Near-net-shape processed ZnS ceramics by aqueous casting and pressureless sintering

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Abstract

In this paper, slip casted ZnS ceramics were pressurelessly sintered at 1000°C under flowing argon atmosphere. The application of cold isostatic pressing enhanced the microstructural homogeneity of the ZnS green body and therefore contributed to the overall densification progress. Highest relative density of 92% was achieved after sintering for 6 hr, accompanied by remarkable grain growth. Phase transition from sphalerite to wurtzite was found by the prolonged soaking time. The mechanisms for grain growth were analyzed.

Keywords: ZnS; slip casting; pressureless sintering; phase transition; sintering mechanism.

1. Introduction

Transparent ceramics have continuously attracted the attentions among material scientists and engineers [1-2]. In the family of transparent ceramics, zinc sulfide (ZnS)--a well-known band gap II-VI semiconductor--has widely been adopted in the long infrared wavelength transmission applications, such as IR windows and domes in the range of 8-12 μm . Besides, ZnS could also be used as phosphors, sensors and photocatalysts [3-5].

The existence of hexagonal phase can cause birefringence which decreases the optical transparency of ZnS. An effective approach to solve this problem is the application of low temperature processing techniques. Methods of chemical vapor deposition (CVD), hot pressing, and spark plasma sintering (SPS) have been successfully employed to prepare bulk polycrystalline ZnS ceramics [5-8]. However, several drawbacks have been found relating to these methods: high cost as well as dimensional restriction of products. The advantages of large-scale fabrication accompanied by near-net-shape processing as well as microstructural homogeneity are preferred for practical usages. Advanced wet forming methods can address this problem well [9-12]. Slip casting is a simple and facile technique to fabricate ceramic components into pre-designed shapes. In the past few decades, slip casting has been adopted into various ceramic systems, such as Al_2O_3 , SiC, Si_3N_4 and ZrB_2 , et al [13-16]. Up till now, very few studies have been focused on the slip casting of ZnS, which is quite promising due to its advantages as described above. Clothier et al and Ravichandran et al reported slip casting of ZnS ceramics in their patents by

respectively, yet the information provided was not sufficient, e.g. processing details, dispersants, etc [17, 18].

In the current study, research on aqueous slip casting of ZnS ceramics was performed, using nano-sized ZnS powder synthesized in a laboratory-scale according to our previous study [4]. Organic dispersant of an alternative copolymer of isobutylene and maleic anhydride, with its commercial name as ISOBAM [19], was introduced for the stable dispersion of ZnS nano powder. Cold isostatic pressing (CIP), followed by pressureless sintering were performed before obtaining final ceramic products. Microstructure evolution upon sintering was revealed as well. Our current study provided a feasible low-cost technique for the fabrication of ZnS ceramics by slip casting and pressureless sintering.

2. Experimental procedure

Nano-sized ZnS powder was synthesized by wet chemistry method. Detailed information can be referred in our earlier report [4]. A water solvable copolymer of isobutylene and maleic anhydride, with a commercial name of ISOBAM (Kuraray Co., Ltd.) was used as the dispersing agent. ZnS powder, ISOBAM, together with de-ionized water, was homogenized by constant stirring of 300 rpm for 12 hr: the volume ratio of solid ZnS and liquid water was 1:4, and the added dispersant content was 0.8 wt% of the ZnS powder. Then the stable slurry was degassed in vacuum before casting into a gypsum mould. The green bodies experienced complete drying in oven before transferring into CIP machine. The parameters for CIP procedure were:

200 MPa with a dwelling time of 3 min. Pressureless sintering was carried out after CIP: the ZnS samples were heated in a tube furnace under flowing argon atmosphere, with a firing temperature of 1000°C. This temperature was chosen for preventing phase transition effectively. The heating rate was 3°C·min⁻¹.

Bulk density was measured using the Archimedes' Principle method. The relative density was calculated by Archimedes' density over theoretical density (4.1 g cm⁻³). The phase identification was determined by X-ray diffraction (XRD) data using a Bruker D2 Phaser diffractometer (Bruker-AXS, Madison, WI). Microstructure observation was performed on an FEI Quanta 200 FESEM (Hillsboro, OR).

3. Results and discussion

The self-synthesized ZnS nano powder was 300-500 nm in particle size approximately. Besides, its spherical morphology is favored for the flow behavior [4]. After casting, the green body experienced drying first before further CIP to homogenize the microstructures. Slight relative density increase from 44% to 47% was found after CIP, compared with un-CIPed counterpart. Yet just as shown in Fig. 1, more attention should be paid to the microstructural homogeneity, which was critical for achieving subsequent densification [20].

The green body was near-net-shape formed in-situ after complete drying. The heating schedule for the dried green body was 3°C min⁻¹ till 1000°C without external pressure. The reason that heating was conducted at such a slow rate is based on the consideration of de-binding without the formation of unwanted excessive porosity.

1 The TG/DTA curves are shown in Fig. 2. The mass decreased continuously, first
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3 rapidly and then slowly, until approaching the peak temperature. Due to the presence
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5 of stabilizing polymer ISOBAM, the completely-dried green body experienced further
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7 mass decrease upon temperature increment. The mass decrease percentage was around
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9 ~0.9 wt%, which was in good accordance with the added ISOBAM content.
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14 The relative density as a function of soaking time was plotted and displayed in Fig.
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17 3. Initially, the relative density of CIPed green body was 47%. After firing, the value
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19 increased rapidly. The density increased steadily with the increase of soaking time
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21 until 6 hr, and then decreased by the prolonged holding time. A highest relative
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23 density (92%) was found in ZnS samples sintered by 6 hr. The relative density
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25 decreased afterwards, down to merely 72% corresponding to the sample soaked for 12
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27 hr. This rapid density decrease was assumed to be strong decomposition of ZnS
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29 ceramics due to excessive sintering: A piece of evidence showed that the sample was
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31 broken into several parts with hollow microstructures. During the densification
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33 progress, the ceramic particles underwent notable neck formation and therefore the
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35 inter-particle distance was significantly reduced by the elapsed time, displaying
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37 increased density and enhanced sinterability. This sintering characterize was preferred,
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39 as along as the decomposition of ZnS ceramics was suppressed.
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50 The XRD curves of the ZnS ceramics before and after sintering are shown in Fig. 4.
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53 The ZnS nano powder was generally in cubic phase (sphalerite) [4]. The current slip
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55 casting followed by CIP processing can hardly influence phase transformation but
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57 high temperature firing rather does. The sphalerite phase was beneficial for achieving
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1 transparency, due to its advantageously isotropic properties [21]. Cubic ZnS was
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3 replaced by hexagonal phase upon a high temperature soaking. Therefore from our
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5 result it is clear that the intrinsic nature of unpreventable high temperature phase
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7 transition need to make a balance with the material density.
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11 The microstructures of sintered bulks are displayed in Fig. 5. It can be clearly seen
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13 that neck formation was increasingly obvious by the steady increase of soaking time,
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15 accompanied by gradual pore elimination. Considering the aspects of pore-boundary
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17 interaction and the ‘pore coordination number’ theory [22]: the pore coordination
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19 number (N) of initial large pores were basically less than the critical pore coordination
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21 number (N_c), meaning that they had a tendency to shrink and therefore porosity
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23 decrease would be expected. Meanwhile, in view of average grain size: it was 4.1 μm
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25 for the sample sintered by 6 hr, augmenting 64% as compared with that sintered
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27 merely by 1 hr. On the basis of classic sintering theory, the development of grain size
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29 was found to have a strong relationship of direct proportion to sintering time ($G^m \propto t$)
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31 [22]. The initial ZnS particle was in nano-size (400 nm) after the CIP process. Upon
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33 firing at 1000°C, distinctive grain growth was detected, in which the grain size
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35 developed into micron-scale. The soaking time and relative density as a function of
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37 average grain size was plotted and revealed in Fig. 6. Both curves followed the same
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39 regularity (which could be explained by previous analysis): the average grain size
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41 increased by the increase of soaking time and relative density. Besides, the exponent
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43 m in the exponential relationship that mentioned above was calculated to be 3.7 after
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45 fitting. This value falls between 3 and 4, indicating the sintering process was driven
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1 by the joint-effects of volume diffusion and evaporation-condensation mechanisms
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8 **4. Conclusions**

10 In this paper, advanced forming techniques of slip casting in combination with cold
11 isostatic pressing were applied. Pressureless sintering was preformed afterwards, in
12 order to fulfill the task of densification. The ZnS samples that sintered at 1000°C for 6
13 hr exhibited a highest relative density of 92%, and an average grain size of 4.1 μm .
14 With the prolonged dwelling time up till 6 hr, gradual grain growth occurred and
15 pores were wiped off the ceramic body step by step. Further increase in soaking time
16 to 12 hr would result in rapid decrease in material density. The results demonstrated
17 that sintering was driven by the combined effects of volume diffusion and
18 evaporation-condensation mechanisms. Differing from traditional fabrication methods,
19 our current study provided a feasible and low-cost tactic to prepare ZnS ceramics.
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Figure captions

Figure 1. SEM figures of as-casted ZnS green body: (a) before CIP, and (b) after CIP.

Figure 2. TG/DTA curves of the as-casted and dried green body.

Figure 3. The relative density of sintered ZnS ceramics as a function of dwelling time.

Figure 4. The XRD curves of the ZnS ceramics before and after sintering.

Figure 5. SEM morphology of sintered ZnS ceramics at different sintering time, soaking for (a) 1 hr, (b) 2 hr, (c) 3 hr, (d) 6 hr and (e) 12 hr by respectively.

Figure 6. Soaking time and relative density as a function of average grain size at the temperature of 1000°C.

Figure 1 (a)

Figure 1 (b)

Figure 2

Figure 3

Figure 4

Figure 5(a)

Figure 5(b)

Figure 5(c)

Figure 5(d)

Figure 5(e)

Figure 6