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Original Article

Microstructural and optical properties of the ZnS ceramics sintered by vacuum hot-pressing using hydrothermally synthesized ZnS powders

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ABSTRACT

ZnS nanopowders annealed at low temperatures (≤550 °C) have a pure cubic structure, while a small amount of hexagonal phase formed in specimens annealed at temperatures ≥700 °C. The particle sizes of the ZnS nanopowders increased with the annealing temperature. ZnS ceramics that were sintered using ZnS nanopowders annealed at low temperatures (≤550 °C) exhibited low transmittance, because of their porous microstructure. ZnS ceramics that were synthesized using ZnS powders annealed at high temperatures (≥800 °C) containing large agglomerated particles, also exhibited low transmittance, due to the presence of a liquid phase. A carbonate absorption band was found from the ZnS ceramics with small grains, because carbon ions diffused from the graphite mold into the ZnS ceramics during sintering, probably through the grain boundaries, and formed carbonates. A ZnS ceramic that was sintered at 1020 °C using the nanopowders annealed at 750 °C exhibited dense microstructure, with a large transmittance, 68%, in the wavelength range 6.0–12 μm.

1. Introduction

Zinc sulfide (ZnS) is an important wide band gap II–VI semiconductor that has been widely investigated for application to optoelectronic, photoelectric, and luminescent devices [1–4]. Moreover, ZnS has high transparency at the infrared wavelengths, and thus is a good candidate material for infrared windows and missile domes in defense applications in the wavelength region 8–12 μm [5–7]. ZnS has a cubic sphalerite structure at low temperature, and it changes to hexagonal wurtzite structure at 1020 °C [8,9]. It has been reported that the presence of the hexagonal wurtzite phase reduced the infrared transmittance of ZnS due to the birefringence of the hexagonal structure, and the scattering caused by the refractive index difference between the hexagonal and cubic matrix phases [10]. In general, germanium single crystal has been mainly used for infrared optical devices, but it is rare, and very expensive [11,12]. In order to replace the germanium single crystal, chalcogenide glasses have been investigated, but the mechanical properties of chalcogenide glass are weak, despite their promising transmittance properties [13]. ZnS ceramics have been investigated for use as infrared optical devices, because of their good optical and mechanical properties [14,15].

Hot pressing has been used to produce infrared-transparent ZnS ceramics, but the results were unsatisfactory [16]. The chemical vapor deposition (CVD) method was applied to synthesize polycrystalline ZnS, which showed good optical transparency. Moreover, a large number of polycrystalline ZnS window plates are commercially produced using CVD [17,18]. However, CVD is expensive and requires long processing times. Furthermore, the mechanical properties of ZnS produced by CVD are too low to be used in harsh conditions [10,15]. Therefore, vacuum hot-pressing (VHP) has been used to produce transparent ZnS ceramics to overcome the problems caused by the CVD method, and the ZnS ceramics produced by VHP have exhibited promising characteristics [19,20]. In addition, the spark plasma sintering (SPS) method has also been used to synthesize ZnS ceramics at low temperature [6,10,21–23]. According to previous works, the microstructure and optical properties of ZnS ceramics produced by the VHP or SPS methods are considerably influenced by the purity and size of the ZnS nanopowders [10,15]. ZnS powders were therefore specially produced by various methods, such as colloidal processing and wet chemical process methods, for use in the synthesis of ZnS ceramics with good optical properties [14,17].

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Moreover, ZnS powders have been annealed under various conditions, to remove defects, and to control their particle sizes [6,17].

In present work, ZnS nanopowders were synthesized via a hydrothermal process, and they were annealed at various temperatures to control particle size and remove defects. Moreover, the ZnS ceramics were sintered by the VHP method using the hydrothermally-synthesized ZnS nanopowders for the first time, and the effects of the size and structure of the ZnS nanopowders on the structural and optical properties of the ZnS ceramics have been systematically investigated. The ZnS ceramics synthesized in this work showed high transmittance in the infrared region and can thus be used in infrared optical devices.

2. Experimental procedure

ZnS nanopowders were synthesized by a hydrothermal method using $ZnSO_4{\cdot}7H_2O$ (≥ 99.5%, Aladdin, China) and $Na_2S{\cdot}9H_2O$ (≥99.99%, Aladdin, China) powders as starting materials. Water was used as solvent. The $ZnSO_4{\cdot}7H_2O$ powders were added to the water, and the $Na_2S{\cdot}9H_2O$ powders were then added to the mixed solution, to form ZnS nanopowders with a S/Zn ratio of 1.3. The mixed solution was stirred for 1 h, placed in a Teflon-lined vessel that was filled to 40% capacity, and left in an oven at 220 °C for 12 h. The detailed conditions for the hydrothermal process were reported previously [24]. The hydrothermally synthesized ZnS nanopowders were annealed at various temperatures (550 °C–850 °C) under a vacuum condition. The annealed ZnS powders were sintered by VHP at various temperatures ranging between 950 °C and 1040 °C under a vacuum level of 10^{-3} mtorr. The heating rate was approximately 10 °C/min, and 20 MPa pressure was applied to the specimens at the sintering temperature. A graphite mold of 16 mm in diameter was used for the sintering of the ZnS ceramics.

The densities of the ZnS ceramics were measured using the Archimedes method. X-ray diffraction (XRD; Rigaku D/Max-RC, Tokyo, Japan) with CuKα radiation was used to determine the crystal structure of the specimens. The particle size of the ZnS nanopowders and microstructure of the ZnS ceramics were investigated using scanning electron microscopy (SEM; Hitachi S-4800, Osaka, Japan). Thermogravimetric and differential thermal analysis (TG/DTA) were performed on ZnS powders in air using SDT Q-600 (TA Instruments, New Castle DE, USA). The specific surface area of the ZnS nanopowders was determined by the Brunauer-Emmett-Teller (BET) single point method using ASAP2020: Micromeritics (Tristar, USA). Fourier Transform Infrared (FT-IR) spectra of ZnS nanopowders were obtained by FT-IR spectrometry (FT-IR, iS 10; Thermo Fisher Scientific, Massachusetts, USA) in the spectral range 600–4000cm^{-1}, and the same equipment was used to obtain the Infrared transmission spectra of ZnS ceramics in the wavelength range 3.0–16.0 μm.

3. Results and discussion

The XRD patterns of the ZnS nanopowders annealed at various temperatures under vacuum condition are shown in Fig. 1(a)–(f). All the specimens show the pure ZnS phase without any secondary phase, indicating that the ZnS phase was well formed in these specimens, and it is stable without evaporation, even at high temperature of 850 °C under vacuum. The ZnS nanopowders without annealing or annealed at 550 °C have pure cubic sphalerite structure. However, reflections for the hexagonal wurtzite structure, indicated by asterisks in Fig. 1, were observed from the specimen annealed at 700 °C, and their intensities increased as annealing temperature increased; thus, the ZnS nanopowders annealed at 850 °C are considered to have a large amount of hexagonal wurtzite phase (see Fig. 1(f)), despite the fact that the cubic-hexagonal phase transition temperature is 1020 °C. The sizes of the ZnS nanoparticles used in this work were very small, approximately 130 nm. Therefore, they have high surface energies, resulting in high reactivity between the particles, which induced the formation of the wurtzite phase at temperatures lower than the transition temperature.

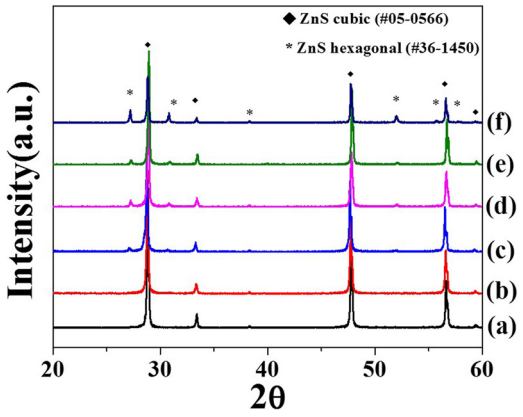

Fig. 1. XRD patterns of the ZnS nanopowders annealed at various temperatures: (a) RT, (b) 550 °C, (c) 700 °C, (d) 750 °C, (e) 800 °C, and (f) 850 °C.

Formation of the wurtzite phase at temperatures lower than the transition temperature (1020°C) was also observed in other ZnS ceramics synthesized using ZnS nanopowders [7,17].

Fig. 2(a)–(f) exhibit the SEM images of the ZnS nanopowders annealed at various temperatures. The average size of the ZnS nanopowders without annealing is approximately 0.13 μm (see Fig. 2(a)), and it increased slightly to 0.22 μm for ZnS nanopowders annealed at 550 °C, as shown in Fig. 2(b); interaction between ZnS nanopowders did not occur for these ZnS nanopowders. For the ZnS nanopowders annealed at 700 °C, some of the particles interacted with each other to form large particles, as indicated by arrows in Fig. 2(c); the average particle size is approximately 0.44 μm. For the ZnS powders annealed at 750 °C, most of the ZnS nanopowders interacted with each other, forming slightly larger particles with an average particle size of 0.52 μm (see Fig. 2(d)). Finally, for the ZnS nanopowders annealed at high temperatures (≥ 800 °C), agglomeration occurred between the ZnS nanopowders, resulting in the development of large particles, as shown in Figs. 2(e) and (f). The size of the nanoparticles increased with the annealing temperature through their agglomeration; similar results have also been observed for various different nanoparticles [25]. Figure S1 of the Supplementary Material 1 shows the variation of the average particle size. The surface area of the ZnS nanopowders was also measured, and it decreased with the increase in the annealing temperature (see Fig. S1 of the Supplementary Material 1). The decrease in the surface area with the increase in the annealing temperature can be explained by the increase in the particle size.

The results of FTIR analysis conducted on ZnS nanopowders annealed at various temperatures are exhibited in Fig. 3(a)–(f). The hydrothermally synthesized ZnS nanopowders without annealing exhibited several absorption peaks between 600 cm^{-1} and 4000 cm^{-1}: a broad absorption peak at 3400 cm^{-1} corresponds to the O—H stretching vibration, an absorption band at 1640 cm^{-1} is assigned to the H—O—H bending mode, while the absorption peaks at 1416 cm^{-1} and 1130 cm^{-1} can be assigned to the S—O vibrational bands, and the peak in the region 600–900 cm^{-1} to Zn—O vibrations [14,26]. The intensities of these absorption peaks decreased with the increase in the annealing temperature, but a small number of absorption peaks were still observed for the ZnS powders annealed at high temperatures (≥ 750 °C). According to previous work, residual water and oxide related defects, including Zn—O and S—O, were also observed in the ZnS nanopowders produced by other methods, and these defects were reported to assist the formation of carbonates in ZnS ceramics [14]. In order to eliminate the Zn—O and S—O defects, it is necessary to remove the oxygen ions from the ZnS nanopowders [14,15]. Most of the oxygen ions in the ZnS nanopowders evaporated during the annealing at high temperatures under vacuum. Therefore, the intensities of the Zn—O and S—O bands decreased after the annealing at high temperatures.