Research Article  
Enhancing the Quality of the Characteristic Transmittance Curve in the Infrared Region of Range 2.5–7 µm of the Optical Magnesium Fluoride (MgF₂) Ceramic Using the Hot-Pressing Technique in a Vacuum Environment  

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1. Introduction  
The optical polycrystalline magnesium fluoride (MgF₂) ceramic is used widely in infrared optical filters due to its high transmittance in the infrared region and mechanical-physical-thermal strengths. The most important characteristic of magnesium fluoride (MgF₂) is the ability to allow well-infrared radiation at the wavelength range of 2.5–7 µm. Recently, the hot-pressing technique has been a popular way to manufacture this optical ceramic. There have been numerous works dealing with this technology, for example, Chang and Hon [1, 2] and Buckner [3] studied the magnesium fluoride (MgF₂) hot-pressing technology in the open air. In [4], it is presented clearly that the optimal set of technological parameters when hot-pressing MgF₂ in the open air were temperature \( T = 650°C \), time \( t = 30 \) min, and pressure \( P = 200 \) MPa. In comparison with single-crystal magnesium fluoride (MgF₂) ceramic, which is created by a single-crystal growth method, the hot-pressed polycrystalline magnesium fluoride allows infrared light in the wavelength range of 0.1–2.5 µm to be transmitted less well [2]. Moreover, when using the hot-pressing technique in the open air, the transmittance in the wavelength regions 2–4 µm and 6–7 µm is mostly not as good as that in the wavelength region 4–6 µm. The cause is that there is the formation of pores inside crystal particles...
during the hot-pressing process in the open air. There is the
fact that it is hard to remove these pores by using other
approaches, for instance, hot isostatic pressing (HIP) was
employed in [5, 6] by Tsai and Yashina, respectively. When
investigating the characteristic transmittance curve in the
infrared range of magnesium fluoride (MgF₂) ceramic, we
can capture the peak points corresponding to the absorption
stretches. There are some important point as follows. The
peak point at 2.8 µm wavelength corresponds to the hy-
droxylate absorption stretching band (OH stretching), the
peak point at 4.3 µm wavelength corresponds to the carbon
dioxide absorption stretching band, the peak point at 5 µm
wavelength corresponds to the bifluoride absorption
stretching band, the peak point at 6.7 µm wavelength cor-
responds to the OH- banding, and other peak points at 3 µm
and 6.1 µm wavelengths correspond to the bands caused by
the humidity [7]. In general, it is difficult to manufacture
magnesium fluoride ceramic without infrared absorption
bands by operating the hot-pressing technique in the open
air. Therefore, in order to cut down the formulation of pores
during the manufacturing process, scientists consider using
the hot-pressing technique in a vacuum environment. At
that time, the optimal technological parameters such as
temperature, time, and pressure need to be adjusted. It is
the main motivation for our team to carry out an experimental
study to find out the optimal function of the working system
with the highest quality of the characteristic transmittance
curve of hot-pressed magnesium fluoride (MgF₂) ceramic.
Besides, we also evaluate the effect of the hot-pressing
 technique in a vacuum environment on the density and
quality of the characteristic transmittance curve in the
infrared range of 2.5–7 µm.

This paper is divided into 4 main sections. Section 1
presents briefly some works dealt with the hot-pressing
specimen: MgF₂ ceramic type I (hot-pressed specimen in the
open air with optimal parameters: temperature T=650°C, 
time t = 30 min, and pressure P = 200 MPa) and MgF₂ ce-
ramic type II (hot-pressed specimen in the 0.04 bar vacuum
environment). By comparing the density and quality of the
characteristic transmittance curve of two mentioned spec-
imens, we can figure out the efficiency of the use of the
vacuum hot-pressing technique. Besides, in order to determine
the optimal technological parameters (temperature, time, and
pressure) of the vacuum hot-pressing technique by using the experimental planning
approach, herein, we use the orthogonal second-order
planning method; the nonlinear compatibility using the
quadratic polynomial with three deformation components
are expressed as follows:

\[ f = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3, \]

where \( x_1, x_2, \) and \( x_3 \) are the technological parameters corresponding to temperature \( T \) (°C), time \( t \) (min), and pressure \( P \) (MPa), respectively.

By selecting the experimental planning option with the
center given by Box and Wilson [8], the number of ex-
periments is defined as follows [9]:

\[ N = 2^k + 2k + n_0, \]

where the structure has three impact factors \( k = 3 \), and the
number of the center of the option is \( n_0 = 3 \). Thus, according
to equation (2), we can find the number of the experiment is
\( N = 17 \). In order to be convenient to calculate the experi-
mental coefficients of the mathematical regression model
and process the data, we convert to the nondimensional
value encoding with the upper bound (+1), the lower bound
(−1), and the average value (0) in the extended space
\( \alpha = 1, 215 \):

\[ \frac{X_j^\prime - X_j^0}{\Delta X_j^0} = 1.215 \rightarrow X_j^\prime = 1.215\Delta X_j^0 + X_j^0, \]

\[ \frac{X_j^\prime - X_j^0}{\Delta X_j^0} = -1.215 \rightarrow X_j^\prime = -1.215\Delta X_j^0 + X_j^0, \]

\[ X_j^\prime = X_j + \beta, \quad \alpha = 1.215, \quad \alpha^2 = 1.476, \quad \beta = 0.73. \]

Based on the optimal technological parameters of the
hot-pressing technique in the open air, we choose the values
of the technological parameters of the hot-pressing tech-
nique in the vacuum as listed in Table 1. Then, we measure

![Figure 1: The SEM of the MaF₂ powders.](image)
the transmittance of the specimens at the 4.5 \mu m wavelength to obtain the experimental planning values.

In order to conduct the experimental planning investigation, we manufacture seventeen specimens in the 0.04 bar vacuum environment following the data set as presented in Table 2.

The experimental cylinder specimens with \( \Phi 30 \times 10 \) mm are created from the same hot processing mold, which is made from the heat-resistant Nickel alloy-Inconel 718, and the mold is covered with a boron nitride nonstick layer. The hot-pressing process does not need to use additional adhesive additives. The diagram of the hot-pressing technique in a vacuum environment is shown in Figure 2.

The specimens need to be ground and polished to ensure the following requirements: the degree of parallelism of two working surfaces is not over 30,' the surface roughness \( R \) does not exceed 0.050 \mu m, and the surface cleanliness must be from level IV or higher based on GOST 11141 standard.

The density of the specimens is measured by the hydrostatic weighing method on the device CY 323 GT. In order to obtain the characteristic transmittance curve, we measure the transmittance using a single-beam spectrometer with a Michelson interferometer. In detail, herein, we use the infrared spectrometer Nicolet Summit FTIR Spectrometers with the measuring spectral range of 1.28–28 \mu m. The transmittance is measured in the direction of hot-pressing.

From the transmittance of seventeen specimens at the 4.5 \mu m wavelength, we obtain the experimental planning data set by using the experimental planning method to determine the coefficients of the regression function as shown in equation (1). Then, we use Maple 2016 application (Waterloo Maple Inc, Waterloo, Ontario, Canada) to find out the optimal value of the regression function and the optimal data set of the working system.

### Table 1: The values of the experimental planning.

| Variable | \(-\alpha\) | -1 | 0 | 1 | \(\alpha\) |
|----------|-------------|----|---|---|-----------|
| \(x_1\) Temperature \(T \) (°C) | 480 | 500 | 600 | 700 | 720 |
| \(x_2\) Time \(t \) (min) | 5 | 10 | 30 | 50 | 55 |
| \(x_3\) Pressure \(P \) (MPa) | 80 | 100 | 200 | 300 | 320 |

3. Results and Discussions

Firstly, we obtain the results as follows. The density of the hot-pressed specimen in a vacuum environment is 3.178 g/cm³, while the density of the hot-pressed specimen in the open air is 3.173 g/cm³. We can see clearly that by using the hot-pressing technique in a vacuum environment, the density of the specimen increases. The reason can be easily explained that when operating in the open air, the air will diffuse into the specimen structure and then the porosity of the pressed product increases. However, when employing the hot-pressing technique in a vacuum environment, we can overcome this disadvantage; as a result, the porosity of the pressed product decreases (Figure 3).

Figure 4 presents the characteristic transmittance curve in two cases (specimen type I and specimen type II) at the same technological conditions: temperature 650°C, time 30 min, and pressure 200 MPa.

Secondly, we can see that the quality of the characteristic transmittance curve of specimen type II (the blue line, in a vacuum environment) is higher than that of the characteristic transmittance curve of specimen type I (the red line, in the open air). The hot-pressed specimen in a vacuum environment has a 4–10% higher transmittance in the range of 2–7 \mu m than that of the hot-pressed specimen in the open air with the same technological condition. Others depend on the wavelength.

Next, the characteristic transmittance curve of the hot-pressed specimen in a vacuum environment is smoother than that of the hot-pressed specimen in the open air, it has fewer peak points, and the width of the peak points is smaller. The first peak point of the characteristic transmittance curve of magnesium fluoride (MgF₂) ceramic can be observed at the 2.8 \mu m wavelength. This peak point is the most easily identifiable characteristic of the nature of MgF₂ ceramic compared with that of other optical ceramics. This can be explained that, when operating the system in the high-temperature environment, the powder hydrolysis phenomenon appears. In other words, there is an interaction between MgF₂ powder and the steam in the high-temperature environment. The finer the powder MgF₂ is, the stronger the thermal hydrolysis reaction is. The cause is the powder MgF₂ makes it easy to absorb the high-temperature steam. The interaction between MgF₂ powder and the steam and the formulation of the substance are expressed as follows [10, 11]:

(i) The reaction of steam absorption is based on the following chemical equation:

\[
\text{MgF}_2 + \text{H}_2\text{O} \rightarrow \text{MgF}_2 \cdot \text{H}_2\text{O} \quad (6)
\]

(ii) The process of forming hydroxy fluoride complex compounds is based on the following chemical equation:

\[
\text{MgF}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Mg(OH)F} + \text{HF} \quad (7)
\]

The formation of hydroxyl compounds is the cause of the peak point corresponding to the 2.8 \mu m wavelength. From Figure 4, we can observe that, for the specimen type I (the red line, in the open air), this peak point is relatively wide, spreading to the 3 \mu m wavelength, while for the hot-pressed specimen in a vacuum environment (the blue line), this peak point is very narrow and it is only located at the 2.8 \mu m wavelength. The decrease in transmittance at the 3 \mu m wavelength is due to the steam getting into the particles of the product in the open air. So, using the hot-pressing technique in the vacuum can thoroughly resolve this drop. The other effect of the hydrolysis of ceramic powder MgF₂ is that, in addition to hydroxyl compounds,
it also produces bifluoride (HF). This is the cause of the peak point corresponding to 5 µm wavelength. This effect has a relatively strong effect on the application scope of the optical MgF₂ ceramic, because the 5 µm wavelength is in the best transmittable infrared region (3–6 µm) of the MgF₂ optical ceramic. 

On the other hand, regarding the decrease in transmittance at the 5 µm wavelength, we need to pay attention to the decomposition temperature of hydroxy fluoride as follows [10, 11]:

\[
\text{Mg(OH)F} \rightarrow \text{MgO} + \text{HF} 
\]

The effects of thermal hydrolysis are greatly reduced when operating in a vacuum environment due to the steam restriction. The peak points corresponding to the 2.8 µm and 5 µm wavelengths can be clearly seen on the characteristic transmittance curve of the hot-pressed specimen in a vacuum environment and is narrower and much shorter than those of the hot-pressed specimen in the open air.
Besides, we can see the peak point at the 6.7 µm wavelength. This decrease is due to the OH bending. This peak point of the red line (the hot-pressed specimen in the open air) is not only deeper than that of the blue line (the hot-pressed specimen in a vacuum environment), but also there is a larger wide spreading to 7 µm wavelength. The reason is that, when hot-pressing the fluoride ceramic, there is a formation of carbonate impurities due to the interaction of the hydroxide group (OH) with CO₂ in the air by the following reactions [12–14]:

\[
2\text{OH}^- + \text{CO}_2 \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \tag{9}
\]

\[
\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^- \tag{10}
\]

A decrease at the 7 µm wavelength of a vacuum-pressed specimen is virtually absent due to the removal of CO₂ in the pressing environment.

Table 3 shows the experimental results at the 4.5 µm wavelength of seventeen hot vacuum-pressed specimens to obtain the optimal technological parameters in a vacuum environment by the experimental planning approach.

The results of the regression coefficients in equation (1) are listed in Table 4.

The regression function coefficient is confirmed based on the Student standard; firstly, we need to calculate the reproductive variance \(S_{RV}\). According to the results of the experimental data table, we can find the reproductive variance \(S_{RV}\) as shown in Table 5.

After some efforts including finding the variances of coefficients in the regression function \(S_{bi}\), identifying statistical tests, and comparing with the Student standard \(t(0.05; 2) = 4.3\), we get the regression function coefficient values as listed in Table 6.

Then, we obtain the regression function as follows:

\[
f = 84.53 + 4.77x_1 + 2.52x_2 + 2.67x_3 + 2.63x_1x_3 - 3.38x_2x_3 - 6.84x_1^2 - 4.81x_2^2 - 5.15x_3^2, \tag{11}
\]

where \(x_1 = (T - 600/100)\), \(x_2 = (t - 30/20)\), and \(x_3 = (P - 200/100)\).

The results of the regression function test using the Fisher standard are as follows:

(i) Residual variance:

\[
S^2_{RV} = 17.91, \tag{12}
\]

\[
f_1 = 6, \tag{13}
\]

\[
f_2 = 2.
\]

(ii) The Fisher standard:

\[
F = 17.91, \tag{13}
\]

\[
F_{a} = F_{0.05}(6, 2) = 19.3.
\]
We can see that $F < F_a$, so the function is compatible. Therefore, the regression function written in equation (11) is verified.

Now, we use Maple 2016 application (Waterloo Maple Inc, Waterloo, Ontario, Canada) to find out 86.25% highest transmittance at the optimal technological parameters as follows:
We can see that the optimal technological parameters in a vacuum environment are not much different than those in the open air. In the case of operating in a vacuum environment, the pressure is higher. Therefore, the residual pressure decreases and the air in the particles is removed. Consequently, the density and quality of the product increase (Figure 5).

Figures 6–8 present the dependence of the transmittance on 2 of the 3 technological factors (temperature, time, and pressure).

It can be seen the dependency of the transmittance on the technological parameters when hot-pressing in a vacuum environment is similar to that in the open air. The effect of temperature and pressure on the quality of the hot-pressed product is greater than the effect of time. We can see that the curvature of the surface in Figure 6 is greater than that in Figures 7 and 8.

4. Conclusions

By operating the hot-pressing technique in a vacuum environment, the impact of moisture and other disturbances in the open air on the quality of hot-pressed MgF₂ ceramic is overcome. The transmittance at the infrared band 2–7 µm of the hot-pressed specimen in a vacuum environment is about 4–10% higher than that of the hot-pressed specimen in the open air. Moreover, the characteristic transmittance curve of the hot-pressed specimen in a vacuum environment is smoother, has fewer peak points, and decreases. We also find out the optimal technological parameters of the system when running in a vacuum environment are as follows: temperature $T = 640.9°C$, time $t = 33.0$ min, and pressure $P = 231.4$ MPa.
Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References

[1] C.-S. Chang and M.-H. Hon, “Texture effect of hot-pressed magnesium fluoride on optical transmittance,” Materials Chemistry and Physics, vol. 81, no. 1, pp. 27–32, 2003.
[2] C.-S. Chang, M.-H. Hon, and S.-J. Yang, “The optical properties of hot-pressed magnesium fluoride and single-crystal magnesium fluoride in the 0.1 to 9.0 μm range,” Journal of Materials Science, vol. 26, no. 6, pp. 1627–1630, 1991.
[3] D. A. Buckner, C. H. Harold, and J. K. Norbert, “Hot-pressing magnesium fluoride,” Journal of American Ceramic Society, vol. 45, no. 9, pp. 435–438, 1962.
[4] Magnesium fluoride for hot pressing, Calcined. Technical conditions TU 6-09-689-76, Russia State Committee 1977: 9, State Committee for Standards of Government of Russia, Moscow, Russia, http://www.docum.ru/tu.asp?id=84047.
[5] D. S. Tsai, C. T. Wang, S. J. Yang, and S. E. Hsu, “Hot isostatic pressing of MgAl2O4 spinel infrared windows,” Materials and Manufacturing Processes, vol. 9, no. 4, pp. 709–719, 1994.
[6] E. V. Yashina, E. M. Gavrishchuk, and V. B. Ikonnikov, “Compaction mechanisms of polycrystalline ZnS obtained by the sub-method during high-temperature gas-static pressing,” Inorganic Materials, vol. 40, no. 9, pp. 1035–1038, 2004.
[7] M. H. Moghim and M. H. Paydar, “Hot-pressing of bimodally distributed magnesium fluoride powder,” Infrared Physics & Technology, vol. 53, no. 6, pp. 430–433, 2010.
[8] G. E. P. Box and K. B. Wilson, “On the experimental attainment of optimum conditions,” Journal of the Royal Statistical Society. Series B (Methodological), vol. 13, no. 1, pp. 1–38, 1951.
[9] C. David and R. Nancy, The Theory of Design Experiments, Chapman & Hall/CRC, Boca Raton, FL, USA, 2000.
[10] D. R. Messier, “Kinetics of high-temperature hydrolysis of magnesium fluoride: I, evaluation of reaction mechanism,” Journal of the American Ceramic Society, vol. 48, no. 9, pp. 452–459, 1965.
[11] D. R. Messier and A. P. Joseph, “Kinetics of high-temperature hydrolysis of magnesium fluoride: II, influence of specimen geometry and type and of product layers,” Journal of the American Ceramic Society, vol. 48, no. 9, pp. 459–463, 2006.
[12] P. P. Fedorov, V. V. Osiko, T. T Basiev et al., “Optical fluoride nanoceramics,” Russian Nanotechnology, vol. 2, no. 5-6, pp. 95–105, 2007.
[13] V. M. Reuters, “The effect of heat treatment on the transmission of windows of fluoride crystals in the vacuum ultraviolet region of the spectrum,” WMD, vol. 7, pp. 43–45, 1976.
[14] V. K. Komar, “The effect of heat treatment on IR absorption in zinc selenide crystals,” Collection of Abstracts of the VII All-Union Meeting “Crystal Optical Materials”, vol. 57, 1989.