Formation of ceramic bodies using submicron MSnO$_3$ (M = Ba, Zn, Ca) particles and evaluation of their electric behaviour in different atmospheres

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Abstract

In this work, the most suitable conditions were determined for shaping ceramic bodies of the MSnO$_3$ system (M = Ba, Zn, Ca), using submicron particles of these perovskites synthesized by a chemical route. For this, the rheological behaviours of colloidal suspensions of the MSnO$_3$ powders (M = Ba, Zn, Ca) were studied considering the effects of solid content and concentration of ammonium polyacrylate (APA). The results indicated that the optimal solids contents for stable suspensions in each system were 13.8 (BaSnO$_3$), 19.4 (ZnSnO$_3$), and 21.5 vol.% (CaSnO$_3$). The suspensions containing BaSnO$_3$ and ZnSnO$_3$ showed large reductions in viscosity, approximately 87%, when APA (0.5–0.8 wt.%) was added. In contrast, the CaSnO$_3$ suspension did not show significant changes after addition of APA. Slip casting of the stable suspensions allowed formation of porous green bodies, which were subsequently sintered in the range 1000–1500 °C. Considering their potential use as gas sensors, a preliminary study of the sintered bodies showed high detection responses (R_a/R_g) toward 80 ppm reducing gas at operating temperature of 270 °C, especially ZnSnO$_3$ to acetone and ethanol vapours, BaSnO$_3$ to ethanol vapour and CaSnO$_3$ to toluene vapour.

Keywords: perovskites, processing, rheology, slip casting, electrical behaviour

I. Introduction

Perovskites MSnO$_3$ (M = Ba, Zn, Ca) are outstanding materials due to the great diversity of their technological applications, which include use as dielectric materials [1–3], gas sensors [4–6], solar cells [7–9] and anodes for lithium-ion batteries [10–12]. To obtain these perovskite-like structures, different synthesis methods have been used, including sol-gel [10,13,14], hydrothermal [4,15,16], co-precipitation [3,6] and solid-state reaction [2,17] processes. In particular, the polymer complex or Pechini method has been used to obtain a great variety of advance ceramic powders, including a range of stannates [18,19], thereby enabling purity and homogeneity in the product and control of the physicochemical properties of the particles.

One of the potential uses of these perovskites is as active material in gas sensors [20,21]. Significant research has been carried out with ZnSnO$_3$ that has shown a significant sensing capacity against different gases [22], among them: acetone [23], ethanol [24,25], formaldehyde [22,26], CO [27], NO$_2$ [28], H$_2$ [29], etc. This does not rule out the possibility of studying the potential use of other perovskites of interest for gas sensors [4,30,31], with a more careful and systematic study of them being required, considering this potential technological use. For the evaluation of their ability as gas sensors, syn-
themselves stannate powders have been used directly or as a thin film [28,29], but it is not easy to find evaluation reports on ceramic bodies formed from these ceramic powders. Therefore, it is of interest to determine the electrical behaviour of the sintered bodies of these perovskites in the presence of certain gases. To do this, it is necessary to form the ceramic bodies, for which the most suitable conditions for shaping and sintering of dense bodies of these compounds should be determined. Although there are few reports on the forming of these ceramic bodies, several of those that deal specifically with sintering [32–36] have been patented [37,38]. This indicates that there is technological interest in the forming of ceramic bodies using powders of different stannates, which is the central theme of this work.

The colloidal process is a widely used method for obtaining advanced ceramic bodies. This technique integrates several ceramic forming processes, including tape casting, dip coating, screen printing and slip casting [39,40]. In colloidal processing methods, stable slip is initially formed with ceramic powders of interest in a liquid medium. With this slip, ceramic products with very good characteristics can be formed, considering different applications, among which the following stand out: biosensors, gas sensors, varistors, condensers and fuel cell films [41–45]. To obtain these devices, both the composition and the stabilization of the ceramic slurry must be optimized.

When ceramic powders are suspended in a solvent such as water, attractive Van der Waals-type forces arise. These cause the particles to join and form groups or “soft” agglomerates that can eventually cause flocculation of the system, as well as sites of high stress that would negatively affect the final properties of the formed object [46]. Therefore, it is necessary to form a stable suspension with adequate dispersion of solids and good rheological behaviour. This ensures controlled slip casting to form a green body with reduced number of heterogeneities, better microstructural control and enhanced properties [47].

One strategy frequently used to stabilize colloidal suspensions, including nanofluids, is to coat the particles with a layer of a substance that is primarily organic in nature and acts as a dispersant (steric stabilization) [48–51]. However, it is also possible to change the electrical charge of the particle surface, which increases the electrostatic repulsion between particles and favours stabilization [46,51,52].

Moreover, previous studies considered different variables involved in the colloidal process, such as the concentration of solids and the nature of solvent and deflocculant (dispersing agent). These mainly affect the viscosity of the suspension and its dispersion state. Slips giving the best results in the production of ceramic bodies have a certain degree of thixotropy (the gradual recovery of the structure of the suspension at the micro and macroscopic level) [39,46,47,51,53].

The values of viscosity, and therefore of thixotropy, depend not only on the total amount of deflocculant added to the suspension, but also on the relative proportion of each of the components of the system (solid - solvent - deflocculant). For example, the thixotropy of a slip is reduced when increased amounts of deflocculant are used [51–53]. To form the appropriate slip needed to obtain a desired ceramic body, it is necessary to carry out a careful rheological study of the corresponding suspensions, since parameters such as viscosity and sedimentation time affect the quality of the ceramics formed from these slips.

To obtain ceramic bodies of the MSnO₃ system (M = Ba, Zn, Ca) using colloidal processing, and particularly slip casting, it is necessary to form a stable slip with controlled dispersion of stannate powders. Unfortunately, there is a limited number of reports on this issue in which powders of these particular perovskites were used, which is why the aim of this work is to study the rheological behaviour of aqueous colloidal suspensions containing MSnO₃ nanoparticles (M = Ba, Zn, Ca) synthesized by the modified Pechini method. Initially, colloidal suspensions were formed and a surfactant or dispersant (ammonium polyacrylate (APA)) was added. After that, the suspensions were characterized rheologically. Finally, based on the results of the rheology tests, green bodies were obtained using the slip casting method. The sinterability of these bodies was evaluated by means of dilatometry and relative density tests, and their microstructures were examined by scanning electron microscopy (SEM). Finally, considering a potential technological application of these sintered bodies based on MSnO₃ (M = Ba, Zn, Ca) they were tested as gas sensors to the detection of several volatile organic compounds, known as VOCs (acetone, ethanol, and toluene), as well as other gases (CO, H₂ and NO₂), at a fixed concentration.

II. Experimental

MSnO₃ (M = Ba, Zn, Ca) powders were obtained by the polymer complex method described in previous work [18,54]. The crystalline structures of the synthesized particles were determined with X-ray diffraction (XRD) using the PANalytical X’Pert PRO diffractometer with a Cu source having Kα₁ = 1.540598 Å and Kα₂ = 1.544426 Å and working voltage and current of 45 kV and 40 mA, respectively. Scanning and transmission electron microscopy images were obtained by using a JEOL microscope, model JSM 6490 LV in secondary electron mode with an acceleration voltage of 20 kV and a JEOL 2010 F TEM with an acceleration voltage of 400 kV to determine the morphologies and sizes of particles, particularly secondary particles, as well as their state of agglomeration.

The average particle size was determined by laser granulometry in a Mastersizer 2000 particle size analyser (Malvern Instruments). Brunauer-Emmett-Teller (BET) specific surface areas of synthesized pow-
ders were calculated from N$_2$ adsorption/desorption isotherm plots recorded on a Quantachrome Nova 1000e. Density measurements were made using a helium pycnometer (Anton Par, Ultrapyc 3000). The state of agglomeration $FA$ of the synthesized powders was defined by the $D_{50}/D_{BET}$ ratio [55,56]:

$$FA = \frac{D_{50}}{D_{BET}} \quad \text{where} \quad D_{BET} = \frac{6}{S.S.A \cdot \rho} \quad (1)$$

$D_{50}$ is the median volume diameter determined by laser granulometry, $D_{BET}$ is an average diameter calculated from the specific surface area ($S.S.A$) measured by nitrogen adsorption (BET) and $\rho$ is the powder density measured by helium pycnometry.

The stability of the stannate powders was evaluated as a function of pH through measurements of zeta potential (ZP), using a Zeta Meter 3.0 and diluted suspensions (0.1 mg/l) of the powders while maintaining constant ionic strength. The pH of the suspension was adjusted by adding HCl and NaOH in a controlled manner and the particles were dispersed using a magnetic stirrer until the pH of the system was constant. Ten measurements were taken for each pH value.

Rheological tests were performed using a Haake Mars III rheometer from Thermo Scientific with a concentric cylinder configuration. The tests were carried out at room temperature while maintaining a gap of 4.2 mm between the cylinders and the shear rate was set from 10 to 1000 s$^{-1}$. Evaluation of rheological parameters for all suspensions was based on the flow curves determined using Haake RheoWin software. Slurries were prepared with distilled water, ammonium polyacrylate (Darvan 821-A, produced by Vanderbilt Minerals) concentrations of 0 to 0.8 wt.% and MSnO$_3$ powder concentrations (M = Ba, Zn, Ca) between 5–30 vol.%. The solid contents were previously determined to ensure the fluidity of the suspensions under shear conditions. The evaluated suspensions were initially subjected to ultrasound agitation to break up "soft" agglomerates using a Branson digital sonifier probe, model S450-D, for 10 min. In parallel, a sedimentation study of the suspensions was carried out in which all samples were settled in a vibration-free environment and the heights of the sediments formed were monitored for several hours. After the rheological analysis, the appropriate parameters required to form stable slips, i.e. solid content and amount of deflocculant, were defined. For the shaping, the suspensions were poured into plaster-type moulds (Corona brand) used to obtain two types of samples: cylindrical rods, to perform dilatometry tests, and discs, to complement the studies of sinterability and specifically to determine their microstructure. The procedures described above are represented by the diagram in Fig. 1a. Once the bodies had been removed from the moulds, the samples were dried at room temperature in a desiccator for 24 h. The ceramic specimens were sintered in a Carbolite RHF 1600 electric furnace at temperatures between 1000–1500 °C for 1 h. The sintered samples were characterized by helium pycnometry to determine the density and by SEM to observe their surfaces. Also, the apparent porosity ($AP\%$) was calculated using Eq. 2, described in the ASTM Standard C20 and in Ref. [57]:

$$AP\% = \frac{W - D}{W - S} \times 100 \quad (2)$$

where $D$ is the weight in air, $W$ is the soaked weight and $S$ is the suspended weight. The apparent porosity is a percentage of the volume of the open pores in the total specimen volume.

The sintered ceramic bodies (sensor material) were manually coated with silver paint on both sides and placed in equipment with two platinum electrodes located in a chambers system (see Fig. 1b). A preliminary gas sensing test was carried out using a system equipped with 6 chambers connected in parallel (with a volume of ~3.2 ml) with continuous flow and mass flow controllers that allowed the mixing of dry air and target gas calibrated to achieve the desired concentration. An adjustable hotplate (Combiplac, J.P. SELECTA) was used to heat the sensor setup. Temperature was monitored during the test. Measurement of the sensors DC resistance was performed with an electrometer (Keithley 6517B) with relay multiplexer to monitor several sensors simultaneously. The response of the sensors was defined as $R_a/R_g$, where $R_a$ and $R_g$ are the sensor resistance in air and in the target gas, respectively.

III. Results and discussion

3.1. Characterization of synthesized powders

Figure 2 shows XRD patterns corresponding to the MSnO$_3$ samples (M = Ba, Zn, Ca) synthesized by the
polymer complex method and heat treated at temperatures of 700 °C (BaSnO$_3$ and ZnSnO$_3$) and 800 °C (CaSnO$_3$). The characteristic peaks of the crystalline phases of BaSnO$_3$ (JCPDS 15-780), ZnSnO$_3$ (JCPDS 28-1486) and CaSnO$_3$ (JCPDS 31-312) and no secondary phases were observed.

SEM and TEM micrographs of the synthesized perovskites are shown in Fig. 3. In these cases, the presence of polyhedral agglomerates greater than 1 µm in size and smaller primary particles with sizes between 20 and 100 nm (Figs. 3a and 3b) were observed. The spheroidal morphology predominated in the BaSnO$_3$ and ZnSnO$_3$ primary particles (Figs. 3a and 3b), while the CaSnO$_3$ particles had thin laminar forms with lengths of ∼500 nm (Fig. 3c).

Particle size distributions were measured by laser granulometry (Fig. 4). The BaSnO$_3$, ZnSnO$_3$ and CaSnO$_3$ powders had mean particle sizes of approximately 200, 160 and 60 nm, respectively. Additionally, the N$_2$ adsorption/desorption isotherms indicated that the specific surface areas of the BaSnO$_3$, ZnSnO$_3$ and CaSnO$_3$ samples were 38.913, 4.560 and 8.056 m$^2$/g, respectively. An overview of the results obtained with Eq. 1 is given in Table 1. By correlating information from Table 1, it indicates that the BaSnO$_3$ particles show serious agglomeration.

Figure 5 shows the variations in zeta potential (ZP) versus pH for the stannate particles in aqueous media. For the particles without additives, the negative electric charge predominated for a wide range of pH values in the suspension, since the isoelectric point was obtained as pH$_{iep}$ ≈ 3.3. This pH$_{iep}$ value is consistent with those reported by Shukla [58] and Lü [59], which indicated pH$_{iep}$ values of 3.82 and 4.96, respectively. The differences in pH$_{iep}$ values can be justified if the physical and chemical characteristics of the nanoparticles differed because the synthesis methods used to prepare

<table>
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<tr>
<th>Sample</th>
<th>Density [g/cm$^3$]</th>
<th>$D_{V50}$ [µm]</th>
<th>$D_{BET}$ [µm]</th>
<th>FA</th>
</tr>
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<tbody>
<tr>
<td>BaSnO$_3$</td>
<td>4.66</td>
<td>0.209</td>
<td>0.033</td>
<td>6.33</td>
</tr>
<tr>
<td>ZnSnO$_3$</td>
<td>6.81</td>
<td>0.163</td>
<td>0.193</td>
<td>0.84</td>
</tr>
<tr>
<td>CaSnO$_3$</td>
<td>4.26</td>
<td>0.0679</td>
<td>0.174</td>
<td>0.39</td>
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Ammonium polyacrylate (APA) is characterized as a “weak” polyelectrolyte, such that its dissociation and adsorption are favoured in moderately alkaline media. Therefore, the increases in the magnitudes of ZP may have arisen because the APA molecules were adsorbed on the surfaces of nanostannates, an effect that ought to promote colloidal stabilization, according to Davies and Binner [60]. The stability presented by suspensions containing APA can be justified by considering that the polymer is efficiently adsorbed on the surface of the stannates, giving rise to the formation of loops and tails in the adsorbed layer, as proposed by Davies and Binner [60]. The stability of stannates against sedimentation is a critical parameter for assuring the uniformity of the suspension during the period of time sufficient for handling and forming before a green body is formed [51].

### 3.2. Rheological behaviour of the suspensions

**Suspensions without dispersing agent**

Flow curves for the MSnO₃ suspensions (M = Ba, Zn, Ca) with different solids contents (φ) are shown in Fig. 6. The stress (τ) and viscosity (η) show an approximately linear relationship (near-Newtonian flow) for φ ≤ 8 vol.%. In these suspensions, the distances between particles increased and the Van der Waals forces weakened, leading to the viscosity not changing significantly with the shear rate (γ). For solids contents greater than 8 vol.%, increases in both resistance to flow (yield stress) and viscosity were observed, resulting in shear thinning with the variation of the shear rate, which results from the interactions between apparent volumes in concentrated suspensions of anisotropic particles such as ceramic suspensions [61,62]. Thus, as γ and τ increased, the particles increasingly aligned in the flow direction. This reduced the apparent volume of the particles, which finally meant a decrease in suspension viscosity. It can also be seen that in all three stannate

<table>
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<th>Sample</th>
<th>Time [h]</th>
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<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>BaSnO₃</td>
<td></td>
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<tr>
<td>without</td>
<td>1.15</td>
</tr>
<tr>
<td>0.1 wt%</td>
<td>3.5</td>
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<tr>
<td>ZnSnO₃</td>
<td></td>
</tr>
<tr>
<td>without</td>
<td>1.20</td>
</tr>
<tr>
<td>0.1 wt%</td>
<td>3.01</td>
</tr>
<tr>
<td>CaSnO₃</td>
<td></td>
</tr>
<tr>
<td>without</td>
<td>1.67</td>
</tr>
<tr>
<td>0.1 wt%</td>
<td>2.00</td>
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</table>
systems, an initial shear stress was required for the suspensions to begin to flow (from $\varphi \geq 13$ vol.%). This was the most pronounced for the BaSnO$_3$ suspension with $\varphi = 15$ vol.%, which was reflected in the initial viscosity (Fig. 6a) and may have been due to the presence of particle agglomerates observed in the micrographs in Fig. 3 and calculated in Table 1. The ZnSnO$_3$ and CaSnO$_3$ suspensions have initial viscosities lower than that of BaSnO$_3$, with values below 20 Pa·s (Fig. 6b,c). Meanwhile, upon increasing and decreasing the shear rate, hysteresis was observed in the flow curves, primarily for the highest load of solids; this could be caused by the increase in solids content since the movement of the slip layer was difficult and, therefore, particles interactions cause disturbances [53].

To determine the effect of shear rate on the flow behaviour of the suspensions (Fig. 6), it was necessary to know the influence of their volumetric solids fractions to adequately characterize their rheological behaviour. However, this is not easy to determine, particularly for suspensions in which the solids fraction is relatively high. The effect of the dynamic interactions between particles was modelled with the maximum packing fraction $\varphi_m$ [63–65]. A value close to the maximum particle packing fraction can be determined by plotting the viscosity of the suspension as a function of the volumetric fraction of solids.

As shown in Fig. 7, for suspensions with a shear rate of 100 s$^{-1}$, a value commonly used in casting techniques, small increases in the solids content ($\varphi$) led to significant increases in viscosity. A tangent line to the curve of the relative viscosity increase was drawn in the region where $\eta_r \to \infty$ (Fig. 7), such that this line, intercepting the baseline (i.e. the minimum viscosity), allowed us to determine the values of the maximum optimal load ($\varphi_{op}$) of solids. The volumes of solids were 13.8%, 19.4% and 21.5% for the suspensions containing BaSnO$_3$ (Fig. 7a), ZnSnO$_3$ (Fig. 7b) and CaSnO$_3$ (Fig. 7c) powders, respectively. The $\varphi_{op}$ values for each of the perovskites corresponded to the highest volumetric fraction of solids in the suspensions required to favour a reduction in the constriction of the ceramic body during drying and sintering processes.

To verify the validity of the results obtained from Fig. 7, the model proposed by Liu [66] was used. This model allows us to predict the maximum particle packing den-
sity ($\varphi_{\text{max}}$) by providing a simple method to obtain $\varphi_{\text{max}}$ directly from experimentally obtained viscosity data for the corresponding colloidal suspension. The model that has been used in the rheological studies of other metal oxide powders, such as ZnO and In$_2$O$_3$-SnO$_2$ [67,68], resulted in $\varphi_{\text{max}}$ values that agreed well with the fitted results. The curve for the function $1 - \eta_r^{-1/2}$ versus $\varphi$ shows that when extrapolating the curve-fitted line in 

$\left(1 - \eta_r^{-1/2}\right) \rightarrow 1$, the $\varphi_{\text{max}}$ values for the MSnO$_3$ system ($M = \text{Ba, Zn, Ca}$) could be obtained; these were 15.8, 24.3 and 28.0 vol.% respectively (Fig. 8a-c). The values determined using the Liu model (Fig. 8) were comparable to the $\varphi_{\text{op}}$ values obtained experimentally in this work (Fig. 7). The differences between the $\varphi_{\text{op}}$ and $\varphi_{\text{max}}$ values could be explained by the wide ranges in particle size distribution, forms and the chemistries of the synthesized stannates.

**Effect of ammonium polyacrylate (APA)**

Figure 9 shows the flow curves for the suspensions that contained the optimal values of solid contents ($\varphi_{\text{op}}$) and to which the dispersant APA was added. In these curves (Fig. 9), greater pseudoplastic and thixotropic behaviour was observed than in the curves for the suspensions that did not contain dispersing agent. With the addition of 0.1 wt.% APA, $\tau$ and $\eta$ decreased appreciably for the BaSnO$_3$ and ZnSnO$_3$ systems (Fig. 9a,b), an effect associated with weaker interactions between the particles due to the steric repulsion caused by the dispersant. Therefore, the stabilization of these stannate suspensions would be increased by amounts of APA greater than 0.1 wt.%.

The viscosity results (Figs. 7 and 9) were consistent with the results of the sedimentation tests (Table 2). In all colloidal suspensions, the stability times (sedimenta-
Figure 9. Flow curves for different APA contents (mass fraction) in BaSnO$_3$ (a), ZnSnO$_3$ (b) and CaSnO$_3$ (c) slips

Figure 10. Relative viscosity ($\eta_r$) as a function of the APA concentration for the optimal solid content ($\varphi_{op}$): BaSnO$_3$ (a), ZnSnO$_3$ (b) and CaSnO$_3$ (c)
nanoparticles in the aqueous medium, thereby significantly reducing the viscosity of the suspension. As shown in Figs. 10a,b, the viscosities of the suspensions were reduced by approximately 88 and 86% upon adding between 0.5 and 0.3 wt.% of the dispersing agent to slurries with the optimal solids contents ($\varphi_{op}$) of BaSnO$_3$ and ZnSnO$_3$, respectively.

3.3. Sintering of the green bodies

The BaSnO$_3$ and ZnSnO$_3$ suspensions stabilized electrostatically with APA were used to consolidate green bodies by slip casting using plaster moulds. In the same way, bodies were also formed for the CaSnO$_3$ system but without the addition of the dispersant, considering that the sedimentation time for this sample was adequate for this process. Figure 11 shows the surfaces of the green bodies formed with the nanoparticles observed in Fig. 3. The bodies presented different porous microstructures and small fractions of agglomerates. This demonstrates that the dispersion process was not entirely effective in eliminating the agglomerates present in the starting material, e.g. in the ZnSnO$_3$ samples where flakes composed of nanoparticles were formed (Figs. 11b,e).

Figure 12 shows the relative densities and the apparent porosity of the stannate ceramic bodies subjected to heat treatments at temperatures between 1000 and 1500°C. The densification rates for the bodies were different and depended on the chemical nature of the stannate and its green density. The three systems achieved densities higher than 75% at 1000°C. The ZnSnO$_3$ system obtained an appreciable increase in its relative density to ~90%TD after sintering at 1300°C and the densities of the BaSnO$_3$ and CaSnO$_3$ samples were higher than 90%TD after sintering at 1400°C. The apparent porosity, an indirect measure of the estimation of the degree of porosity of the sintered bodies, decreased with increasing temperature at 1300°C; the AP% presented values around 11% for all three systems. These results, as well as the degree of densification of the sintered bodies, allowed the selection of the appropriate temperature to thermally treat the shaped bodies that were used as gas sensitive materials. The selection criterion of this temperature was, on one hand, to have densification values that would allow manual adaptation of the ceramic body to the electrode system shown in Fig. 1b and, on the other hand, to obtain an apparent porosity with similar values between samples that favours the interaction between the sensor surface and the test gas. Therefore, the selected sintering temperature was 1300°C for all three systems. At this temperature, the desired degrees of densification and apparent porosity between 9–11% were obtained.

The shrinkage behaviours of the cylinders formed by slip casting different stannates were determined by means of dilatometry tests (Fig. 13a). The sample containing CaSnO$_3$ showed a small shrinkage of 0.4% at
1074 °C. Its densification began at ~1420 °C and shrinkage of 4.85% occurred at 1500 °C, but the system did not reach its stability point. The ZnSnO$_3$ sample began to densify at 1200 °C, a lower temperature than that of the CaSnO$_3$ body, and also had higher shrinkage at 1500 °C (10.7%). The contour of the shrinkage curve for this body (Fig. 13a) clearly showed that the sintering was close to the point of stabilization, reiterating what was observed in the densification curve (Fig. 12). For the BaSnO$_3$ sample, densification began at 1000 °C and exhibited shrinkage of 17.5% at 1500 °C, which was the highest temperature between these three systems. The shrinkage curve for this body showed three regions (Fig. 13a). There was a region below ~950 °C in which no shrinkage of the cylinder was observed, and this was followed by another zone between ~950 and ~1130 °C in which a first important shrinkage of the solid with a smooth shrinkage rate was found (Fig. 13b). Finally, in the third region (between ~1130 and 1500 °C), the greatest shrinkage occurred with a high rate. A similar behaviour was exhibited by the body formed with powder of the CaSnO$_3$ system, but it occurred at higher temperatures. The ZnSnO$_3$ body meanwhile presented shrinkage behaviour different from the others. It only

Figure 14. SEM micrographs of the samples sintered at 1000, 1300 and 1500 °C: a) BaSnO$_3$, b) ZnSnO$_3$, and c) CaSnO$_3$
showed a large shrinkage (Fig. 13a) that occurred between \( \sim 1200 ^\circ C \) with a high shrinkage rate (Fig. 13b).

The differences in the shrinkage curves observed in Fig. 13 for different stannate samples formed by slip casting were evident in the microstructures of the sintered bodies at temperatures between 1300 and 1500 °C. Figure 14 shows micrographs of freshly fractured surfaces of bodies formed with BaSnO\(_3\), ZnSnO\(_3\) and CaSnO\(_3\) powders sintered at 1000, 1300 and 1500 °C. The sintering temperatures were defined by taking as a reference the minimum of the shrinkage rate curves, \(-\frac{d(dL/dL_0)}{dt}\) (Fig. 13b). Porosity was observed in all three samples, especially in the ZnSnO\(_3\) body (Fig. 14b), which has the largest grain size (\( < 1 \mu m \)). The highest densification and the smallest grain size (\( < 500 \text{ nm} \)) were found for the ceramics formed with the BaSnO\(_3\) powders (Fig. 14a), results that were consistent with those obtained from the curves for densification (Fig. 12) and shrinkage (Fig. 13). The CaSnO\(_3\) bodies (Fig. 14c) showed a heterogeneous microstructure and melting of the sintered grains at 1300 °C was observed in certain regions of the samples.

Considering the microstructures of the MSnO\(_3\) bodies (\( M = \text{Ba, Zn, Ca} \)) as well as their chemical compositions, it is expected that their functionalities, which depend on technological interests, will be different. Moreover, the results obtained in this work can be used as a reference when it is necessary to form a sintered body of one of these stannates for a specific application, such as for a dielectric, anode for lithium batteries or a gas sensor, a functionality that was tested in this work.

### 3.4. Preliminary results of the gas sensing

The selectivity of the developed gas sensors, which is the ability of a sensor to distinguish different kinds of gases, was evaluated. For this test, 270 °C was selected as the operating temperature, a value close to that reported by other studies [31,70]. The response of the sensors based on the MSnO\(_3\) porous bodies (\( M = \text{Ba, Zn, Ca} \)) to the detection of several volatile organic compounds, known as VOCs (acetone, ethanol and toluene), as well as other gases (CO, H\(_2\) and NO\(_2\)), at a fixed concentration of 80 ppm can be seen in Fig. 15a. It is appreciated that the ZnSnO\(_3\) sensor shows the highest responses to acetone, ethanol and hydrogen. Specifically, this sensor presented the highest selectivity for acetone, with a response of 37. The BaSnO\(_3\) sensors in the presence of ethanol vapours and CaSnO\(_3\) in toluene vapours reached responses of 14 and 11, respectively, higher responses than those reported in recent literature [31,71].

Figures 15b-d show dynamic response/recovery curves of the MSnO\(_3\) sensors (\( M = \text{Ba, Ca, Zn} \)) at the operating temperature (270 °C) selected in this work. Initially, the responses were recorded by repeatedly exposing and purging 80 ppm of the test gases (ethanol, toluene or acetone) for three consecutive cycles. Then, the concentrations were varied from 60 to 5 ppm and again to 80 ppm. Reversible cycles were observed, in
which the sensor materials maintained their base electrical resistance (in air). The BaSnO$_3$ and ZnSnO$_3$ sensors exhibited particularly good sensitivities at concentrations lower than 80 ppm of the ethanol and acetone gases, respectively (Figs. 15b,c). The CaSnO$_3$ sensor presented good sensitivity of toluene gas at concentrations from 80 to 20 ppm, while at low concentrations, from 10 ppm, the sensor losses sensitivity, indicating detection limits close to this concentration (Fig. 15d). Furthermore, this compound showed a good sensing response to CO and NO$_2$ (Fig. 15a).

Taking into account the structural advantages of the formed bodies, the porous surfaces of the sensor materials had a large number of adsorption sites for gas molecules and were favourable for the diffusion of these molecules. Therefore, it is expected that the characteristics of the sensors, including sensitivity, may be one of the important reasons that lead to considering colloidal processing as a low-cost simplified shaping method that does not require complex instrumentation, such as screen printers and vacuum chambers [72], thus allowing study of the potential application of advanced materials in the field of gas sensing. Given the interesting and promising results shown in Fig. 15, a more rigorous and systematic evaluation of the electrical behaviour against the presence of the indicated gases of these ceramic bodies, formed with the submicronic MSnO$_3$ powders (M = Ba, Zn, Ca), is needed to determine their potential use as a sensor materials in gas sensor devices.

IV. Conclusions

MSnO$_3$ nanoparticles (M = Ba, Zn, Ca), obtained via polymer complex route, were used to form stable suspensions with the help of suitable amounts of ammonium polyacrylate (APA) as dispersing agent. Electrostatically stable suspensions with solid concentrations of 13.7 (BaSnO$_3$), 19.2 (ZnSnO$_3$) and 21.3 vol.% (CaSnO$_3$) were obtained. Optimal amounts of dispersing agent (0.5 and 0.3 wt.%) reduced the viscosities of the BaSnO$_3$ and ZnSnO$_3$ samples by ~88 and ~86%, respectively. For the CaSnO$_3$ suspension, the addition of APA had little effect on their rheological behaviour. Additionally, sinterability of the green bodies formed by slip casting was also investigated. It was shown that maximum shrinkage appeared at $T_m \approx 1300^\circ$C for the ZnSnO$_3$ system, but at much higher temperature (~1450°C) for the CaSnO$_3$ and BaSnO$_3$ systems and did not reach shrinkage stability at 1500°C.

Colloidal processing allowed the formation of gas sensitive materials, at low cost and in a reproducible way. The preliminary gas sensing test for the BaSnO$_3$, ZnSnO$_3$ and CaSnO$_3$ samples showed good selectivity and high responses to 80 ppm of ethanol, acetone and toluene at operating temperature of 270°C. Based on these results, it can be concluded that the MSnO$_3$ sensors (M = Ba, Ca, Zn) present good selectivity to the target gases, suggesting potential applications in the detection of these vapours. Specifically, they could be used to evaluate environmental pollution (mainly VOCs) and in medical applications for the early diagnosis of diseases as human breath analysers.

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