

## Preparation of ThO<sub>2</sub> as a Structural Analogue for Nuclear Fuel via Surfactant-Templated Sol-Gel Route

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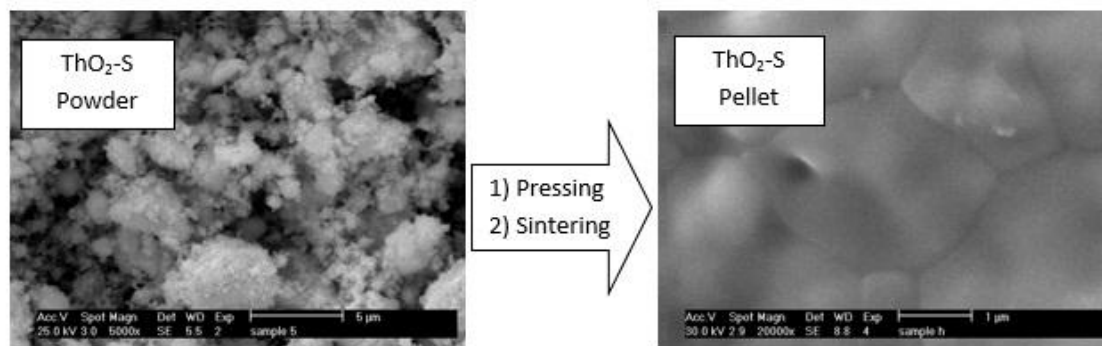
### KEYWORDS

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### ABSTRACT

Sol-gel synthesis of surfactant-templated nanostructured ceramic materials is usually carried out via controlled hydrolysis and condensation of a starting material in the presence of micelles of a polymer, followed by its removal by extraction or calcination. In this work, surfactant template sol-gel route for the synthesis of thorium dioxide gels using thorium nitrate and octyl phenol ethoxylate polymer as a structure directing agent was described, and the sinter ability of the produced ThO<sub>2</sub> powder (ThO<sub>2</sub>-S) was investigated in comparison with commercial one (ThO<sub>2</sub>-C). Prepared ThO<sub>2</sub>-S composed of micro and meso pores and exhibited high surface area as 31.23 m<sup>2</sup>/g and particle size as 15.1 nm. The produced powder ThO<sub>2</sub>-S was pressed and sintered to form the high density ThO<sub>2</sub> pellet. The final grain size of the pellets reached below micrometer size. The calculated green and sintered densities of the fabricated pellets, and their microstructural characteristics studies, utilizing SEM images, show that this synthesizing route yielded a good sinter ability of the synthesized ThO<sub>2</sub> Nano powder at low temperature. Prepared ThO<sub>2</sub>-S sample and commercial ThO<sub>2</sub> were sintered under the atmospheres "Ar" and "Ar-8%H<sub>2</sub>", and comparison of data from samples sintered under the both of two different atmospheres at 1500 °C, show that the atmosphere had no effect on density value. Furthermore, the green density of ThO<sub>2</sub>-S pellets is less than ThO<sub>2</sub>-C but the pellets which were fabricated from the ThO<sub>2</sub>-S have reached better sintered density than the pellets fabricated by ThO<sub>2</sub>-C.

### GRAPHICAL ABSTRACT



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## Introduction

Sustainable development is the development that meets the needs of the present generation without compromising the needs of future generations. To attain this goal, one of the imperatives is to adopt nuclear power. In spite of the disaster at Fukushima, nuclear power remains a clean viable alternative to fossil fuels that have wreaked havoc on the environment by way of global warming, climate change, melting ice caps and rising sea levels. Alternative nuclear technologies have been suggested as a means of delivering enhanced sustainability with proposals including fast reactors, the use of thorium fuel and tiered fuel cycles [1].

Already in the pioneering years of nuclear energy but mainly over the last 30 years, thorium ( $\text{ThO}_2$ ) has been investigated as fuel matrix as an alternative to uranium dioxide ( $\text{UO}_2$ ) [2]. Decrease of available uranium resources incites attention to the fertile elements such as thorium. Hence, in the last two decades extensive research and development has been carried out on the thorium fuel cycle [3]. In the thorium fuel cycle, the isotope of thorium,  $^{232}\text{Th}$ , is used as a fertile material. In the reactor,  $^{232}\text{Th}$  is transmuted into the fissile artificial uranium isotope,  $^{233}\text{U}$ , which is the nuclear fuel. Unlike natural uranium, natural thorium

contains only trace amounts of fissile materials (such as  $^{231}\text{Th}$ ), which are insufficient to initiate a nuclear chain reaction. Additional fissile material (such as  $^{235}\text{U}$ ) or another neutron source is necessary to initiate the fuel cycle [4]. Oxide fuel comes in the form of cylindrical pellets, about 1 cm in height and diameter. Such pellets could fabricate by the cold press and sinter technique [5]. Thorium dioxide is a refractory ceramic material and is difficult to sinter to high density. The usual temperatures for efficient sintering of  $\text{ThO}_2$  exceed  $1700^\circ\text{C}$  [6]. Sintering is a key step in most of the processes which deal with the elaboration of ceramic materials. It is a complicated process that contains microstructural evolution by densification through several different transport mechanisms. The main factors which influence the sintering are temperature, annealing time, green density, and bulk composition [7].

The fuel density is an important property of the fuel and is a function of the following factors: fuel composition, temperature, amount of porosity, O/M ratio, and burn-up [8]. So, in nuclear fuel pellet fabrication, the control of composition, porosity, surface area and particle size of powder is important. The manner and mechanisms involved on the sintering process are essential investigation to achieve the

required microstructure and final properties in solids. During the conventional sintering of a compacted powder, densification and grain growth occur simultaneously through atomic diffusion mechanisms. Many researchers have been working on reducing the grain size below 1 µm aiming to improve some properties, such as strength, toughness and wear resistance in ceramics. It is accepted that the sinterability of fine nanoparticles is superior due to the higher surface stress. However, densification of these powders is often accompanied by grain growth.

Most sinterable thorium oxide powder was obtained by precipitating thorium oxalate at 10 °C followed by digestion. Pellets of 96% TD were obtained without resorting to milling. Simultaneous separate introduction of the oxalic acid and thorium nitrate solutions into the continuous precipitation reactor produces precipitated particles which are agglomerates of inter-grown crystals distinctly different from the particles precipitated by direct strike. In the production of thorium oxide powder from oxalate, the decomposition and calcining heat cycle must include enough time between 300 °C and 400 °C to thoroughly decompose the oxalate hydrate [1].

Nanocrystalline thoria was synthesized on laboratory scale at Kalpakkam [9-11] and a master sintering curve for ThO<sub>2</sub> was

developed by Kutty *et al.* [12]. Optimal operating conditions for the sintering of the samples were determined through dilatometric studies under argon atmosphere from room temperature to 1500 °C (heating rate of 5 °C/min) achieving densities of 94% to 99% TD. The use of hydrothermal conditions in precipitation improved the cationic distribution in the sintered samples [1].

At Japan Atomic Energy Research Institute [13], ThO<sub>2</sub> powder of specific surface area 4.56 m<sup>2</sup>/g was ball milled to 9 m<sup>2</sup>/g, compacted at 2 to 5 t/cm<sup>2</sup> without binder and sintered at 1550 °C to get densities in the range 96% - 98% TD.

The sinterability of ThO<sub>2</sub> has been studied by several researchers [14, 15]. For this purpose, high specific surface area fine powders are needed since surface energy reduction is the driving force in sintering procedure. The extrusion of sol-gel derived pastes is one of several methods studied for preparation of fine particle nuclear fuels [16]. The sol-gel template procedure for preparing fine nanostructured powders entails synthesis of the desired ceramic materials on the surface of surfactant polymer micelles. The resulting materials possess many advantages such as easy synthesis, tunable pores size, thick pore walls, high specific surface area, and good textural properties [4, 17].

In this work, surfactant templating sol-gel route for the synthesis of thorium dioxide using thorium nitrate and octyl phenol ethoxylate was described, and the sinterability of the produced  $\text{ThO}_2$  powders was investigated in comparison with commercial  $\text{ThO}_2$  powder.

According to the literatures, several types of sintering have been developed and it is reported that sintering at high temperatures in reducing atmosphere seems to be the most favored production route [1]. In this research, sinterability of sol-gel derived  $\text{ThO}_2$  powder in Ar and Ar-8%  $\text{H}_2$  atmosphere was studied.

## Materials and methods

### Materials

Nuclear grade thorium nitrate pentahydrate ( $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ) and thorium dioxide ( $\text{ThO}_2$ ) were purchased from BDH Merck. Concentrated ammonium hydroxide (25%  $\text{NH}_3$  in  $\text{H}_2\text{O}$ ), octyl phenol ethoxylate ( $\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$ ,  $n = 10$ ), and absolute ethanol (99.8 %) were bought from Sigma Aldrich.

### $\text{ThO}_2$ ceramic preparation pellet fabrication

In a round-bottom flask, 5mL octyl phenol ethoxylate,  $\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$  ( $n=10$ ), was dissolved in 50 mL absolute ethanol and stirred for 18 hours. Then in a beaker, 8.45 g thorium nitrate pentahydrate,

$\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ , was dissolved in 15 mL absolute ethanol. Then 2.25 mL ammonium hydroxide 25% was slowly added drop by drop to the beaker. With each drop of ammonium hydroxide, a white precipitate formed. This precipitate must be allowed to dissolve before the next drop of  $\text{NH}_4\text{OH}$  added. Then the contents of beaker transferred to the round-bottom flask and the mixture was stirred for three more hours. The solution was allowed to age in room temperature. The prepared gel dried at room temperature and finally was calcined at 723 K for one hour. Prepared sample was denoted as  $\text{ThO}_2\text{-S}$ .

### $\text{ThO}_2$ Ceramic Preparation Pellet Fabrication

The synthesized  $\text{ThO}_2$  and commercial powder samples were cold-pressed into cylindrical pellets of 11 mm diameter and about 5 mm height without binder and lubricant at compaction pressure of 300 MPa using a double action hydraulic press (Tajhiz Ceram-Iran), separately. The pellets were sintered under different sintering conditions at 1500 °C and two flowing Ar and Ar-8%  $\text{H}_2$  atmospheres. Table 2 describes sintering conditions of the prepared pellet samples and obtained density data.  $\text{ThO}_2\text{-C1}$  and  $\text{ThO}_2\text{-S1}$  were sintered at Ar atmosphere and  $\text{ThO}_2\text{-C2}$  and  $\text{ThO}_2\text{-S2}$  were sintered at Ar- $\text{H}_2$  atmosphere.

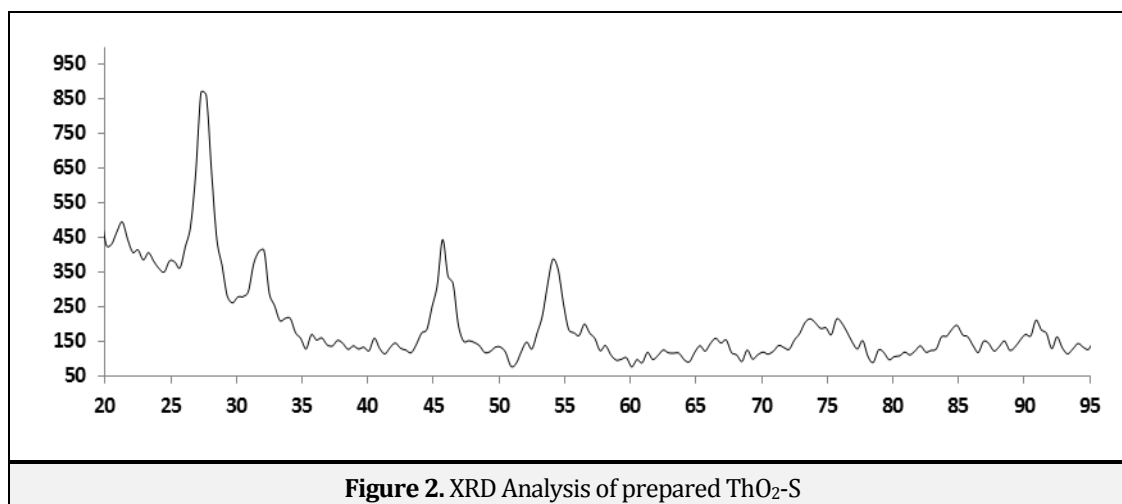
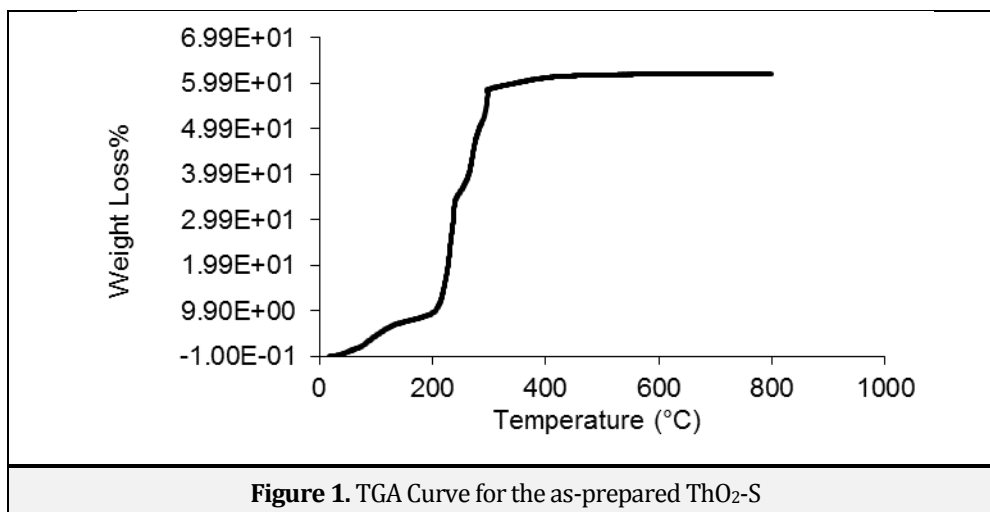
## Results and discussion

### Characterization of ThO<sub>2</sub> Powders

The TGA curve recorded for the dried gel of ThO<sub>2</sub>-S sample is depicted in Figure 1. According to TGA analysis in Fig.1, there are three weight loss stages. The first stage up to 200 °C corresponds to the evaporation of molecular water and hydroxide groups. The second stage from 200 to 350 °C is attributed to the release of the surfactant from the ThO<sub>2</sub>. Finally, the slight thermal effect at 350 to 450 °C confirms the crystallization of the amorphous

phase to the thorium dioxide.

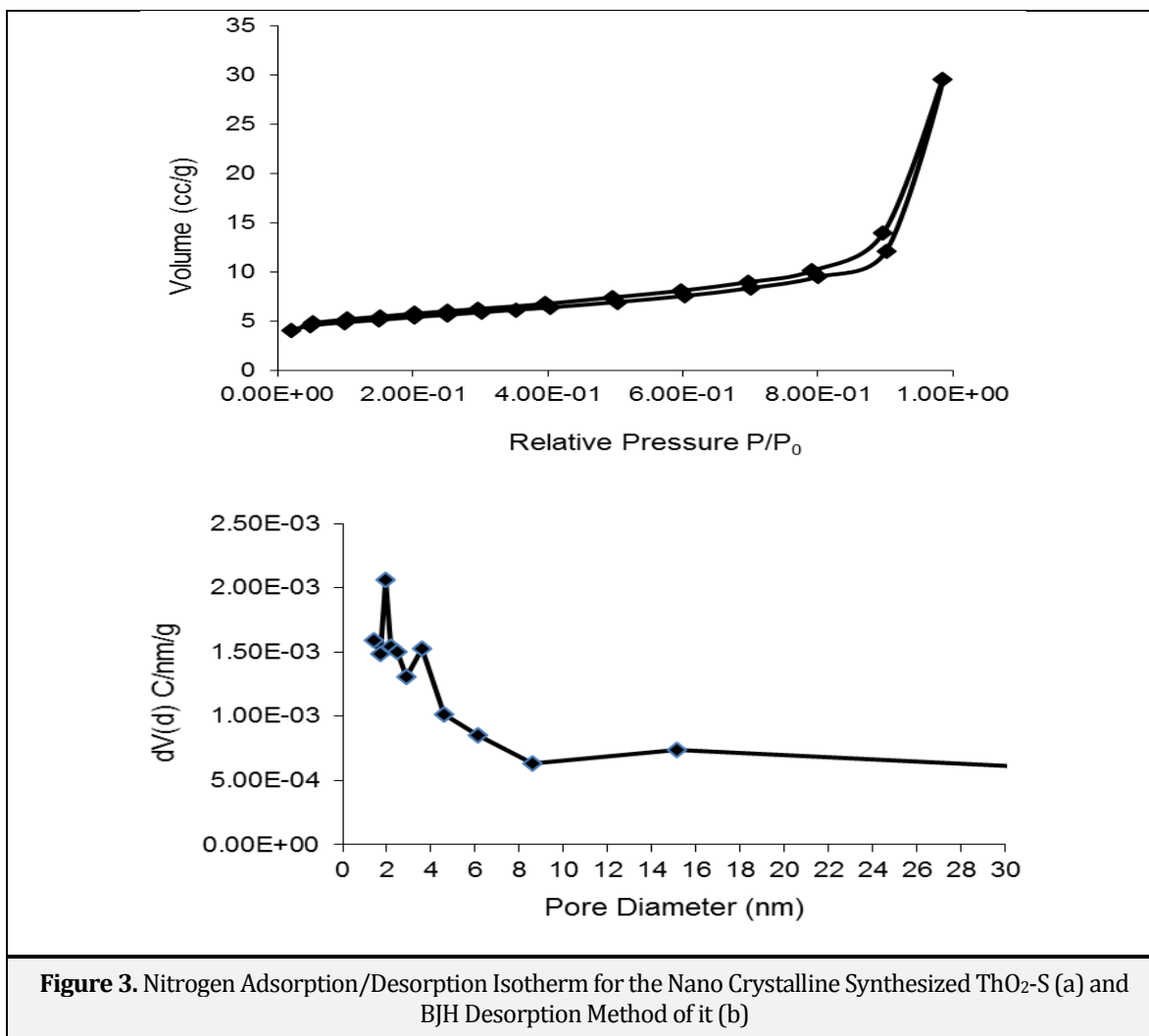
The crystalline structure of synthesized sample was investigated by XRD measurement. The XRD pattern obtained for ThO<sub>2</sub>-S sample is shown in Figure 2. The result confirms the formation of thorium dioxide crystals and the line broadening in the all XRD patterns indicated that the powders consisted of Nano crystallites [18]. According to Scherer's equation, the average crystallite sizes of pure ThO<sub>2</sub> sample is 15.1 nm.



The BET and BJH analyses were carried out for the prepared sample. The nitrogen adsorption/desorption isotherms as a function of relative pressure ( $P/P_0$ ) for the prepared powders was depicted in Figure 3. According to the results, isotherms are of type IV indicating the presence of mesopores within the synthesized materials [19,20]. According to the BJH analysis for the Nano crystalline  $\text{ThO}_2\text{-S}$  sample, the pore volume, and pore size of the powder were determined. The results are

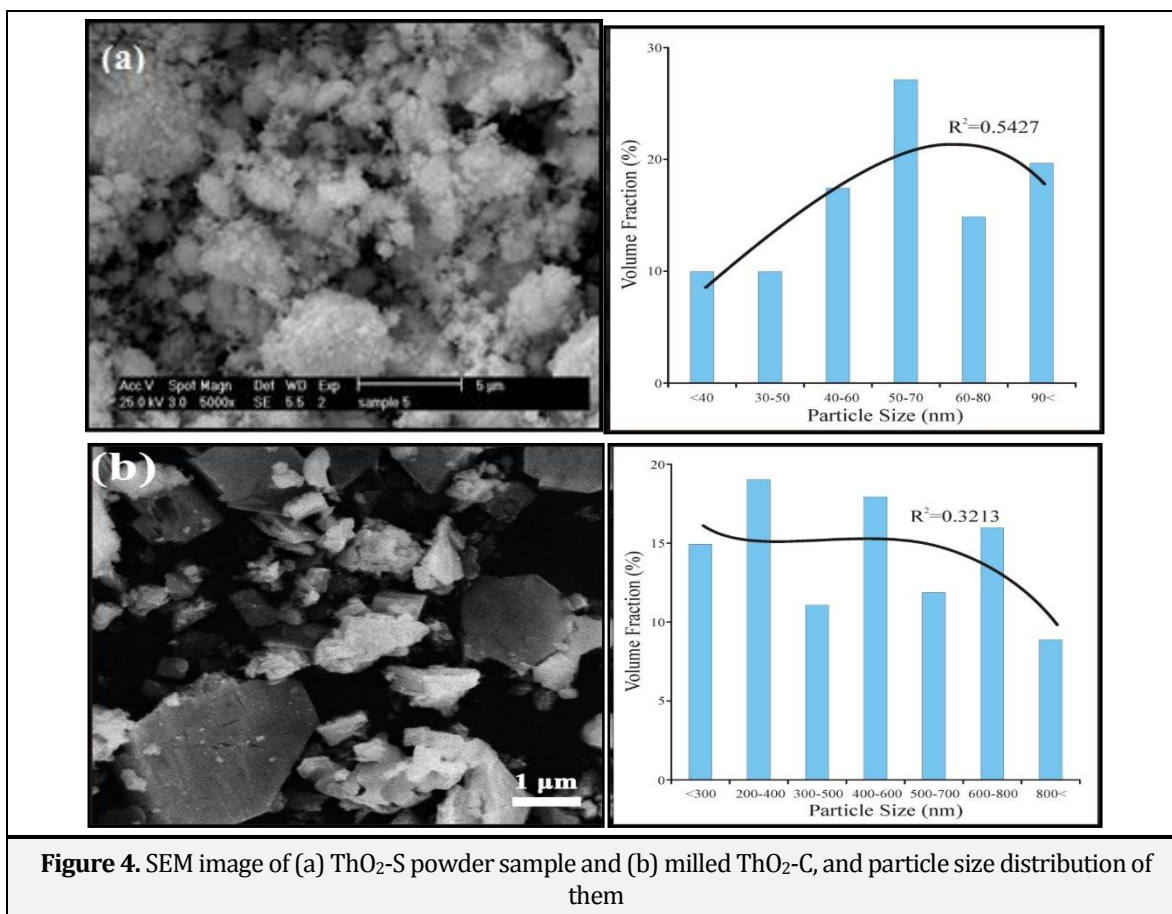
summarized in Table 1.

Figure 4 shows the SEM images of the  $\text{ThO}_2\text{-S}$  and the  $\text{ThO}_2\text{-C}$  powders and their average particle size distribution. These images illustrate a general view of morphology of the particles. The structural morphology showed that all the synthesized powder samples were spherical. The average particle size distribution was estimated by means of a microstructure measurement program and Minitab statistical software.



**Table 1.** Characteristics of the synthesized and commercial powder samples

	Crystalline size (nm) XRD Result	Surface area ( $\text{m}^2/\text{g}$ ) BET Result	Pore volume ( $\text{cm}^3/\text{g}$ ) BJH Result	Pore size (nm) BJH Result
$\text{ThO}_2\text{-S}$	15.1	31.23	0.09159	1.954
$\text{ThO}_2\text{-C}$	-	24.50	0.07672	1.368



### Pellets Characterization

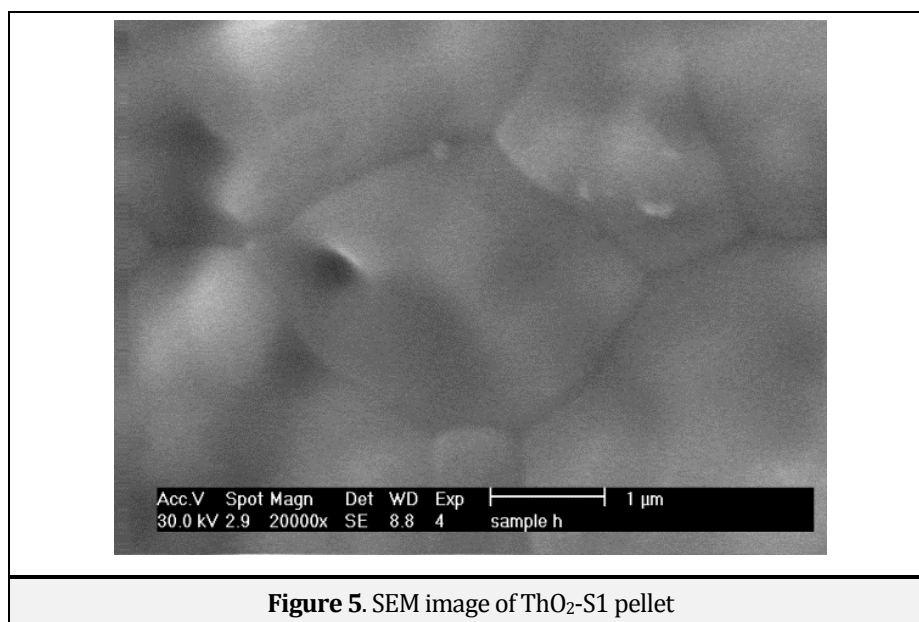
Figure 5 shows the SEM image of the pellet fabricated by  $\text{ThO}_2\text{-S}$  powder and sintered at Ar atmosphere ( $\text{ThO}_2\text{-S1}$ ). Comparison of Figure 5 and Figure 4a exhibits that, the sintering process result in grain growth, and particle size in  $\text{ThO}_2\text{-S1}$  pellet are larger than particle size of  $\text{ThO}_2\text{-S}$  powder. Green densities of pellets were

geometrically determined and densities of the sintered pellets were measured using Archimedes' method. Density of one sample was measured three times and the average was reported as the result (RSD,  $n=3$ ). The density calculation results are presented in Table 2. The average grain sizes of the sintered pellets were calculated using heyn intercept method [21]



the results are reported in Table 2. In Table 2, plette sample sintered at Ar atmosphere were

marked with 1, and samples sintered at Ar-8% H<sub>2</sub> atmosphere were marked with 2.



**Figure 5.** SEM image of ThO<sub>2</sub>-S1 pellet

**Table 2.** Average grain size, green and sintered pellet density of 4 pellet samples

	Average Grain Size nm	Green Pellet Density (% of the th.d.) ±RSD% (n=3)	Sintered Pellet Density (% of the th.d.) ±RSD% (n=3)
ThO <sub>2</sub> -C1	8136	57.1 ± 0.11	95.2 ± 0.12
ThO <sub>2</sub> -C2	8024	57.1 ± 0.12	95.1 ± 0.13
ThO <sub>2</sub> -S1	542	56.7 ± 0.13	97.5 ± 0.14
ThO <sub>2</sub> -S2	563	56.8 ± 0.13	97.4 ± 0.13

## Conclusion

In this research, ThO<sub>2</sub> was prepared utilizing one nonionic structure directing agents (octyl phenol ethoxylate) via the -sol gel route. Then, in order to investigate the sinterability and grain growth process of the powder, some pellet samples were consolidated using syntesized ThO<sub>2</sub> and ThO<sub>2</sub> commercial powder samples by the cold press and sinter technique. Comparison of data from samples sintered at 1500°C under the both of two different atmospheres

(Ar and Ar-8% H<sub>2</sub>), show that the atmosphere had no effect on density value of fabricated pellets. Furthermore, the green density of ThO<sub>2</sub>-S pellets is less than ThO<sub>2</sub>-C but the pellets which were fabricated from the ThO<sub>2</sub>-S have reached better sintered density than the pellets fabricated by ThO<sub>2</sub>-C. The wider particle size distribution of ThO<sub>2</sub>-C powder makes the better packing at green stage of the pellet. Moreover, the smaller size of ThO<sub>2</sub>-S and high surface area of this sample could facilitate the sintering



procedure result in better sintering density.

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