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GRAIN BOUNDARIES IN DOPED-CERIA NANOFILMS USED AS ELECTROLYTES FOR IT-SOFC FUEL CELLS

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Resumen
Las cerámicas de ceria (CeO_2), dopadas con Y_2O_3 (CYO) o con samaria Sm_2O_3 (CSO son consideradas como materiales promisorios para electrolitos sólidos de celdas de combustible de tipo SOFC- Solid Oxide Fuel Cells, debido a su alta conductividad por iones oxígeno. Los requerimientos necesarios para electrolitos de las pilas de combustible son: estabilidad química, alta conductividad, condiciones adecuadas de sinterizado, alta densidad y ausencia de porosidad abierta. En este trabajo, se utilizó CeO_2 dopada con 10% molar de samaria, material ya estudiada en algunos aspectos por los autores, tratándoselo térmicamente por "fast-firing" durante un corto tiempo (3 min) a 850ºC y a 1450ºC para producir el sinterizado del material. En el DEINSO-CITEDEF se realiza una planificación completa de los efectos del "fast-firing" para comprender el comportamiento de estas cerámicas, estudiando: el crecimiento de grano; velocidad de sinterizado, cambios en las características de los bordes de grano, tamaño de cristalitas, densidad de poros, densificación e interacción de defectos. En este trabajo, se consideran especialmente, los efectos del "fast-firing" respecto de la estructura de los bordes de grano para contribuir a lograr electrolitos sólidos que exhiban mayor estabilidad y mejor calidad. La caracterización de las cerámicas fue realizada por técnicas de adsorción BET, DRX, SEM and HRTEM.

Abstract
Ceria (CeO_2) ceramics as doped with Y_2O_3 (CYO) or with Sm_2O_3 (CSO) are considered promising materials as electrolytes for SOFCs Solid Oxide Fuel Cells due to their high conductivity by oxygen ions. The necessary requirements for fuel cells electrolytes are chemical stability, high conductivity, convenient sintering conditions, high density and absence of open porosity. In this work, the already studied materials in some aspects by the authors: doped CeO_2 with molar 10% samaria, was thermally treated by fast-firing for a short time (3 min) at 850ºC and at 1450ºC to produce the material sintering.
A complete planning of the fast-firing effects to understand these ceramics defects behavior is performed at DEINSO-CITEDEF, studying: the grain growth, sintering velocity, changes in the grain boundaries, crystallites size measurements, pores density, densification and defects interaction. In this work, the fast-firing effect on grain boundaries structure is considered.
This study also contributes to synthesize solid electrolytes with higher chemical stability and improved quality. The ceramics characterization was performed by BET adsorption techniques, XRD, SEM and HRTEM.

***Palabras clave**: ceria dopada con samaria, sinterizado, "fast-firing", bordes de grano asimétricos y simétricos.*
***Key-words**: samaria doped ceria, sintering, "fast-firing", asymmetric and symmetric grain boundaries.*

1. Introduction

Fuel cells are considered as promising devices to generate clean energy by conversion of chemical energy into electric energy. Among them, the SOFC-solid oxide fuel cells which can be operated with pure H_2 but, exhibiting the advantage of working also with hydrocarbons because of their property of inner reforming. The actual commercial type SOFC fuel cells are the HT-SOFCs, operated at high temperature: HT= (800-1200 ºC, to produce energy to be applied for rural zones or in areas far situated from urban centres. The disadvantages of HT-SOFCs come from their high operation temperature (T_{op}) which considerably damages the materials used to build them and by their requirement of noble elements for connectors. Consequently, important efforts are devoted to find new materials for the SOFCs electrolytes and electrodes enabling to decrease the T_{op}. The IT-SOFCs, functioning at an intermediate temperature range: IT = (550-700) ºC, avoid the materials degradation caused by thermal cycling, enable the use of materials in nano-scale to build the cells, avoid fast diffusion in the interfaces allowing, at the same time, to reduce the cost of connection materials.

Ceria (CeO_2) ceramics as doped with Y_2O_3 (CYO) or with Sm_2O_3 (CSO) are considered as promising materials for SOFCs electrolytes due to their high conductivity by oxygen ions. Otherwise, if IT-SOFCs operate at a lower T_{op}, nanocrystalline CYO and CSO may be used to build the fuel cells with considerable advantages. In previous works, the authors studied the electrical properties of CYO and CSO as a function of grain size using EIS (Electrochemical Impedance Spectroscopy) [1, 2]; the structure of grain boundaries was also studied. It was found a remarkable increase of the whole ionic conductivity (one magnitude order or more) in comparison with the intrinsic bulk conductivity of conventional microcrystalline ceramics. This fact has been attributed to a predominating conductivity by grain boundary [3]. CYO and CSO have been characterized by BET adsorption technique, XRD, SEM and TEM (HRTEM) considering how the nanofilms microstructure affects conductivity.

The necessary requirements for fuel cells electrolytes are: chemical stability, high conductivity, convenient sintering conditions, high density and absence of open porosity. These properties have been considered in ceria-ceramics as doped with molar 10% Y_2O_3 (CYO) or with molar 10% Sm_2O_3 (CSO). If ceria is doped with trivalent cations, oxygen vacancies are created which result necessary for the conduction process by oxygen ions. As already mentioned, it was found by the authors that the ionic conductivity in these ceramics increased in one order of magnitude or more [1, 2] in small grained or in nanocrytalline materials in comparison with the conductivity of the same materials with microcrystalline scale, being this fact attributed to the fast oxygen vacancies migration produced by a delocalized translating movement by large jumps (big hops*)* through the grain boundaries [3].

In this work the doped ceria (CSO) ceramic was thermally treated with a previous fast-firing (FF) for 3 min at 850 ºC and at 1450 ºC to sinterize them. Several FF effects were studied: grain boundaries growth, sintering rate, changes in grain boundary characteristics, crystallites size, pores density, films densifying and defects interaction. All these subjects are considered to be applied in diffusional models of nano-CSO and CYO in development at DEINSO. Particularly in this work, the thermal FF effect on the structural characteristics of grain boundaries (GB) of nanocrystalline CSO is studied. The final aim is the preparation of nano-solid electrolytes exhibiting a higher stability and improved quality. The characterization of CSO before and after FF was performed by: BET (Brunauer-Emmett-Teller isotherms) adsorption techniques to determine the specific area which is used to evaluate the crystallites size; by XRD to also determine the crystallites size using Scherrer equation; by Scanning Electron Microscopy (SEM) to observe the specimen surface and by High Resolution Transmission Electron Microscopy (HRTEM) to observe the grain boundaries characteristics.

2. Materials and Methods

Nano CSO (doped ceria with molar 10% samaria) specimens were prepared as described in [1, 2] departing from commercial (Nextech) powders. The powders purity resulted: 99.8% (in agreement with CSO manufacturers information). The specific area (in m^2/g) is determined by BET (Brunauer-Emmett-Teller isotherms) nitrogen adsorption techniques using an Autosorb-1 Quantachrom Equipment, DEINSO-CITEDEF.

Microstructure studies of ceramics surface were performed with a SEM-Philip 505, DEINSO-CITEDEF and films observation with a HRTEM, JEM-2100 (Jeol, Tokyo, Japan) the Jožef Stefan Institute, Ljubljana, Slovenia.

The crystallite mean size was evaluated by XRD (using Scherrer equation) [4] in a Philips PW 3710 diffractometer using Cu-Kα radiation.

The oxide nanoparticles were dispersed in ethanol being afterwards dried under controlled conditions. The FF was performed at 850 ºC and at 1450 °C for: 3 min and with heating and cooling temperatrure: 200 $ºC.min^{-1}$ for both treatments. The fast-firing (FF) is a conventional thermal method to densify the ceramics performed at high temperature. If FF is applied for a short time it is possible to avoid an important increase of grain growth during the process.

Sintering process, occurs when powders are packed together and heated at high temperature, approximately 2Tm/3 (Tm: melting point) in which case, diffusion becomes significant, This definition is not completely certain for nanocrystals because several material properties change in the nanoscale, i.e. Tm is generally lower than for the same material but microcrystalline..

The lattice parameter was evaluated by Rietveld analysis [4]. BET (Brunauer-Emmett-Teller isotherms) N_2 adsorption technique, with an Autosorb-1 Quantachrom Equipment (DEINSO-CITEDEF), enables to determine the particle size using the classical BET approach [5], surface observation of CSO were performed with Scanning Electronic Microscopy (SEM) using a Philip 505 SEM equipment (DEINSO-CITEDEF) and structure of materials was observed by High Resolution Electron Microscopy (HRTEM) with a JEM-2100 Jeol-Tokyo Transmission Electron Microscope belonging to the Jožef Stefan Institute, Ljubljana, Slovenia. The particles size was also calculated by the conventional method of lines intersection in SEM micrographs. In this work, we shall refer too to data taken from HRTEM micrographs which enabled to know the GB type and density: symmetrical GB twinned GB, tilt GB or low misorientation GB to understand the relation between diffusion through different GB types now in calculation at DEINSO [6]. It must be considered that grain growth occurs in polycrystalline materials to reduce the system overall energy. GB are non-equilibrium defects. In nanomaterials where the GB constitutes a significant proportion of the whole volume, the growth tendency should be particularly strong and the main task during the nanomaterials processing is, as far as possible, to prevent this for happening [7].

3. Results and discussion

The CSO material characterization results were:

- *Specific area* (228 m^2/g) as evaluated by BET isotherms N_2 adsorption technique;
- *Microstructure studies of ceramics surface* were performed with a SEM-Philip 505, **Figures 1** and **2.** The classical method of crossing lines enabled too the measurement of particles size in micrographs taken before and after FF treatments. XRD and BET data were in agreement.

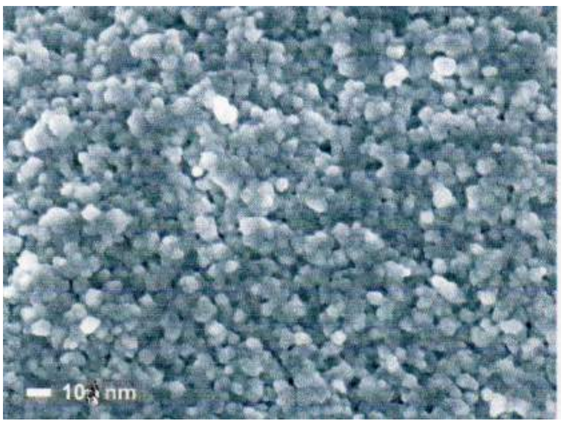

Figure 1: CSO SEM micrograph before FF thermal treatment

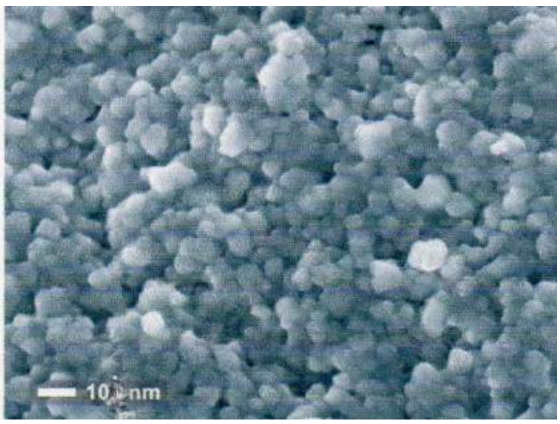

Figure 2: CSO SEM micrograph after FF at 1450ºC for 3min

- *The crystallites mean size* was measured by XRD (using Scherrer equation) [6] in a Philips PW 3710 diffractometer using Cu-Kα radiation and the resulted data were: (3.6 ± 0.2) nm (mean initial value in material without FF treatment); (6.2 ± 1) nm and (15 ± 2.5) nm mean values after fast-firing (FF) treatments at 850 ºC and 1450 ºC, respectively.
- *The lattice parameter was evaluated by Rietveld analysis* [4] considering in the CSO that the space *Fm3m* group exhibited the Sm^{3+} cations and the O^{2-} anions in the 4a and 8c sites, respectively.
- *Observation of grain boundaries* was performed with a HRTEM, JEM-2100 (Jeol, Tokyo, Japan) Stefan Institute, Ljubljana, Slovenia. **Figures 3 /4.**

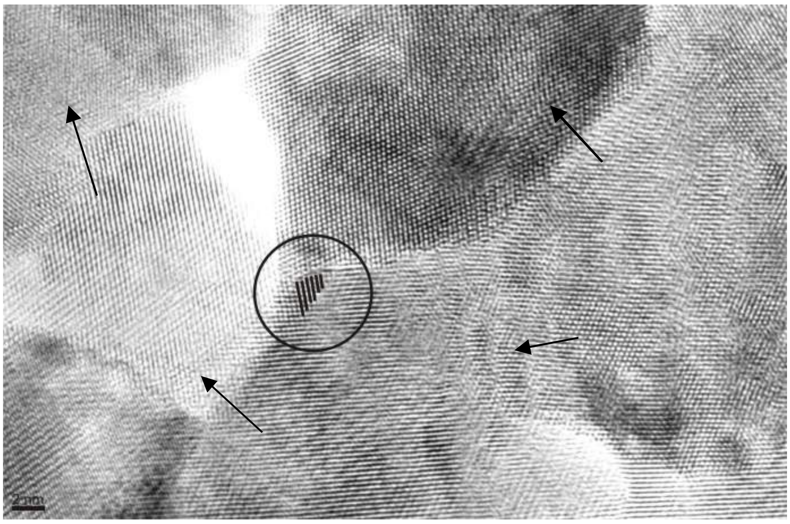

Figure 3. HRTEM micrograph of thermally treated specimen, FF= 850ºC for 3 min**.**
Numerous asymmetric GB are observed shown by arrows. In the circle: dislocations ending in GB.

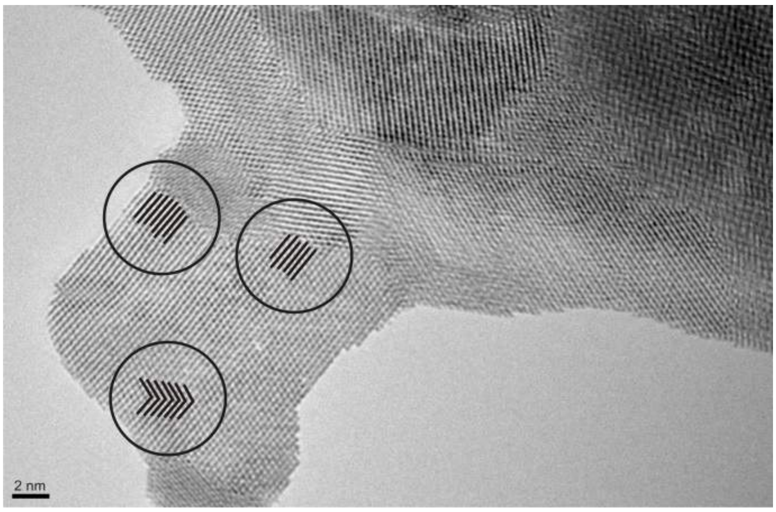

Figure 4. CSO HRTEM micrograph of thermally treated specimen, FF=1450ºC for 3 min.
In the two upper circles, numerous dislocations are ending in GBs

The fast-firing (FF) is a convenient process to sinterize the nanofilms but it is necessary to know how the GB structure is affected by the FF temperature and duration. More important changes in the GB structure are probable as the treatment temperature increases. It was necessary to recognize the asymmetric and symmetric GB to afterwards evaluate the density of both types of GB in specimen treated at FF= 850ºC and at FF= 1450ºC. The asymmetric GBs are found in high proportion in recently prepared material, before being thermally treated with FF. In case of nano-CSO specimens asymmetric GBs are low-angle disordered GBs without a coordination line, containing, dislocations, interfaces, holes and other defects which facilitate the impurities drag, Symmetric GBs are ordered boundaries with a straight coordination line and exhibiting two parts of lattice as specular images at both sides of the coordination line. If there are not defects in the GB this kind of boundary represents a simple direction change of the lattice, it is a real twinned boundary. If the boundary contains isolated dislocations symmetrically placed at both sides of the straight coordination line, it is a tilting GB. From the point of view of diffusion, in the symmetrical GB the mass transport is performed through the lattice (the GB does not contain defects) then it is a bulk transport or volume diffusion. But, diffusion is much more easily accomplished along surfaces, interfaces, holes, GBs or via dislocations than through the lattice because those defects exhibit a more open structure and defects act as "short circuits". A tilting GB in spite of being a symmetrical arranged GB, enables to increase diffusion along dislocation core, dislocations are really short circuits. Before the FF treatment, the percentage of asymmetric GB is higher than 95% appearing few symmetric GB (**Figure 3** which is a HRTEM image of a specimen with FF at 850ºC for 3 min). Numerous asymmetric BG are observed with dislocations ending on the GB, defects and holes but it was difficult to find symmetric GBs.

Symmetric GBs are known to grow also during the preparation procedures [7- 9] or by stresses relaxation at high temperature. Afterwards, in spite that the symmetric grain density may increase, it maintains lower than 10% (**Figure 4,** which is a HRTEM image of specimen thermally treated by FF a 1450ºC for 3 min). The temperature increase facilitates the atomic re-ordering at the GBs interface changing the local potential. This fact probably drives to a decrease of the system energy which turns more stable if some GBs become symmetric.

In order to statistically evaluate the percentage of symmetric and asymmetric GBs in the two types of fast-fired specimen (FF=850ºC and FF=1450ºC), 10 specimen were taken in each case and numerous GBs images were observed with HRTEM, finding that for a fast-fired specimen at 850ºC, there were only few symmetric GBs (**Figure 3**) and for fast-fired at 1450ºC more symmetric GBs appeared but always in low concentration (**Figure 4)**. In spite of these differences, the sintering results are useful for sintering the material in both cases without diffusion (or conduction) decrease in the system [10-11]. Actually, these results are going to be proved, at DEINSO by microstructure and diffusion studies since diffusion (and ionic conduction in case of CSO) in nanocrystalline ceramics is still far from being well understood [11].

4. Conclusions

The doped cerium oxide (CSO) nanocrystalline particles, to be used as electrolytes for fuel cells of IT-SOFC type, were treated by fast-firing at 850ºC and at 1450ºC for 3 min to sinterize it. The grain growth was measured as comparing the grain size in non-thermally treated material by FF: (3.6 ± 0.2) nm and after the two FF at 850ºC: (6.2 ± 1) nm and at 1450ºC: (15 ± 2.5) nm. This experimental fact is going to be compared with diffusion calculations and conductivity measurements which are actually running at DEINSO. The HRTEM observations of GBs structure and density were analysed considering the percentage of symmetric and asymmetric grain boundaries. Finally, if the specimens as thermally treated in this work with a high temperature fast-firing (even at the highest temperature) for a very short time, results has shown that the treatment is useful to sinterize the material without an appreciated decrease of intergrain diffusion.

5. References

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