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Controlled precipitation methods: formation mechanism of ZnO nanoparticles

J.E. Rodríguez-Paéz[a,*], A.C. Caballero[b], M. Villegas[b], C. Moure[b], P. Durán[b], J.F. Fernández[b]

[a]*Departamento de Física, Universidad del Cauca, Popayán, Colombia*
[b]*Departamento de Electrocerámica. Instituto de Cerámica y Vidrio (CSIC), 28500 — Arganda del Rey/Madrid, Spain*

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Abstract

Zinc oxide nano-particles with different morphologies have been obtained by controlling different parameters of the precipitation process: solution concentration, pH and washing medium. The reactions leading to the formation of zinc metastable complexes were followed by potentiometric and conductimetric titrations. During the ethanol washing step the intermediate zinc complexes have been modified by weathering and solution processes which drived both the phase transformation reactions and the particles recrystallization. The nucleation of zinc alkoxides during this process is an "organic matrix-mediated" process, where the matrix is formed on the intermediate zinc complexes surface during the NH_4OH addition to the solution of the zinc precursor. The existence of this matrix has been supported by FTIR. The transformation of the zinc metastable complexes during the washing with ethanol was followed with XRD. Through this process it is possible to obtain agglomerates of zinc oxide nanoparticles from a random network, as was revealed by SEM and TEM. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There is a growing interest in the production of ultrafine powders (UFP) as well as in their consolidation. For decades, the studies of small particles and catalysis particles have been a focused topic of scientific research. The physical and chemical properties of nanoparticles, suggest them as ideal building blocks for two and three dimensional cluster self-assembled structures.[1] UFP allows the use of low sintering temperatures and are the base to obtain fine grain size ceramics with relevant properties in microelectronics.[2] A reduction in particle size to the nanometer scale results in quantum size effects when the dimensions become comparable or lower than the length of the de Broglie electron, the wavelengh of phonons and the mean size of excitons.[3] Recently, an incredible number of fabrication routes for ultrafine starting particles have emerged.[4–6] Most of these routes can be divided into three major classes: chemical, mechanochemical and thermophysical methods.[4] The chemical routes use direct, often very simple, chemical reactions to produce a product in the powder form. These techniques have in common the fact that they do not offer underlying of physical or chemical principles (except to silica). Thus, the generalisation of the processes involved must require the understanding of the formation mechanism of nanoparticles.[6]

The method of controlled precipitation is a process to obtain large quantities of ceramic powders with reproducible properties for their use as industrial products.[7] The three stages of the process are: (1) the formation of metastable zinc complexes through a slow addition of ammonia, (2) the partial phase transformation of metastable zinc precursors to zinc oxide after washing the initial colloidal suspension with ethanol and (3) the complete transformation to ZnO by thermal treatment. The main phenomenon of this method is the controlled release of cations from an homogeneous suspension. This work discusses the kinetics of the precipitation of the zinc complexes and the formation mechanism of ZnO particles during the process.

2. Experimental procedure

Zinc acetate dihydrate aqueous solutions 0.34 M acidified with 0.25 N HNO_3 were titrated using both a

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* Corresponding author.

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conductivity dip-type cell (conductivity meter WTW LF 320/SET Tetracon 325) to measure the conductivity changes in the solution and a Titrino DMS 716-Metrohm for the potentiometric titration. Both the specific conductivity and the pH were measured simultaneously as a function of the volume consumed until pH 9 was reached. The titration solution was a 12 M NH_4OH solution added by 0.1 ml increments by means of a Teflon capillary tube submerged below the solution-gas interface while the solution was continuously stirred.

The precipitation process was controlled by the potentiometric and conductimetric titration results. Two precipitates were formed, the first at pH 7.7, ETOH77, and the second at pH 8.5, ETOH85. In both cases the precipitation process was carried out at room temperature.

The resulting precipitates were filtered and redispersed in ethanol several times. The redispersion of the cake was carried out using a high speed turbine. The resultant sediments of ETOH77 and ETOH85 were dried after several washings at 60°C for 2 days. Pure ZnO was not obtained after drying, and for this purpose a thermal treatment in air at 320°C for 1 h was required.

To determine the crystalline phase evolution, both the 60°C dried precipitate and the ceramic powder obtained after washing with ethanol were characterised by X-Ray Diffraction (XRD), using CuK_α radiation. To characterise the surface groups infrared spectroscopy of non-washed precipitates was used. The particle size and the morphology of ZnO powders obtained after thermal treatment were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Results and discussion

3.1. Formation of the organic matrix

Fig. 1 shows the potentiometric and conductimetric titration curves of 0.34 M $Zn(CH_3COO)_2$ aqueous solution. The potentiometric titration curve shows one initial increase in pH, zone I, that corresponds to the neutralization of the protons by NH_4OH. The extended near-horizontal plateau, zone II, indicates the existence of an OH- consuming process. The second increase in pH, zone III, occurs after this plateau up to a near constant pH value (~8.5).

The conductimetric titration curve presents three linear regions and one transition zone between the two initial ones. The first region corresponds to the titration of normal alkyl carboxylic acid groups. These groups are associated with the COOH surface functional group of zinc acetate complexes. The carboxylic acids have a strong hydrogen-bonding ability. This characteristic allows the formation of open dimmers. The portion of the titration curve due to the weak acid polymer groups is not perfectly linear.[8]

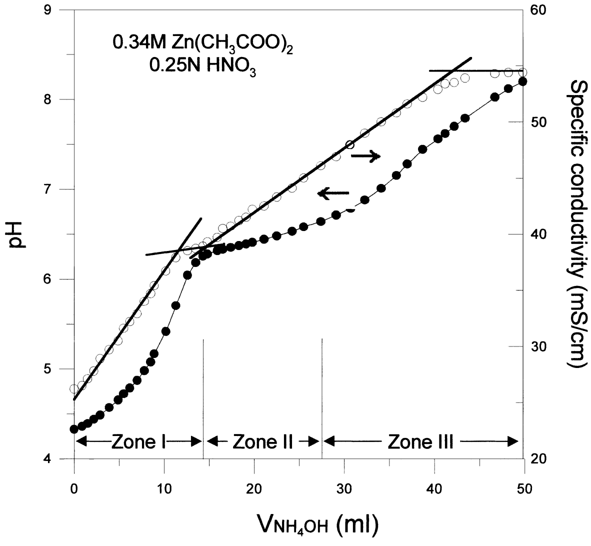

Fig. 1. Potentiometric and conductimetric titration curves of 0.34 M $Zn(CH_3COO)_2$ aqueous solution.

Moreover, hydrogen bonding is of the type $R_1COOH.....B$, where B is a nitrogen base, i.e. NH_3, can occur. The transformation from $R_1COOH.....B$ into a hydrogen-bonded $R_1COO^-.....B^+$, ion pair, at a critical pK difference between the acid and the nitrogen base has been demonstrated.[9] For that, the middle portion can correspond to the titration of $R_1COOH.....R_2NH_3$ and the last one to the titration of the ammonium surface groups.

In the transition zone and in the intermediate linear region the colloids can be progressively formed. In the last linear region the addition of the weakly ionized base to the solution causes the conductivity to almost level off.

The kinetics of the solid–water interactions are dominated by chemical reactions occurring at such an interface. The formation of cations at the surface complexes and the adsorption of ligands involve the coordination of the zinc ions with nitrogen donor atoms and ligand exchange, respectively.[10]

Infrared spectra of precipitates of ETOH77 and ETOH85 before washing are shown in Fig. 2. In these spectra the characteristic bands of carboxylic acid and ammonia salts were recorded. The bands around 1500 cm^{-1} can be assigned to the $\nu_a(COO^-)$ [1551 cm^{-1}] and $\nu_s(COO^-)$ [1450 cm^{-1}] vibrations. Their frequency separation ($\Delta\nu = 104$ cm^{-1}) is typical of an acetate ion acting as a chelating bidentate ligand.[11] Another assignation of these two bands around 1500 cm^{-1} can be: $\nu_a(COO^-)$ [1587 cm^{-1}] and $\nu_s(COO^-)$ [1445 cm^{-1}] vibrations. In this case, the frequency separation ($\Delta\nu = 142$ cm^{-1}) corresponds to acetate bridges.[11] On the other hand, the broad band at ~3500 cm^{-1} indicates the existence of inter and intra-hydrogen bonds between

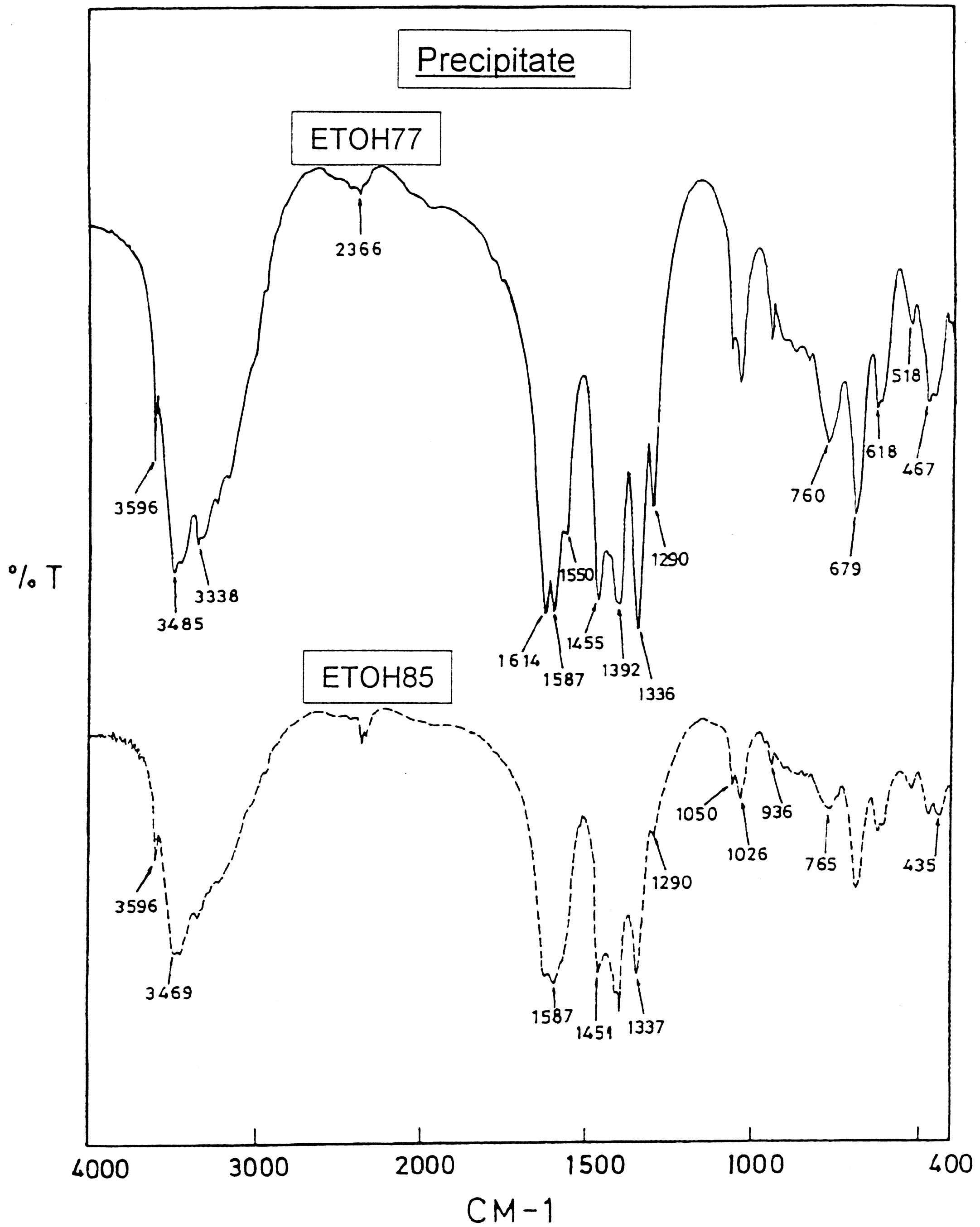

Fig. 2. Infrared spectra of precipitates of ETOH77 and ETOH85 before washing.

chemical units that could be associated with dimmer and polymer structures.[11]

These surface complexes are the basic components of the organic matrix. These complexes are located on the surface of the intermediate zinc compounds obtained during NH_4OH addition.

3.2. Nucleation of zinc alkoxides

The nucleation of zinc alkoxides occurs during the washing of the colloidal suspension with ethanol. At this step, the intermediate zinc compounds could be modified by both weathering and solution processes. The chemical reactions at the interface control the solution process rate. This is due to the interaction between surface species and the solid solution because the inner sphere surface complexes polarize and weaken the critical metal–anion bonds surrounding the surface metal centers. This facilitates the detachment of the reacting metal surface species.[10] The main chemical reaction on the solid surface during the washing with ethanol is:

$$\equiv \mathrm{Zn-OH(s)} + \mathrm{C_2H_5OH(l)} \Longleftrightarrow \equiv \mathrm{Zn{-}O{-}CH_2CH_3(s)} + \mathrm{H_2O(l)} \quad (1)$$

where ≡Zn– is a Zn surface site. Another possibility of surface reaction is the exchange involving the carboxylic and ethoxide functional groups as indicates the following reaction:

$$\mathrm{Zn(CH_3COO)_2{+}C_2H_5OH} \Longleftrightarrow \mathrm{Zn(CH_3COO)(C_2H_5O)} + \mathrm{CH_3COOH} \quad (2a)$$

$$\mathrm{Zn(CH_3COO)(C_2H_5OH)} + \mathrm{C_2H_5OH} \Longleftrightarrow \mathrm{Zn(C_2H_5O)^2{+}CH_3COOH} \quad (2b)$$

As in other systems[12] a chemical modification of the molecular precursor is observed as a result of the chemical substitution of CH_3COO^- by $C_2H_5O^-$. This two step-reaction allows the formation of the zinc dialkoxide. On the other hand, in these situations surface complexes formation facilitate the release of Zn^{2+} and/or Zn^+–O–CH_2CH_3 from the surface to the adjacent solution. In summary, during the ethanol washing the bulk suspension is enriched in Zn^{2+} and/or Zn^+–O–CH_2CH_3.

On the organic matrix carboxylic ligands and carboxylate headgroups are present. These groups can facilitate the nucleation of the zinc alkoxides as they occurs in other systems.[13] The nucleation can occur through an ionotropic process.[14] The ionotropic model assumes that the zinc binding moiety is spatially fixed on a macromolecular scaffolding. The zinc is bounded to the matrix through carboxyl groups. The bounded zinc would then attract a local concentration of $C_2H_5O^-$. These anions attract a local secondary concentration of zinc ions as free ions and/or ion pairs. Zinc alkoxide nucleation results from this high local concentration of the precursor ions.

3.3. Zinc alkoxide to zinc oxide transformation

The zinc alkoxide to zinc oxide transformation occurs during the drying step and it can be considered both as a Greenler's transformation[15] and an Arai's desorption.[16] Although the diethyl zinc (DEZ) is the more common zinc alkoxide,[17] it oxidised rapidly to zinc dialkoxide,[18] being both a high chemical activity species. In fact, the DEZ is an electron deficient compound with two vacant orbitals, so the presence of these vacant orbitals available for bonding explains its high chemical reactivity.[19]

ZnO films have been prepared by the oxidation of diethyl zinc. Epitaxial films have been achieved at temperatures of 400 and 730°C by the reaction of DEZ with H_2O/H_2 and N_2O/N_2 as oxidizing gasses, respectively.[19] Roth et al.[20] reported reasonable ZnO conducting films with a substrate temperature of 280–480°C. Vogel et al.[21] obtained ZnO powder by hydrolysis of a dilute solution of zinc ethoxide in dry ethanol. In this work the transformation of the zinc alkoxide to zinc oxide occurs between room temperature and ~60°C.

Fig. 3 shows the X-ray diffraction patterns of the precipitates and the powders after the washing with ethanol for ETOH77 (a) and ETOH85 (b). In both cases, the XRD results show two crystalline phases

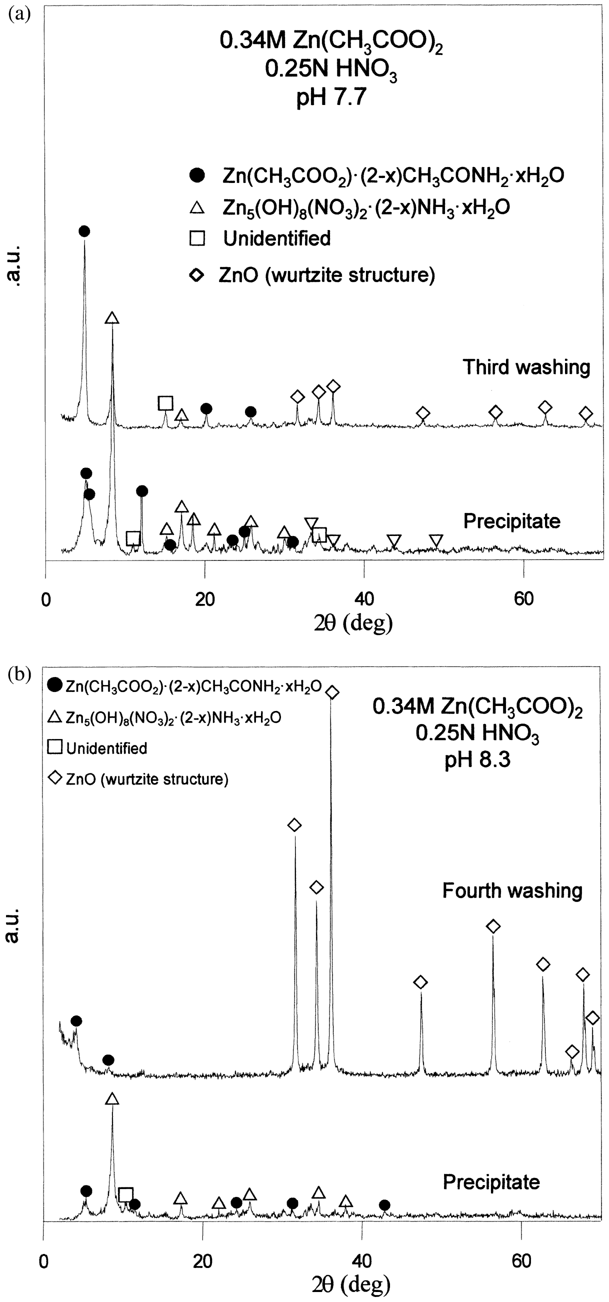

Fig. 3. X-ray diffraction patterns of the precipitates and the powders after the washing with ethanol for ETOH77 (a) and ETOH85 (b).

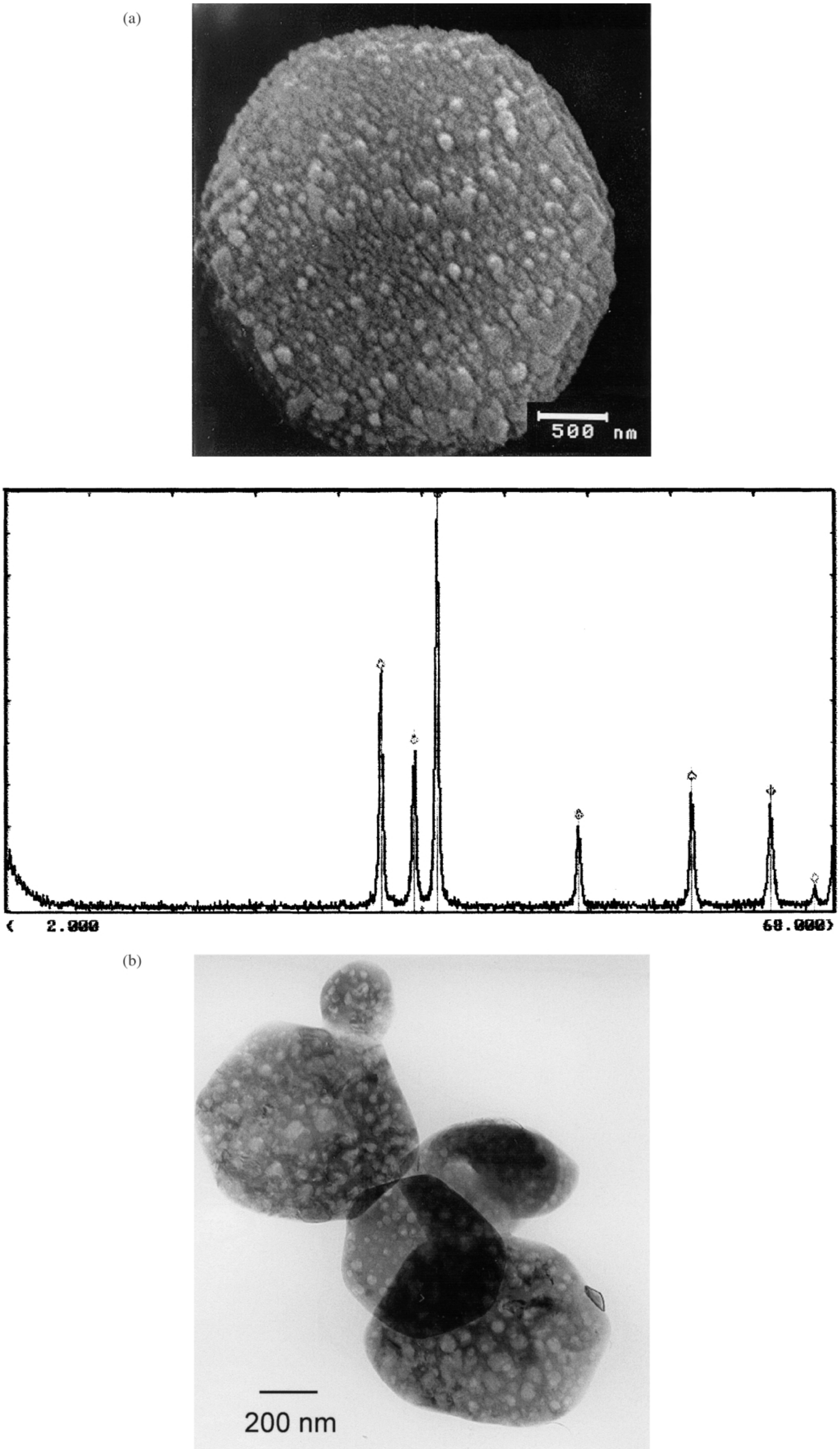

Fig. 4. (a) SEM micrograph of an individual self-assembled structure of the ETOH85 powder. (b) TEM micrograph of the same self-assembled structure.

identified as: ammine zinc hydroxide nitrate (AZHN), $Zn_5(OH)_8(NO_3)_2\cdot(2-x)H_2O\cdot xNH_3$ (JCDP 45-593 and 40-1459), and zinc acetate acetamide hydrate (ZAAH), $Zn(CH_3COO)_2\cdot(2-x)H_2O\cdot xCH_3CONH_2$ (JCDP 33-1977, 35-1647 and 34-819). In both powders after washing with ethanol the main crystalline phase was ZnO (zincite).

In Fig. 4(a), a SEM micrograph, an individual self-assembled structure of the ETOH85 powder is presented. Fig. 4(b) shows a micrograph of the same self-assembled structure obtained by TEM. As can be seen, these self-assembled structures (particles) are agglomerates consisting of nanoparticles. The agglomerates size is ~1 μm, whereas the nanoparticles size is ~50 nm.

4. Conclusions

The controlled precipitation method allows the control of the different stages of ceramic powder processing, and in this way the preparation of ceramic powders with reproducible properties. From the potentiometric and conductimetric titrations three processes can be followed and identified: (a) the neutralization of existing acid in the solution; (b) the embryonation and nucleation of the solid phase and (c) the growth of the nuclei. The conductimetric titration curves indicate the endpoints of the process which correspond to the titration of different functional groups: carboxylic acid, weak acid polymer, $R_1COOH.....R_2NH_3$ complexes and ammonia groups.

Chemical weathering, solution processes and phase transformation occur during the washing stage with ethanol. These processes are produced by shear action and solute–solvent interaction. The nucleation of zinc alkoxides during the washing step with ethanol is an "organic matrix-mediated" process. The organic matrix is formed on intermediate surface zinc complexes during the addition of NH_4OH to zinc solution. The nucleation is an ionotropic process. Zinc alkoxide nucleation results from this high local concentration of the Zn^{2+} and Zn^{+}–O–CH_2CH_3 precursor ions.

The last stage is the transformation of the zinc alkoxide to zinc oxide through both a Green's transformation and an Arai's desorption.

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