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# Semiconducting densified $SnO_2$-ceramics obtained by a novel sintering technique

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**Abstract**

Dense and electroconductive $SnO_2$ ceramics, important for special electrodes applications, with the $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ final composition were densified by applying the Field Activated Sintering Technique (FAST). The same composition, obtained starting both from the initial oxides (i. e. $SnO_2$, $Sb_2O_3$ and CuO) and from $SnO_2$ and the $CuSb_2O_6$, was conventionally sintered by thermal treatment at 1100 °C–3 h. High relative density values (i.e. 99%) and a consolidated microstructure (grain size below 1 μm) were obtained only by applying FAST. The resulting $SnO_2$-based solid solutions, presented a semimetallic behaviour sustained by the conductivity vs. temperature dependence and the obtained negative values for the Seebeck coefficients, with electrons as major charge carriers. For the conventional sintered specimens, the poor sintering capabilities evidenced by density and porosity measurements limited the electrical applications of the obtained materials as densified ceramics.

*Keywords:* Dense ceramics; Electrical properties; Sintering; $SnO_2$

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## 1. Introduction

The use of n-type semiconductor $SnO_2$ materials as dense ceramics for obtaining electrodes for electric glass melting furnaces[1] and in the production of aluminium by electrolysis[2] is limited by its low densification during sintering. This is due to the dominance of non-densifying mechanisms such as surface diffusion or evaporation–condensation which promote grain coarsening of $SnO_2$ and thus leads to poor densification capabilities of this ceramic.[3]

Several processes and sintering aids have been used to improve the densification of $SnO_2$ ceramics by forming a lattice solid solution or liquid phase. Park et al.[4] have obtained 97% of theoretical density of $SnO_2$ (without additives) by using hot isostatic pressing (150 MPa) at 1400°C during 12 h. Zuca et al.[5] observed that $SnO_2$ densifies up to 94% of theoretical density when 2 mol% of $Sb_2O_3$ and 1 mol% of CuO are used as additives. The benefit of using the latter additives to the sintering of $SnO_2$ was extensively studied in our laboratory.[6,7] As previously reported, the supplementary addition of CuO and $Sb_2O_3$ has been found to significantly increase the electrical properties of the obtained $SnO_2$ based materials by improving both the sintering capabilities and the conduction mechanism.[5,8]

Field activated sintering technique (FAST) is a non-conventional densification method, which was successfully applied to difficult to sinter materials, resulting in obtaining 98% densities for ceramic powders without any sintering additives.[9,10] For the $SnO_2$-based ceramics, the use of the FAST technique on the 0.90 $SnO_2$–0.10 $Sb_2O_3$ initial composition achieved 92.4% density value.[9]

The aim of this work is to study the ability of the FAST technique to sinter the $SnO_2$–$CuSb_2O_6$ based ceramics and to evaluate the electrical properties of the as-obtained densified ceramics.

## 2. Experimental

The $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ final composition samples was prepared by classical ceramic method[9] starting both from the initially oxides as well as from $SnO_2$ and $CuSb_2O_6$ binary compound (prepared in our laboratory)[11] and then thermally treated at 1100°C-3 h.

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FAST densification was carried out using a SPS machine (Sumitomo Coal Mining Co, Japan). Loose powders from the ground pellets resulted when using the 0.90 $SnO_2$ and 0.10 $CuSb_2O_6$ initial mixture, and were loaded in a die and punch unit, transferred into the SPS machine and sintered at 890 °C for 10 h under a 40 MPa pressure in vacuum ($5\times10^{-5}$ MPa).

For phase determination, a Scintag Automated Diffractometer fitted with a solid state counter and Cu$K_\alpha$ radiation ($\lambda_{K_{\alpha1}} = 1.54059$ Å), was used over the range of $2\theta = 10$–$80°$ with supplementary step scans (0.01° step size, 2.5 s counting time) to measure the unit cell parameters.

The ceramic properties were determined by the classical methods detailed in refs 7 and 9 The electrical properties were evaluated in the −196 to 850 °C temperature range using a direct current bridge operating in four points scheme and the Seebeck coefficient was measured at room temperature, using the warm point method and a platinum reference.[5,6]

## 3. Experimental results and discussion

### 3.1. Structural characterization

Table 1 presents the lattice parameters of the studied composition conventionally sintered, as well after applying FAST. As previously reported,[5,7,11] the heat treatment of the initial 0.82 $SnO_2 + 0.09\ Sb_2O_3 + 0.09$ CuO and 0.90 $SnO_2 + 0.10\ CuSb_2O_6$ mixtures results in a single stable phase ($SnO_2$ based solid solution) after annealing at 1100 °C for 3 h. All the XRD peaks were found to be shifted to the right (larger angle or smaller both *a* and *c* lattice parameters) with respect to pure $SnO_2$ after the tetragonal *rutile* type solid solution was formed, while after applying FAST to the sintered specimen, there is a dilatation instead of a contraction (Table 1).

### 3.2. Ceramic properties

As seen from the ceramic properties of the obtained samples (Table 1), the conventional sintering leaves high porosity (Fig. 1a and b) as well as relative low-density values, pointing to difficulties in sintering of the $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ composition. In contrast, FAST sintering of the same composition results in lower open porosity values (i.e. 0.00%), and relative density of 99.06% typical for highly densified ceramics. Consequently, the SEM photographs (Fig. 1c) indicate the obtaining of a consolidated microstructure with essentially no pores and grain size of 1 μm.

For the electroconducting ceramics as are the $SnO_2$ based ceramics, the electrical properties are strongly related with the sample mono-phase characteristic.[12] This condition is fully accomplished in the present work since according to the XRD results all the studied samples are formed, after the conventionally as well as FAST sintering process, from a unique phase consisting of a $SnO_2$ based solid solution. However, the conventional sintering process has developed a higher relative density value only when starting with the $SnO_2$, $Sb_2O_3$ and CuO initial oxides (Table 1). The high 5.03% porosity value obtained for this latter sample points to the presence on its surface of a high amount of open pores, with size dimensions of 20 μm, visualized in Fig. 1a. The grains with regular shape but different sizes may result from a sample surface enriched in $Cu_4SbO_{4.5}$ microphase,[8] as well as from the recrystallization process of the high temperature melt.[11]

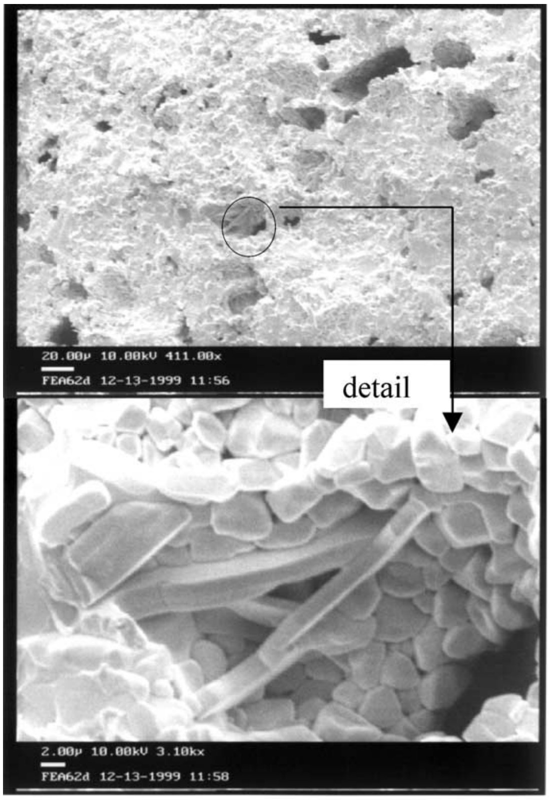
Moreover, the relative density obtained for the latter is higher than the 4.3 value previously reported for the 0.90 $SnO_2$–0.10 $Sb_2O_3$ equivalent initial composition, conventionally sintered in the same conditions,[9] pointing to the positive effect of the supplementary addition of CuO on the conventional sintering of the $SnO_2$ based materials.

For the sample obtained starting with $SnO_2$ and $CuSb_2O_6$ initial components, the resulting 8.45% porosity value (Table 1) shows even a great amount of open pores (5 μm size) uniformly shaped and distributed on the surface visualized in Fig. 1b.

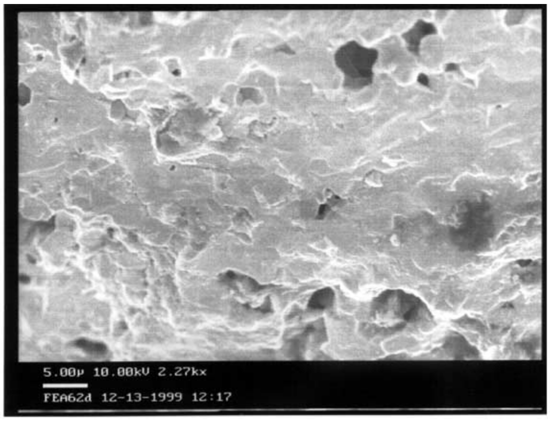
This difference in the obtained relative density values may be related only to the better sintering capabilities of the sample prepared starting from the initial oxides; as a result of the simultaneously proceeding of the sintering and the formation process of the $SnO_2$ based solid solution, the latter taking place in stages and thus increasing the whole reactivity of the system.[5,7] On the other hand, the presence of some un-reacted CuO may develop the formation of a liquid phase at high temperatures.[7,11] Such a liquid phase rich in CuO was evidenced in the

Table 1
Lattice parameters and ceramic properties of the sintered $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ composition

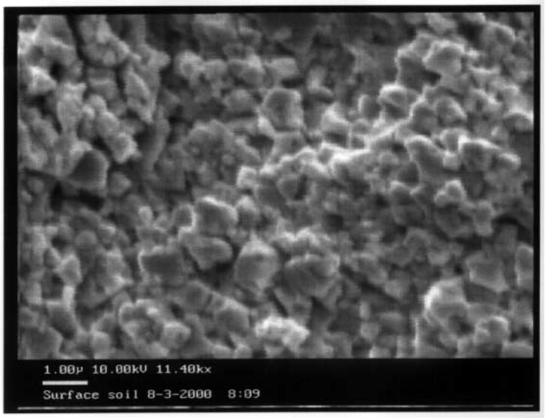
| Sample | Initial composition (mol%) | | | | $a_o \equiv b_o$ | $c_o$ | $d_{theor}$ | $d_{exp}$ | $d_{rel}$ | $P_a$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SnO_2$ | CuO | $Sb_2O_3$ | $CuSb_2O_6$ | (Å) | (Å) | (g/cm³) | (g/cm³) | – | (%) |
| Pure $SnO_2$ | 100 | – | – | – | 4.7357 | 3.1861 | – | – | – | – |
| Conventional sintering | 82 | 9 | 9 | – | 4.7020 | 3.1630 | 6.96 | 5.02 | 72.12 | 5.03 |
| | 90 | – | – | 10 | 4.7251 | 3.1703 | 6.88 | 4.44 | 64.53 | 8.45 |
| FAST | 90 | – | – | 10 | 4.7824 | 3.2240 | 6.60 | 6.59 | 99.06 | 0.00 |



*a)* 0.82 $SnO_2$ + 0.09 $Sb_2O_3$ + 0.09 CuO, 1100°C–3 h.



*b)* 0.90 $SnO_2$ + 0.10 $CuSb_2O_6$, 1100°C–3 h.



*c)* 0.90 $SnO_2$ + 0.10 $CuSb_2O_6$, 1100°C – 3 h + FAST.

Fig. 1. SEM micrographs of the sintered $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ composition.

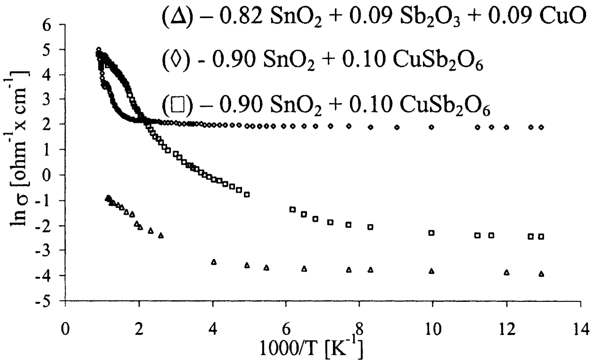


Fig. 2. The variation of electrical conductivity with temperature for the $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ compositions: (◇) obtained by FAST and conventionally sintered samples: (□) annealed at 1100 °C–10 h; (Δ) annealed at 1200 °C–3 h.

$SnO_2$–$Sb_2O_3$–CuO based compositions even for short sintering times[7] and its presence may thus significantly improve the densification properties of the latter sample.

As previously discussed, only for the $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ composition sintered by FAST, data presented in Table 1 and Fig. 2c) pointed to the obtaining of a highly densified ceramic. Even though the exact mechanism of the enhanced FAST densification is not yet known, it is assumed that the pulsed electrical current creates favourable conditions for the removal of impurities and activation of powder particle surfaces. Some arcing or electrical discharge phenomena at particle-to-particle contacts may be responsible for adsorbate elimination or surface "cleaning", thus creating favourable conditions for subsequent particle bonding. This activation explained the high densities obtained in ceramics without additives and direct grain-to-grain contact at atom scale observed by HREM in ceramics and metals.[13] In addition to the little coarsening due to a very short time at high temperatures, the final nanometer grain sizes by FAST sintering also reflect a minimal coarsening during the heating up stage.[14]

### 3.3. Electrical properties

The dependence of the electrical conductivity on temperature of the conventional and FAST sintered samples is plotted in Fig. 2. As expected,[5,9] both conventionally sintered samples as well as the FAST sintered $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ compositions exhibit a typical semiconducting behaviour with electrons as

Table 2
Activation energies $E_d$ (eV) and Seebeck coefficient values (μV/°C) for the sintered $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ composition

| Sample | Initial composition | | | | $E_d$ | Temperature range | | Seebeck coefficient |
|---|---|---|---|---|---|---|---|---|
| | $SnO_2$ | CuO | $Sb_2O_3$ | $CuSb_2O_6$ | (eV) | °C | 1000/K | (μV/°C) |
| conventional sintering | 82 | 9 | 9 | – | 0.093 | 27–827 | 0.9–3.3 | −1.6 |
| | | | | | 0.012 | 97–201 | 2.11–2.7 | |
| | 90 | – | – | 10 | 0.45 | 502–562 | 1.2–1.3 | −2.3±0.5 |
| | | | | | 1.00 | 697–837 | 0.9–1.03 | |
| FAST | 90 | – | – | 10 | 0.37 | 267–317 | 1.7–1.85 | −2.6±0.5 |

major charge carriers. While by conventional sintering and starting from $SnO_2$ and $CuSb_2O_6$ initial components there are three reported values for the $E_d$ activation energy (Table 2) indicating a steps conduction mechanism, for the sample densified by FAST only one value was calculated. As seen from Table 1, the conventionally sintered samples, now matter their initial composition, have lower density and high open porosity values. It is this high open porosity that probably affords the existence of some adsorbed chemical species on the grains surface. Their desorbtion process is expected to occur up to 600 °C and result in some changes in the slope of the conventionally sintered samples,[15] leading to additional values for the activation energies of the sample obtained using $SnO_2$ and $CuSb_2O_6$ initial components (Table 2). A different slope associated with such a desorption process was not seen in the FAST sintered specimen (Fig. 2). Since the semiconducting behaviour was evident in all the studied sintered samples, the higher conductivity obtained in the FAST case can be attributed only to its denser microstructure, sustained by the data from Fig. 2, especially below room temperature. The higher degree of densification obtained in the FAST sample resulted in negative but lower values of the Seebeck coefficient—typical for materials with metallic conduction, indicating a higher charge carrier density than for conventionally sintered samples.

## 4. Conclusion

The *rutile* type solid solution as $SnO_2$ unique phase, of the $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ initial composition, was sintered to 99% high-density values under an external applied electrical field. Conductivity measurements and negative values of the Seebeck coefficients showed a high charge carrier concentration (i.e. electronic conduction). The higher conductivity of the FAST specimen resulted in only one donor level in the $SnO_2$ energy gap as compared to conventionally sintered $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ solid solution. This behaviour was attributed to the higher degree of densification obtained by FAST and, therefore, the wider conduction path of the charge carriers due to the absence of pores.

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