FINAL REPORT

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Precipitation Hardening of Infrared Transmitting ZnS Ceramics

Principal Investigators: B. Dunn and A. J. Ardell

Department of Materials Science and Engineering
University of California, Los Angeles
Los Angeles, CA 90024-1595

The contract N00014-91-J-1664 was an extension of a previous ONR contract (N00014-87-K-0531). For the purpose of completeness, research accomplished under both contracts is covered in this report so that the results of the entire program can be reviewed. A separate report was issued for N00014-87-K-0531.

A. Scientific Research Goals

Precipitation strengthening is a potentially attractive technique for hardening and toughening infrared transmitting materials. The controlled precipitation of a finely dispersed second phase offers the opportunity to improve mechanical properties without degrading optical properties. It is well established that the presence of an appropriate dispersion of second phase particles can improve the mechanical behavior of ceramics, and, by maintaining a particle size < 100 nm, scattering losses in the infrared will be circumvented.

The overall objectives of the research program have been (1) to demonstrate that ZnS-based ceramics can be precipitation-strengthened and (2) to characterize the resulting mechanical and optical properties of the multiphase materials. An important research goal has been to identify ZnS-based systems suitable for strengthening and to determine the composition ranges and annealing treatments required to produce precipitate phases or other solid-state reaction products. Another important research objective has been to determine why "alloys" in the ZnS-Ga_2S_3 system exhibit an increase in both fracture toughness and hardness, and to establish the composition ranges and annealing treatments which produce this behavior. The research has also sought to quantify the effects of size and volume fraction of various second phase constituents on infrared scattering. The relationship between mechanical behavior and microstructural development has been of central importance in this research program.

B. Summary of Research Accomplishments

Candidate systems for precipitation strengthening have been identified, i.e., the ZnS-CdS and ZnS-$ZnGa_2S_4$ systems. The phase equilibria in the ZnS-rich region of these two systems have been established. CdS is very soluble in ZnS and the two-phase microstructure envisioned in this system will consist of sphalerite and wurtzite solid solutions. Ga_2S_3 exhibits limited solubility in ZnS and the pseudobinary ZnS-$ZnGa_2S_4$ system is characterized by a eutectoid reaction. The equilibria phase diagrams for both systems were published.

The research program focused on the ZnS-$ZnGa_2S_4$ system. We developed hot pressing methods for ZnS and ZnS-Ga_2S_3 "alloys" which routinely produced samples exceeding 99.0% of their theoretical density. These high quality specimens were used to characterize mechanical and optical properties of materials containing 8 to 16 mol% Ga_2S_3.

The most significant result obtained during the program was the observation that the various ZnS-Ga_2S_3 compositions exhibit considerably higher fracture toughness and hardness than pure ZnS. The increase in hardness was proportional to the amount of Ga_2S_3 added, with the 16 mol% sample exhibiting a value nearly two times larger than ZnS. A sizeable increase in fracture toughness was also observed in all samples. At 12 mol% Ga_2S_3, the fracture toughness value was more than 50% greater than that of pure ZnS. In these studies, all samples were solid-solution treated in the wurtzite phase (at 940°C), and no precipitated phases were detected by x-ray diffraction. The mechanism responsible for the observed increase in hardness and fracture toughness has yet to be determined.

The optical properties of several ZnS-Ga_2S_3 solid solutions have been measured. As expected, the infrared transmission exhibited no change from that observed for pure ZnS, with excellent transmission until the infrared cut-off in the 12 μm range. In addition to this experimental work, a model based on Mie theory was developed to calculate the amount of spectral infrared scattering caused by the presence of a porous second-phase. Various in-line transmission curves were calculated and used to characterize the scattering effects of pore size and concentration. The in-line transmission from 2.5 - 10 μm of ZnS samples hot-pressed at 137.8, 172.3 and 206.7 MPa was measured and compared with calculated transmission curves. A model based upon the use of a single pore size was unable to produce a transmission curve which fit the experimental results, however, a model which incorporated the size dispersion effect of the scatterer was able to generate a transmission curve that matched the experimental results. A bimodal distribution of pores provided far better agreement than did a single distribution function. The good agreement between the model and the experimental results suggests that characterization of the infrared transmission data may be used as an effective, non-destructive analytical technique for the determination of the pore size distribution in optical ceramics

Another significant result is the successful development of a method for measuring fracture toughness using an indented miniaturized ring-on-ring disk-bend fracture toughness test (MDBFTT). Samples 3 mm in diameter and 300 to 400 µm thick are indented using a Vickers indenter and the load to fracture is measured in the MDBFTT. This is repeated for several loads, after which already developed fracture toughness equations are applied to the data, yielding a value of K_{Ic}. The fracture toughness can be obtained by this method without measuring actual crack lengths, thereby eliminating the uncertainties associated with such measurements. Initial measurements on standard samples, including CVD-grown ZnS, have yielded values which are in excellent agreement with conventional fracture toughness measurements.

C. Publications Acknowledging ONR Support

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