Hindawi
Advances in Materials Science and Engineering
Volume 2020, Article ID 7258431, 8 pages
https://doi.org/10.1155/2020/7258431

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 (MgF_2) Ceramic Using the Hot-Pressing Technique in a Vacuum Environment

Nguyen Tuan Hieu ,[1] Van Thom Do ,[2] Nguyen Dinh Thai,[1] Tran Duc Long,[1] and Phung Van Minh[2]

[1]*Hanoi Institute of Technology, Hanoi City, Vietnam*
[2]*Faculty of Mechanical Engineering, Le Quy Don Technical University, Hanoi City, Vietnam*

Correspondence should be addressed to Nguyen Tuan Hieu; hieuhtip@gmail.com and Van Thom Do; thom.dovan.mta@gmail.com

Received 21 March 2020; Revised 5 June 2020; Accepted 22 June 2020; Published 24 July 2020

Academic Editor: Simo-Pekka Hannula

This paper carries out an experimental study to enhance the quality of the characteristic transmittance curve in the infrared range of 2.5–7 μm of the optical magnesium fluoride (MgF_2) ceramic. This work evaluates the effectiveness of using vacuum environment in the MgF_2 ceramic hot-pressing technique by comparing the density and the quality of the transmittance characteristic curve of two types of specimens manufactured by the hot-pressing technique corresponding to open air and vacuum environment under the same technological parameters including temperature 650°C, time 30 min, and pressure 200 MPa. The results present that, in comparison with using the hot-pressing technique in the open air, when using the hot-pressing technique in a vacuum environment, the transmittance increases about 4–10%, the characteristic transmittance curve is smoother and has fewer peak points, and the wide of peak points are smaller. When hot-pressing in a vacuum environment, the temperature can be up to 750°C in order to obtain the magnesium fluoride (MgF_2) ceramic with the highest quality of characteristic line in the infrared range of 2.5–7 μm. Seventeen specimens are manufactured to conduct the experimental study in order to figure out the optimal set of technological parameters (temperature $T = 640.9$°C, time $t = 33.0$ min, and pressure $P = 231.4$ MPa) when hot-pressing in a vacuum environment by the experimental planning approach.

1. Introduction

The optical polycrystalline magnesium fluoride (MgF_2) 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 (MgF_2) 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 (MgF_2) hot-pressing technology in the open air. In [4], it is presented clearly that the optimal set of technological parameters when hot-pressing MgF_2 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 (MgF_2) 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 (MgF_2) 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 hydroxylate 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 corresponds to the OH-banding, and other peak points at 3 μm and 6.1 μm wavelengths correspond to the bands caused by the humility [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 (MgF_2) 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 technique in the open air as well as its disadvantages. The research object and governing equations are introduced in section 2. Section 3 presents the experimental results and discussions. Some important points are concluded in the last one, Section 4.

2. Experiment

In this work, the experimental specimens are manufactured using the hot-pressing technique from the same kind of powder magnesium fluoride with size is about 80–100 nm and the purity is over 99%. The SEM of the MaF_2 powders is shown in Figure 1.

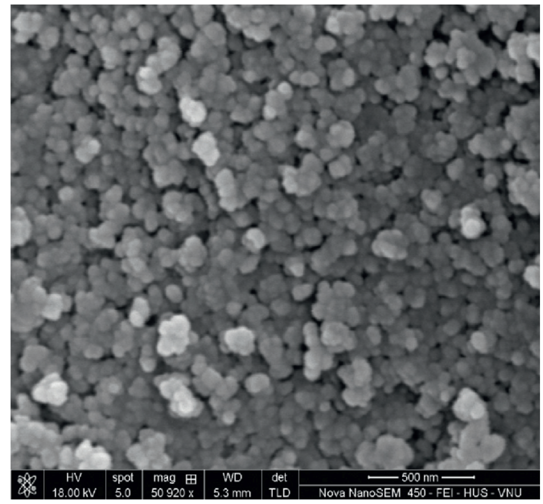


Figure 1: The SEM of the MaF_2 powders.

To evaluate the efficiency of the vacuum hot-pressing technique, we consider two types of the experimental specimen: MgF_2 ceramic type I (hot-pressed specimen in the open air with optimal parameters: temperature $T = 650^{\circ}$C, time $t = 30$ min, and pressure $P = 200$ MPa) and MgF_2 ceramic 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 specimens, 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:

$$\begin{aligned} f = {} & b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 \\ & + b_{23} x_2 x_3 + b_{11} x_1^2 + b_{22} x_2^2 + b_{33} x_3^2, \end{aligned} \tag{1}$$

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 experiments is defined as follows [9]:

$$N = 2^k + 2k + n_0, \tag{2}$$

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 experimental 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 $\alpha = 1,215$:

$$\frac{X'_{j\max} - X_j^0}{\Delta X_j^0} = 1.215 \longrightarrow X'_{j\max} = 1.215 \Delta X_j^0 + X_j^0, \tag{3}$$

$$\frac{X'_{j\min} - X_j^0}{\Delta X_j^0} = -1.215 \longrightarrow X'_{j\min} = -1.215 \Delta X_j^0 + X_j^0, \tag{4}$$

$$X'_j = X_j^2 - \beta, \quad \alpha = 1.215, \quad \alpha^2 = 1.476, \quad \beta = 0.73. \tag{5}$$

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 technique in the vacuum as listed in Table 1. Then, we measure

Table 1: The values of the experimental planning.

Variable	$-\alpha$	-1	0	1	α
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

the transmittance of the specimens at the 4.5 μm 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 μm, and the surface cleanness 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 μm. The transmittance is measured in the direction of hot-pressing.

From the transmittance of seventeen specimens at the 4.5 μm wavelength, we obtain the experiment 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.

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/cm^3, while the density of the hot-pressed specimen in the open air is 3.173 g/cm^3. 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 μm 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 (MgF_2) ceramic can be observed at the 2.8 μm wavelength. This peak point is the most easily identifiable characteristic of the nature of MgF_2 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 MgF_2 powder and the steam in the high-temperature environment. The finer the powder MgF_2 is, the stronger the thermal hydrolysis reaction is. The cause is the powder MgF_2 makes it easy to absorb the high-temperature steam. The interaction between MgF_2 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:

$$MgF_2 + H_2O \longleftrightarrow MgF_2 \cdot H_2O \tag{6}$$

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

$$MgF_2 \cdot H_2O \longleftrightarrow Mg(OH)F + HF \tag{7}$$

The formation of hydroxyl compounds is the cause of the peak point corresponding to the 2.8 μm 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 μm 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 μm wavelength. The decrease in transmittance at the 3 μm 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 MgF_2 is that, in addition to hydroxyl compounds,

Table 2: The technological data set of specimens.

Order	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
x_1 Temperature T (°C)	500	700	500	700	500	700	700	480	720	600	600	600	600	600	600	600	600
x_2 Time t (min)	10	10	50	50	10	10	50	50	30	30	5	55	30	30	30	30	30
x_3 Pressure P (MPa)	100	100	100	100	300	300	300	300	200	200	200	200	80	320	200	200	200

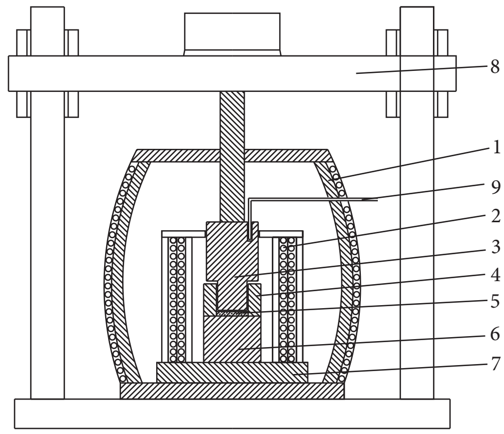
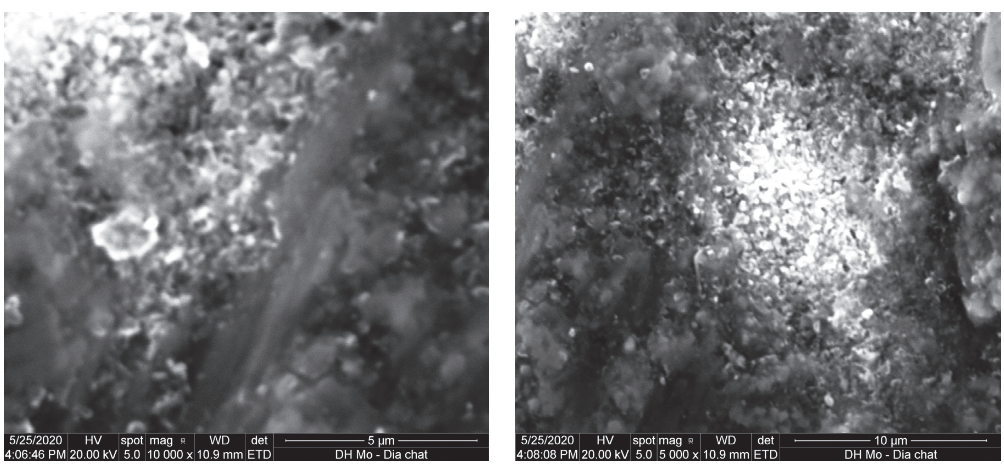


Figure 2: The diagram of the hot-pressing technique in a vacuum environment. 1, vacuum chamber; 2, heating furnace; 3, pestle; 4, shell mold; 5, pressing material; 6, mortar; 7, pedestal; 8, pressing table; 9, thermocouple.



(a) (b)

Figure 3: Microstructure of the ceramics sintered in the open air (a) and in a vacuum environment (b).

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 MgF_2 ceramic, because the 5 μm wavelength is in the best transmittable infrared region (3–6 μm) of the MgF_2 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]:

$$Mg(OH)F \longleftrightarrow MgO + HF \tag{8}$$

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.

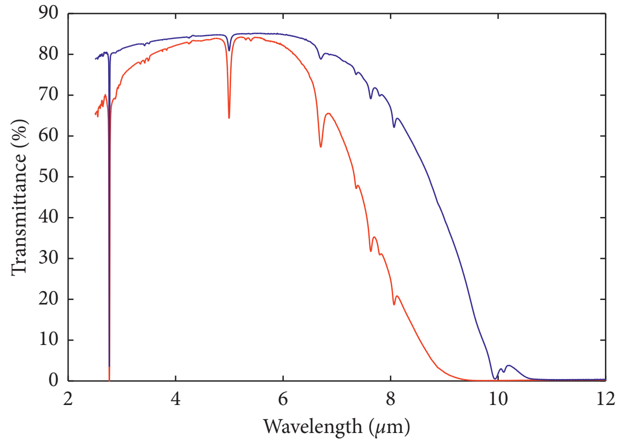


FIGURE 4: The characteristic transmittance curve.

TABLE 3: The experimental results of the transmittance.

Order	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
x_1 Temperature T (°C)	500	700	500	700	500	700	700	480	720	600	600	600	600	600	600	600	600
x_2 Time t (min)	10	10	50	50	10	10	50	50	30	30	5	55	30	30	30	30	30
x_3 Pressure P (MPa)	100	100	100	100	300	300	300	300	200	200	200	200	80	320	200	200	200
The transmittance at 4, 5 $\mu m\tau$ (%)	57	66	70	73	63	79	59	76	77	71	83	71	84	69	86	85	87

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 CO_2 in the air by the following reactions [12–14]:

$$2OH^- + CO_2 \longleftrightarrow {CO_3}^{2-} + H_2O \quad (9)$$

$$OH^- + CO_2 \longleftrightarrow {HCO_3}^- \quad (10)$$

A decrease at the 7 μm wavelength of a vacuum-pressed specimen is virtually absent due to the removal of CO_2 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_{th}. According to the results of the experimental data table, we can find the reproductive variance S_{th} 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:

$$\begin{aligned} f &= 84.53 + 4.77x_1 + 2.52x_2 + 2.67x_3 + 2.63x_1x_3 \\ &\quad - 3.38x_2x_3 - 6.84x_1^2 - 4.81x_2^2 - 5.15x_3^2, \end{aligned} \quad (11)$$

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:

$$\begin{aligned} S^2_{RV} &= 17.91, \\ f_1 &= 6, \\ f_2 &= 2. \end{aligned} \quad (12)$$

(ii) The Fisher standard:

$$\begin{aligned} F &= 17.91, \\ F_\alpha &= F_{0.05}(6.2) = 19.3. \end{aligned} \quad (13)$$

Table 4: The results of the regression coefficients.

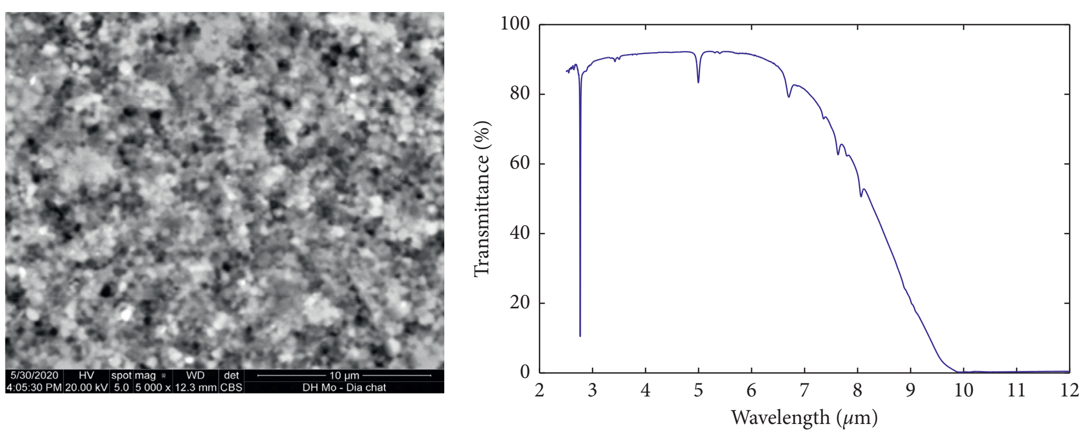
b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{11}	b_{22}	b_{33}
72.27	4.77	2.52	2.67	−0.63	2.63	−3.38	−6.84	−4.81	−5.15

Table 5: The reproductive variance.

Order	y_0	$\overline{y}$	$(y_0 - \overline{y})$	$(y_0 - \overline{y})^2$	$n_0 - 1$	S^2_{th}	S_{th}
1	86		0	0			
2	85	86	−1	1	2	1	1
3	87		1	1			

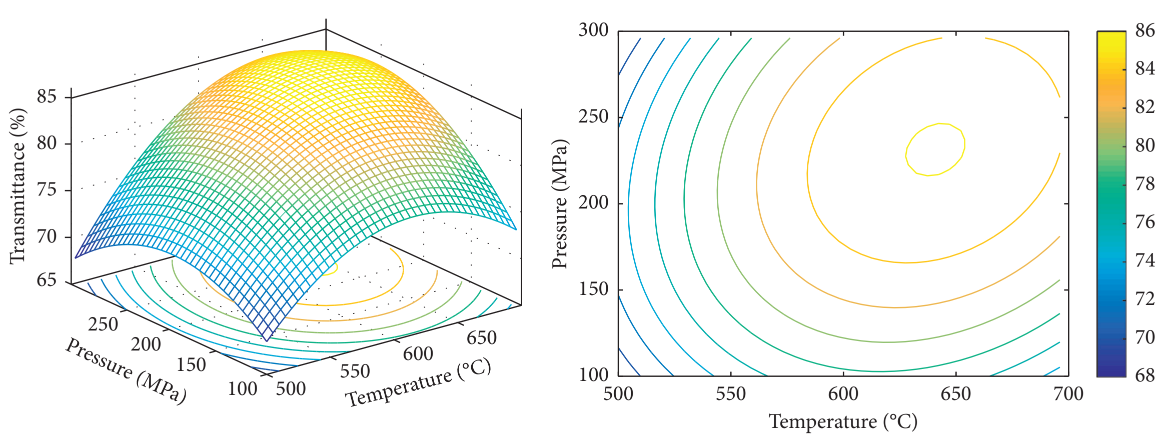
Table 6: The regression function coefficient values.

b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{11}	b_{22}	b_{33}
72.27	4.77	2.52	2.67	0.00	2.63	−3.38	−6.84	−4.81	−5.15



(a) (b)

Figure 5: The transmittance (a) and microstructure (b) of the ceramics sintered at the optimal parameters.

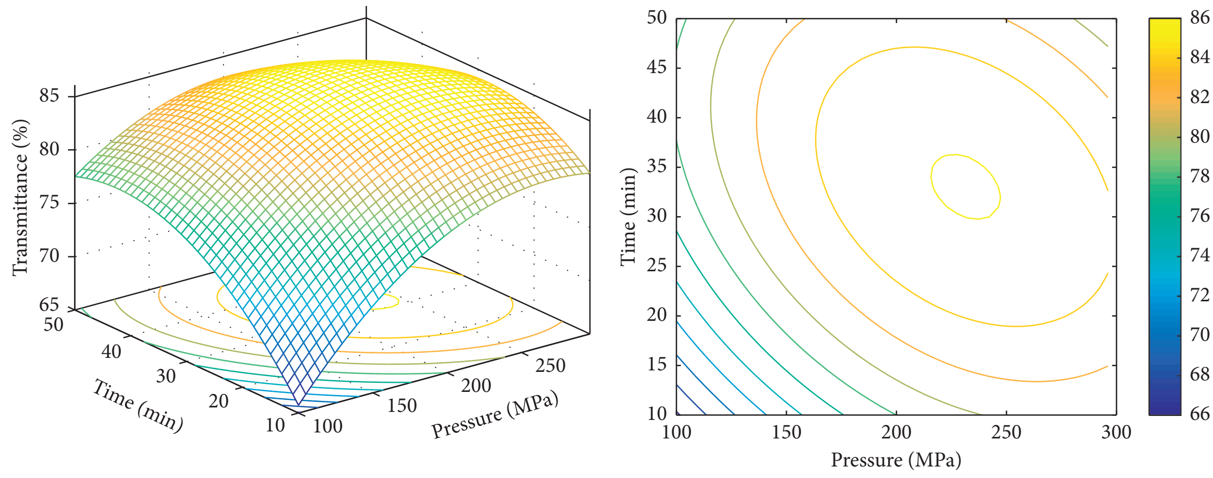


(a) (b)

Figure 6: The optimal transmittance surface depends on the temperature and pressure.

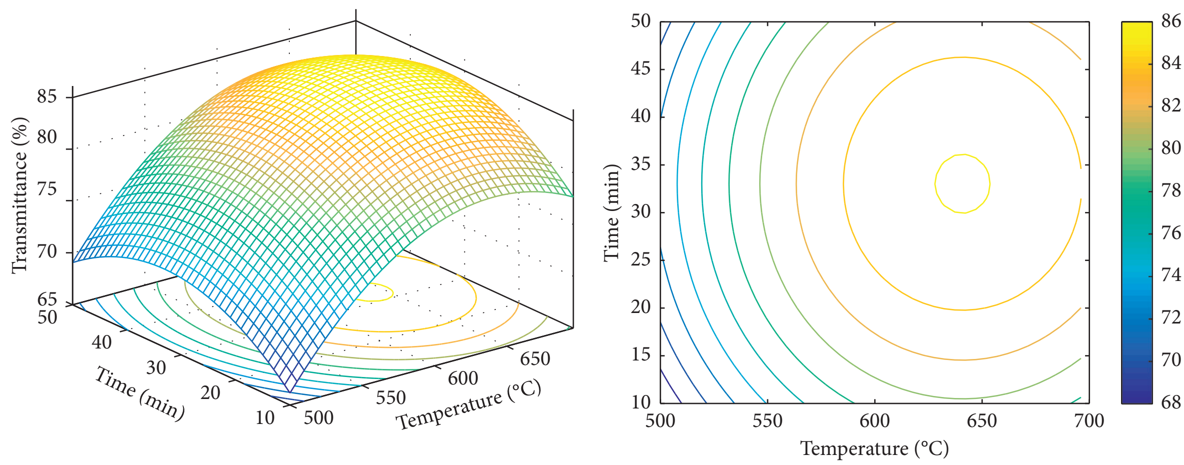
We can see that $F < F_{\alpha}$, so the function is compatible. Therefore, the regression function written in equation (11) is verified.

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:



(a) (b)

Figure 7: The optimal transmittance surface depends on the time and pressure.



(a) (b)

Figure 8: The optimal transmittance surface depends on the temperature and time.

(i) Temperature $T = 640.9^{\circ}$C

(ii) Time $t = 33.0$ min

(iii) Pressure $P = 231.4$ MPa

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 in turn 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 MgF_2 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 $T = 640.9^{\circ}$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

This research was funded by the Hanoi Institute of Technology under grant number 10.02–2020.26.

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 $MgAl_2O_4$ 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.