Effects of Heat Treatment of ZnS Nanoparticles Prepared by Hydrothermal Synthesis on Microstructure and Optical Properties in Spark Plasma Sintering (SPS)

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ABSTRACT

In this study we have investigated the effects of heat treatment of ZnS nanoparticles prepared by hydrothermal synthesis and commercial CVD method for comparison on microstructure and optical properties of spark plasma sintered (SPS) ZnS. The heat treatments of ZnS nanoparticles were carried out at 550℃ for 10 min. in a vacuum. According to heat treatment, the reactivity of ZnS nanoparticle surface decreased and pyrolysis phenomenon appeared, which were tentatively considered to affect the infrared transmittance of SPS sintered body. Also wurtzite phase may causes birefringence due to the optical anisotropy began to be produced in more than 950℃. Good optical properties of sintered ZnS were shown in 950℃ by SPS. When sintering with SPS method, it could be deteriorated in the optical properties by light scattering caused by the refractive index difference among ZnS, impurities (especially carbon originated from the graphite mold and punch), defects, and pores.

Keywords: ZnS, Hydrothermal Synthesis, Spark Plasma Sintering, Microstructure, Optical Property

1 INTRODUCTION

Zinc sulfide (ZnS) is one of the most widely used infrared transmitting window and lens materials for systems operating in the long wave range (8~12 μm) [1]. ZnS nanoparticles have been intensively studied because of their unique electrical and optical properties and potential applications (optical sensor, solid state solar window layers, photoconductors, phosphors, and catalysts) [1]. Therefore various synthetic methods to prepare ZnS nanocrystals in order to obtain desired physical and chemical properties have been developed such as sol-gel, electrochemical deposition, sonochemical, solvothermal, hydrothermal technique and so on [2]. Chemical-vapor-deposited ZnS (CVD-ZnS) has less optical absorption from impurities and can be made in larger sizes with greater homogeneity than hot-pressing (HP) or spark plasma sintering (SPS) of ZnS [3]. There have been many attempts to produce ZnS directly with more or less success for reducing the cost. Since ZnS nanoparticles are prepared by various synthesis methods, the final sintering properties are different. In addition, the optical properties of the sintered body vary depending on the heat treatment of the raw powders. In this study we have investigated the effects of heat treatment of ZnS nanoparticles prepared by hydrothermal synthesis and commercial CVD method for comparison on microstructure and optical properties of spark plasma sintered (SPS) ZnS. To observe the change of crystal phases, morphologies and optical characteristics of heat-treated nanoparticles was conducted using XRD analysis, FE-SEM, and FT-IR spectroscopy.

2 EXPERIMENTAL

Reagent grade of $ZnSO_4 \cdot 7H_2O$ (≥99.0%, Sigma-Aldrich, USA) and $Na_2S \cdot 9H_2O$ (≥99.99% Sigma-Aldrich, USA) were used as the precursors in the hydrothermal synthesis of the ZnS. A molar ratio of $ZnSO_4 \cdot 7H_2O$ vs. $Na_2S \cdot 9H_2O$ was 1:1.2. First of all, the pre-mixed water solution of $Na_2S \cdot 9H_2O$ was added to the mixed solution of $ZnSO_4 \cdot 7H_2O$ stirring at 85℃ on a hot-plate. This mixture was stirred for 1 h and placed in a Teflon-lined vessel (500 cc) that was filled to 80% and heated in an oven at 180℃ for 70 h durations. The products were then filtered and washed with distilled water, and dried at 100℃ for 20 h. In addition, the hydrothermal synthesized ZnS and a commercial ZnS powder (purity of 99.999%) were heat-treated at 400℃ to 550℃ for 2h in vacuum (~10^{-3} torr). Sintering was conducted using SPS (spark plasma sintering; WT4000A, Weltech, Korea) method with condition of 50 MPa, ~10^{-3} torr in vacuum, at 900~1000℃ for 10 minite with heating rate of 100 ℃/min. using graphite mold and punch (10 mmϕ). The structural properties of the powders and SPSed specimens were examined via X-ray diffraction (XRD, PANalytical, X'pert pro, Netherland). Furthermore, the microstructure of the nanoparticles were examined by using FE-SEM (LSM-6700F, JEOL, Japan). The optical transmittance of SPSed ZnS speciments were conducted with FT-IR (4100, Jasco, Japan) range of 2~20 μm.

3 RESULTS AND DISCUSSION

3.1 Heat-treatment of Hydrothermal Sysnthesized ZnS Powder

Figure 1 shows the pparent colors of hydrothermal synthesized ZnS powders with temperature to 550℃ in vacuum. Non-heat treated nanoparticles appears white color, however heat-treated powders changed the color from gray (400℃) to light yellow (550℃). It is considered that the color changes to light yellow as the heat treatment temperature increases due to thermal decomposition of ZnS.

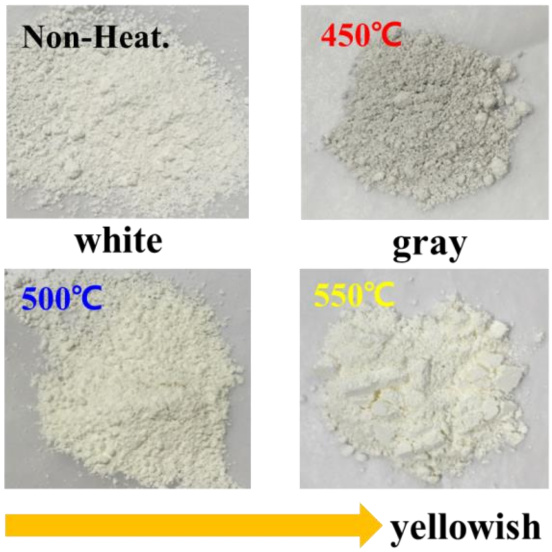
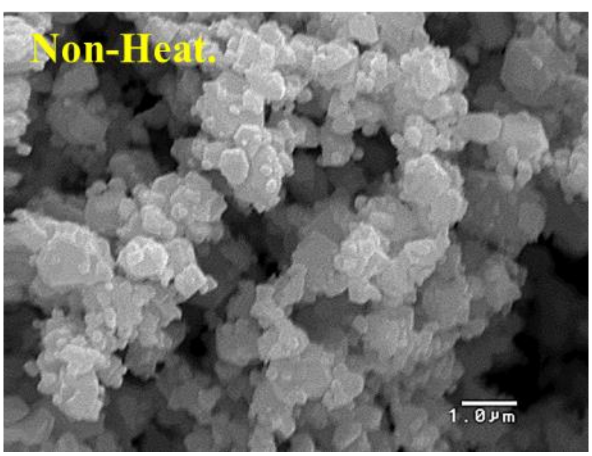


Figure 1: Apparent colors of hydrothermal synthesized ZnS powders with temperature to 550℃ in vacuum.

Figure 2 shows Microstructures of as-hydrothermal synthesized ZnS powders and heat-treated powders at 550℃ for 2h in vacuum [4]. It can be seen that the shape of the powder changes to polygonal shape through the heat treatment. This means that the particles are more stabilized by heat treatment because it does not change XRD patterns as shown in Figure 3.



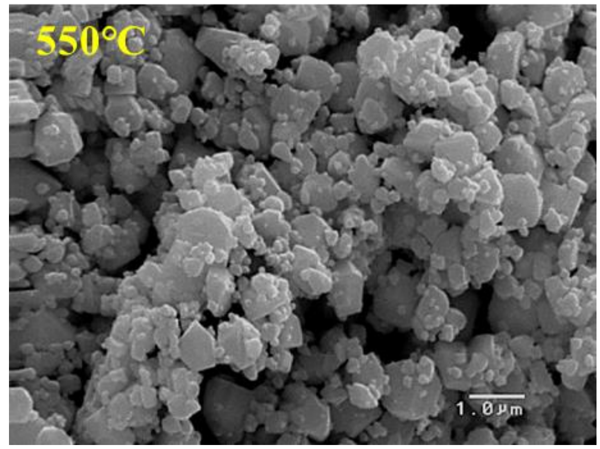


Figure 2: Microstructures of hydrothermal synthesized ZnS powders with heat-treatment at 550℃ for 2h in vacuum.

Figure 3 shows XRD patterns of heat-treated ZnS powders for several temperatures in vacuum. There are no change of crystal structure with cubic.

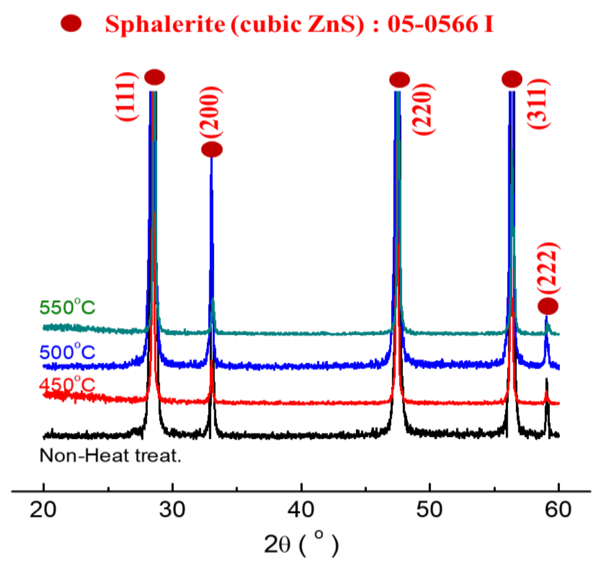


Figure 3: XRD patterns of heat-treated ZnS powders for several temperatures in vacuum.

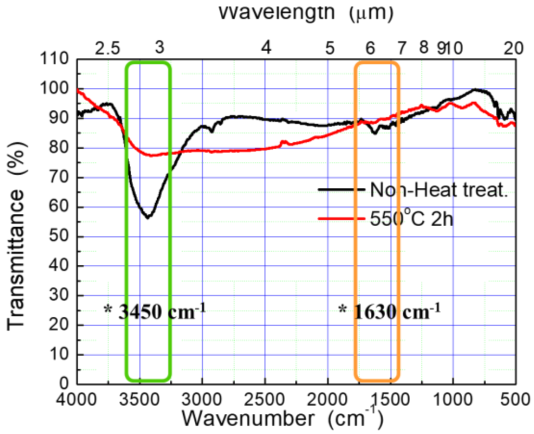


Figure 4: Fourier transform infrared analysis of heat-treated ZnS powders in vacuum.

Figure 4 shows Fourier transform infrared analysis of heat-treated ZnS powders in vacuum. The band at 3450 cm-1 indicates O-H stretching vibration whereas the band at 1630 cm-1 is assingned to the H-O-H bending mode. It showed the presence of oxygen in powders and its removal after heat-treatment at 550℃ 2h.

Therefore, it is thought that the heat treatment of the synthesized ZnS powders removes impurities remaining during synthesis but plays a role of stabilizing the crystal structure without changing it. It is believed that this can provide an effect that does not react with carbon that can be introduced from the graphite mold during sintering.

3.2 Sintering and FT-IR Properties of Commercial ZnS Powder

As previously mentioned, it was found that when the powder prepared by hydrothermal synthesis was heat-treated at 550℃ in vacuum, impurity removal and powder crystal structure stability were secured. Therefore, in this study, SPS study on commercial ZnS powders was conducted first.

Figure 5 shows Photo of the inside of the furnace taken during sintering (SPS) with graphite mold.

Figure 6 shows Microstructure of commercial ZnS powder (purity 99.999%) SPSed at (a) 900℃ and (b) 950℃ for 10 minite in vacuum. At 900℃, ZnS grain size is about 2 μm, but at 950℃ it is grown at 20 μm or more.

Figure 7 shows the optical transmittance of SPSed ZnS speciments for non heat-treated commercial powder using FT-IR for various sintering temperature for 10 minite [3]. Various impurities and bonding in SPSed ZnS are identified as shown in the figure 7 such as O-H stretching vibration, S-H, Zn-H or H-O-H bending, Carbonate or S-O, C-S, and S-O and so on. Inset figure of XRD pattern of SPSed ZnS with sintering temperature revealed that the structure of ZnS changed partially to hexagonal form according to increasing temperature (above ~920℃).

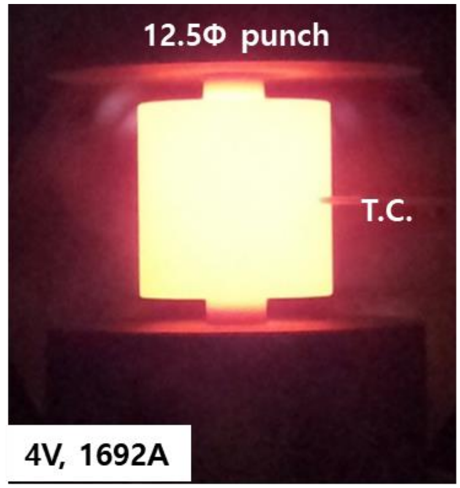


Figure 5: Photo of the inside of the furnace taken during sintering (SPS) with graphite mold.

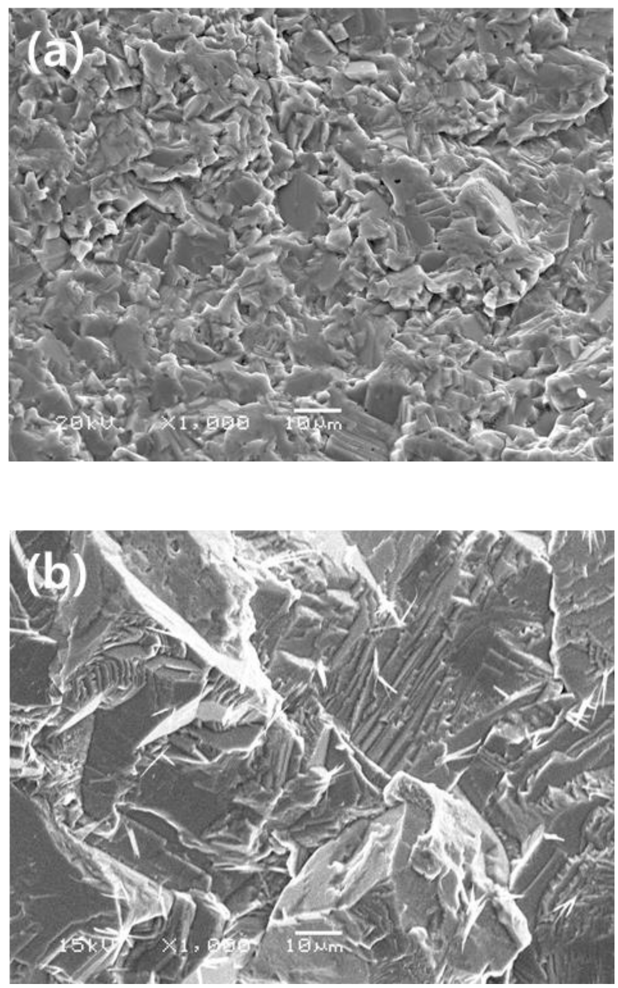


Figure 6: Microstructure of commercial ZnS powder (purity 99.999%) SPSed at (a) 900℃ and (b) 950℃.

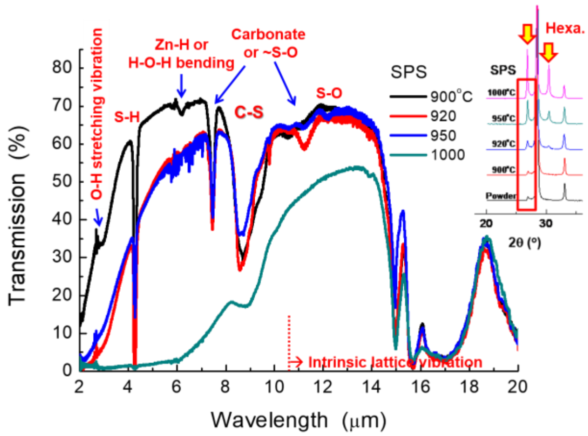


Figure 7: Optical transmittance of SPSed ZnS (non heat-treated commercial powder) using FT-IR for various sintering temperature for 10 minite.

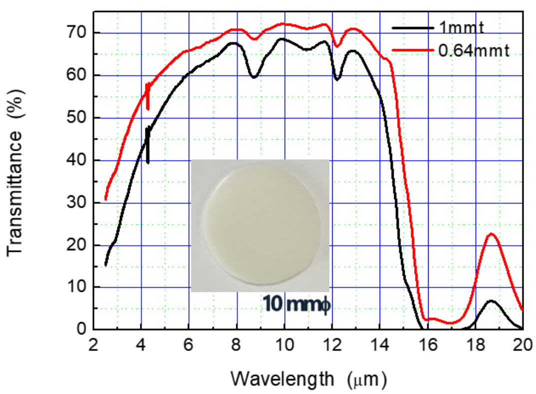


Figure 8: Optical transmittance of SPSed ZnS (heat-treated commercial powder at 550℃ for 2h in vacuum) at 950℃ for 10 minite.

Figure 8 shows the optical transmittance of SPSed ZnS (heat-treated commercial powder at 550℃ for 2h in vacuum) at 950℃ for 10 minite and appearent photograph of sintered ZnS. As we can see the results of FT-IR transmittance at Figure 7, after heat-treatment of ZnS powders at 550℃, the SPSed ZnS speciments have been reduced dratiscally the impurities in it exept the trace of C-S and S-O bonding.

4 SUMMARY

The heat treatments of ZnS nanoparticles were carried out at 550℃ for 10 min. in a vacuum. According to heat treatment, the reactivity of ZnS nanoparticle surface decreased and pyrolysis phenomenon appeared, which were tentatively considered to affect the infrared transmittance of SPS sintered body. Also wurtzite phase may causes birefringence due to the optical anisotropy began to be produced in more than 950℃. Good optical properties of sintered ZnS of heat-treated powders were shown in 950℃ by SPS.

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