Hot-Pressed Cesium Iodide

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Polycrystalline CsI disks were fabricated by hot-pressing in a nitrogen-purged glove box. Densification during hot-pressing occurred by plastic flow resulting from lattice dislocation glide. Primary recrystallization and extensive grain growth were observed. Both the optical and mechanical properties of this material were significantly affected by grain growth, but in opposite ways. Transmittance increased and strength decreased as grain size increased. The hot-pressed CsI had transmittance of about 85% in the extra-long-wavelength infrared range, a value equivalent to that of single-crystal CsI. The flexural strength of theCsI that was hot-pressed under conditions that minimized grain growth was about 8 times higher than that of single-crystal CsI. [Key words: cesium iodide, hot-pressing, grain growth, optical properties, mechanical properties.]

I. Introduction

There are numerous applications for materials that are transparent to infrared radiation; but, at the same time, the degree of sophistication and the performance criteria for such optical systems are increasing. The requirements for such materials in state-of-the-art optical devices include high transmittance, high mechanical strength, and chemical stability with respect to the environment. The material of choice for a specific application depends mainly on the wavelength of the infrared to be employed. For near- (0.75- to 2.5-μm wavelength) and mid-infrared (3.0 to 5.0 μm) applications, there are a relatively wide range of materials available, including silicate glasses, calcium aluminate glasses, fluoride glasses, halides, chalcogenides, fluorides, oxides and oxinitrides. For far-infrared (8 to 12 μm) systems, the list of applicable materials is relatively short, but still includes germanium, halides, chalcogenides, and III-V compounds such as GaAs. For even longer wavelengths, i.e., for extra-long-wavelength-infrared (XLWIR, 15 to 60 μm) transmission, the only choices are a few halide materials such as CsI, CsBr, and TlBr-TlI solid solutions. Among these, CsI has the highest intrinsic transmittance (about 90%) over the entire XLWIR range. Even with this excellent and unique optical property, CsI has not been widely used, because it has low mechanical strength and strong hygroscopicity. The hygroscopicity can be avoided by the application of appropriate protective coatings. However, the mechanical strength of CsI must be substantially improved for some potential applications. The strengthening of single-crystal CsI by introducing impurities (such as Ba and Cr) during crystal growing has been reported. However, introduction of impurities may affect the optical performance of the material. Other halide materials, such as KCl and KBr, have been strengthened by the introduction of subgrains and low-angle grain boundaries during press forging of single-crystal billets. The limitations of this technique are edge crack initiation and propagation during forging, and rapid grain growth at room temperature after forging.

In the present study, polycrystalline CsI was prepared by an alternate technique—hot-pressing. Powder processing techniques have generally been avoided in the fabrication of alkali halide optical components because these materials are strongly hygroscopic. Any moisture adsorbed on particle surfaces can result in increased adsorption and scattering of radiation. This moisture sensitivity problem was minimized in our work by starting with ultradry powder and conducting all powder processing and hot-pressing operations in a glove box purged with dry gas. The goal of this research was to develop procedures for hot-pressing polycrystalline CsI optical material that is stronger and, at the same time, transparent in the XLWIR range as single-crystal material. As part of this effort, the densification behavior and microstructural changes during hot-pressing were studied. The optical and mechanical properties of CsI hot-pressed under various conditions were measured and compared to those of single-crystal CsI.

II. Experimental Procedure

All the powder preparation operations and hot-pressing were done in a glove box to avoid moisture attack on the samples. The glove box and associated entrance chamber were purged with flowing gas from liquid nitrogen. Water vapor and oxygen contents in both the glove box and entrance chamber were continuously monitored with a hygrometer and an oxygen analyzer, respectively. The water vapor pressure and oxygen partial pressure in the glove box were kept below $1.0 \times 10^{-4}$ and $3.0 \times 10^{-5}$ atm (10 and 3 Pa), respectively. Hot-pressing was performed using a hydraulic press (25-ton ($2.3 \times 10^5$ kg) capacity) and stainless steel dies wrapped with a tubular, stainless-steel-clad heating element. Pressure was applied to the sample after the pressing temperature was reached. A linear voltage differential transformer (LVDT) was installed to monitor the ram movement continuously during pressing. A thermocouple was inserted in a small hole in the die to precisely measure the sample temperature. Two different grades of powder were used as starting materials: ultrapure (99.999% CsI) and ultrapure/ultraladry (99.999% CsI, H₂O and OH⁻ < 1 ppm). The as-received powders were in spherical form, with average diameter of 600 μm. The powders were ground in the glove box for about

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**Model 5300, Panametric, Inc., Waltham, MA.


Fred S. Carver, Inc., Menomonee Falls, WI.

*6101F demodulator, Automatic Timing and Controls Co., King of Prussia, PA.

*asar, Johnson Matthey, Inc., Seabrook, NH.
20 min, using a laboratory mill. The size and distribution of the milled powders were determined by using a light-scattering particle-size analyzer. Hot-pressing variables were temperature, applied stress, and pressing time. After hot-pressing, the relative density, microstructure, transmittance, and strength of the samples were measured as a function of those variables. The transmittances of the samples were measured by an infrared spectrophotometer. The strengths of the materials were determined by a four-point-flexure test of as-pressed bars having dimensions 0.4 cm x 0.635 cm x 2.54 cm. The inner and outer spans of the four-point-bend test were 0.635 cm and 1.905 cm, respectively. The 2.54 cm x 0.635 cm faces of the die punches were polished so that no sample preparation was needed prior to testing. The microstructures of the samples were observed by optical and scanning electron microscopy. For optical microscopy, the samples were ground with 800-grit Sic abrasive paper and polished with 3-μm diamond paste without using lubricant. The grain-size distribution was measured by an image analyzer.

III. Results and Discussion

(1) Densification Behavior

A particle-size distribution representative of the powders after being milled and screened in the glove box is shown in Fig. 1. The powder has the lognormal distribution generally found in many ceramics. The average particle size of the powder was typically about 10 μm. The densification behavior of CsI was studied by monitoring the movement of the hydraulic press ram as samples were pressed under various conditions. For uniaxial hot-pressing in a cylindrical die, the densification rate (dp/dt) and the deformation rate (de/dt) are related by the following equation:

\[ \frac{de}{dt} = \frac{1}{\rho} \left( \frac{dp}{dt} \right) = (dp/dt) \]  

where \( \rho \) and \( \varepsilon \) are the density and thickness, respectively, of the sample. The densities of the samples were converted according to this relationship from the ram movement monitored by the LVDT. Figure 2 shows the density change of CsI disks as a function of pressing time at different pressing temperatures. The applied stress was 34.5 MPa. Densities greater than 98% of theoretical were achieved in 1 h when the pressing temperature was higher than 100°C. When the temperature was too high (>250°C), discoloration of the sample was observed, apparently as a result of decomposition of the CsI.

Fig. 1. Typical particle size distribution of CsI powder after milling for approximately 20 min.

Therefore, most of the experiments were performed at temperatures between 100° and 250°C.

During the hot-pressing of ceramics, a relationship for the kinetics during densification is generally expressed as follows:

\[ \rho = \rho_0 + k_1 \ln t \]  

where \( \rho \) is the density of the material at time \( t \), and \( \rho_0 \) and \( k_1 \) are constants. The relative densities of CsI as a function of time at \( T = 125°C \) are plotted in Fig. 3 for various applied stresses. The linear relationships between the density (\( \rho \)) and log \( t \) show that the densification of CsI follows the classical densification behavior frequently observed in many other ceramics.

Generally, to identify the exact densification mechanism of ceramics during hot-pressing, the following relationship between the densification rate (dp/dt) and applied stress (\( \rho_c \)) is used:

\[ dp/dt = (AD\mu b/kT)(b/G)^n(gp_c/\mu)^m \]  

Fig. 2. Relative densities of CsI as a function of pressing time at different pressing temperatures; applied stress = 34.5 MPa.

Fig. 3. Relative densities of CsI as a function of log \( t \) at different applied stresses; pressing temperature = 125°C.

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**Notes:**
- **A-20 universal mill, Tekmar Co., Cincinnati, OH.**
- **Microtrac particle-size analyzer, Leeds & Northrup Instruments, North Wales, PA.**
- **983G infrared spectrophotometer, Perkin-Elmer Corp., Norwalk, CT.**
- **Kontron Electronics, Inc., Mountain View, CA.**
where \( A \) is a constant, \( D \) the diffusion coefficient, \( \mu \) the shear modulus, \( b \) the Burgers vector, \( k \) the Boltzmann constant, \( G \) the grain size, \( g \) the stress multiplication factor, \( p_a \) the applied stress, and \( m \) and \( n \) are the exponents characteristic of the densification mechanism. When the temperature is constant, and assuming the microstructures of the materials are similar at the same porosity level, Eq. (3) can be simplified as follows:

\[
d_{p}/dt = k_2(p_a)^n
\]

where \( k_2 \) is a constant characteristic of each material. From the value of \( n \), which is the slope of the plot of \( \log (dp/dt) \) vs \( p_a \), the densification mechanism of a material can be clearly identified. For example, when the main densification mechanism is lattice- or grain-boundary diffusion, \( n \) is close to 1; and when grain-boundary sliding plays an important role, \( n \) is larger than 1. When plastic flow by lattice dislocation glide is the densification mechanism, \( n \) is larger than 3. These relations are discussed in more detail by Rahaman et al.\(^7\)\(^8\).

Figure 4 is a plot of \( \log (dp/dt) \) vs \( p \) for CsI at different applied stresses. This figure shows that \( \log (dp/dt) \) decreases linearly with density \( (p) \) and that the slope becomes steeper as the stress increases. This change in the slope implies that the applied stress plays an important role in the densification of CsI. Taking the data from Fig. 4, the relationship between densification rate \( (dp/dt) \) and applied stress \( (p_a) \) was determined according to Eq. (4). As shown in Fig. 5, the slopes of \( \log (dp/dt) \) vs \( p_a \) are parallel for different densities. The slopes of these lines \( (n) \) are 5.4, implying that plastic flow as a result of dislocation glide is the densification mechanism for this material within this experimental range. Similar behaviors have been observed for other alkali halide materials. For example, slopes of 6.6 and 3.6 were determined for LiF and NaCl, respectively.\(^9\)\(^10\) These results suggest that, despite the difference in crystal structure (simple cubic for CsI and face-centered cubic for NaCl and LiF), alkali halide materials are densified by the same mechanism, i.e., by lattice dislocation glide.

(2) Microstructures

When a material is deformed plastically, a significant amount of strain energy is stored in the system. To relieve this stored energy, new strain-free nuclei are formed and grow at the expense of the plastically deformed matrix. This process is termed primary recrystallization. The microstructure of a material during primary recrystallization is characterized by the existence of relatively large grains randomly distributed in a fine matrix. This primary recrystallization is generally followed by normal grain growth.\(^11\)

The evolution of the microstructure of CsI with pressing time is shown in Figs. 6(A) to (D). The pressing conditions for these samples were \( T = 100^\circ\text{C} \) and \( p_a = 103.4 \text{ MPa} \). The microstructure of a sample pressed for 5 min is shown in Fig. 6(A). This micrograph shows that the grain size is about the same as the particle size of the starting powder, indicating that neither recrystallization nor grain growth has occurred at this time. As the pressing time increases to 20 min, a number of large grains appear in the fine matrix, as shown in Fig. 6(B). These large grains are believed to be formed by the primary recrystallization process. As the time increases further, extensive grain growth occurs, as is evident in the microstructure of CsI after 1 h of pressing as shown in Fig. 6(C). Grain growth continues to occur as the pressing time increases. Figure 6(D) is the microstructure of CsI pressed for 2 h.

The average grain size of CsI, determined by an image analysis technique, is shown in Fig. 7. As seen in this graph, the average grain size of CsI did not change significantly during primary recrystallization, even though some large grains emerged in fine matrix (Fig. 6(B)). The average grain size increased remarkably during the normal grain growth process. These microstructural changes have significant effects on the optical and mechanical properties of CsI, as will be discussed below.

(3) Optical Transmittance

In order for a material to be used as an optical component, the transmittance of the body is of primary importance. For high transmittance, the density of the body must be near the theoretical limit to reduce the scattering at pores. The pressing conditions for optimum optical performance were determined to be \( T = 150^\circ\text{C} \), \( p_a = 103.4 \text{ MPa} \), and time = 1.0 h. Two different grades of CsI (ultrapure and ultrapure/ultrady) were used to observe the effect of moisture adsorbed on the starting powder. As-pressed disks had relative densities >99.8%, and dimensions of 5.08-cm diameter and 0.64-cm thickness. The nondiffusive (specular) transmittances of the hot-pressed CsI samples are shown, compared with that of single-crystal CsI, in Fig. 8. The transmittance of the polycrystalline CsI sample as-pressed from ultrapure/ultrady powder is equivalent to that of single-crystal CsI in the extra-long-wavelength infrared region (\( \approx 15 \mu\text{m} \)), while the transmittance of the sample pressed from the ultrapure powder was ~10% lower. These results indicate that adsorbed
moisture level plays an important role in determining the transmittance of hot-pressed CsI and that, based on transmittance, polycrystalline CsI is a viable alternate material to single crystals for XLWIR optical components.

(4) Mechanical Strength

High mechanical strength is another requirement for optical components in some applications. The strength of hot-pressed CsI samples was measured using a four-point-bend test. The bend-bar specimens were individually hot-pressed in a rectangular cross-section die to avoid the necessity for machining and polishing after hot-pressing. All of these specimens were pressed from the ultrapure/ultradry powder that was milled under one set of conditions to produce powder having an average particle size of 10 μm. Variables in specimen preparation were pressing time and temperature. Five samples were pressed under each set of conditions.

The effect of pressing time on the strength of CsI hot-pressed at $p_a = 103.4$ MPa and $T = 125°C$ is shown in Fig. 9. The maximum strength, which is about 8 times higher than that of single crystal, was obtained when the pressing time was a minimum (5 min). The decrease in strength of this material with pressing time is due to the grain growth described previously. The yield strength of a material is related to the average grain size by the Petch relationship, as follows:

$$\sigma = \sigma_0 + k_3 G^{-0.5}$$  \hspace{1cm} (5)

where $\sigma$ and $G$ are the yield strength and average grain size of the material, respectively, and $\sigma_0$ and $k_3$ are constants. The relation between the flexural strength and grain size of CsI is shown in Fig. 10. The linearity between the flexural strength and $G^{-0.5}$ indicates that the flexural strength of CsI follows the Petch relationship. Typical micrographs of the fracture surfaces of samples pressed for different lengths of time are shown in Fig. 11. Figures 11(A) and (B) are the fracture surfaces of CsI pressed at $T = 100°C$, $p_a = 103.4$ MPa for 5 min and 2 h, respectively. These micrographs clearly show the effect of pressing time on the grain size and, consequently, on the mechanical strength of this material.

The effect of pressing temperature on flexural strength (Fig. 12) was similar to that of pressing time. All of these samples were pressed for 30 min at 103.4 MPa. The increase in strength with pressing temperatures up to 100°C is attributed to an increase in the densification rate with temperature, and the rapid decrease thereafter is due to the grain growth. According to Fig. 12, the optimum temperature range in which to fabricate strong CsI is between 100° and 150°C. This means that, in this temperature range, sufficient densification of the CsI occurs without excessive grain growth. However, transmittance measurements in the XLWIR range of samples pressed at different temperatures (also in Fig. 12) show that higher temperatures than these are desirable. The increase in transmittance with pressing temperature is believed to be due to the decrease in grain-boundary area,
and thus the scattering sites, as grain growth occurs. These results indicate that a trade-off exists between strength and transmittance and that pressing conditions can be changed to meet the requirements of a specific application.

**IV. Summary**

A polycrystalline CsI material useful for extra-long-wavelength infrared optical components was successfully fabricated by hot-pressing. The densification mechanism during hot-pressing was found to be plastic flow that resulted from dislocation glide. Primary recrystallization occurred during the early stages of hot-pressing to release the strain energy stored in the material during deformation, followed by normal grain growth. The nondiffusive transmittance of the hot-pressed material was about 85% in the XLWIR range (15 to 60 μm), a value equivalent to that of single-crystal CsI. The maximum flexural strength observed in hot-pressed CsI was 31 MPa, about 8 times higher than that of single-crystal CsI.

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Fig. 11. Fracture surface of CsI pressed at $T = 100^\circ$C and $p_0 = 103.4$ MPa: (A) pressed for 5 min; (B) pressed for 120 min.

Fig. 12. Effect of pressing temperature on the strength and transmittance of polycrystalline CsI pressed for 30 min at $p_0 = 103.4$ MPa.

References


