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Theoretical and experimental analysis of MgF_2 crystal growth

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Magnesium fluoride crystal growth is studied in a closed graphite chamber. The raw material located at the chamber bottom is kept at temperature higher than MgF_2 melting point (1550 K) and evaporated at reduced pressures ranging from 0.1 to 1.0 Pa. MgF_2 crystal growth occurs on the chamber top at temperatures varied from 1324 to 1374 K. Diaphragms with hole of various diameters are mounted at a certain distance from material source for controlling the growth rate and the crystal shape. A simplified model based on experimental observations [3] is suggested for describing the process. Theoretical analysis shows that the growth rate monotonically increases with the temperature drop for large holes, while small diameters lead to a decrease in the growth rate at high temperature drops due to MgF_2 losses on the diaphragm. Our computations predict 0.8-1.2 mm/h of crystal growth under operating conditions considered. This is consistent with experiments where magnium fluoride crystals (110) are obtained as disks of 100 mm diameter and 10 mm thickness [3].

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1. Introduction

Fluoride crystals such as magnesium fluoride (MgF_2) are widely utilized as various kinds of optical elements, lenses, window materials etc. due to high transmittance within a broad range of wavelengths from the vacuum ultraviolet region to the far infrared region. Usually, a technique based on the Stockbarger method [1] is employed for growing the crystals. The present paper focuses primarily on theoretical analysis of an alternative process to find influence of operating conditions on the growth rate and the crystal properties.

2. Model

Sketch of the MgF_2 growth chamber is presented in Fig. 1. Radii of chamber and diaphragm hole are R_C and r. T_1, T_2, and T_3 denote temperatures at chamber bottom, top and diaphragm, respectively. MgF_2 vapor pressure distribution in lower and upper parts of the chamber is assumed to be uniform and set to equal p_1 and p_2. On the other hand, the pressure can vary considerably within boundary layers near walls, top, bottom and diaphragm of chamber. The pressure of MgF_2 saturated vapor (p^s) is evaluated from data [2] as

$$p^s = 3.62\times 10^{13} \exp\left(-4.42\times 10^4/T\right) \qquad (1)$$

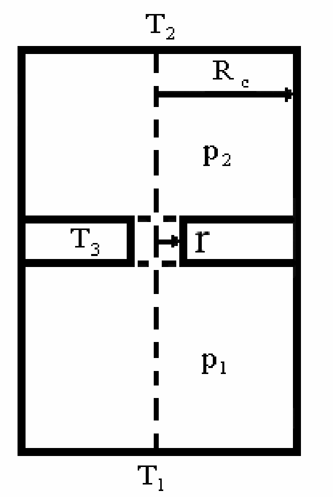

Fig. 1. Sketch of the MgF_2 growth chamber.

Mass flux of MgF_2 from the chamber bottom is determined by p_1^s at $T=T_1$ and the pressure in the lower part p_1 as

$$j_1 = \beta_1 \left(p_1^{s} - p_1 \right) \quad (2)$$

Similarly, the mass flux to the chamber top is given by p_2^{s} at $T=T_2$ and the pressure in the lower part p_2 as

$$j_2 = \beta_2 \left(p_2 - p_2^{s} \right) \quad (3)$$

Mass loss on the lower side of diaphragm at $T=T_3$ is estimated as

$$j_3 = \beta_3 \left(p_1 - p_3^{s} \right) \quad (4)$$

Here $\beta_i = \sqrt{\dfrac{M_{MgF_2}}{2\pi R T_i}}$ is calculated at $T=T_i$, M_{MgF_2} is the molecular weight of MgF_2, R is the gas constant.

Difference in vapor pressures between lower and upper parts of the chamber provides the viscous flow through the diaphragm hole. Using the expression for viscosity from the kinetic theory and calculating the physical parameters inside the hole for averaged pressure $p = 0.5\left(p_1 + p_2\right)$, the following expression can be derived for estimating the mass flux here

$$j = \frac{3\sqrt{2}\pi d^2 r}{2 k T_3 c_3} \left(p_1^2 - p_2^2 \right), \quad (5)$$

where d is the Lenard-Jones' parameter for MgF_2 molecules in the gas phase ($= 3.62\ \mathring{A}$), k is the Boltzmann constant, c_3 is the sound velocity at $T=T_3$.

The mass conservation gives then the following set of equations for calculating p_1 and p_2

$$j_1 R_C^2 = j r^2 + j_3 \left(R_C^2 - r^2 \right) \quad (6)$$

$$j_2 R_C^2 = j r^2 \quad (7)$$

MgF_2 growth rate V is determined by the mass flux on the chamber top j_2 and the density of MgF_2 formed in the solid phase ($\rho_c = 3130$ kg/m^3) on the chamber top and diaphragm as

$$V = \frac{j_2}{\rho_c} \quad (8)$$

Using Eqs. (2)-(8), one can derive the explicit expression for evaluating V

$$V = \frac{1}{1-\gamma^2} \left[V_1 + \gamma V_2 + V_r - \sqrt{\left(V_1 + \gamma V_2 + V_r \right)^2 - \left(1 - \gamma^2 \right)\left(V_1^2 - V_2^2 \right)} \right] \quad (9)$$

where $\gamma = \dfrac{1}{\beta_2} \left[\beta_1 + \beta_3 \left(1 - \dfrac{r^2}{R_C^2} \right) \right]$,

$$V_1 = \frac{1}{\rho_c} \left[\beta_1 p_1^{s} + \beta_3 \left(1 - \frac{r^2}{R_C^2} \right) p_3^{s} \right],$$

$$V_2 = \frac{1}{\rho_c} \left[\beta_1 + \beta_3 \left(1 - \frac{r^2}{R_C^2} \right) \right] p_2^{s},$$

$$V_r = \frac{k T_3 c_3 R_C^2}{3\sqrt{2}\pi d^2 r^3 \rho_c} \left[\beta_1 + \beta_3 \left(1 - \frac{r^2}{R_C^2} \right) \right]^2 .$$

The growth rate in the chamber without the diaphragm is found from (9) at $V_r=0$ and $\beta_3=0$

$$V = \frac{V_1 - V_2}{1+\gamma} = \frac{\beta_1 \beta_2}{\beta_1 + \beta_2} \frac{p_1^{s} - p_2^{s}}{\rho_c} \quad (10)$$

Note the temperature drop between the chamber bottom and top is mostly responsible for the process within the approach above.

3. Results and discussion

The growth rate of MgF_2 crystal was measured experimentally for the process in the chamber without the diaphragm and reached 0.6-2.4 mm/h at the raw material temperature of 1473-1573 K and at the top temperature of 1374 K [3]. Fig. 2 demonstrates the growth rate predicted within the developed model as a function of the temperature drop between the chamber bottom and top at the raw material temperature of 1474 K. As it follows from the plot, our computations are within range of the experimental data [3] and show a monotonic increase in the growth rate with the temperature drop. This is associated with a decrease of the saturated vapor pressure near the growth surface and, hence, the elevation of pressure drop between the chamber top and bottom.

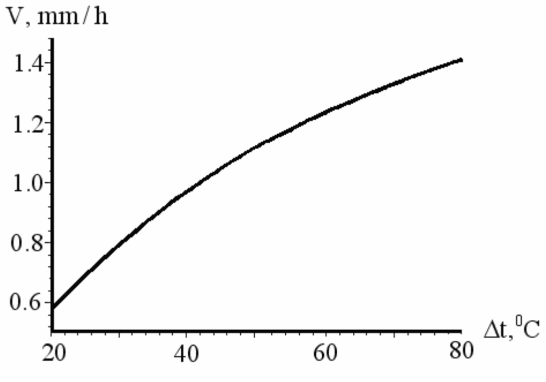

Fig. 2. Predicted growth rate vs. temperature drop without diaphragm. Bottom temperature is 1474 K.

The model is further applied for describing the process accomplished in the chamber with diaphragm (see Fig. 1). Fig. 3 illustrates the growth rate vs. the temperature drop at the diaphragm with holes of various diameters. The modeling results show a non-monotonic increase in the growth rate at the hole diameters smaller than 50 mm. This is mainly due to competition of two phenomena. One is the deposition on the lower part of the diaphragm and, as a result, the material loss. The other is the crystal growth on the chamber top. Note that a monotonic increase in the growth rate manifests itself only at hole diameters closed to the chamber diameter when the loss on the diaphragm becomes negligible.

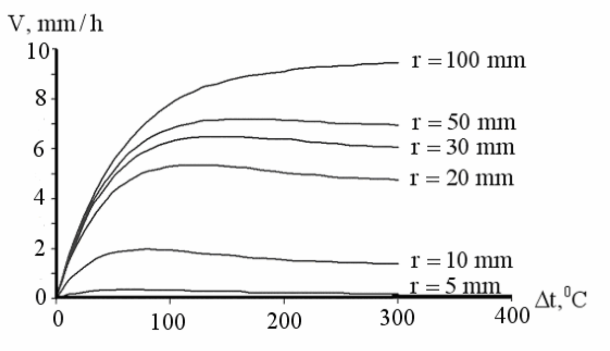

Fig. 3. Predicted growth rate vs. temperature drop at various diameters of diaphragm hole. Bottom temperature is 1474 K.

To get an insight into the process, 2D pattern of the growth rate is presented as a function of the temperature drop and the hole diameter in Fig. 4. As seen from the computations, the temperature drop elevation can cause a drastic decrease in the growth rate at narrow holes. Obviously, the material loss on the diaphragm is then comparable to the MgF_2 consumption on the chamber top and, therefore, an additional increase of the temperature drop fails to improve the process output.

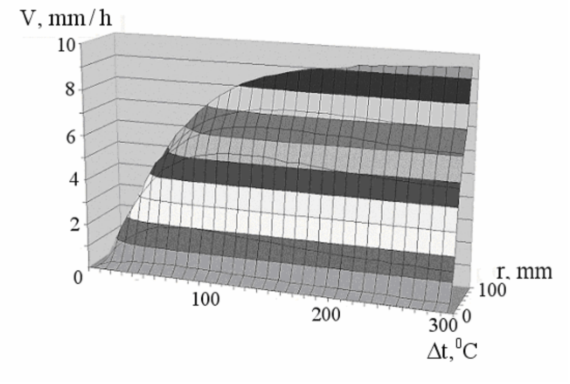

Fig. 4. 2D growth pattern vs. temperature drop and diaphragm hole diameter.

In addition, it is experimentally found from comparison samples of 100 mm diameter and 10 mm thickness that magnium fluoride crystals (110) grown by the above technique are stronger and possesses some optical characteristics better than those obtained by the Stockbarger method [3].

4. Conclusions

The simplified model is developed for prediction of MgF_2 growth rate in the chamber with diaphragm. The growth rate monotonically increases at large diameters of diaphragm hole. On the other hand, the growth rate exhibits a non-monotonic behavior at small diameters of diaphragm hole. High temperature drops cause then a decrease in the growth rate due to increased loss on the diaphragm.

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