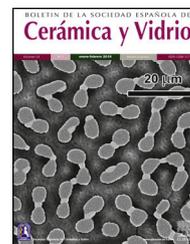




BOLETIN DE LA SOCIEDAD ESPAÑOLA DE

Cerámica y Vidrio

www.elsevier.es/bsecv


Experimental design applied to improving the effect of bismuth oxide as a sintering aid for tin oxide

María-José Sánchez-Rivera^{a,*}, Ana Gozalbo^{a,c}, Valentín Pérez-Herranz^b, Sergio Mestre^{a,c}

^a Instituto Universitario de Tecnología Cerámica, Universitat Jaume I, Castellón, Spain

^b IEC Group, Departamento de Ingeniería Química y Nuclear, Universitat Politècnica de València, Spain

^c Departamento de Ingeniería Química, Universitat Jaume I, Castellón, Spain

ARTICLE INFO

Article history:

Received 28 June 2017

Accepted 24 October 2017

Available online 21 November 2017

Keywords:

Oxides

Sintering

Microstructure

Experimental design

ABSTRACT

Tin oxide has been extensively studied due to its wide variety of applications. However, its poor sinter ability requires the use of sintering aids for its processing. The sintering behaviour of three different SnO₂-based powder mixtures, containing Bi₂O₃ in amounts between 1 and 2 mol%, has been analyzed. The effects of thermal treatment parameters (heating rate, maximum temperature and soaking time) on the densification were obtained by a factorial experimental design 2³. Bi₂O₃ adequate proportion (around 1.5%) combined with a fast heating (15 °C min⁻¹) and a high maximum temperature (1300 °C), allows reaching densifications around 45%. However, soaking time has no significant effect over densification. An interpretation of the significant effects has been proposed based on thermodynamic behaviour of Bi-containing compounds and the mass transport mechanisms.

© 2017 SECV. Published by Elsevier España, S.L.U. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Diseño experimental aplicado a la mejora del efecto del óxido de bismuto como promotor de sinterización del óxido de estaño

RESUMEN

El óxido de estaño es un material ampliamente estudiado dada su gran variedad de aplicaciones. Sin embargo, debido a que sinteriza sin densificar, su procesado requiere la incorporación de promotores de la sinterización. Se ha estudiado el comportamiento de 3 mezclas a base de óxido de estaño que contenían óxido de bismuto como promotor de la sinterización, en proporciones 1-2% mol. A través de un diseño factorial de experimentos 2³, se han evaluado los efectos de los parámetros del tratamiento térmico (velocidad de calentamiento, temperatura máxima y tiempo de permanencia) sobre la densificación. La combinación de una adecuada proporción de Bi₂O₃ (alrededor del 1,5%), una velocidad de

Palabras clave:

Óxidos

Sinterización

Microestructura

Diseño de experimentos

* Corresponding author.

E-mail address: mariajose.sanchez@itc.uji.es (M.-J. Sánchez-Rivera).

<https://doi.org/10.1016/j.bsecv.2017.10.006>

0366-3175/© 2017 SECV. Published by Elsevier España, S.L.U. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

calentamiento rápida ($15\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) y una temperatura de sinterización elevada ($1.300\text{ }^{\circ}\text{C}$), permite alcanzar una densificación del 45%. Sin embargo, el tiempo de permanencia no ejerce un efecto significativo. Se propone una interpretación de los efectos significativos sobre la densificación, basada en el comportamiento termodinámico de los compuestos que contienen Bi y en los mecanismos de transporte de materia.

© 2017 SECV. Publicado por Elsevier España, S.L.U. Este es un artículo Open Access bajo la licencia CC BY-NC-ND (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Introduction

Tin oxide exhibits many attractive physical and chemical properties, such as high conductivity (n-type semiconductor) and corrosion resistance. Traditionally, SnO_2 has been used as raw material for some pigments [1] and as opacifier in ceramic glazes [2]. Nowadays, it is broadly used in the production of gas sensors [3,4], as well as components requiring high chemical corrosion resistance in chemical industry applications [5]. In the last field, an important application is obtaining electrodes for the processing of aluminium by electrolysis [6,7] and electric glass melting furnaces [8].

One of the main drawbacks of SnO_2 is its poor sinter ability since hinders its use [9,10]. According to Kimura et al. [11], two different phenomena can occur during the sintering process in ceramic bodies: densification and particle coarsening. High densification is obtained when bulk transport mechanisms, as grain-boundary diffusion, are predominant. By contrast, surface transport mechanisms, as surface diffusion or evaporation–condensation, generates a non-densified body because of the particle coarsening. In the case of pure tin oxide, the studies describe a decomposition of SnO_2 in SnO and O_2 at temperatures above $1100\text{ }^{\circ}\text{C}$. In consequence, the evaporation–condensation mechanism predominates during sintering, whereby the electrodes obtained from this material showed a very low densification [12,13].

Different approaches have been used to improve densification, namely, hot isostatic pressing [14], Field Activated Sintering Technique (FAST) [15] or the addition of other metallic oxides as “sintering aids” [16,17], those promote the formation of a eutectic liquid between SnO_2 and the “sintering aid” at low temperature favouring a liquid-phase sintering [18,19]. Between the oxides proposed as “sintering aids” for tin oxide, bismuth oxide has been proposed as a non-toxic alternative. The Bi_2O_3 – SnO_2 phase diagram contains three stable solid phases: bismuth oxide (m.p. $840\text{ }^{\circ}\text{C}$), tin oxide (m.p. $1800\text{ }^{\circ}\text{C}$) and $\text{Bi}_2\text{Sn}_2\text{O}_7$ (melts incongruently near $1400\text{ }^{\circ}\text{C}$ and decomposes to solid SnO_2 and a Bi_2O_3 -rich liquid). In addition, a low-temperature eutectic was present for a 2 mol% SnO_2 and 98 mol% Bi_2O_3 ($825\text{ }^{\circ}\text{C}$). In addition, the presence of Bi_2O_3 suppresses SnO_2 sublimation owing to the high pressure of oxygen resulting from Bi_2O_3 or $\text{Bi}_2\text{Sn}_2\text{O}_7$ sublimation [20]. In consequence, the sintering mechanism of SnO_2 through the gas phase is partially blocked.

In this work, a factorial experimental design 2^3 has been used to analyze the effect of thermal cycle parameters (heating rate, maximum temperature and soaking time) over the performance of bismuth oxide as sintering aid for tin oxide. Thermodynamic data have been used to interpret the obtained results.

Experimental procedure

Raw materials were SnO_2 (purity 99.85%, Quimialmel S.A., Spain), and Bi_2O_3 as sintering aid (purity 98%, Fluka AG, Germany). Three different compositions were formulated to evaluate the effect of bismuth oxide proportion over the sintering behaviour of tin oxide (Table 1). 0.8% in weight of polyvinylalcohol (Mowiol 8-88, Clariant Iberica S.A. Spain), was added to each composition as a ligand.

Firstly, raw materials were mixed in a planetary mill (Pulverisette 5, Fritsch GmbH, Germany), at 230 rpm during an hour using water as a fluid and the suspension was dried at $110\text{ }^{\circ}\text{C}$ for 24 h. Secondly, the dried powder was sieved through a $600\text{ }\mu\text{m}$ mesh and was moistened to 5% (kg water/kg dry solid). Thirdly, disc specimens of 2 cm diameter and 0.5 cm thickness were dry-pressed at 450 kg cm^{-2} in a laboratory uniaxial press (Nanneti Spa, Italy). Finally, eight different thermal treatments were carried out in a laboratory furnace in air atmosphere (RHF1600, Carbolite Furnaces, UK) with the experimental design showed in Table 2.

Bulk density of green and sintered specimens was measured by mercury immersion (Archimedes' method), and densification (change in bulk density due to sintering divided by the change needed to attain a pore-free solid), was calculated according to German [21].

Characterization of crystalline structures present on some specimens was performed using an X-ray diffractometer (Theta-Theta D8 Advance, Bruker, Germany), with CuK radiation ($\lambda = 1.54183\text{ \AA}$). The generator applied an intensity light source of 45 kV and 40 mA. XRD data were collected by means of a VANTEC-1 detector in a 2θ from 5 to 90° with a step width of 0.015° and a counting time of 1.2 s/step. SEM images were taken with a FEG-SEM (QUANTA 200F, FEI Co, USA) from polished sections of some samples.

Table 1 – Molar percentages of oxides of the three compositions.

Oxide	A	B	C
SnO_2	99.0	98.5	98.0
Bi_2O_3	1.0	1.5	2.0

Table 2 – Factorial experiment design 2^3 . Two levels for 3 parameters of sintering cycle: heating rate, maximum temperature and soaking time.

Level	Heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$)	Tmax ($^{\circ}\text{C}$)	Soaking time (h)
–1	5	1100	1
+1	15	1300	4

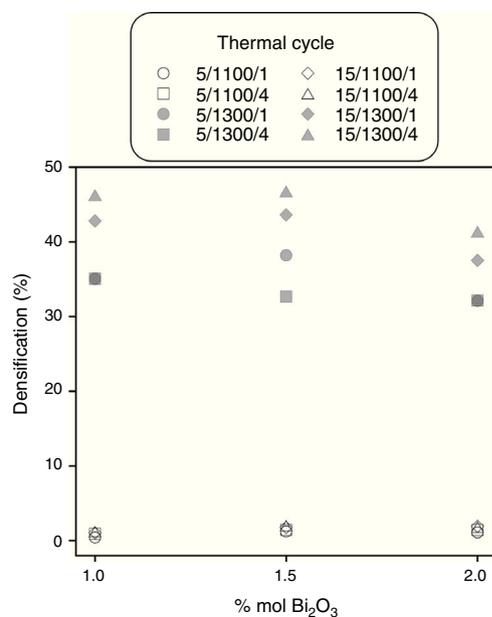


Fig. 1 – Densification samples as a function of the percentage of bismuth oxide and thermal cycle parameters (heating rate/maximum temperature/soaking time).

Experimental results and discussion

Results showed that the addition of bismuth oxide allows to reach densifications of 45% (corresponding to a relative density of 73.8% with respect to pore-free SnO₂). However, sintering aid was only effective at temperatures around 1300 °C and its proportion is limited to 1.5% because higher contents of Bi₂O₃ tend to decrease maximum densification values (Fig. 1). In addition, the faster heating rate seems to increase densification, but an effect of soaking time was not appreciable.

The main effects and interactions (Table 3), as well as their standard deviation σ , were obtained according to Box et al. [22]. It was considered as significant the effects higher than 3σ . Maximum temperature has the greatest effect on densification followed by heating rate and the interaction $T \times r$. However, densification seems not to be influenced by soaking time and the other interactions.

XRD of samples of composition B treated with the 15/1300/4 cycle identified a small proportion of a pyrochlore-type compound Bi₂Sn₂O₇, being cassiterite the main phase (Fig. 2). This pyrochlore showed an inhomogeneous spatial distribution as SEM images demonstrate (Fig. 3). It was concentrated in the centre of the sample and the volume near the surface

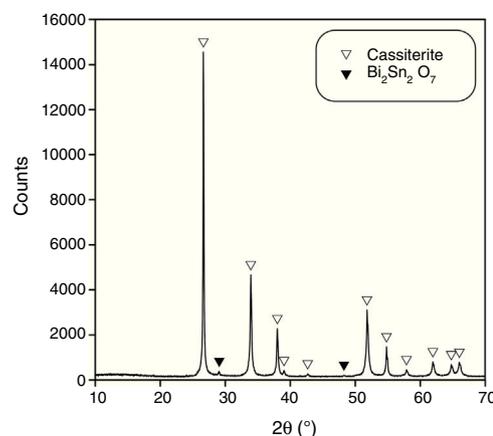


Fig. 2 – XRD of samples treated with the 15/1300/4 thermal cycle.

was practically free of this phase. In consequence, there is a loss of bismuth oxide during the thermal treatment, which mainly comes from the vicinity of the sample surface. In the other hand, the Bi₂Sn₂O₇ was present in discrete agglomerates, showing interphases with the tin oxide particles which points to a wetting by a liquid phase at high temperature.

It can be proposed that Bi₂O₃ reacts with SnO₂ to generate Bi₂Sn₂O₇ at $T > 850$ °C [23], and consequently very small densification is obtained at 1100 °C. This fact is due to the absence of any liquid phase and the predominant surface mass transport mechanisms characteristic of pure SnO₂ sintering. Surface transport which masks any volumetric mass transport mechanism. By contrast, the presence of a bismuth-rich liquid phase at 1300 °C is the way for a volumetric mass transport mechanism which allows densifications around 45%. In parallel, the high oxygen partial pressure generated by Bi-containing compounds reduces the gas-phase transport of SnO₂. Accordingly, it is advisable to add bismuth oxide to promote SnO₂ densification at 1300 °C. By contrast, Bi₂O₃ effect is negligible at 1100 °C.

The effect of heating rate can be related with bismuth oxide losses, because the weight loss of samples treated at 1300 °C and the faster heating rate was slightly lower than their counterparts obtained with the slower heating rate (the mean values were 4.18% and 4.00% respectively). By contrast, the weight losses of samples treated at 1100 °C were around a mean value of 0.96%, slightly higher to the 0.8% content of PVA, meaning that the bismuth oxide losses were clearly inferior. According with this hypothesis, the lower heating rate

Table 3 – Calculation of the effect of firing parameters on the densification for each proposed composition (the effects considered not significant are signalled with an asterisk).

Comp.	Effects and interactions of thermal treatment on densification								σ
	r	T	t	$r \times T$	$r \times t$	$T \times t$	$r \times T \times t$		
A	4.96	38.89	1.02*	4.49	0.77*	0.70*	0.96*	0.44	
B	5.14	38.70	-0.48*	4.58	2.16*	-0.70*	2.16*	0.94	
C	3.96	34.21	1.02*	3.35	0.85*	0.91*	1.05*	0.82	

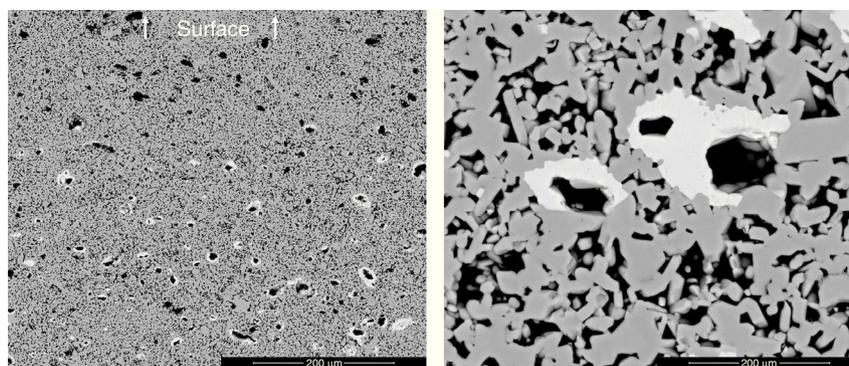


Fig. 3 – SEM images of composition B specimen treated with the 15/1300/4 thermal cycle (bright phase: $\text{Bi}_2\text{Sn}_2\text{O}_7$).

allows the diffusion out of the sample of a bigger fraction of the gaseous species generated by $\text{Bi}_2\text{Sn}_2\text{O}_7$ sublimation. In consequence, the blocking effect over the gas-phase transport of SnO_2 is less intense. On the other hand, the loss of bismuth could also be related to the lack of a measurable effect of soaking time over densification. As a bigger volume fraction of the sample loses the bismuth, the densification mechanism is stopped in those zones, and the effect of larger soaking times is lower. Probably with shorter soaking times the significance of this effect could be evaluated. Further research is needed to confirm this point.

Conclusions

Bismuth oxide promotes tin oxide densification combined with an adequate thermal cycle. The experimental design has shown that the highest densifications (around 47%) are obtained with proportions of Bi_2O_3 between 1.0 and 1.5% molar combined with a fast heating rate ($15^\circ\text{C min}^{-1}$) and a maximum temperature of 1300°C . Heating rate, maximum temperature and their interaction are the parameters with a significant effect over densification. However, soaking time has no significant effect over densification, at least in the range of values investigated.

Bi_2O_3 reacts to generate $\text{Bi}_2\text{Sn}_2\text{O}_7$, which is found in the central volume of the most densified samples but not near their surfaces. In addition, higher densifications are linked with higher mass losses during the thermal treatment due to bismuth compounds volatilization.

The evolution of densification in the presence of bismuth oxide has been interpreted considering the thermochemical behaviour of Bi-containing compounds, and their effect over the mass transport mechanisms.

Acknowledgements

The authors thank to Ministerio de Economía y Competitividad and Fondo Europeo de Desarrollo Regional for the support to this research [Plan Nacional de I+D, project Ref. CTQ2015-65202-C2-2-R (MINECO/FEDER)].

REFERENCES

- [1] G. Monrós, J.A. Badenes, A. García, M.A. Tena, *El Color de la Cerámica: nuevos mecanismos en pigmentos para los nuevos procesados de la industria cerámica*, Athenea 11, Publicaciones de la Universitat Jaume I, Castellón de la Plana, 2003.
- [2] J. Molera, T. Pradell, N. Salvadó, M. Vendrell-Saz, Evidence of tin oxide recrystallization in opacified lead glazes, *J. Am. Ceram. Soc.* 82 (1999) 2871–2875.
- [3] P.P. Tsai, I.C. Chen, M.H. Tzeng, Tin oxide (SnO_x) carbon monoxide sensor fabricated by thick-film methods, *Sensor Actuat. B: Chem.* 25 (1) (1995) 537–539.
- [4] F. Li, J. Xu, X. Yu, L. Chen, J. Zhu, Z. Yang, X. Xin, One-step solid-state reaction synthesis and gas sensing property of tin oxide nanoparticles, *Sensor Actuat. B: Chem.* 81 (2) (2002) 165–169.
- [5] S. Zuca, M. Terzi, M. Zaharescu, K. Matiasovsky, Contribution to the study of SnO_2 -based ceramics, *J. Mater. Sci.* 26 (6) (1991) 1666–1672, <http://dx.doi.org/10.1007/BF00544681>.
- [6] L. Cassayre, T.A. Utigard, S. Bouvet, Visualizing gas evolution on graphite and oxygen-evolving anodes, *JOM J. Miner. Met. Mater. Soc.* 54 (5) (2002) 41–45, <http://dx.doi.org/10.1007/BF02701696>.
- [7] A.M. Popescu, S. Mihaiu, S. Zuca, Microstructure and electrochemical behaviour of some SnO_2 -based inert electrodes in aluminium electrolysis, *Z. Naturforsch. A* 57 (9–10) (2002) 71–75, <http://dx.doi.org/10.1515/zna-2002-9-1010>.
- [8] C. Barry Carter, M. Grant Norton, *Ceramic Materials: Science and Engineering*, Springer Science & Business Media, New York, 2013, <http://dx.doi.org/10.1007/978-1-4614-3523-5>.
- [9] D. Nisiro, G. Fabbri, G.C. Celotti, A. Bellosi, Influence of the additives and processing conditions on the characteristics of dense SnO_2 -based ceramics, *J. Mater. Sci.* 38 (12) (2003) 2727–2742, <http://dx.doi.org/10.1023/A:1024459307992>.
- [10] Z.M. Jarzebski, J.P. Marton, Physical properties of SnO_2 materials. I. Preparation and defect structure, *J. Electrochem. Soc.* 123 (7) (1976) 199C–205C, <http://dx.doi.org/10.1149/1.2133010>.
- [11] T. Kimura, S. Inada, T. Yamaguchi, Microstructure development in SnO_2 with and without additives, *J. Mater. Sci.* 24 (1989) 220–226, <http://dx.doi.org/10.1007/BF00660957>.
- [12] E. Medvedovski, Tin oxide-based ceramics of high density obtained by pressureless sintering, *Ceram. Int.* 43 (2017) 8396–8405, <http://dx.doi.org/10.1016/j.ceramint.2017.03.185>.

- [13] D. Nisiro, G. Fabbri, G.C. Celotti, A. bellosi, Influence of the additives and processing conditions on the characteristics of dense SnO₂-based ceramics, *J. Mater. Sci.* 38 (2003) 2727–2742, <http://dx.doi.org/10.1023/A:1024459307992>.
- [14] S.J. Park, K. Hirota, H. Yamamura, Densification of nonadditive SnO₂ by hot isostatic pressing, *Ceram. Int.* 10 (1984) 115–166, [http://dx.doi.org/10.1016/0272-8842\(84\)90013-0](http://dx.doi.org/10.1016/0272-8842(84)90013-0).
- [15] O. Scarlat, S. Mihaiu, G. Aldica, J. Groza, M. Zaharescu, Semiconducting densified SnO₂-ceramics obtained by a novel sintering technique, *J. Eur. Ceram. Soc.* 24 (6) (2004) 1049–1052, [http://dx.doi.org/10.1016/S0955-2219\(03\)00387-X](http://dx.doi.org/10.1016/S0955-2219(03)00387-X).
- [16] C.R. Foschini, L. Perazolli, J.A. Varela, Sintering of tin oxide using zinc oxide as a densification aid, *J. Mater. Sci.* 39 (18) (2004) 5825–5830.
- [17] J.A. Cerri, E.R. Leite, D. Gouvêa, E. Longo, J.A. Varela, Effect of cobalt (II) oxide and manganese (IV) oxide on sintering of tin (IV) oxide, *J. Am. Ceram. Soc.* 79 (3) (1996) 799–804, <http://dx.doi.org/10.1111/j.1151-2916.1996.tb07949.x>.
- [18] V. Gil, J. Tartaj, C. Moure, P. Durán, Sintering, microstructural development, and electrical properties of gadolinia-doped ceria electrolyte with bismuth oxide as a sintering aid, *J. Eur. Ceram. Soc.* 26 (15) (2006) 3161–3171, <http://dx.doi.org/10.1016/j.jeurceramsoc.2005.09.068>.
- [19] J. Kim, T. Kimura, T. Yamaguchi, Effect of bismuth of oxide content on the sintering of zinc oxide, *J. Am. Ceram. Soc.* 72 (8) (1989) 1541–1544, <http://dx.doi.org/10.1111/j.1151-2916.1989.tb07703.x>.
- [20] N.A. Asryan, T.N. Kol'tsova, A.S. Alikhanyan, G.D. Nipan, Thermodynamics and phase diagram of the Bi₂O₃-SnO₂ system, *Inorg. Mater.* 38 (11) (2002) 1141–1147.
- [21] R.M. German, *Sintering Theory and Practice*, John Wiley & Sons, New York, 1996.
- [22] G.E.P. Box, J.S. Hunter, W.G. Hunter, *Statistics for Experimenters: Design, Innovation and Discovery*, John Wiley & Sons, Hoboken, NJ, 2005.
- [23] V. Ravi, S. Adyanthaya, M. Aslam, S. Pethkar, V.D. Choube, Synthesis of bismuth tin pyrochlore, *Mater. Lett.* 40 (1999) 11–13.