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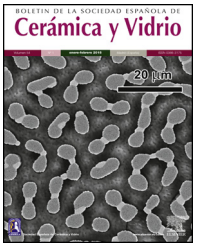

# Experimental design applied to improving the effect of bismuth oxide as a sintering aid for tin oxide

*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*

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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 $SnO_2$-based powder mixtures, containing $Bi_2O_3$ 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 $2^3$. $Bi_2O_3$ 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.



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

*Palabras clave:*
Óxidos
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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 $2^3$, 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 $Bi_2O_3$ (alrededor del 1,5%), una velocidad de

* *Corresponding author.*
E-mail address: mariajose.sanchez@itc.uji.es (M.-J. Sánchez-Rivera).
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calentamiento rápida (15 °C·min$^{-1}$) y una temperatura de sinterización elevada (1.300 °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.



## 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 °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 °C), tin oxide (m.p. 1800 °C) and $Bi_2Sn_2O_7$ (melts incongruently near 1400 °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 °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 $Bi_2Sn_2O_7$ 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 polivinylalcohol (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 °C for 24 h. Secondly, the dried powder was sieved trough a 600 μm 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 ($\lambda = 1.54183$ Å). The generator applied an intensity light source of 45 kV and 40 mA. XRD data were collected by means of a VÅNTEC-1 detector in a $2\theta$ 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 (°C min$^{-1}$) | Tmax (°C) | Soaking time (h) |
|---|---|---|---|
| −1 | 5 | 1100 | 1 |
| +1 | 15 | 1300 | 4 |

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