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The optical properties of hot-pressed magnesium fluoride and single-crystal magnesium fluoride in the 0.1 to 9.0 μm range

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A polycrystalline high-density magnesium fluoride, fabricated into plates or shapes by hot-pressing, exhibits high in-line transmittance from 2.5 to 6.0 μm, and single-crystal magnesium fluoride extends from 0.1 to 6.0 μm. The ultimate and practical transmittance of hot-pressed magnesium fluoride using intrinsic and extrinsic reflectance, absorptance and scattering mechanisms, are investigated. The intrinsic scattering mechanism due to the polycrystalline structure is basically responsible for the tremendous difference in transmittance in the short wavelength region of the spectrum. The in-line transmittance of polycrystalline and single-crystal MgF_2 is discussed in terms of sample thickness.

1. Introduction

A polycrystalline high-density magnesium fluoride, made by the hot-pressing technique [1, 2], has been extensively used as a dome material for missiles which have infrared sensors, because of its excellent transmittance in the infrared region of the spectrum, high mechanical strength and thermal stability. The stringent optical requirements of modern optics permit very little leeway in absorptance or scattering, and the preparation of highly purified starting powders is essential for materials of high optical quality. The starting materials must be chemically pure as well as phase pure [3, 4]. The hot-pressing technique involves sintering with simultaneous application of heat and pressure. The simultaneous effects of pressure and temperature make it possible to lower the sintering temperature considerably.

The present work focuses on the unique optical properties of hot-pressed magnesium fluoride (HP MgF_2) samples with a uniform grain size smaller than 1 μm shown in Fig. 1. The short wavelength transmission cut-off of the best HP MgF_2 sample is shifted considerably towards longer wavelengths than the transmission cut-off of single-crystal MgF_2. Much of the reduction in the best HP MgF_2 sample in the short wavelength transmittance is likely to be caused by the light scattering by residual pores and by optical anisotropy [5–7]. The optical anisotropy becomes significant only when the number of pores is extremely low. Hence HP MgF_2 cannot be used for application in the ultraviolet and visible region of the spectrum. In addition, the transmission curve indicates the most common extrinsic absorptance from the sharp band of OH stretching and the broad band of H_2O at 2.75 μm, OH bending at 6.7 μm and oxyfluoride hydrogen complex at 5.0 μm, as shown in Fig. 2.

The bulk scattering is very difficult to distinguish from true absorptance in the short wavelength transmission measurement. It is therefore important to measure the scattered light from the transparent samples where the absorptance is negligible. The surface scattering contribution can be neglected after optical polishing treatment. Because anomalous results are observed in the transmission curve for HP MgF_2, it was decided to compare this material with single-crystal MgF_2, extending information transmittance through the visible and ultraviolet ranges.

2. Experimental procedure

Submicrometre magnesium fluoride powder for hot pressing was prepared by a solution technique [3, 4]. To hot press the magnesium fluoride powder, addition of a sintering aid is not necessary. Hot pressing takes place in an atmosphere and typical process parameters are temperature, 823 to 973 K, and pressure, 207 to 276 MPa. It is noteworthy that the hot pressing of magnesium fluoride powders has proved to be possible in boron nitride (BN) die, without any permanent sticking to the die wall.

For transmission measurement, slices 2.0, 5.0 and 10.0 mm thick were cut from the same hot-pressed plate and from the same single-crystal bulk. The slices were given an optical surface on both sides through a sequence of cutting, grinding and polishing processes. Samples were prepared so that the in-line transmit-

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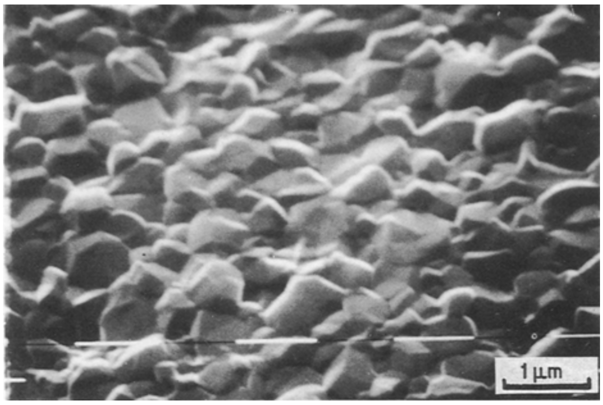

Figure 1 A typical scanning electron micrograph showing the microstructure of hot-pressed magnesium fluoride.

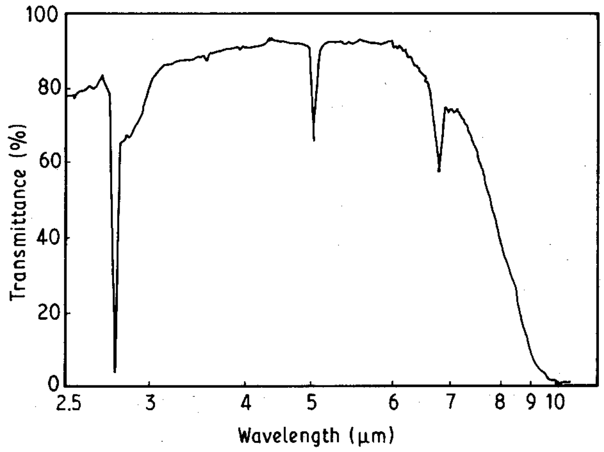

Figure 2 Infrared transmittance spectrum of hot-pressed magnesium fluoride, obtained with a P–E 780 series spectrophotometer; thickness = 2.0 mm.

tance could be measured parallel to the pressing direction and to the *c*-axis direction. Fig. 3 shows schematically the optical path of the apparatus used for the in-line transmission measurement that was carried out with a Perkin–Elmer Model 780 spectrophotometer in the wavelength range 2.5 to 9.0 µm and a Schmadz Model 360 in the wavelength range 0.1 to 2.5 µm. The measured transmittance of HP MgF_2 can be written as [8]

$$T_{meas} = T_{spec} = (1 - R)^2 \exp(-\alpha l) \quad (1)$$

where $R(= (N-1)^2/(N+1)^2)$ is the single surface reflection, N is the refractive index of the material, α is the absorption coefficient due to material and scattering, l is the sample thickness, usually in centimetres.

3. Results and discussion

When electromagnetic radiation is incident upon and passes through a sample whose surfaces are plane-parallel and optically smooth, various loss mechanisms will operate. Broadly speaking, they may be separated into two categories: intrinsic loss and extrinsic loss. Intrinsic loss is characteristic of material and cannot be changed. Extrinsic loss is not characteristic of the material but results from the processing procedures used to make it. According to energy conservation [9]

$$R + T + \alpha = 1 \quad (2)$$

where R is the total specular reflectance at the interfaces between the sample surfaces and the environment, T is the specular transmittance, α is the absorptance due to the material and scattering within the sample. The transmittance, including total internal reflectance, of a completely non-absorbing sample is given by [10]

$$T = T_{calc} = 2N/(N^2 + 1) \quad (3)$$

and the reflectance is given by

$$R = R_{calc} = 1 - T = (N-1)^2/(N^2+1) \quad (4)$$

Fig. 4 illustrates that the transmission curves are identical for wavelengths below 6.0 µm for single-crystal MgF_2 with the different thicknesses 2.0, 5.0 and 10.0 mm. The experimental transmittance is very close to the calculated value which is obtained using Equa-

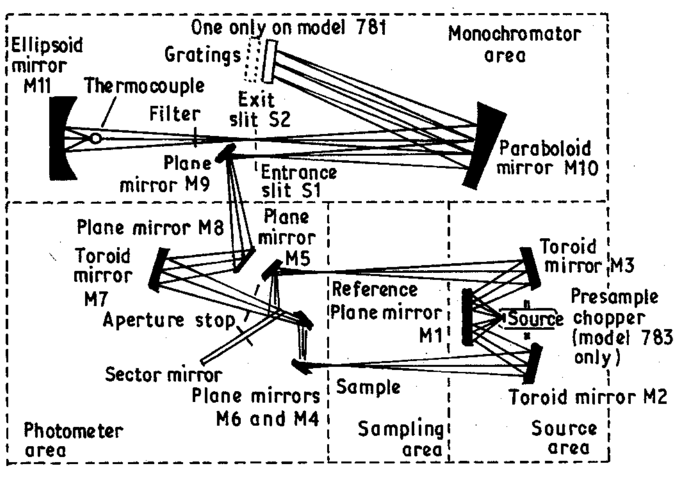

Figure 3 Optical path of Perkin–Elmer 780 series spectrophotometer.

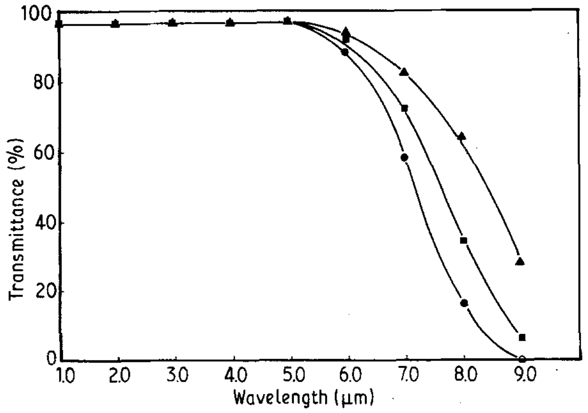

Figure 4 In-line transmittance for single-crystal magnesium fluoride with thicknesses t = (▲) 2.0, (■) 5.0, (●) 10.0 mm.

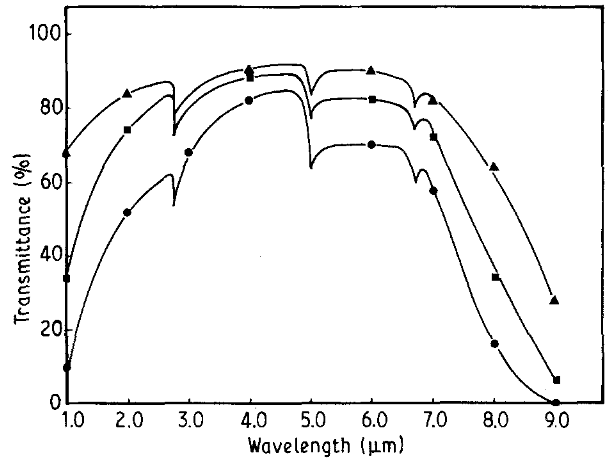

Figure 5 In-line transmittance for hot-pressed magnesium fluoride with thicknesses t = (▲) 2.0, (■) 5.0, (●) 10 mm.

tion 3, i.e. $T_{meas} = T = T_{calc}$ = 95 to 96%. Combined with Equations 2 and 4, $\alpha = 0$. The result makes it reasonable to assume a single-crystal MgF_2 sample with complete non-absorption. At longer wavelengths (> 6.0 μm), the behaviour of the transmission curve shows two properties. One is that the long wavelength cut-off is determined by the first harmonic of fundamental lattice absorption [11]; the other is that the absorption coefficient decreases almost with increasing frequency [12, 13]. Hence the transmittance is dependent on the sample thickness and decreases nearly exponentially with increasing wavelength.

In an HP MgF_2 sample, the transmission loss of incident radiation may inevitably occur due to scattering by the presence of a large number of micropores within the material and by optical anisotropy. The absorption in the short wavelength region of the spectrum is negligible. Therefore, the formula for the transmittance of HP MgF_2 can be modified from Equation 1 as follows [14]

$$\begin{aligned} T_{meas} &= T_{spec} \\ &= (1 - R)^2 \exp[-(\beta + C_{sca})l] \\ &\simeq (1 - R)^2 \exp(-C_{sca} l) \\ &= (1 - R)^2 \exp(-3 Q_{sca} V_p l / 4r) \end{aligned} \qquad (5)$$

where β is the absorption coefficient due to the material, C_{sca} is the absorption coefficient due to scattering, Q_{sca} is the scattering factor that varies between 0 and 4, V_p is the volume fraction of scattering pores, r is the radius of scattering pore. To ensure that there was no variation between separate samples, the HP MgF_2 used for each of the curves shown in Fig. 5 was taken from the same piece of material. The transmission curves illustrating the effect of sample thickness on transmittance qualitatively agree with the results predicted by Equation 5. At wavelengths longer than 6.0 μm, the profile of transmission curves is similar to that of single-crystal MgF_2.

In determining the volume absorption coefficient of magnesium fluoride in the long wavelength region of 3 to 8 μm, the scattered light is negligible. If the in-line transmittance of two samples of different thickness, but otherwise identical, is measured under such circumstances, the experimental absorption coefficient from Equation 5 is given by

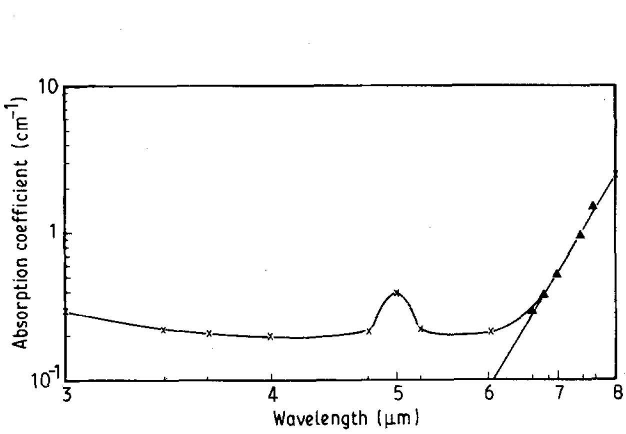

Figure 6 Absorption coefficient from polished magnesium fluoride samples. (———) the contribution predicted for lattice absorption: (×) absorption coefficient observed for HP MgF_2; (▲) indicate absorption coefficient observed for single-crystal MgF_2.

$$\beta = -\ln(T_2/T_1)/l_2 - l_1 \qquad (6)$$

If the frequency of infrared radiation is greater than several times the restrahl frequency of magnesium fluoride, the theoretical absorption will vary nearly exponentially with frequency

$$\beta \sim \exp(-AW) \qquad (7)$$

where A is a material-dependent parameter and W is the frequency expressed in wavenumber units. Fig. 6 shows the extrinsic absorption at wavelengths shorter than 6.0 μm, the intrinsic absorption at longer wavelengths (> 6 μm) for HP MgF_2 and for single-crystal MgF_2 determined using Equation 6. The observed intrinsic absorption of magnesium fluoride fits Equation 7, which yields as a straight line on log–log paper, in the wavelength region 6.0 to 8.0 μm. The extrinsic absorption level measured on the HP MgF_2 is approximately 0.2 cm^{-1} within a broad spectral range, increasing markedly in the vicinity of the selective absorption band. If the exponential dependence is obeyed, the absorption is probably intrinsic, otherwise, probably extrinsic.

The transmission property of HP MgF_2 in the short wavelength region of the spectrum (0.1 to 0.8 μm) is discussed by comparing it with hot-pressed magnesium aluminate spinel (HP $MgAl_2O_4$), because the two materials nearly have the same window region. In scattering theory, the scattering loss mechanism is more sensitive to the transmittance of short wavelength than that of long wavelength and there is an important function, ρ, which is used to describe the scattering effect, and is defined by

$$\rho = 4\pi r|m_1 - m_2|/\lambda_0 \qquad (8)$$

where r is the uniform or average pore size, λ_0 the wavelength in vacuum, m_1 the refractive index of the gas in the pores, and m_2 the refractive index of the medium. The physical meaning of ρ is the phase lag experienced by a central light ray that travels through the sphere along a full diameter, and it is proportional to the scattering factor Q_{sca} as is ρ at low values. Fig. 7 shows the relationship of short-wavelength (0.1 to 0.8 μm) transmission curves of single crystal and polycrystals for both magnesium fluoride with lower refractive index and magnesium aluminate spinel with higher refractive index. The curve for HP MgF_2 is taken as the best one from five different run samples with the same thickness, the curve for HP $MgAl_2O_4$ is obtained in the same way, but for the worst sample. These curves indicate that the worst HP $MgAl_2O_4$ is better than the best HP MgF_2. However, the in-line transmittance for the single-crystal MgF_2 is better than that for the single-crystal $MgAl_2O_4$. Hence experimentally, the opposite result is obtained for transmittance for single crystals and polycrystals by comparison of both materials. According to Equation 8, the short wavelength transmittance of HP MgF_2 should not be far below that of HP $MgAl_2O_4$. Because Equation 8 suggests that, for a given porosity (pore size) of two hot-pressed materials or smaller porosity of the best HP MgF_2, $\rho_{MgAl_2O_4}$ is always larger than ρ_{MgF_2}. In other words, the scattering factor, Q_{sca}, of HP $MgAl_2O_4$ is always larger than that of HP MgF_2. It is said that the fraction of light scattering intensity of HP MgF_2 is smaller than that of HP $MgAl_2O_4$. Hence the ultimate transmittance of HP MgF_2 in the ultraviolet and visible region should be at least comparable to that of HP $MgAl_2O_4$ without considering crystal structure differences. From the results of the preceding analysis, the discrepancy in transmittance between the experimental measurements and the theoretical prediction when comparing HP MgF_2 and HP $MgAl_2O_4$ can be attributed to the secondary transmission loss of HP MgF_2 which is caused by intrinsic birefringent scattering due to variation of the refractive index of the anisotropic crystal structure [17].

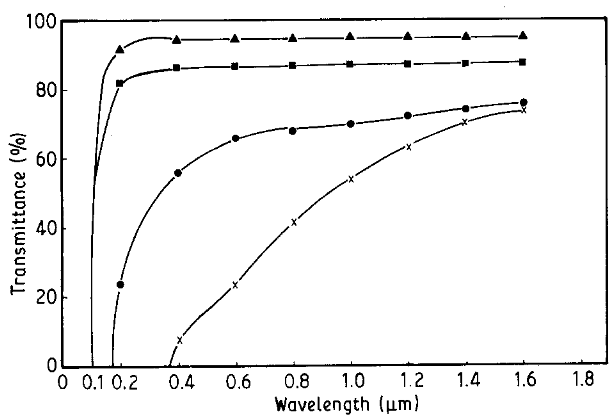

Figure 7 In-line transmittance for single-crystal MgF_2, $MgAl_2O_4$ and HP MgF_2, $MgAl_2O_4$ all with sample thickness t = 2.0 mm: (▲) transmittance observed for single-crystal MgF_2; (■) transmittance observed for single-crystal $MgAl_2O_4$; (●) transmittance observed for the worst of five runs using HP $MgAl_2O_4$ samples; (×) transmittance for the best of five runs using HP MgF_2 samples.

4. Conclusions

1. The intrinsic birefringent scattering mechanism due to crystal structure is responsible for the ultimate transmittance of HP MgF_2 achievable within the window region.
2. Hot-pressed MgF_2 does not result from processing procedures to cause opacity in the ultraviolet and visible region.
3. The profiles of the transmission curves of single-crystal and HP MgF_2 related to sample thickness agree quite well with the calculated values.
4. Hot-pressed MgF_2 exhibits extrinsic absorption at wavelengths shorter than 6 μm. At longer wavelengths, the absorption is intrinsic and is shown by the straight line for single-crystal MgF_2.

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