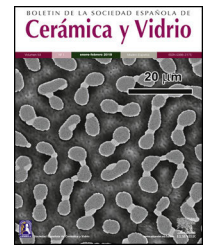




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Study of lithium carbonate as sintering aid for tin oxide densification through experimental designs: Main variables and microstructure changes

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ABSTRACT

Tin oxide is one of the most extensively studied semiconductor materials due to its broad field of applications. On the one hand, its high conductivity and its corrosion resistance are the most remarkable properties. Therefore, one of the most developed uses in the recent decades has been as ceramic electrode for electrooxidation process. On the other hand, its poor sinterability hinders a broader use. As a result, the use of advanced techniques or sintering aids for obtaining low-porosity specimens is necessary. So far, many additives have been studied, CaCO_3 , Co_3O_4 , Nb_2O_5 or MnO_2 , among others. In the present work, the sintering behaviour of SnO_2 -based powder, containing Li_2CO_3 as a sintering aid, which generates a liquid phase, has been analysed, since it is one of the additives that has been studied to a lesser extent. The effect of the amount of sintering aid just like the thermal treatment parameters (maximum temperature, heating rate and soaking time) on volumetric contraction's evolution has been studied through a factorial experiment designs 2^n . The results show that an amount of lithium carbonate greater than 1 mol.% is unfavourable to densification. With regards to the thermal cycle's parameters, it is advisable to have thermal treatments at high temperatures (1300 °C) with moderate soaking times (1 h), as maximum temperatures have the biggest influence on the densification followed by soaking time while the heating rate has a lesser influence. Under these conditions, a microstructure of closed and rounded pores is obtained, in which a residual phase is enclosed, but the small proportion of which prevents its characterisation.

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Estudio del carbonato de litio como ayuda de sinterización para óxido de estaño mediante diseños de experimentos: variables principales y cambios microestructurales

R E S U M E N

Palabras clave:

Óxidos cerámicos
Sinterización
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El óxido de estaño es uno de los materiales más estudiados, dado su extenso campo de aplicación. De entre sus propiedades, cabe destacar su alta conductividad eléctrica y su resistencia a la corrosión, de ahí que entre sus aplicaciones se encuentre la de electrodo cerámico. Sin embargo, su baja capacidad de densificación dificulta su uso. Como consecuencia, se requieren técnicas avanzadas o aditivos de sinterización que faciliten la obtención de piezas con baja porosidad. Hasta el momento han sido muchos los aditivos estudiados, CaCO_3 , Co_3O_4 , Nb_2O_5 o MnO_2 , entre otros. En este trabajo se estudia el proceso de sinterización de piezas de SnO_2 a las que se ha incorporado Li_2CO_3 como aditivo de sinterización, el cual genera una fase líquida, por ser uno de los aditivos en cuyo estudio se ha profundizado en menor medida. A través de diseños factoriales de experimentos 2^n , se han determinado los efectos de los diferentes parámetros del ciclo de cocción (temperatura máxima, velocidad de calentamiento y tiempo de permanencia), así como la cantidad de aditivo de sinterización, sobre la evolución de la contracción volumétrica. Los resultados muestran que la incorporación del carbonato de litio, en porcentajes superiores al 1% molar, no es favorable para la densificación. Respecto a los parámetros de cocción, resultan recomendables tratamientos térmicos a elevada temperatura (1.300°C) con tiempos de permanencia moderados (1 hora), mientras que la velocidad de calentamiento ejerce una menor influencia. En estas condiciones se obtiene una microestructura de poros cerrados y redondeados, en la que queda encerrada una fase residual cuya reducida proporción impide su caracterización.

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Introduction

Tin oxide is a material whose remarkable physicochemical properties, including its high conductivity (n-type semiconductor) and resistance to corrosion, allow it to be used in a wide range of sectors. Traditionally, it has been used in the ceramic industry as a raw material to produce pigments [1] and as opacifier in glazes [2]. But nowadays its use has been extended to the field of electronic and chemical industries, becoming a widely used material in the production of gas sensors [3,4] or components that require high resistance to chemical corrosion [5]. In the latter case, the production of electrodes for the processing of aluminium by electrolysis is noteworthy [6,7].

However, tin oxide is also known to sinter without densifying [8], which makes it difficult to use and requires specific sintering techniques to obtain parts with low porosity, such as hot isostatic pressing [9] or activated sintering [10,11]. Another option is the addition of certain metal oxides that act as sintering promoters to increase densification. In the latter case, the usual mechanism consists of the formation of a eutectic liquid at a low temperature between SnO_2 and the sintering additive, thus favouring a sintering in the presence of liquid phase. Several metal oxides have been studied in recent years for this purpose, including ZnO , CaCO_3 , Co_3O_4 , Nb_2O_5 or MnO_2 , among others [12–17].

In a previous work, the sintering process of SnO_2 electrodes to which Bi_2O_3 had been incorporated as a sintering additive was analysed [18]. In the present work, we study the influence of Li_2CO_3 as sintering aid over the sintering process of SnO_2 with the aim to compare the results with the obtained ones in the aforementioned publication, since lithium oxide is an abundant material, not very expensive, with a high electrochemical potential, which does not contribute colour when introduced into a composition and which, despite having been mentioned, has not received as much attention as those mentioned above.

Respect to the sintering process, Li_2O has been proposed as a dopant for SnO_2 [19], concretely for obtaining transparent conducting films by spray pyrolysis [20]. In addition, Li_2O can also be proposed as sintering additive for SnO_2 , under the hypothesis that it generates a liquid phase during the heat treatment. However, this cannot be confirmed from a thermodynamic point of view as the phase diagram of the system $\text{Li}_2\text{O}-\text{SnO}_2$ has not been published (to our knowledge, the only diagram containing both oxides corresponds to $\text{Li}_2\text{O}-\text{SnO}_2-\text{SiO}_2$ system, but it does not cover the SnO_2 -rich zone [21]). As additional data that support the hypothesis, the crystal structures of two mixed oxides in the $\text{SnO}_2-\text{Li}_2\text{O}$ system, Li_8SnO_6 and Li_2SnO_3 have been described, compounds which have been synthesised by solid state reaction at around 950°C and 1000°C respectively [22,23], but their melting temperature has not been reported. Additionally, one

study indicates that Li_2SnO_3 can be sintered at around 800°C [24]. With these data and considering the melting point of pure Li_2O (1473°C) [25], it is likely that there is an eutectic in the Li_2O – Li_8SnO_6 system capable of generating a liquid phase at moderate temperatures which helps to densify SnO_2 . In addition, their high melting point could reduce the losses of additive along sintering that are characteristic of other sintering aids as Bi_2O_3 [18].

Since lithium oxide reacts violently with water, lithium carbonate was used as an additive in this work. This salt has a melting point of 732°C and decomposes completely at around 1300°C . However, Li_2CO_3 decomposition is a complex multi-stage process, which can start at temperatures of the same order as melting point, depending on the composition of the surrounding atmosphere [26]. Thus, the liquid phase generated by the Li_2CO_3 melt, although its exact nature depends on the temperature and the surrounding atmosphere, could initiate densification at temperatures lower than those required for Li_2O to form a eutectic, especially if sintering is performed at moderate temperatures. If sintering is performed at temperatures close to the decomposition temperature of Li_2CO_3 , a eutectic liquid could already be formed, corresponding to the Li_2O – Li_8SnO_6 system, which in this case would also facilitate densification. In this sense, the use of lithium oxide as a sintering aid has been described for various materials such as garnets [27,28], samarium-doped ceria [29], or yttrium-doped ceria [30], as well as lithium carbonate for the sintering of calcium carbonate [31]. In the case of doped ceria, which would be the closest system to SnO_2 , the results suggest that the key role is played by Li_2O from the decomposition of carbonate, but there is no agreement about the mechanism of action.

In this work, the behaviour of lithium carbonate as a sintering additive for tin oxide has been analysed, together with the effects of heat treatment parameters, by means of 2^n factorial designs of experiments [32]. In a first design, the effects of Li_2CO_3 ratio and heating rate on the sintering evolution during the heating stage have been studied. In a second design, in addition to the aforementioned variables, the effects of maximum temperature and soaking time have been analysed. From the results obtained, it has been possible to define the variables with the greatest effect on the sintering of SnO_2 in the presence of Li_2CO_3 .

Experimental procedure

The raw materials used were SnO_2 , (Quimiamel S.A., purity 99.85%, Spain) and Li_2CO_3 (Panreac S.A., purity 98%, Spain). Polyvinyl alcohol (PVA, Mowiol 4-88, Clariant Iberica S.A., Spain) was used as binder for the green specimens. Two compositions A and B were designed, with $\text{Li}_2\text{CO}_3/\text{SnO}_2$ molar ratios of 1/99 and 2/98 respectively (to compare with a previous work, above mentioned, where the molar ratios for the composition of $\text{Bi}_2\text{O}_3/\text{SnO}_2$ were the same [18]). The PVA was added in a proportion of 0.8 g per 100 g of oxides. The raw materials were weighted and then wet homogenised in a planetary mill (Pulverisette 5, Fritsch GmbH, Germany) at 230 rpm for one hour using water as a fluid. The obtained suspension was dried in a laboratory oven at 110°C for 24 h, after which the dried material was disaggregated in an agate mortar until it passed

Table 1 – Factors and levels of the conducted factorial designs of experiments.

Level	–1	+1
Li_2CO_3 (mol.%)	1	2
Heating rate ($^\circ\text{C min}^{-1}$)	5	15
Maximum temperature ($^\circ\text{C}$)	1100	1300
Soaking time (h)	1	4

through a $600\ \mu\text{m}$ mesh. The powder was then moistened to a water content of 5 wt.% (dry basis). A fraction of each mixture was used for experiments on a heating microscope (Misura 3, Expert Systems Solutions Srl, Italy). The rest of the mixture was shaped as cylinders (20 mm in diameter and about 5 mm thick) in a laboratory uniaxial press (Robima, Spain), at a pressure of $450\ \text{kg cm}^{-2}$. After drying in a laboratory oven, the specimens were subjected to the selected heat treatments for sintering in an electric laboratory furnace (RHF1600, Carbolite Furnaces Ltd., UK).

The experiments with the heating microscope constituted a 2^2 design in which the factors evaluated were the Li_2CO_3 proportion and the heating rate (keeping the maximum temperature of the test at 1300°C and taking images every 5°C). The sintering experiments in the furnace constituted a 2^4 design in which the factors evaluated, in addition to those already mentioned, were the maximum temperature and the soaking time (they correspond to the first three rows of Table 1 and to the whole table respectively).

In this work, the use of heating microscopy is proposed to deduce the behaviour of the samples during heating, since this equipment makes it possible to evaluate the shrinkage with respect to the initial section of the specimen by means of image analysis (hereinafter sectional shrinkage, S_s), which makes it possible to measure the temperatures when shrinkage starts (T_{ss} , corresponding to a 1% shrinkage) and the shrinkage ends (T_{se} , when the specimen stops shrinking). In addition, it has been used to measure the shrinkage corresponding to the point at which the maximum temperature of the sintering experiments in the furnace was reached. This data allowed to estimate the value of the volumetric shrinkage (S_{Ve}) to which these values corresponded using the model described in the annex, and thus to compare them with the volumetric shrinkage experienced by the sintered specimens. To obtain this parameter, the bulk density of both dry and sintered specimens was determined using the mercury immersion method (based on Archimedes' principle). From these values, the volumetric shrinkage after each thermal cycle (S_V) was calculated. Additionally, these values allow the calculation of relative density and densification (the change in bulk density due to sintering divided by the change required to obtain a porosity-free material).

The crystalline phases present in the sintered specimens were identified by X-ray diffraction to determine whether any mixed oxide of the SnO_2 – Li_2O system had formed. For this purpose, the specimens were reduced to powder and analysed with a Theta-Theta D8 Advance (Bruker, Germany), with CuK radiation ($\lambda = 1.54183\ \text{\AA}$), operating at 45 kV and 40 mA, using a VANTEC-1 detector in a 2θ range between 5° and 90° (step length of 0.015° at 1.2 s/step). Scanning electron microscopy (FEG-SEM QUANTA200F, FEI Co., USA) was also used to anal-

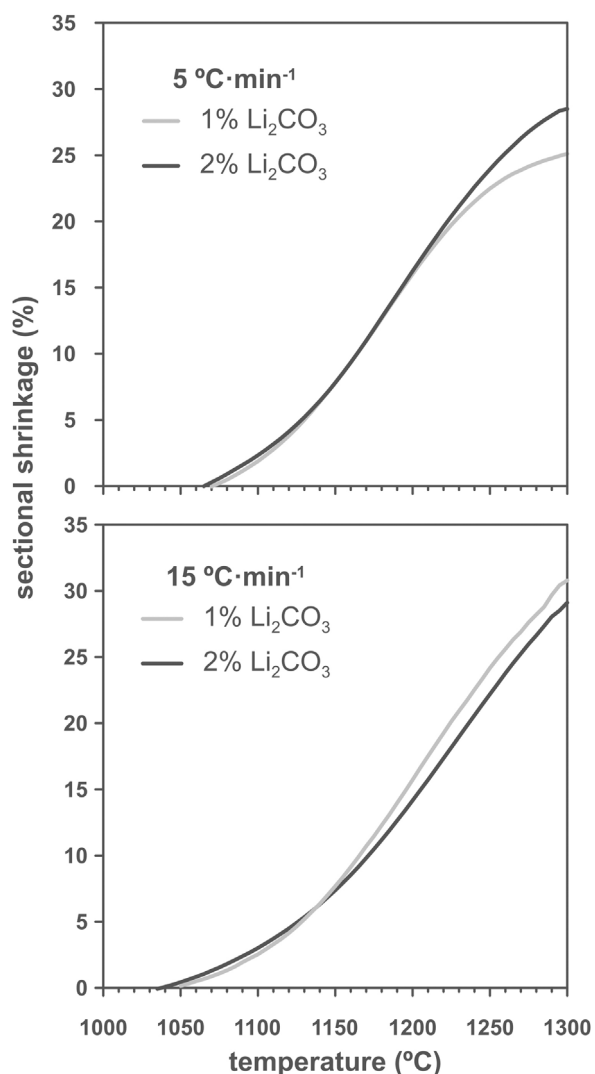


Fig. 1 – Sectional shrinkage–temperature curves obtained for the two compositions with two different heating rates.

use the microstructure in polished sections of the sintered samples, without additional treatments.

Results and discussion

The shrinkage–temperature curves obtained in the heating microscope (Fig. 1), as well as the shrinkage initiation temperatures (Fig. 2) allowed estimating the effects of the Li₂CO₃ ratio and the heating rate. Firstly, it was found that the chosen additive allowed SnO₂ to start sintering during the heating section of the thermal cycle, as under the same conditions a pure tin oxide specimen did not show any shrinkage (the curve of pure SnO₂ is not included in Fig. 1 because at 1300 °C it has not yet started to shrink). Secondly, the heating rate slightly affects the position and shape of the curves. By increasing the heating rate from 5 to 15 °C min⁻¹ the shrinkage onset temperature decreases by about 20 °C and the initial slope of the curve decreases. Thirdly, all four curves show an increase in slope around 1150 °C but the final evolution is different. Heating at

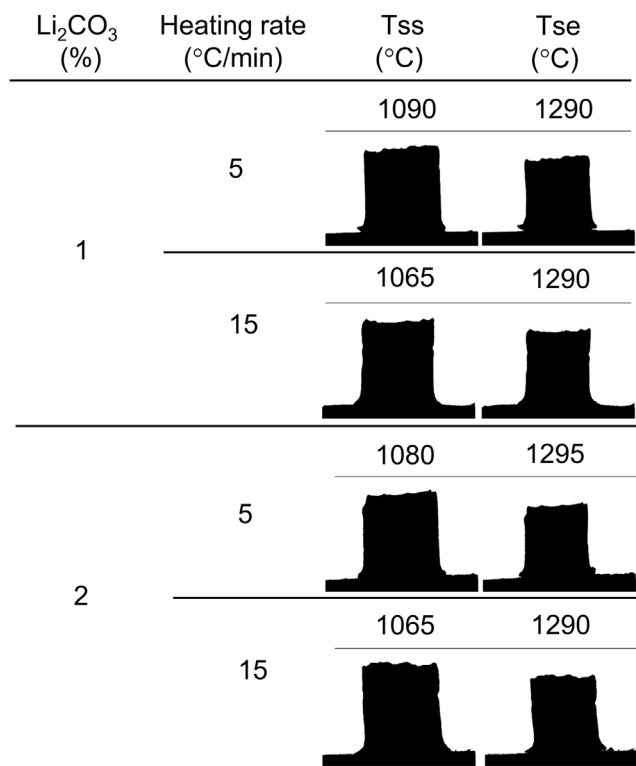


Fig. 2 – Images obtained on the heating microscope for the two compositions with two different heating rates as well as the shrinkage starts/ends temperatures registered.

5 °C min⁻¹ shows a progressive reduction in the slope from about 1250 °C, while heating at 15 °C min⁻¹ the slope remains stable almost until 1300 °C. In no case the end of sintering was reached in a definite way, which suggests that the samples would continue to shrink as the temperature increases (or maintain the final temperature of the test for a certain time). No clear effect of the Li₂CO₃ proportion was seen on the curves, except in the case of the 1 mol.% at the lowest heating rate and in the higher temperature range, where a further decrease in the slope of the curve is seen, leading to a lower final shrinkage. In contrast, for the higher heating rate, the differences between the two curves are much smaller. Consequently, it follows that there is an important interaction between the lithium carbonate proportion and the heating rate during this part of the heat treatment.

As increasing the heating rate usually delays the onset of sintering in the heating microscopy test, the detected anomaly can be assigned to the melting and decomposition process of Li₂CO₃ and the subsequent interaction of the generated liquid with the SnO₂ particles, which could generate the eutectic liquid of the Li₂O–Li₂SnO₃ system as a secondary effect. The appearance of a liquid phase causes a rearrangement of the particles under capillary forces if no rigid bridges have previously formed in the structure [33]. However, the significant difference between the melting temperature of lithium carbonate (732 °C) and the onset of shrinkage (from 1.065 °C) seems to indicate that after Li₂CO₃ melting, the liquid phase is either too viscous or does not reach enough proportion to cause particle rearrangement, and the temperature needs to

Table 2 – Comparison between the theoretical loss on ignition and the average values obtained with the heat treatments at each maximum temperature.

Loss on ignition (%)	Li ₂ CO ₃ (mol.%)	
	1	2
Theoretical	1.08	1.38
T _{max} = 1100 °C	0.93	1.18
T _{max} = 1300 °C	1.12	1.44

be raised to initiate rearrangement. Considering that a heating microscope test of pure Li₂CO₃ confirmed the melting point of the bibliography and showed that the liquid has a low viscosity, the second option was the case. This would imply a further advance in the decomposition of the carbonate, and therefore the presence of a higher proportion of Li₂O, which would be the real sintering-promoting agent, if the mechanism is like the case of doped ceria [29,30]. For the lower heating rate, more time would be available for interaction between Li₂O and SnO₂, which could mean a lower proportion of effective liquid phase involved in sintering, thus delaying shrinkage. Conversely, with the higher heating rate, the time available for Li₂O–SnO₂ interaction would be shorter, so there could be a higher proportion of effective liquid phase and therefore shrinkage could be initiated at slightly lower temperatures. The lack of a defined effect of the Li₂CO₃ ratio on T_{ss} would be because this temperature is defined for a fixed shrinkage of 1%, which would depend more on the viscosity of the liquid phase, which in turn depends more on the temperature, than on its ratio.

The proposed interpretation is supported by the average calcination loss data of the sintered specimens at each temperature, compared to the theoretical values obtained by assuming complete decomposition of the lithium carbonate and combustion of the PVA (Table 2). The specimens sintered at 1100 °C do not reach the theoretical loss, suggesting that the lithium carbonate has not completely decomposed at that temperature, and if it has not done so after treatments of one or four hours, it can be considered that at the end of the heating ramp the proportion of undecomposed lithium carbonate will be even higher. On the contrary, after treatments at 1300 °C the losses are of the same order or slightly higher than the theoretical ones, which points to the complete decomposition of the lithium carbonate. The fact that the losses are slightly higher than the theoretical ones may be due to a slight volatilisation of SnO₂, which is a consequence of its sintering’s mechanism in absence of additives, by surface diffusion at moderate temperatures or transfer of matter through the gas phase at high temperatures [34]. However, a partial volatilisation of Li₂O at 1300 °C cannot be excluded.

The volumetric shrinkage data obtained with the eight thermal treatments showed a very wide range of values, between 22% and 46% approximately (Fig. 3), which corresponds to densifications in the range of 29% to 86%. In a first approximation, there are two main groups of experiments, differentiated by the maximum temperature reached during the firing cycle. A dominant effect of this variable in the sintering process is thus revealed, with the highest S_V values being obtained in the experiments carried out at a maximum

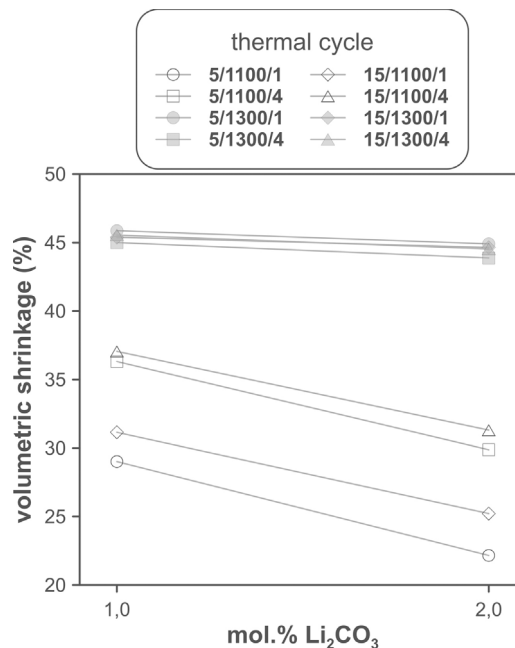


Fig. 3 – Variation of volumetric shrinkage with the percentage of lithium carbonate for each of the sintering experiments performed (legend: heating rate/maximum temperature/soaking time).

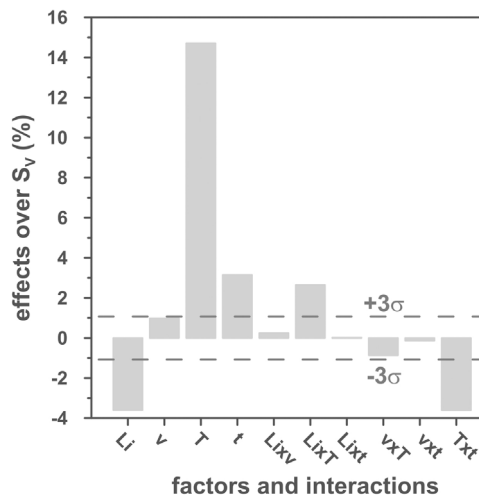


Fig. 4 – Effect of the analysed variables and their interactions on the volumetric shrinkage of SnO₂ specimens.

temperature of 1300 °C. To evaluate the influence of the rest of the parameters investigated, it is necessary, starting from these data, to calculate the effect of each one of them, as well as the value of their interactions as described by Box et al. [32]. Fig. 4 shows the main effects and their interactions, highlighting those that an ANOVA analysis has identified as significant. Of the four parameters studied, only the heating rate is not significant. In addition, among the second-order interactions, the Li₂CO₃ proportion with temperature (Li × T) and soaking time with temperature (t × T) are significant, while none of the higher-order interactions are significant.

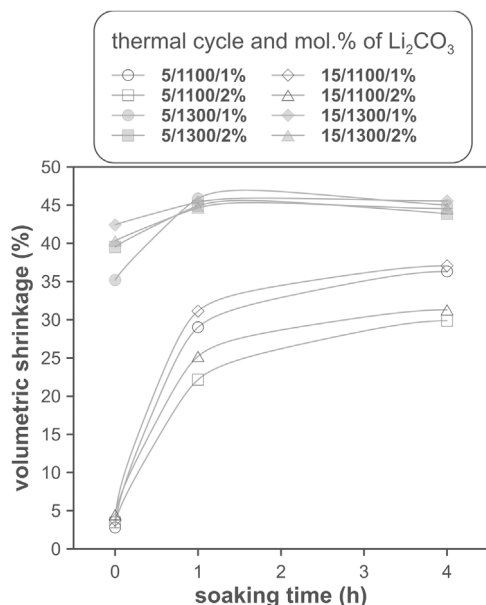


Fig. 5 – Evolution of volumetric shrinkage as a function of soaking time at T_{max} (legend: heating rate/maximum temperature/mol.% of Li_2CO_3).

The statistical calculation suggests that the maximum temperature is the parameter with the greatest influence on the sintering process of tin oxide in the presence of lithium carbonate. Additionally, the proportion of Li_2CO_3 and the soaking time, and their interactions with the temperature would be the rest of the effects to be considered to define sintering conditions. In other words, considering the values of the effects, the best combination of parameters would be to use the high level of temperature and the lower level of Li_2CO_3 , while the level of time is almost indifferent, since the effect of the $T \times t$ interaction practically compensates the main effect of time. This result indicates, on the one hand, that the addition of Li_2CO_3 is limited to around 1 mol.%, and that, on the other hand, the residence time can be shortened considerably by operating at 1300 °C, but not at 1100 °C.

The effect of time is much more evident when comparing the volumetric shrinkage achieved for each set of conditions as a function of dwell time (having considered the shrinkage at the end of the heating ramp as the S_{Ve} from heating microscope test, Fig. 5). The data indicate that when 1300 °C is reached, the shrinkage of the specimens is very close to the maximum shrinkage. This maximum shrinkage seems to be reached within one hour, and if soaking time is prolonged for much longer, a certain tendency towards expansion is observed, which would be an indication of over-sintering. On the other hand, increasing the heating rate influences the shrinkage reached at the end of the ramp when a Li_2CO_3 ratio of 1 mol.% is used, but not when the ratio is 2 mol.%. In the case of the specimens sintered at 1100 °C, the differences in the shrinkage reached at the end of the heating stage are not relevant, but there is a clear effect of soaking time. Under these conditions, it is clearly favourable to use the lower Li_2CO_3 ratio and the higher heating rate, although it is obviously not possible to reach such high values of volumetric shrinkage as those

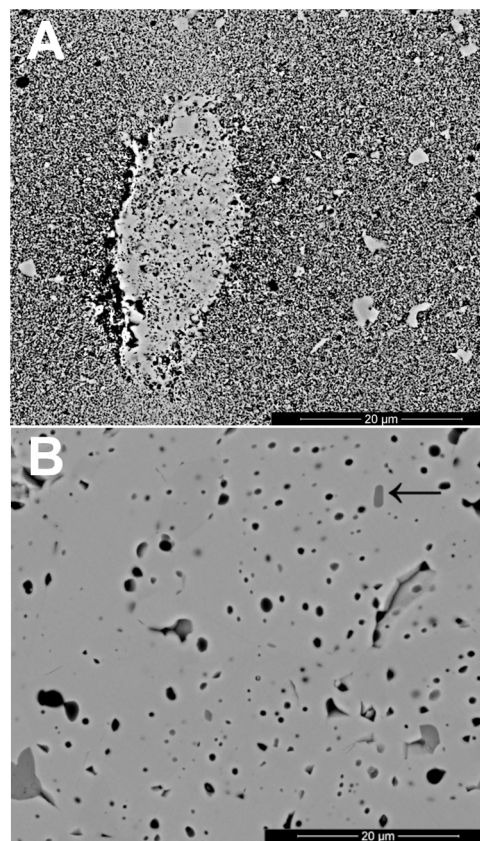


Fig. 6 – Photograph of a section of a specimen (A) composition A sintered for 1 h at 1100 °C (heating at 5 °C min⁻¹); and (B) composition B sintered for 4 h at 1300 °C (heating at 5 °C min⁻¹). One of the possible areas of lithium accumulation is highlighted.

obtained at the highest temperature, in the range of dwell times explored. These results suggest that the mechanisms involved in densification are highly temperature dependent.

The changes in volumetric shrinkage are clearly reflected in the microstructure of the specimens. The samples sintered at 1100 °C show a microstructure in which the submicronic particles of the SnO_2 used as raw material are still visible (Fig. 6A), a sign that the initial stage of sintering has not been overcome. These specimens show the presence of voids that could be assigned to lithium carbonate particles that have melted, decomposed, and interacted with the surrounding SnO_2 particles, generating a more densified zone. The darker grey level of the material surrounding the pore is consistent with the lower atomic weight of Li, but this could not be confirmed because this element cannot be detected by EDX. By contrast, the specimens sintered at 1300 °C show a microstructure with grains much larger than the original SnO_2 particles and rounded closed pores (Fig. 6B), characteristic of sintering's final stage. Darker areas can be detected in these specimens, which can be assigned to high Li concentrations, indicating that during sintering there was a liquid phase which facilitated densification, and which has remained embedded in the microstructure, possibly in a glassy form, since no crystalline phase containing lithium has been detected by XRD, even in

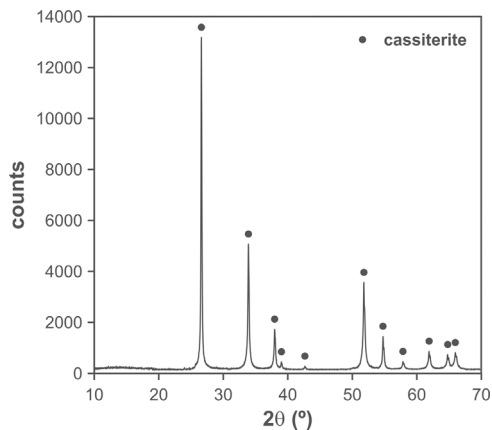


Fig. 7 – Diffractogram a micronized specimen of composition B sintered for 4 h at 1300 °C with heating at 5 °C min⁻¹ (PDF file 04-008-8135).

the composition richest in Li₂CO₃ sintered under the most energetic conditions (Fig. 7). However, given the low proportion of Li₂O in the compositions (below 1 wt.%), the presence of lithium-containing crystalline phases cannot be completely ruled out as they would possibly be below the detection limit of this technique.

Results indicate that the effectiveness of lithium carbonate as a sintering agent is possibly due to the formation of a liquid phase, which is more active at higher temperatures, which is probably related to a higher progress of Li₂CO₃ decomposition reaction. This reaction generates Li₂O, which would be the real sintering agent, as described in the case of (Sm,Ce)O₂ [29]. In addition, the high volatility of Li₂O would facilitate its diffusion throughout the volume of the specimens at the higher operating temperature [35]. As the SEM images show, the presence of rounded pores, as well as the presence of areas with darker shades, are consistent with sintering in the presence of a liquid phase, part of which has been encapsulated between the SnO₂ grains. Whether this liquid phase has generated any compounds of the SnO₂-Li₂O system or has remained as an amorphous liquid could not be discerned with the employed instrumental techniques due to their small proportion.

In general terms, lithium carbonate is an additive that facilitates the sintering of tin oxide, reaching values close to total densification, specifically volumetric contractions in the region of 46% in the most favourable conditions, which correspond to densifications of 86% and relative densities of 93%. Comparing these results with those obtained in a previous publication, better densification values were obtained with lithium oxide as a dopant than with bismuth oxide [18], with which the best results were around 45% densification, due to the high degree of volatilisation of the latter during the sintering process. Obviously, this study does not reach relative densities around 99% as obtained with a 0.5 mol.% of CoO [15] but the sintering cycle could be improved using the obtained information, to approximate these values. On the other hand, comparison with zinc oxide showed that for the same molar proportion of doping as used in this work, it was necessary sintering temperatures higher than 1400 °C to obtain relative densities around 97-98% [36]. Consequently, the use of ZnO

as sintering aid at lower temperatures could give relative densities not far from the ones obtained with lithium carbonate. From the economic point of view, using CoO as sintering aid is more expensive than Li₂CO₃, whereas ZnO is cheaper. As a consequence, lithium carbonate could be an economic alternative to CoO when high densifications are not necessary, but the election between lithium carbonate and zinc oxide would need a detailed study.

Conclusions

Lithium carbonate promotes the densification of tin oxide, although the result depends on its proportion and the parameters of the heat treatment (heating rate, maximum temperature, and soaking time). The experimental designs carried out have made it possible to evaluate the degree of influence of each of the variables studied on the sintering process, determining that the most important factor to consider when designing a heat treatment to obtain high densification is the maximum temperature, followed by the proportion of Li₂CO₃, the residence time at T_{max} and the interaction between the proportion of additive and the T_{max} . Specifically, relative density values of 93% can be achieved with an additive percentage of 1 mol.%, using a maximum temperature of 1300 °C and short soaking times (1 h). In addition, relative densities close to the maximum values can be obtained only with the heating section. This results in a microstructure of closed, rounded pores, in which a residual phase is enclosed, most likely including part of the lithium introduced, but whose exact nature has not been determined.

Annex

The volumetric shrinkage of the fired specimens has been related to the sectional shrinkage recorded under the heating microscope by the following assumptions.

Given the mass and bulk density of both pressed and sintered specimens, the volumetric shrinkage (S_V) is obtained with the following equation.

$$S_V = \frac{V_P - V_S}{V_P} = \frac{m_P/\rho_P - m_S/\rho_S}{m_P/\rho_P}$$

where V_P and V_S are the volume of the pressed and sintered specimen respectively, m_P and m_S their masses and ρ_P and ρ_S their bulk densities.

The heating microscope, on the other hand, measures the variation in the cross-section of the specimen. As the specimen is cylindrical in shape, its side section is a rectangle of height h and base equal to twice the radius R . Assuming that during sintering the height/radius ratio remains constant and equal to α , the volumetric and surface shrinkage of the specimen is given by the following expressions:

$$S_V = \frac{\pi R_0^2 h_0 - \pi R_T^2 h_T}{\pi R_0^2 h_0} = \frac{\alpha R_0^3 - \alpha R_T^3}{\alpha R_0^3} = 1 - \left(\frac{R_T}{R_0}\right)^3$$

$$S_S = \frac{2R_0 h_0 - 2R_T h_T}{2R_0 h_0} = \frac{\alpha R_0^2 - \alpha R_T^2}{\alpha R_0^2} = 1 - \left(\frac{R_T}{R_0}\right)^2$$

where R_0 and h_0 are the initial radius and height of the specimen, and R_T and h_T are the radius and height when a given temperature T is reached.

With this reasoning the two measurements of shrinkage can be related.

$$\frac{R}{R_0} = \sqrt{1 - S_S} = \sqrt[3]{1 - S_V} \rightarrow S_{Ve} = 1 - \sqrt[2]{(1 - S_S)^3}$$

Consequently, it is possible to estimate the volumetric shrinkage of the specimens that would correspond to a given value of sectional shrinkage measured with the heating microscope.

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