 50% (volumetric percentage) aqueous solutions of the organic compound, except for ethanol where percentages of 10, 50 and 100% were used. The pH of ethanolic solutions and NaOH single solution was adjusted to 12. The pH of the precipitating medium was maintained constant (pH = 12) by continuous addition of a 10M solution of NaOH. The details of the experimental apparatus used in this work have already been reported.[21] Once the addition of the cation solution was completed, the powders were allowed to settle. Then, the supernatant solution was poured off and the powders were washed in glass-sintered G5 filters (nominal maximum pore size ranging from 1·0 μm to 1·6 μm) with distilled water to remove sodium. Washing with water was assumed accomplished when flame photometry measurements indicated that the concentration of sodium in the washing water had fallen below 1 ppm. Control experiments showed that this procedure ensured less than 100 ppm in the precipitated powders. A last washing cycle was then performed with acetone–toluene–acetone. Powders were subsequently dried in an agate mortar submitted to previous heating at 110°C. Powders were submitted to X-ray diffraction with a Philips PW 1840 apparatus (Philips, Eindhoven, the Netherlands) and examined with transmission and scanning electron microscopy using Hitachi H9000-NA equipment (Hitachi, Tokyo, Japan). Crystallite sizes were determined by X-ray line broadening measurements and specific surface area by N_2 adsorption (multipoint BET method) using a Quantasorb surface area analyser (Quantachrome Corp., Syosset, NY, USA). Compacts were prepared by isostatic pressing at $2000\,kg\,cm^{-2}$. Pressed samples were submitted to a constant heating rate firing up to 1080°C. Pore size distributions in green and fired compacts were determined by mercury porosimetry in a Micromeritics PoreSizer 9320 (Micromeritics Instrument Corp., Norcross, GA).

3 Results and Discussion

3.1 Nucleation and growth

The powders precipitated in the different experimental conditions previously stated (A, B, C and D) were identified as crystalline ZnO by X-ray diffraction. It was already known that using pure water as solvent and under the experimental conditions described, ZnO was the only reaction product.[21] Therefore the presence of the organic molecules in the medium had no effect on the chemical nature of the precipitated powder. On the other hand, they had a marked role on the physical characteristics of the particles obtained, since they were different for the

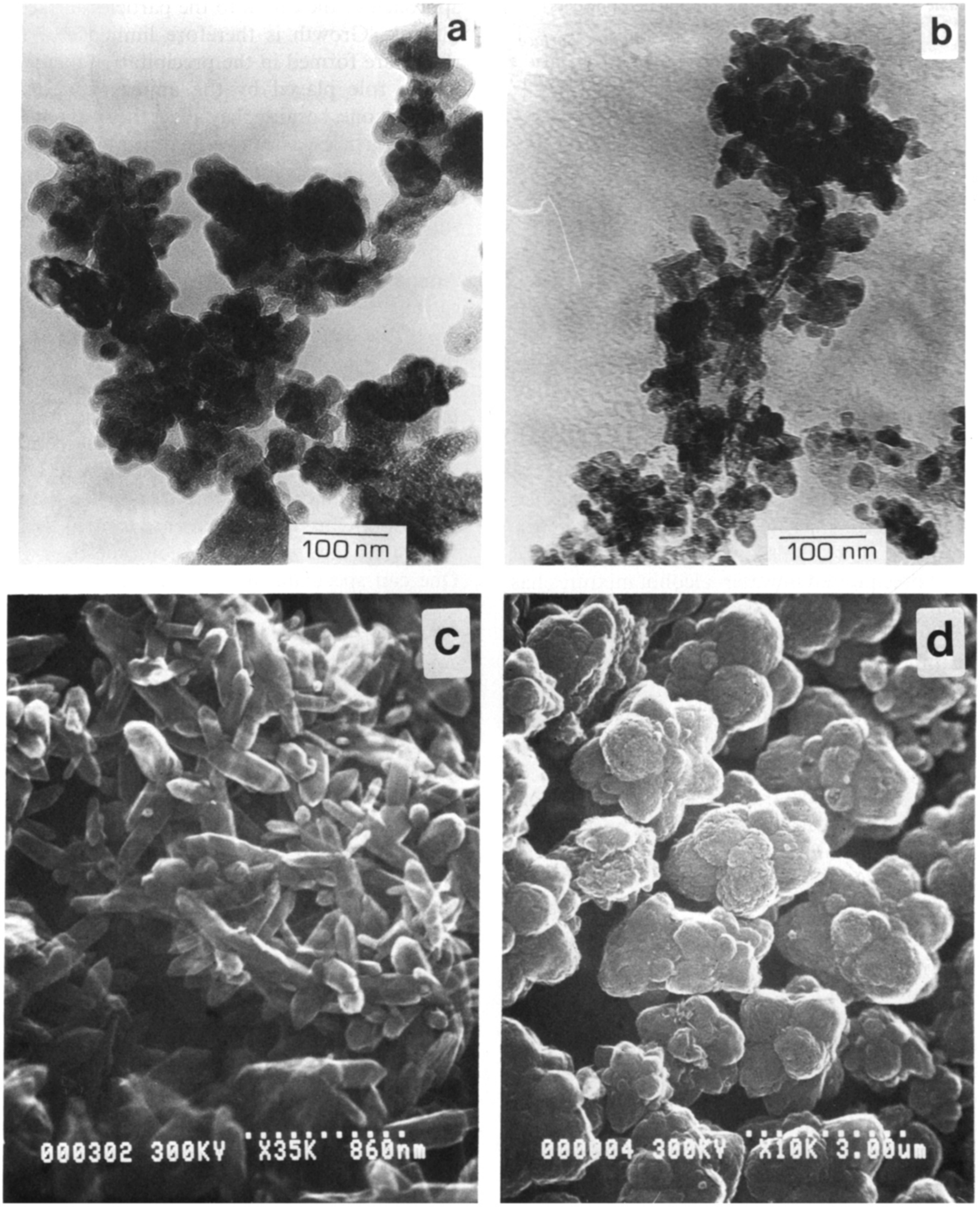

Fig. 1. SEM and STEM micrographs of powder particles precipitated in presence of: (a) no organic additive; (b) ethanol starting volume: 100%); (c) ethanolamine (starting volume: 50%); (d) triethanolamine (starting volume: 50%).

different precipitation media. Figure 1 illustrates the differences concerning the sizes and shapes of the particles. Powders A and B have similar particle shape (some kind of irregular platelet) revealing that ethanol did not affect their morphology. A different role was played by MEA and TEA which tailored very different shapes: particles C are elongated hexagonal prisms while particles D have rounded 'cauliflower'-type shapes.

The size of the particles were also sensitive to the presence of the organic additives. Powders A and B have on the average smaller dimensions than powders C and D, the latter having the larger dimensions. The macroscopic evidence is complemented by the results of surface measurements (BET) and crystallite size calculations presented in Table 1. These data are in agreement with a smaller particle size for samples A and B and permit an

Table 1. Characteristics of the precipitated powders

Powder	*Additive*	*Starting additive volume (%)*	*Crystallite size (nm)*	*Surface area (BET) $m^2 g^{-1}$*
A	No additive	—	25·2	18·2
B	Ethanol	10	23·6	26·6
		50	20·6	28·0
		100	19·4	45·7
C	Ethanolamine	50	66·0	19·4
D	Triethanolamine	50	37·2	1·3

easier differentiation between the several sizes of B type powders. The data of Table 1 also enable the conclusion to be made that the particles of powder D, which have a comparatively rather small surface area, are not formed by soft agglomeration of smaller particles, as could be inferred from the micrograph. Agglomeration of the particles in samples with the smallest particle sizes are however clearly seen in the micrographs of Fig. 1((a) and (b)).

The effect of alcohols on the characteristics of powders precipitated in water–alcohol mixtures has been observed for other systems such as hematite[22,23] and lead selenide.[24] In zinc oxide, obtained by heating in ethanolic media a zinc oxide salt precursor previously prepared,[17] it was assumed that the growth of the particle surface was controlled by the diffusion of Zn^{2+} ions through an ethanolic layer surrounding the particles. The effectiveness of ethanol in retarding the transport of the cation from the solution to the surface of the solid particle was invoked to explain the equiaxed morphology of the obtained particles.

The powders obtained in the present work by precipitation in media with different mixtures of ethanol and water are smaller than those obtained by precipitation in pure water (Table 1). When the highest concentration of ethanol was used the smallest particles were formed. It seems therefore that, at high ethanol concentration, a high nucleation rate competes favourably with a lower growth rate of the already formed particles, allowing a large number of nucleations to take place before suitable environment conditions allow the growth of the nuclei. These conditions seem to be the increasing concentration of water in the precipitation medium, as more and more $ZnCl_2$ solution and NaOH solution are added to it as the precipitation proceeds. The strongest effect of ethanol as retarder of the particle growth is present even when using 10% of ethanol in the starting mixture, since the surface area was increased to $26{\cdot}6\,m^2\,g^{-1}$ from the $18{\cdot}2\,m^2\,g^{-1}$ obtained when pure water was used. Probably, as has been suggested,[17] the role played by the ethanol molecules takes place after the nucleation of the particles. Ethanol adsorption on the surface could form a kind of layer that makes the approach of the cation to the particles surface more difficult. Growth is therefore limited and further nuclei are formed in the precipitation media.

The role played by the amines is probably a different one, because they affect the sizes and shapes of the particles, as can be seen in Fig. 1((c) and (d)). The bigger dimensions of particles C and D suggest that, in precipitation media containing amines, a smaller number of nuclei is formed and that their growth rate is faster than the nucleation rate. Amines have a well-known ability to complex metal cations through their nitrogen atom. At the beginning of the cation addition it is reasonable to expect that Zn^{2+} ions become complexed by the amines in the solution.[25,26] Nucleation of ZnO will probably take place in limited regions of the medium where local conditions, made possible by the continuous addition of reagents, allow nucleation to be either thermodynamically favoured or faster than complexation. Once a few nuclei are formed the results show that they are able to continue their growth. One can speculate that the presence of the amine molecules could even contribute to the enhancement of the growth of the particles. In the high pH conditions of the precipitation medium, and in the absence of amine molecules, Zn and O exist mainly as $Zn(OH)_3^-$ and OH^-, both negative ions.[27] In the presence of amines the metal cations are complexed and a helpful participation of the complexes themselves in the growth process could be envisaged as providing a less negatively charged metal ion whose approach to the negatively charged surface site would suffer a smaller electrostatic repulsion than the $Zn(OH)_3^-$ ion.

However, the role of the amine molecules is not confined to that just described. Their interaction with the growing particle surface has to be responsible for the different shapes exhibited by particles C and D. In the presence of MEA, where elongated particles were formed, some crystal planes had a faster growth than others, whereas in the case of TEA the individuality of the crystal planes seems to be smeared off, with a tendency for more rounded-type particles to be formed. According to current theories of crystal growth,[28] the entrance of a solvated solute molecule into the solvation layer of the powder particle involves the desolvation of both the solute and the surface site of the powder particle. Once this step is accomplished surface diffusion of the solute takes place until a favourable growth site is found and the solute is incorporated into the crystal lattice. In all of this process, solvent–solute molecule interactions can play an important role. Depending on the strength of these interactions, the desolvation of the surface site may become the rate determining step for the growth of the faces where it takes place. As a consequence, these faces grow more slowly than the others and appear as large developed faces. In the particular case of ZnO, differences in the surface properties of the different faces have been reported[19] and used to explain the adsorption–desorption behaviour of organic molecules. Three important features were shown to condition the interaction of the different organic functional groups: (i) dipolar interaction between adsorbates and surface, (ii) different ionic charge of the Zn ion on different surfaces planes and (iii) the degree of steric hindrance of the surface Zn ions on different faces. Being polar molecules with considerable dipole moments (MEA—2·27 debye; TEA—3·57 debye), ethanolamines are expected to interact with ZnO polar surfaces.[19] Accordingly, these faces are supposed to dominate the morphology of the particles, becoming larger than the remaining ones. Because experimental evidence does not agree with this conclusion, it must be considered that the adsorption of ethanolamine molecules also occurs on non-polar faces, probably favoured by other features like bond formation between the amine nitrogen with a surface metal ion and the ethanol hydrogen with a surface oxygen. Two surface sites would then be blocked by the MEA molecule, resulting in a consequent relative decrease of the perpendicular growth rate for the prismatic faces. In the TEA medium, the almost isotropic growth of the particles seems to indicate that the adsorption of this molecule occurs with the same probability on all faces. This rather speculative sequence of events can only be clarified by a better knowledge of the crystal face characteristics and of the type of their interaction with solute molecules.

3.2 Compaction and sintering

Green and sintered densities obtained after the firing cycle for the various samples are presented in Table 2. Figures 2 and 3 present the pore size distributions of samples before and after the firing cycle. From these results it can be seen that densification did not occur to any significant extent, the results for samples from powder D indicating even a small decrease in density. Also, the total volume of pores did not change upon firing, although the pore size distribution has moved to higher average sizes in the fired samples. All this evidence indicates that the powder agglomerates are controlling the porosity evolution. Intra-agglomerate pores were easily eliminated during the firing cycle upon full densification of the agglomerates of finer particles, leading to the formation of interconnected larger pores between the densified regions.[10] The microstructure of the samples after the firing cycle can be seen in the micrographs of Fig. 4. They confirm the evolution of porosity described in Fig. 3 and point out that for applications as atmospheric sensors, powders C seem to develop most adequate microstructure upon firing. The exact firing schedule and the higher permitted temperature, to achieve the exact balance between open porosity, mechanical strength and the degree of surface sensibility towards specific gas

Table 2. Characteristics of the powder compacts

Powder	Green compact		Sintered compact	
	Density (% theoretical density)	*Total pore volume ($cm^3 g^{-1}$)*	*Density (% theoretical density)*	*Total pore volume ($cm^3 g^{-1}$)*
A	48	0·16	49	0·18
B	50	0·15	51	0·17
C	55	0·14	59	0·18
D	49	0·14	46	0·12

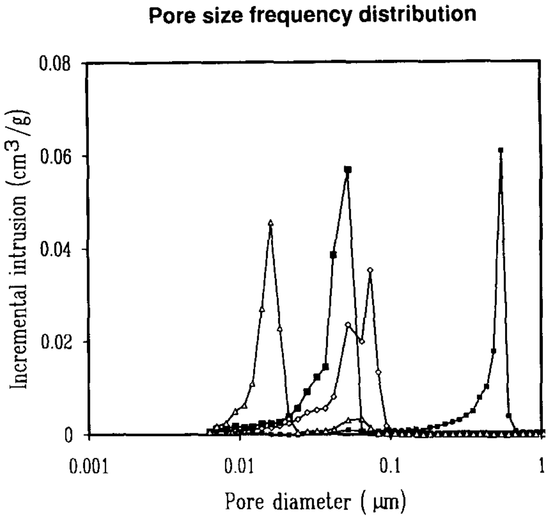

Fig. 2. Pore size distributions of green powders compacts: ■, powder A (no organic additive); △, powder B (ethanol starting volume: 100%); ◇, powder C (ethanolamine starting volume: 50%); ■, powder D (triethanolamine starting volume: 50%).

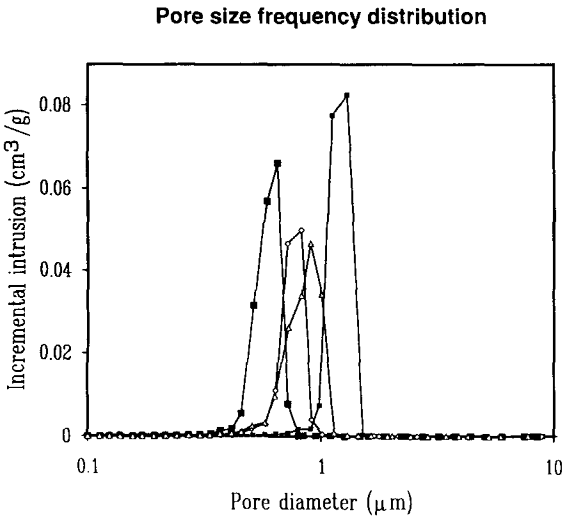

Fig. 3. Pore size distributions of powders compacts fired up to 1080°C: ■, powder A (no organic additive); △, powder B (ethanol starting volume: 100%); ◇, powder C (ethanolamine starting volume: 50%); ■, powder D (triethanolamine starting volume: 50%).

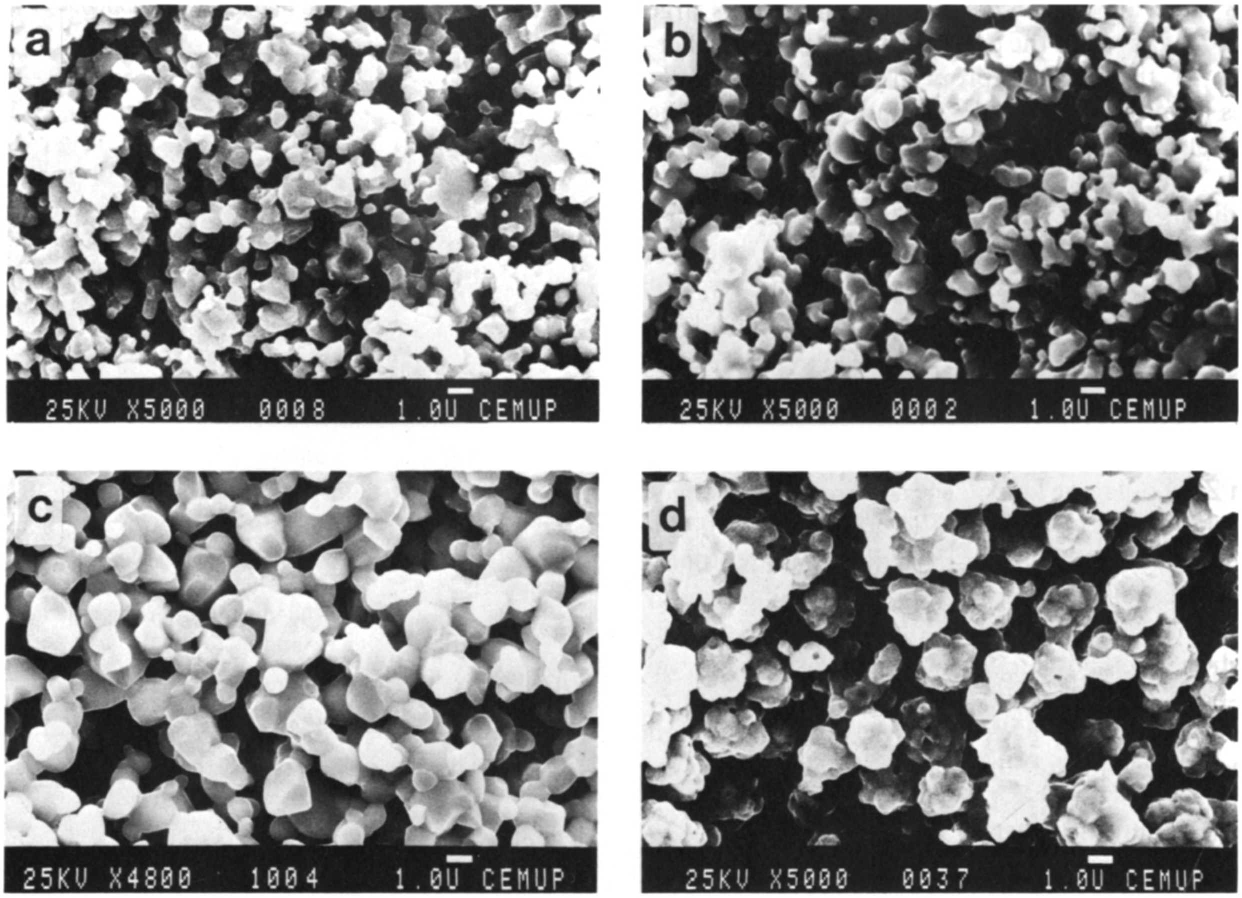

Fig. 4. SEM micrographs of fractured surfaces of fired powder compacts: (a) powder A (no organic additive); (b) powder B (ethanol starting volume: 100%); (c) powder C (ethanolamine starting volume: 50%); (d) powder D (triethanolamine starting volume: 50%).

molecules, can probably only be determined by direct experiments of adsorption–desorption of the gas molecules.

4 Conclusions

The morphological characteristics of ZnO powders obtained by direct precipitation in basic medium are affected by the presence of organic molecules in the precipitation medium. The presence of ethanol decreases the size of the particles, without affecting their shape, while the presence of amines (MEA and TEA) strongly affects the shape of the particles.

Pressed pellets of the precipitated powders can be sintered at low temperatures, leading, in some cases, namely for samples precipitated in the presence of monoethanolamine, to microstructures that seem suitable for the application of the sintered pellets as atmospheric sensors.

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