JOURNAL OF MATERIALS SCIENCE **32** (1997) 5101–5106

Sintering behaviour of monodispersed ZnS powders

Y.-D. KIM, K. SONEZAKI, H. MAEDA, A. KATO*
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Fukuoka 812-81, Japan

The sintering behaviour of monodispersed ZnS powders having particle size of 0.1–0.9 μm, which were prepared from aqueous zinc nitrate solution by a homogeneous precipitation method using thioacetamide, was studied. Dry-pressed pellets of ZnS powders were fired at 900–1250 °C for 2 h in a nitrogen atmosphere. Monodispersed ZnS powders showed high sinterability in comparison with agglomerated or aggregated ZnS powders. The sinterability increased with decrease in particle size, and ZnS powders with particle size of 0.1 μm were densified to above 98% theoretical density by conventional sintering at 1000 °C for 2 h. Ultrafine monodispersed, spherical particles gave a uniform and fine-grained microstructure.

1. Introduction

Zinc sulphide (ZnS) has found many applications in various fields such as phosphors [1], solar cells [2], pigment [3] and infrared-windows [4], etc. It is a difficult substance to densify by conventional sintering methods, because of its tendency to sublime. To overcome this, hot-pressing has been used in the preparation of highly densified ZnS ceramics [5–8].

On the other hand, monodispersed ZnS particles can be prepared by homogeneous precipitation techniques [9]. Such powders are very suitable for elucidating the particle-size effects in various fields. As raw powder for sintering, the following characteristics are generally accepted to be desirable: (1) small particles with a narrow size distribution, (2) spherical particles, (3) no aggregation, and (4) controlled or uniform chemical composition. Thus, monodispersed spherical particles are ideal as raw powders for sintering, because they give a uniform and dense compact. Although there are some reports on the preparation of monodispersed ZnS powders by the homogeneous precipitation method [10, 11], their sintering behaviour has not been examined.

In the present work, the sintering behaviour of monodispersed, spherical ZnS particles was investigated with emphasis on the effect of particle size.

2. Experimental procedure

2.1. Preparation of monodispersed ZnS powders

Synthesis procedures of monodispersed ZnS powders were described elsewhere [9]. The reacting solution was prepared by dissolving zinc nitrate in deionized water and then filtering through 0.1 μm cellulose nitrate membrane filters. The pH of the solution was adjusted to 1.52 ± 0.01 with nitric acid. The solution was heated in a 300 ml flask to 70 °C and thioacetamide was dissolved into the solution with stirring for 5 min. During reaction, the flask was sealed and the reacting solution was not stirred. After a given reaction time, the solution was cooled in cold water to stop the reaction and the product was washed twice with distilled water and finally with ethanol using ultrasonic agitation and centrifuging. The product was dried at 70 °C under a reduced pressure.

2.2. Sintering

The as-synthesized powders were pressed into pellets of 10 min diameter and about 1 mm thick by uniaxial pressing at 3 t cm^{-2} for 3 min followed by isostatic pressing at 4 t cm^{-2} for 3 min. The green compacts were embedded in commercial ZnS powders and fired in nitrogen atmosphere for 2 h at temperatures from 900–1250 °C

2.3. Characterization

The morphology of as-synthesized powders and microstructure of the sintered bodies were observed by scanning electron microscopy (SEM) and powder X-ray diffraction (XRD) using CuK_α radiation. The densities of the sintered bodies were measured by the Archimedes method using water as the immersion liquid.

---

*Author to whom all correspondence should be addressed.

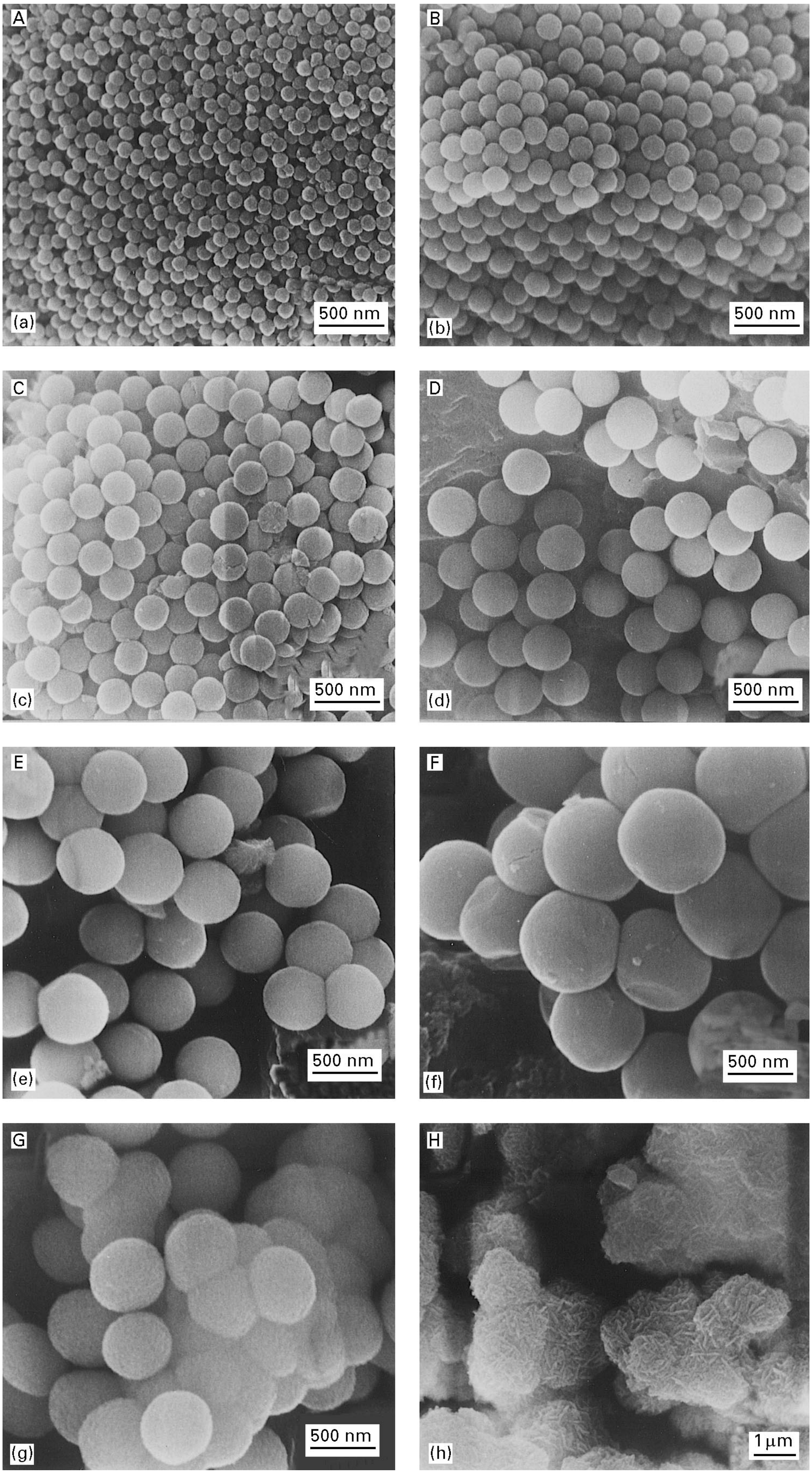

Figure 1 (a–h) Scanning electron micrographs of ZnS powders A to G, respectively. The details of samples A–G are given in Table I.

3. Results of discussion

3.1. Synthesis of monodispersed ZnS powders

The reaction conditions for the synthesis of ZnS powders and its properties are summarized in Table I. As-synthesized powders were β-ZnS. ZnS particles synthesized under various conditions are shown in Fig. 1. The size of ZnS particles was obtained from scanning electron micrographs by measuring approximately 50 particles.

3.2. Sinterability of ZnS powders

The XRD pattern of a sintered body is illustrated in Fig. 2. The equilibrium transformation temperature from cubic β-ZnS into hexagonal α-ZnS is 1020 °C. The transformation is observed in the sintered body. The α-phase appears at 1000 °C and the amount increases with increasing sintering temperature, becoming almost single phase at 1250 °C. Based on the results of XRD, the relative density of the sintered body was calculated using the theoretical density of β-ZnS ($4.102\,\mathrm{g\,cm^{-3}}$) for sintering at 900 °C and 1000 °C, and that of α-ZnS ($4.087\mathrm{g\ cm^{-3}}$) for sintering above 1100 °C.

The effect of sintering temperature on the densification of monodispersed and aggregated ZnS powders is shown in Fig. 3. Because the β–α transformation occurs gradually, the effect of the transformation in the density–sintering temperature curves, shown in Fig. 3, cannot be observed. The monodispersed powders show a higher sinterability than the aggregated ones. Similar results have been observed in the sintering of MgO powders prepared by chemical vapour deposition (CVD) and solid-state reactions [12]. CVD–MgO powders consisted of discrete single crystalline particles, whereas MgO powders prepared by solid-state reactions were agglomerated or aggregated.

The effect of sintering temperature on the densification is relatively small above 1000 °C. This may partly be due to the increase in the sublimation pressure of ZnS. In Fig. 4, the sintered density is plotted against the particle size of monodispersed ZnS powders. The sinterability of monodispersed ZnS powders increases sharply with decrease in the particle size, especially when the particle size is below 0.3 μm. The powder having a particle size of 0.1 μm densified nearly to the theoretical density at a temperature as low as 1000 °C. The increase in sinterability with decrease in particle size may be interpreted by two factors: the increase in driving force for sintering, and shortening of mass transport distance needed for densification.

3.3. Microstructure of sintered ZnS

Fracture surfaces of sintered ZnS are shown in Figs 5–7. Fig. 5 shows the change in microstructure with particle size in starting ZnS powders. When the particle sizes are 0.1 and 0.2 μm, the sintered bodies

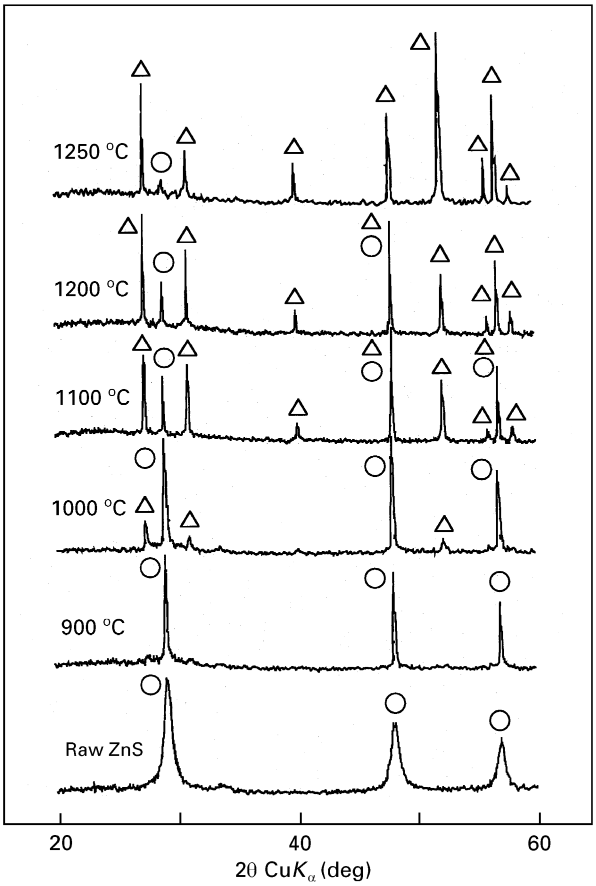

Figure 2 X-ray diffraction patterns of a sintered body fired at various temperatures (△) α-ZnS, (○) β-ZnS.

TABLE I Particle size and reaction conditions for the preparation of ZnS powders

Run no.	[Zn^{2+}] ($\mathrm{mol\,l^{-1}}$)	[TAA] ($\mathrm{mol\,l^{-1}}$)	Reaction time (min)	Reaction temp. (°C)	Particle size (μm)	Remarks[a]
A	0.06	0.4	20	70	0.13 ± 0.01	M
B	0.06	0.4	30		0.22 ± 0.01	M
C	0.05	0.4	30		0.31 ± 0.02	M
D	0.04	0.4	25		0.42 ± 0.02	M
E	0.04	0.5	30		0.58 ± 0.02	M
F	0.03	0.5	30		0.93 ± 0.06	M
G	0.4	0.4	50			A
H[b]						A

[a] M = monodispersed, A = aggregated.
[b] Commercial ZnS powders (Huruuchi Chemical Ltd, Japan).

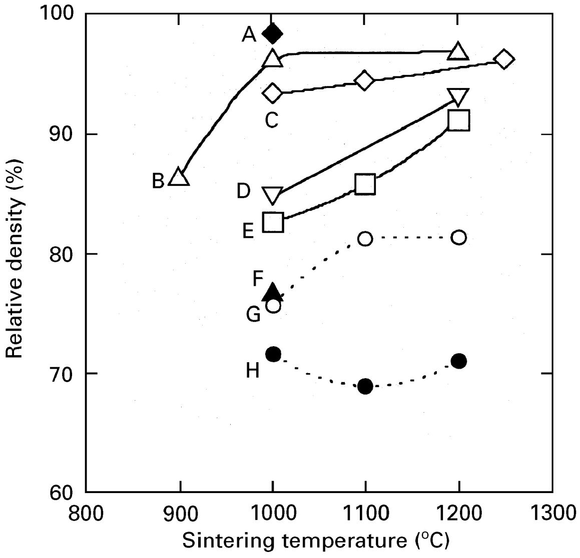

Figure 3 Sintering temperature and densities of sintered bodies. See Table I.

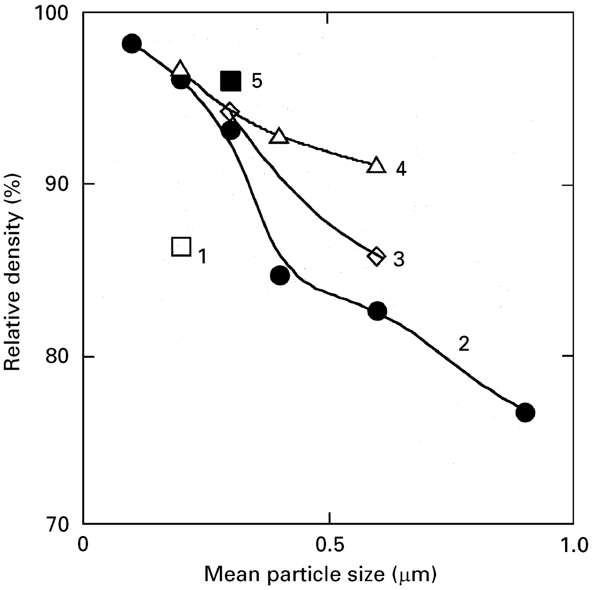

Figure 4 Particle size and densities of sintered bodies derived from monodispersed ZnS powders. Sintering temperature: 1, 900 °C; 2, 1000 °C; 3, 1100 °C; 4, 1200 °C; 5, 1250 °C.

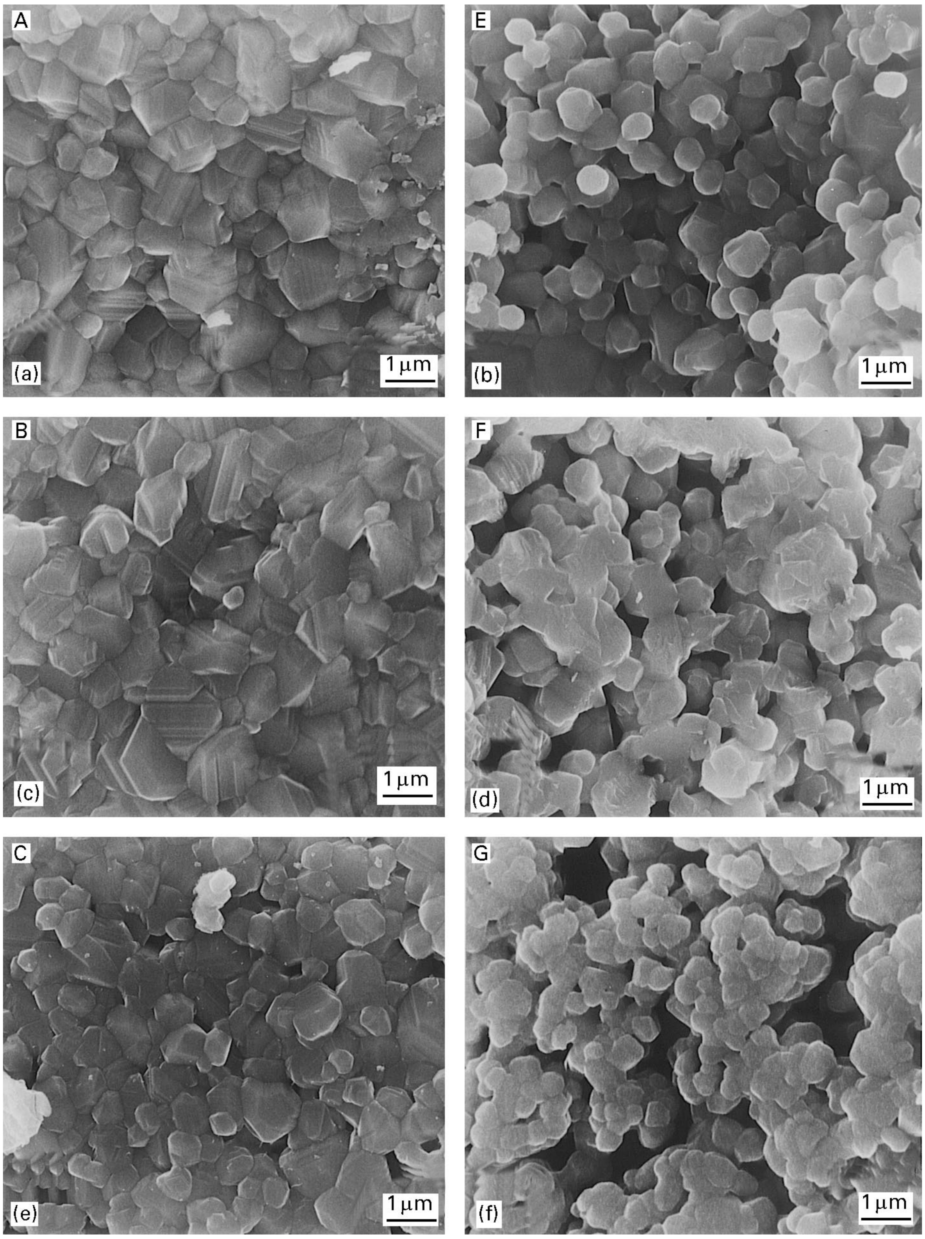

Figure 5 Microstructure of ZnS ceramics (a) A, (b) E, (c) B, (d) F, (e) C and (f) G, See Table I.

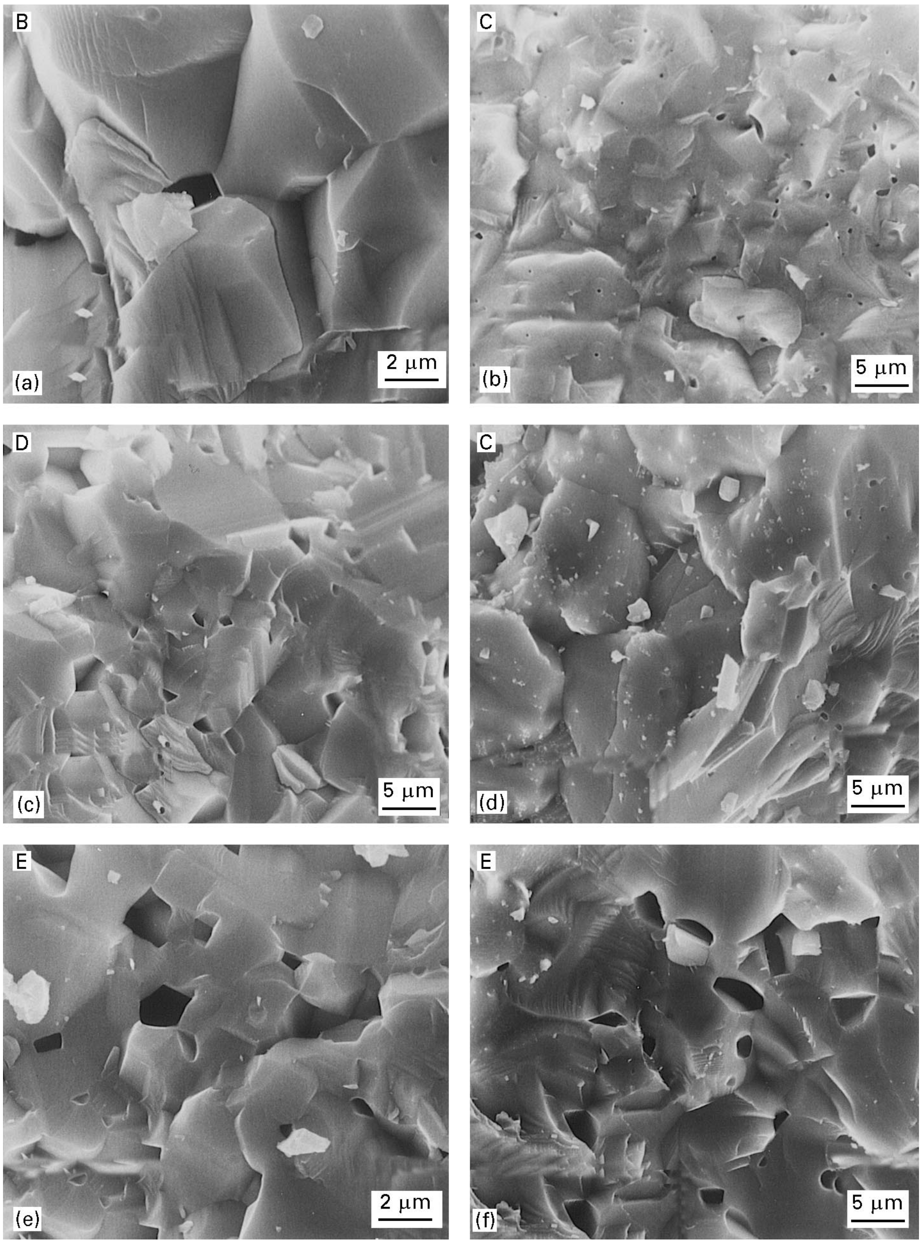

Figure 6 Change in microstructure with sintering temperature of ZnS ceramics (a) B, (b) C, (c) D, (d) C, (e) E and (f) E, derived from monodispersed ZnS powders. See Table I. Sintering temperatures: (a, c, f) 1200 °C, (b, e) 1100 °C, (d) 1250 °C.

have fine-grained structures. When the particle sizes become large, grain growth occurs in such a manner that a network structure develops. The change in microstructure with sintering temperature is illustrated in Fig. 6 on the sintered bodies derived from monodispersed ZnS particles. When the sintering temperature rises from 1000 °C (Fig. 5) to 1100 °C or above, the grain growth becomes remarkable, although the densification proceeds only a little. The increase in sublimation pressure and β–α phase transformation of ZnS will be responsible for the enhanced grain growth. In addition, it should be noted that the sintered body obtained by sintering of 0.2 μm ZnS powder (B) at 1200 °C rarely has isolated pores in the grains, whereas less dense sintered bodies from 0.3–0.6 μm ZnS powders (C, D, E) have isolated pores in the grains. Fig. 7 shows the change in microstructure with sintering temperature of sintered bodies prepared from aggregated ZnS powders. Network structures develop at 1000 °C by preferential sintering within aggregated grains, and grain growth also becomes remarkable above 1100 °C, similar to the sintering of coarse monodispersed ZnS powderes as shown in Figs 5 and 6. Grain growth without densification may occur by means of the evaporation–condensations mechanism. From above results, it can be concluded that monodispersed ZnS particles as fine as 0.1 μm give a sintered body with nearly theoretical density by pressureless sintering, and that in order to obtain fine-grained ZnS ceramics, the sintering temperature should be below 1100 °C.

4. Conclusion

The sintering behaviour of monodispersed ZnS powders prepared by homogeneous precipitation were

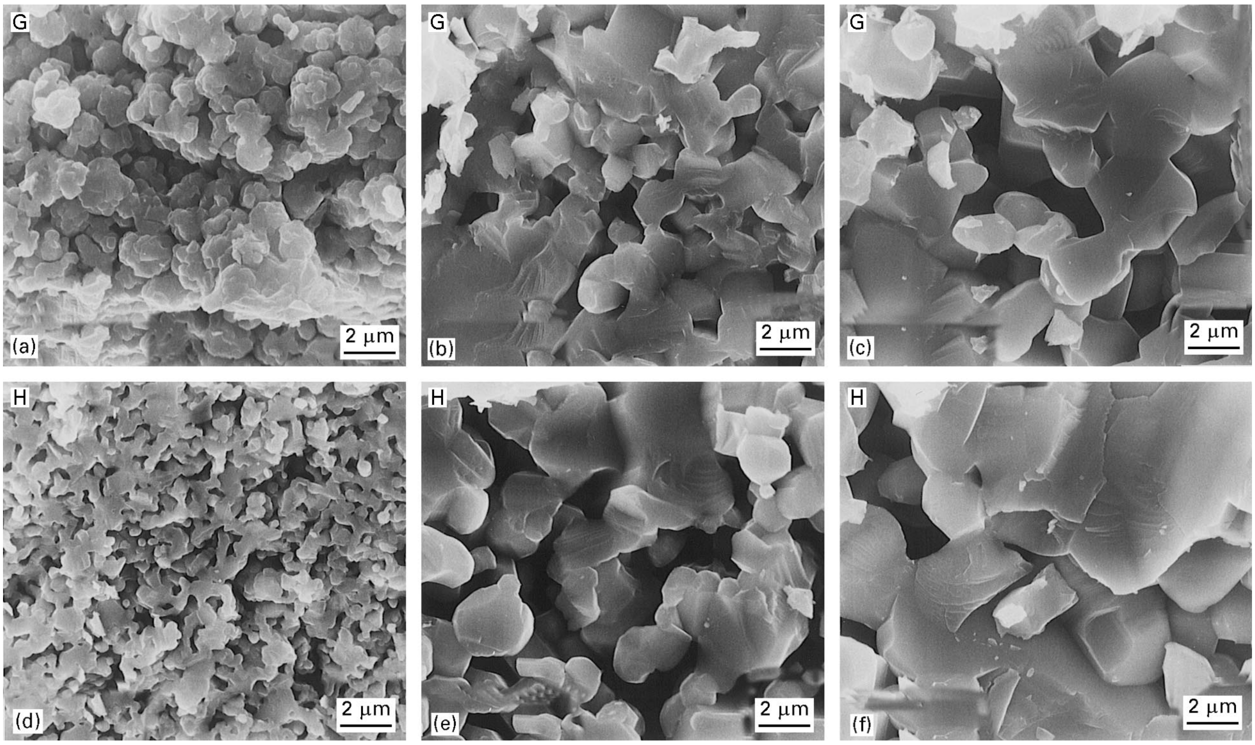

Figure 7 Change in microstructure with sintering temperature of ZnS ceramics (a–c) G, and (d–f) H, derived from aggregated ZnS powders. See Table I. Sintering temperatures: (a, d) 1000 °C, (b, e) 1100 °C, (c, f) 1200 °C.

studied. Monodispersed ZnS powders showed a high sinterability in comparison with agglomerated or aggregated ZnS powders, and ZnS powders with particle size of 0.1 μm could be densified nearly to the theoretical density by pressureless sintering at 1000 °C. A fine-grained ZnS ceramic can be obtained by sintering below 1100 °C.

References

1. PHOSPHOR RESEARCH SOCIETY, in "Phosphor Handbook", edited by S. Shionoya *et al.* (OHM, Japan, 1987) p. 147.
2. A. CLANDRA and M. MISHIRA, *Energy Conver.* **25** (1985) 387.
3. L. T. WORK and H. ODELL, *Ind. Eng. Chem.* **25** (1933) 411.
4. P. MILES, *J. Opt. Soc. Am.* **63** (1973) 1323.
5. H. J. McQUEEN and G. C. KUCZYNSKI, *J. Am. Ceram. Soc.* **45** (1962) 343.
6. E. CARNALL Jr, *ibid.* **55** (1972) 582.
7. Y. FUJITA and T. NITTA, *ibid.* **65** (1982) C-18.
8. K. UEMATSU, K. SAWADA, I. KATO, N. UCHIDA and K. SATO, *J. Ceram. Soc. Jpn* **95** (1980) 299.
9. Y.-D. KIM, T. YONEIMA, S. NAGASHIMA and A. KATO, *Nippon Kagaku Kaishi* **9** (1995) 505.
10. D. M. WILHELMY and E. MATIJEVIC, *J. Chem. Soc. Farad. Trans. 1* **80** (1984) 563.
11. A. CELIKKAYA and M. AKINC, *J. Am. Ceram. Soc.* **73** (1990) 245.
12. A. KATO and Y. TADA, *Mem. Fac. Eng. Kyushu Univ.* **47** (1987) 135.

Received 13 June 1996
and accepted 10 February 1997