ZnS wurtzite ceramic fabrication by a simple and cost–effective pressureless sintering method: A microstructure development overview

Radenka Krsmanović Whiffen,[1] Elena Salernitano,[2] Selene Grilli,[2] Giuseppe Magnani,[2] Francesca Mazzanti,[2] Luciano Pilloni,[1] Amelia Montone[1]

[1]ENEA SSPT-PROMAS-MATPRO, Materials Technology Division, Casaccia Research Centre, Rome
[2]ENEA SSPT-PROMAS-TEMAF, Laboratory of Materials Technologies, Faenza (RA), Italy

Corresponding author: Elena Salernitano, ENEA TEMAF, Via Ravegnana 186, 48018 Faenza (RA), Italy.
Tel. +39.0546.678549.
E-mail: elena.salernitano@enea.it

Key words: ZnS; two step sintering; SEM; ceramics; density; microstructure; grain size.

SUMMARY

The Two-Step Sintering (TSS) process is a useful method to obtain sintered materials of high density and to limit the grain growth associated with the final stage of the sintering process. One of the main advantages of this method is the lowering of the sintering temperature. The development of bulk, dense and small grain size in the wurtzite phase of the ZnS ceramic was investigated by using a micron-sized ZnS powder as a precursor material. The microstructure and morphology of the TSS-fabricated ZnS ceramic pellets were observed by Scanning Electron Microscopy (SEM) and compared to those produced by the conventional sintering process. The ZnS ceramic produced using the TSS method at 1100°C showed comparable density and a much finer microstructure (five times smaller grain size) than the ZnS ceramic produced using conventional sintering at 1250°C. It was demonstrated that the TSS process is a pressureless, simple and cost-effective sintering method, able to deliver high density bulk, wurtzite phase ZnS ceramics with controlled grain size.

Received for publication: 23 June 2020. Accepted for publication: 7 July 2020.

microscopie 2020; 31:9203
doi:10.4081/microscopie.2020.9203

Introduction

Zinc Sulfide (ZnS) is an important wide band-gap II-VI semiconductor, with unique optical and electronic properties that have found numerous applications in optoelectronic, electroluminescent and photoelectric devices, in IR sensors, in biomedical labelling and in photocatalysis for hydrogen production (Wang *et al*., 2013). Zinc Sulfide has two structural forms: a room temperature, stable cubic phase (zinc blende or sphalerite, c-ZnS), that transforms to a metastable, hexagonal wurtzite phase at high temperatures (1020°C for bulk). However, it has been shown that in its nanocrystalline form, wurtzite ZnS is a stable material at room temperature (Wang *et al*., 2005). Moreover, it has been demonstrated several times that both phases can co-exist in the same ZnS sample (Liu *et al*., 2011; Lee *et al*., 2018).

Wurtzite-based materials have the advantages of being cheap, non-toxic and offering excellent opto-electrical properties. Due to their non-centrosymmetric nature, all wurtzite crystals have both piezoelectric and pyroelectric properties. The hexagonal wurtzite phase of ZnS was chosen as the topic of this study, due to its pyroelectric potential in harvesting wasted thermal energy. The development of dense ceramics by the Two-Step Sintering (TSS) fabrication process was investigated, using as a precursor material a micron-sized commercial powder of a mixture of ZnS cubic and hexagonal phases (80% hexagonal, 20% cubic).

The TSS was chosen since it is a pressureless, simple and cost-effective sintering method for obtaining very high density materials with controlled grain growth, operating at a lower temperature than the conventional sintering process. Another advantage of the TSS method is the ability to provide high density materials with reduced grain growth without any dopant or additive. It has been observed that a fine-grained microstructure enhances the mechanical, electrical, magnetic or piezoelectric properties of ceramics, widening their applications (Sutharsini *et al*., 2018; Kambale *et al*., 2019); similar advantages for the pyroelectric properties of a finer-grained ZnS wurtzite ceramic are expected. The TSS fabrication process is also an easily scalable process which can be used to develop bulk and dense ceramics. The TSS has been used for various materials with the main goal of avoiding grain growth in the final stage of sintering. Some applications of the two-step sintering method have focused on materials where high density and small grain size are required, e.g. the electrolytes of solid oxide fuel cells, as ceramics based on Y_2O_3 and CeO_2, alumina-zirconia ceramics, Ni-Cu-Zn Ferrite and ZnO (Lóh *et al*., 2016). Ceramic samples with a relative density higher than 97% of their theoretical density and a grain size at the sub-micrometer level have also been obtained in some cases (Pinto Ferreira *et al*., 2012).

In this paper, the sintering behaviour of the micron-size ZnS powder and the development of a bulk and dense ZnS ceramic by the conventional Single-Step Sintering (SSS) and TSS fabrication processes were investigated. To the best of our knowledge, this is the first time that a wurtzite ZnS ceramic has been prepared using the TSS method without any additive or binder. As the precursor material was a mixture of the cubic and hexagonal phases of ZnS, one of the goals of this study is to identify the right sintering conditions in order to obtain the pure hexagonal phase of ZnS in a bulk ceramic form. Scanning Electron Microscopy helped us to swiftly investigate the microstructure and morphology of both the precursor powder and the prepared ceramics, and also to study the sintering behaviour of the precursor powder. In the next stage of the NanoPyroMat project, the influence of the microstructure on the pyroelectric properties of the ZnS wurtzite ceramic samples will be explored.

Materials and Methods

A commercial micron-sized ZnS powder (a mixture of 20% cubic phase and 80% hexagonal phase) without any binder or sintering additive, was used as the starting powder. Discs with a diameter of 8 mm and a thickness of 4 mm were prepared by the uniaxial pressing of the powder at 100 MPa, followed by cold isostatic pressing (CIP) at 150 MPa. The green compacts were then embedded in a powder pack of the same ZnS powder and put in a graphite crucible. The thermal treatment was performed under a flowing nitrogen atmosphere using a graphite element furnace (Astro - Thermal technology - Model 1000-4560-FP20) in a temperature range from 900°C to 1250°C.

Two sintering processes were tested:

- the SSS process, consisting of heating the green compact up to the selected temperature (1250°C), with a dwell time of 1 h, followed by cooling it down to room temperature; the resulting ceramic was named the SSS sample.
- the TSS process, in which the ZnS disc (green compact) was heated up to a peak temperature (T_1=1150°C), then the temperature was reduced to a lower value (T_2=1100°C), and kept constant for 5 hours before cooling; the ceramic prepared in this way was named the TSS sample.

The microstructure of the ZnS powder and the sintered samples was characterized by X-ray powder diffraction using a SmartLab Rigaku powder diffractometer, equipped with a Cu Kα radiation source and a graphite monochromator in the diffracted beam, operated at 40 kV and 30 mA; small pieces of the ceramic samples were ground into powder prior to taking measurements. The morphology of the samples was investigated by scanning electron microscopy, and two SEM instruments were used: a LEO 438 VP and a LEO 1530 (both Zeiss). The LEO1530 is a hot cathode field emission SEM equipped with a high-resolution in-lens secondary electron detector, a conventional secondary electron detector, a Centaurus back Scattered detector and a XACT microanalysis unit (OXFORD) and it was used to provide high resolution images.

The density of the produced ceramic samples was calculated by measuring their dimensions (+/- 5 μm) and weight (+/- 0,1 mg) (geometrical density).

Results and Discussion

The microstructure of the commercial micron-sized ZnS powder (80% wurtzite, 20% sphalerite), used as the precursor material, is displayed in Figure 1a, and its XRD pattern is shown in Figure 1b. An agglomeration of mostly spherically shaped, smooth surface particles is shown, ranging between 100 and 300 nm in size.

Preliminary tests were performed, consisting of heating the ZnS green pellets up to a specific temperature in the range 900-1250°C, without a holding time. The effect of the applied temperature on the densification process is shown in Figure 1c; a maximum density of around 90% of theoretical density (T.D.) was achieved at the highest temperature of 1250°C. In the conventional SSS process, the grain growth is accelerated due to grain boundary migration and diffusion in the holding stage of sintering, whereas the rapid cooling before the second stage of TSS should limit the grain growth associated with the final stage of the sintering process (Sutharsini *et al*., 2018). For efficient TSS, it is generally necessary to achieve a sufficiently high relative density of the sample (70% or greater) after the T_1 step (Chen, 2000; Chen and Wang, 2000). Once this critical density is reached, a lower temperature, T_2, is used for the isothermal hold to achieve the final density (Pinto Ferreira *et al*., 2012). On the basis of this consideration and the experimental results reported in Figure 1c, 1150°C was the temperature chosen as T_1, while T_2 was set to 1100°C with a holding time of 5 h. The XRD patterns of the SSS (1250°C for 1 h, 93% TD) and the TSS ceramic samples are presented in Figure 1d. Both samples show the main diffraction peaks corresponding to the wurtzite (hexagonal) phase, in agreement with JCPDS card No. 36-1450. A small presence of a cubic ZnS structure (sphalerite, JCPDS card No. 05-0566) was revealed in the TSS sample, probably due to the gradual transformation of the cubic phase to the hexagonal phase (Kim *et al*., 1997). Given the XRD results, the relative density of the sintered samples was calculated using a theoretical density of the wurtzite ZnS phase of 4.087 g cm^{-3} (Kim *et al*., 1997).

The SEM images of the fractured surfaces of the SSS sample are presented in Figure 2a (1250°C, t=0) and Figure 2b (final sample, after sintering at 1250°C for t = 1 h). The SEM observations provide a clear insight into the microstructure changes, as the porosity decreases greatly after the sintering step; however, the final SSS sample still exhibits some residual porosity (Figure 2b). A detailed overview of the microstructure of the SSS sample, obtained by SEM-BSE, is provided in Figure 2 c,d. Here it is possible to observe the typical porosities along the triple grain joints (Figure 2c), while at higher magnification (Figure 2d) the presence of some higher atomic number material within the porosities and grain boundaries is shown. The porosity shown in Figure 2c was

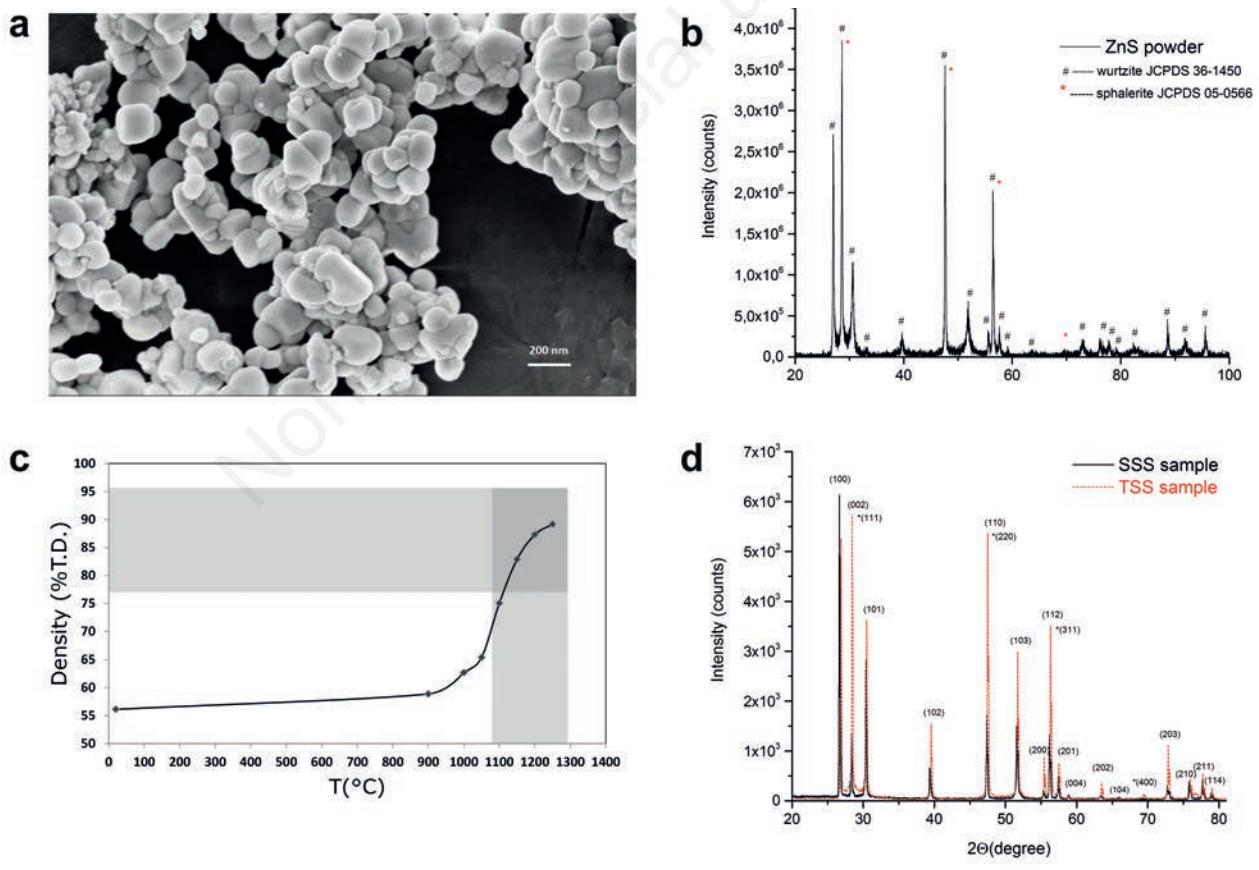

Figure 1. (a) FEG-SEM micrograph and (b) XRD of the ZnS powder; (c) diagram density of the ceramic samples vs applied temperature at holding time t=0; (d) XRD of both the SSS (black) and TSS (red) ceramic samples.

measured using the software ImageJ. The results show that the theoretical open porosity is in the order of 2% with a mean Feret diameter of about 4.3 µm.

Figure 2 e,f show the morphology of the fractured TSS sample (T_1=1150°C and T_2=1100°C). After the first heating stage at T_1 the grains are less than 3 µm in size, while after the second stage, following 5 h holding at T_2 , they grew up to a maximum of 5 µm. The residual porosity in this sample is only slightly greater than that observed for the SSS sample after sintering with an isothermal holding time of 1 h.

These results confirmed that the TSS process made it possible to obtain ceramics with density values comparable to the ceramic obtained via the SSS process, but at a reduced sintering temperature. Moreover, this process facilitates a significant reduction in the grain size, with the grains being up to five times smaller than those produced by the conventional SSS process.

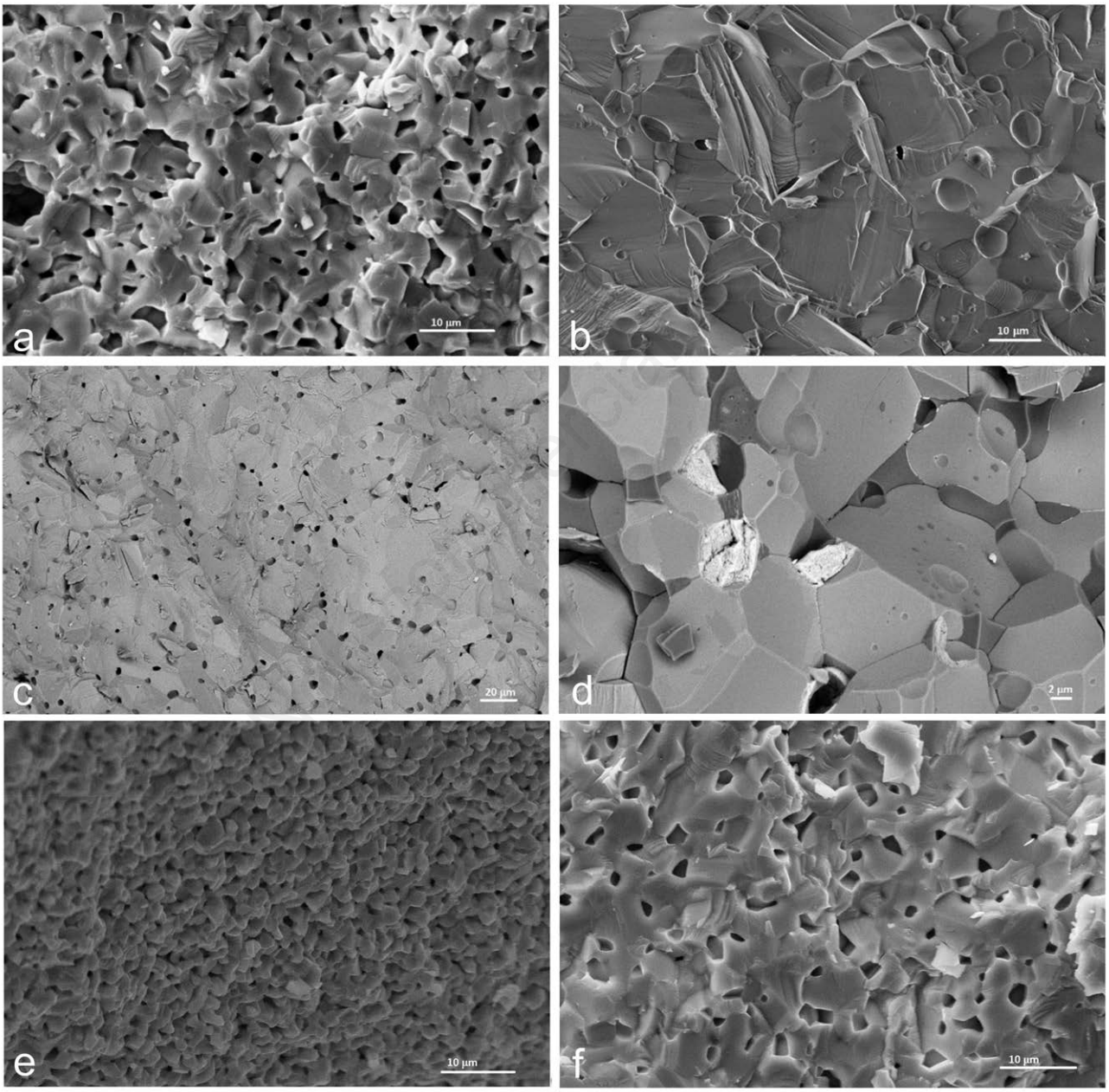

Figure 2. **Microstructure, observed by SEM on fractured sintered ZnS ceramics: SSS at 1250°C and t=0 (a) and t=1 h (b), low (c) and high (d) magnification of the SSS sample (BSE image) and TSS (T1=1150°C and T2=1100°C) at t=0 (e) and t=5 h (f).**

Conclusion

A ZnS commercial powder, a mixture of the wurtzite (80%) and sphalerite (20%) phases, was used as a precursor material. Using the conventional pressureless sintering method (SSS) at a sintering temperature of 1250°C and a holding time of 1 hour, the ZnS powder transformed into a highly dense (93% TD) wurtzite ZnS ceramic with a grain size of about 25 μm. The same precursor, when subjected to the pressureless Two Step Sintering process (TSS) at T_1=1150°C (t=0) and T_2=1100°C (t=5h), resulted in a ceramic of comparable density (approximately 90% T.D.), but with a grain size of approximately 5 μm. This result was a consequence of the lower working temperature and longer sintering time applied during the TSS process than that found in the SSS process.

The suitability of the two-step sintering process for the production of high density ZnS with a controlled grain size was thus demonstrated. A comparable density to the conventionally sintered ZnS ceramic was achieved, but with a much finer microstructure. Considering that obtained ZnS ceramic is a wurtzite-based material, whose pyroelectric properties have not yet been properly studied, we believe that the TSS method, although requiring further testing, could be an excellent tool to obtain fine grained wurtzite with a minimal presence or perhaps total, absence of sphalerite. Therefore, we plan to optimize the TSS process for ZnS wurtzite ceramic production and investigate in more detail the relationship between the microstructure and the pyroelectric response of the ceramic produced.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No.797951.

This project was also partially supported by the Piano triennale di realizzazione 2019-2021 della ricerca di sistema elettrico nazionale – Progetto 1.3 Materiali di frontiera per usi energetici (C.U.P. code: I34I19005780001).

References

Chen I. Grain boundary kinetics in oxide ceramics with the cubic fluorite crystal structure and its derivatives. Interface Sci 2000;8:147-56.

Chen I, Wang X. Sintering dense nanocrystalline ceramics without final-stage grain growth. Nature 2000;404:168-71.

Kambale KR, Mahajan A, Butee SP. Effect of grain size on the properties of ceramics. Met Powder Rep 2019;74:130-6.

Kim Y-D, Sonezaki K, Maeda H, Kato A. Sintering behaviour of monodispersed ZnS powders. J Mater Sci 1997; 32:5101-6.

Lee K-T, Choi B-H, Woo J-U, Kang J-S, Paik J-H, Chu B-U, et al. Microstructural and optical properties of the ZnS ceramics sintered by vacuum hot-pressing using hydrothermally synthesized ZnS powders. J Eur Ceram Soc 2018;38:4237-44.

Liu J, Guo Z, Wang, W, Huang, Q, Zhu K, Chen X. Heterogeneous ZnS hollow urchin-like hierarchical nanostructures and their structure-enhanced photocatalytic properties. Nanoscale 2011;4:1470-3.

Lóh NJ, Simão L, Faller CA, De Noni A, Montedo ORK. A review of two-step sintering for ceramics. Ceram Int 2016;42:12556-72.

Pinto Ferreira G, Silva Jr J, do Nascimento R, Umbelino U, Eduardo A. Two-step sintering applied to ceramics. In: A. Lakshmanan, editor. Sintering of ceramics - New emerging techniques. InTech Open: 2012; pp. 423-36.

Sutharsini U, Thanihaichelvan M, Singh R. Two-step sintering of ceramics. In: I. Shishkovsky, editor. Sintering of functional materials. InTech Open: 2018; pp. 3-21.

Wang Z, Daemen LL, Zhao Y, Zha CS, Downs RT, Wang X, et al. Morphology-tuned wurtzite-type ZnS nanobelts. Nature Mater 2005;4:922-7.

Wang X, Huang H, Liang B, Liu Z, Chen D, Shen G. ZnS nanostructures: Synthesis, properties, and applications. Crit Rev Solid State Mater Sci 2013; 38:57-90.