STABILIREA CONDIȚIILOR DE CREŞTERE A MONOCRISTALELOR DE LiF PENTRU COMUTATOARELE Q ALE LASERILOR YAG:Nd
THE ESTABLISHMENT OF GROWING CONDITIONS OF LiF SINGLE CRYSTALS FOR YAG:Nd LASER Q-SWITCH

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The paper deals with the analysis of LiF single crystals growth conditions in order to establish the main parameters that are involved in the crystal quality. Taking into account the experimental data, correlations between the growing conditions and the single crystals quality used as active media or Q-switches were made. The dependence of the crystals length, fixed as driving property function, on the growth process independent variables was achieved.

Articolul prezintă o analiză a condițiilor de creştere a monocristalelor de LiF în scopul stabilirii parametrilor principali care condiționează calitatea monocristalului. Pe baza datelor experimentale s-au stabilit corelații între condițiile de creştere şi calitatea monocristalelor utilizate ca medii active sau comutatoare Q. S-a obținut o funcție de dependență între lungimea monocristalelor considerată ca fiind proprietatea de bază şi variabilele independente ale procesului de creştere.

Keywords: *lithium fluoride, optical materials, Q-switches, high purity, crystal growth*

1. Introduction

Lithium fluoride (LiF) single crystals with small diameters are interesting materials because of their optical properties such as: active medium in tunable solid-state lasers in the visible and near infrared spectral range, Q- switch for solid-state lasers, dosimeter applications, created color center materials etc. [1]. The method used for obtaining simultaneously LiF single crystals with small diameters was presented in [2, 3], where the activities were focused on substances purifying and synthesizing, growth installation design and growth experiments in different conditions. In these previous works, our target was the achieving of crystals with a minimal length of 50 mm, diameter of 8mm and good optical transmission in VIS-NIR domain, without optimization of the processing.

For Q- switch applications, LiF crystals must have a structure without any kind of defects, as other authors reported [4 - 6]. We can not obtain controlled color centers with gamma or electron irradiation when the starting crystal has an imperfect structure due to the improper growth conditions are not possible to be obtained[7].

2. Experiments

All experiments were performed with the help of a single crystals growth installation based on Bridgman-Stockbarger method, which is presented in [3]. It has an original design, which reveals a modified thermal profile, unlike the original set-up. This new thermal profile along the furnace length means a long time for crystals growth, but allows the obtaining of crystals with a low number of defects as result of low internal stress [8, 9]. The installation component parts represent individual systems for: automatic temperature control, vacuum control and speed of crucible control. Optical grade polycrystalline LiF used as raw material for single crystals growth was obtained by chemical synthesis, followed by vacuum distillation [3]. The furnace dimensions,

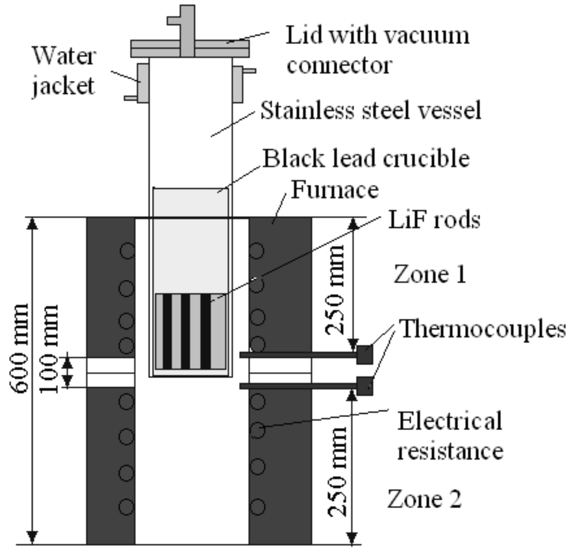

Fig. 1 - Furnace dimensions, thermocouples positioning and crucible initial position/ *Dimensiunile cuptorului, poziționarea termocuplelor şi poziția inițială a creuzetului.*

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thermocouples positioning and crucible initial position for LiF single crystals growth are shown in Figure 1.

It is easy to depict the main differences between the installation from Figure 1 and the well-known single crystals growth installations from melting: two zones without shield, two similar heating zones, graphite crucible with multiple nests and stainless steel container as crucible transporter.

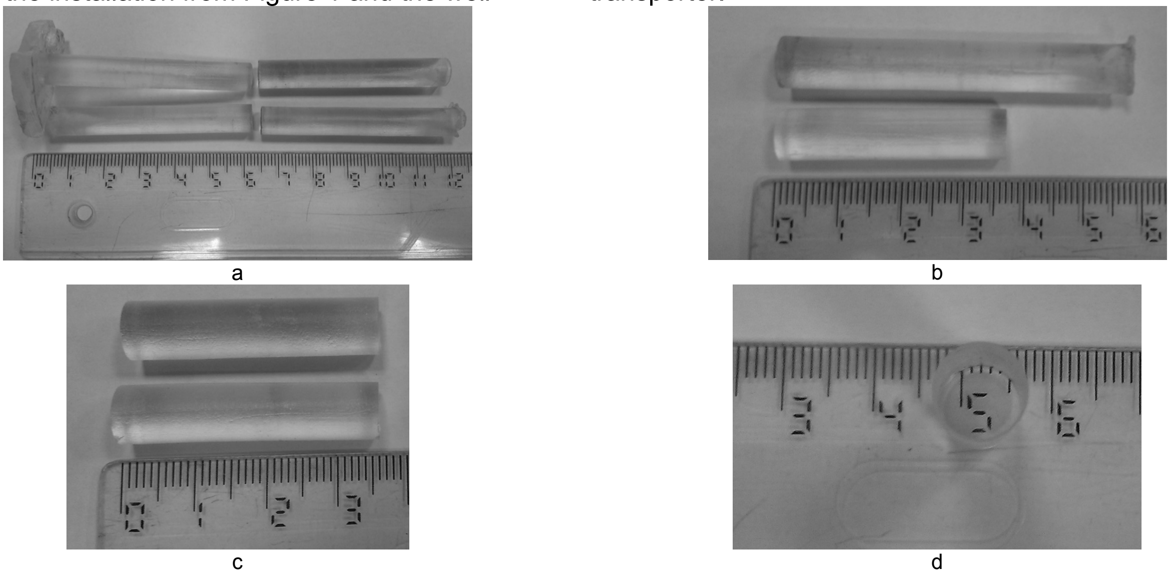


Fig. 2 - (a) LiF single crystals grown and extracted after one growing cycle, (b) the ratio between the as-grown and Q-switch single crystal rods, (c) LiF single crystal rods after parallel cutting and optical polishing and (d) axial transparency of LiF single crystal rod./ *(a) monocristale de LiF crescute şi extrase după un ciclu de creştere, (b) raportul dintre baghetele monocristaline neprelucrate şi cele pentru comutatoare Q, (c) baghete monocristaline de LiF după tăiere paralelă şi polizare optică şi (d) transparența axială a baghetei monocristaline de LiF.*

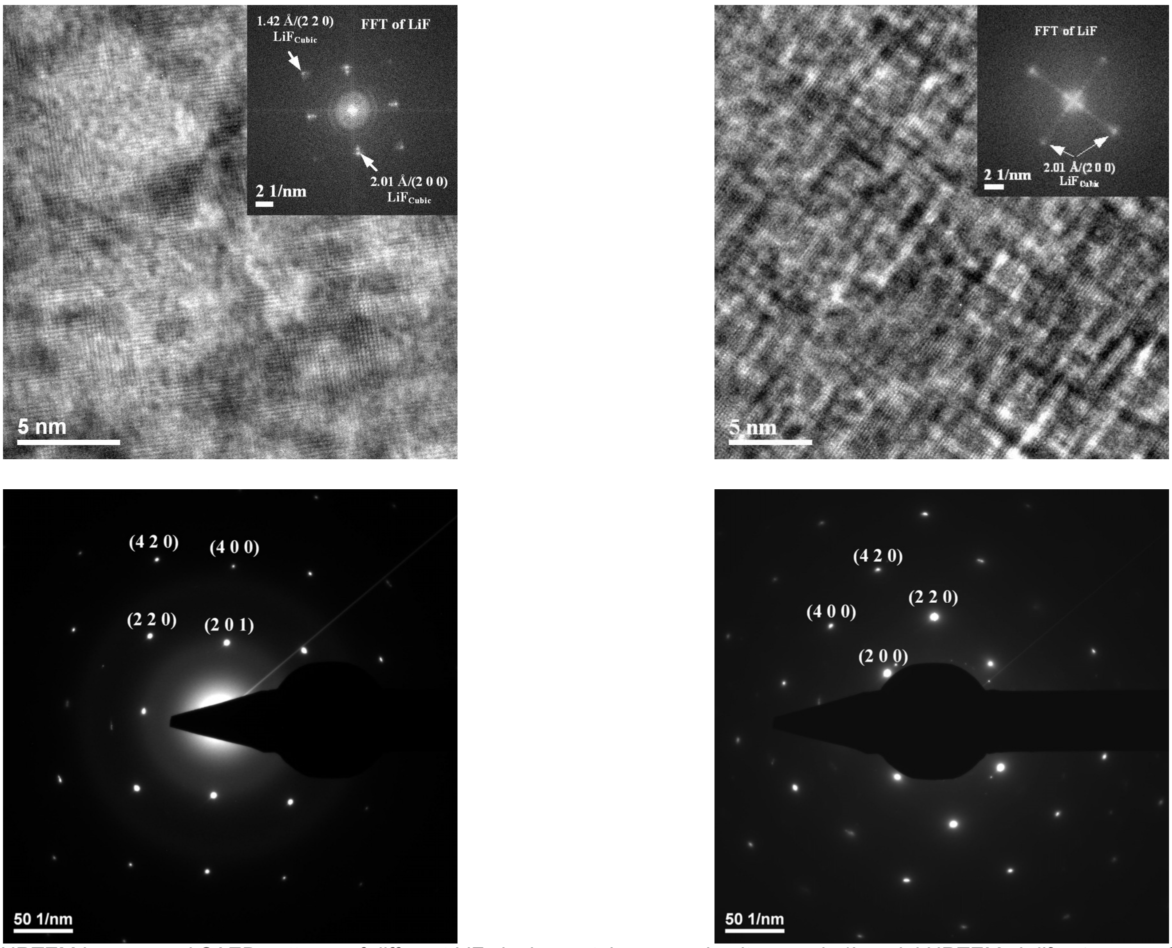


Fig. 3 - HRTEM images and SAED patterns of different LiF single crystals grown simultaneously /*Imagini HRTEM şi difractograme SAED ale unor monocristale de LiF crescute simultan.*

Figure 2a presents images with LiF single crystals grown and extracted after one growing cycle; they exhibit lengths up to 60 mm. Concerning the assurance of the best quality for LiF single crystals, Figure 2b shows that the rod for Q- switch is shorter than the as-grown rod (35 mm compared with about 60 mm), this difference allowing one to chose the best cutting zone. After parallel cutting and optical polishing, LiF single crystal rods have 35 mm length (Figure 2c) and high level of transparency (Figure 2d).

From this level of examination, when dimensions are evaluated in millimeters and one can certify that the growing parameters were well defined, the proof which is able to make differences between polycrystalline LiF rods and single crystal LiF rods is the structure analysis. In this case, one must take into account the crystalline structure in terms of single crystal theory.

High quality single crystals were investigated using Transmision Electron Microscopy (TEM) tools, such as High Resolution Transmision Electron Microscopy (HRTEM) images and Selected Area of Electron Diffraction (SAED) patterns. Figure 3 demonstrates that LiF rods achieved by this method present a cubic structure and the same orientation of crystals growth.

3.Discussions

Using the experimental data presented in Table 1, we can establish the optimal working conditions for obtaining LiF single crystals considering simple or multiple regression analysis, for the considered obtaining method.

The resulting single crystal length for different growing conditions was set as dependent variable. The length of defects-free single crystals is associated with a good optical quality, assuming that the installation architecture was correctly realized.

The independent variables influence upon single crystals quality can be assessed by mathematical modeling based on linear regression with one variable. The experimental conditions and obtained results concerning good single crystals lengths are presented in Table 1.

Because the finding of a function with five variables is a difficult task, it was tried to determine a linear dependence for every variable. The regression equation helps us to predict the single crystals length values for another parameter value than the experimental one [10].

Figure 4 displays the variation of the single crystals length function for the high temperature zone. The length decreases with temperature increasing. This normal evolution can be explained by the extension of the furnace hot zone towards the gradient zone. At lower temperature values, the length increases while the translation speed has low values, which eliminates the defects generation. The prediction function is able to calculate the single crystals length for every Celsius degree when we want to maintain the quality and to reduce the production cost by saving energy.

The low temperature zone provokes changes of the single crystals length in a large range of values. For the temperature close to 700^{o}C, the length reaches the optimal value.

Analyzing the values calculated with the regression equation, it can be concluded that it is possible to achieve very good results if the low temperature zone decreases near 700^{o}C (Figure 5). This phenomenon can be explained by the growing of the temperature gradient and minimization of crystallization section. The consequence is the shifting of the crystallization interface towards the hot zone.

The melt quenching leads to a stressed structure, as a result of the inadequate relaxation temperature.

Table 1

Experimental results for different growing conditions/ *Rezultate experimentale pentru diferite condiții de creştere.*

No *Nr.*	T_{zone1} T_{zona1} [^{o}C]	T_{zone2} T_{zona2} [^{o}C]	Preheating time / *Timp de preincălzire* [h]	Vacuum *Vid* [Pa]	Translation speed *Viteză translație* [mm/h]	Cooling head form *Forma capului de răcire*	Crystal length *Lungime cristal* [mm]	Time *Timp* [h]
1	910	845	8	$3.3\ 10^{-2}$	5	flat lid	3.4	72
2	880	815	8	$3.3\ 10^{-2}$	5	flat lid	2	72
12	870	780	10	3×10^{-2}	1.5	flat lid	50	54
13	870	780	10	3.5×10^{-2}	2.4	flat lid	45	38
14	870	780	10	5×10^{-2}	3	flat lid	27	25
15	870	700	10	6×10^{-2}	4.8	flat lid	8	20
16	870	780	8	3.3×10^{-2}	0	flat lid	0	16
17	880	750	8	2.5×10^{-2}	2.5	flat lid	30	48
18	900	800	8	2×10^{-2}	2.5	flat lid	15	68
19	870	780	6	2×10^{-2}	2.5	flat lid	30	63
20	870	780	6	2.5×10^{-2}	2.5	flat lid	14	80
21	850	780	15	3×10^{-2}	2.5	flat lid	15	55
22	870	700	8	2×10^{-2}	2.5	flat lid	50	45

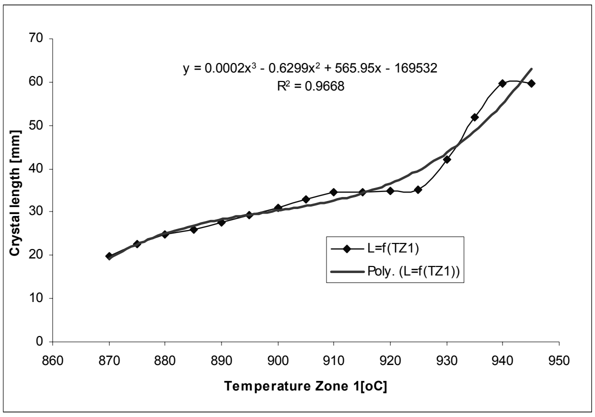


Fig. 4 - The dependence of the single crystals length on the temperature from zone 1 L=f(s)./ *Dependența lungimii monocristalelor de temperatura din zona 1 L=f(s).*

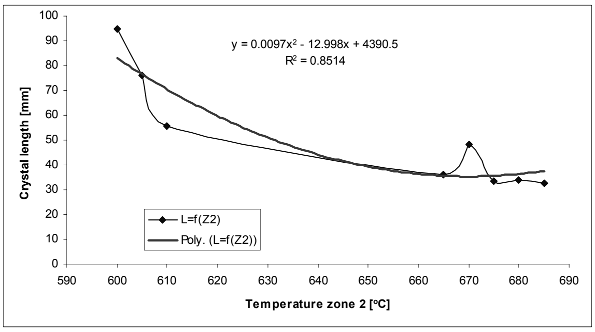


Fig. 5 - The dependence of the single crystals length on the temperature from zone 2 L=f(i) / *Dependența lungimii monocristalelor de temperatura din zona 2 L=f(i).*

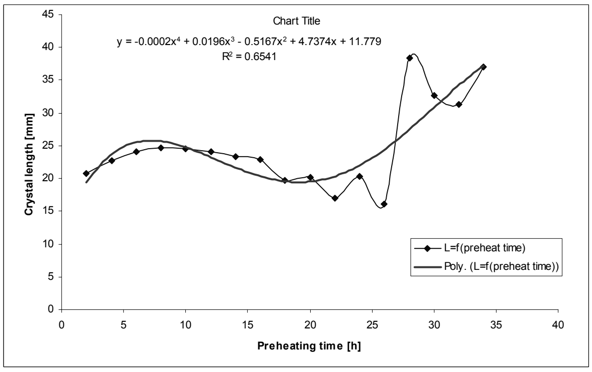


Fig. 6 - The dependence of the single crystals length on the preheating time L=f(p)./ *Dependența lungimii monocristalelor de timpul de preîncălzire L=f(p).*

The experimental data indicate that the batch preheating time has no important influence on the single crystals length. A variation with 2 mm of the length requires up to 30 hours of the preheating time (Figure 6). The preheating time plays an important role in the case of single crystals quality at the beginning of the crystallization zone and single crystals orientation. The values calculated with the regression equation show that the preheating time can be minimize only if LiF is in liquid phase, without gaseous species, at the beginning of the growing procedure.

Regarding the vacuum realized in the crucible chamber, the prediction analysis indicates

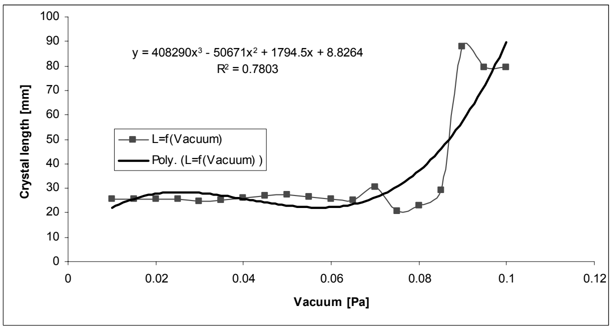


Fig. 7 - The dependence of the single crystals length on the pressure L=f(v). *Dependența lungimii monocristalelor de presiune L=f(v).*

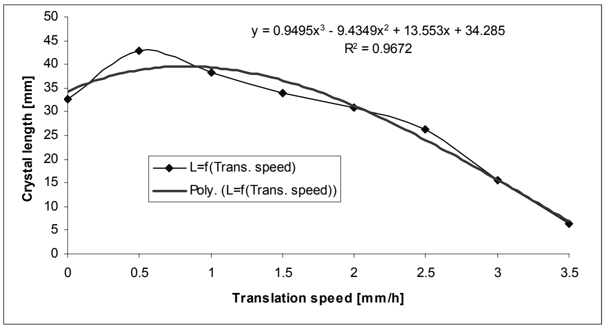


Fig. 8 - The dependence of the single crystals length on the translation speed L=f(w)./ *Dependența lungimii monocristalelor de viteza de translație L=f(w).*

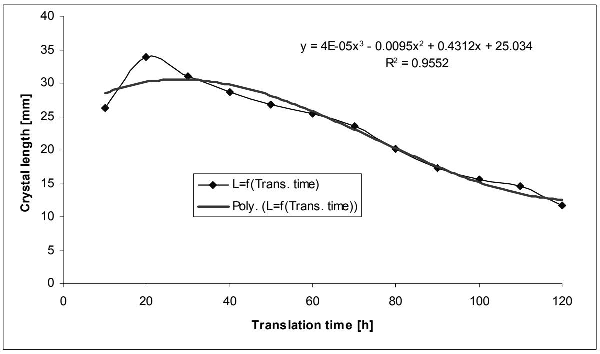


Fig. 9 - The dependence of the single crystals length on the translation time L=f(t)./ *Dependența lungimii monocristalelor de timpul de translație L=f(t).*

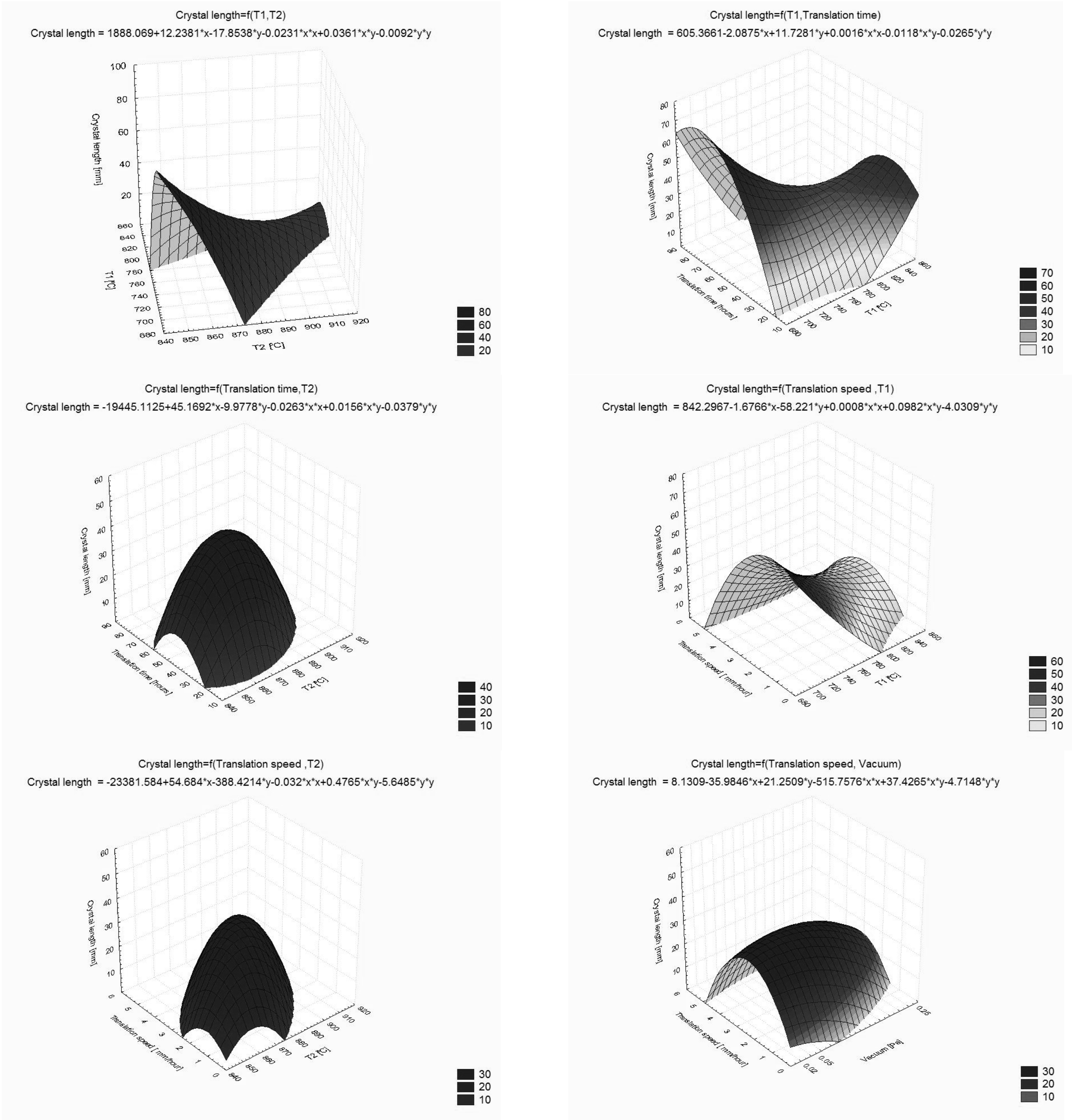
that it is possible to obtain longer single crystals when the pressure decreases with two orders of magnitude (Figure 7).

A greater variation of the single crystals length occurs when the single crystals translation speed inside the furnace is modified. When the translation speed ranges between 0.5 and 5 mm/hour, the length increases three times (Figure 8).

The obtained dependence shows an inefficient growing process when the translation speed is higher than 5 mm/hour. The increase of the time for one batch has no effect on the single crystals length (Figure 9).

In these conditions, the installation reliability has an important effect on the single crystals quality and length.

In conclusion, the dependence of crystal



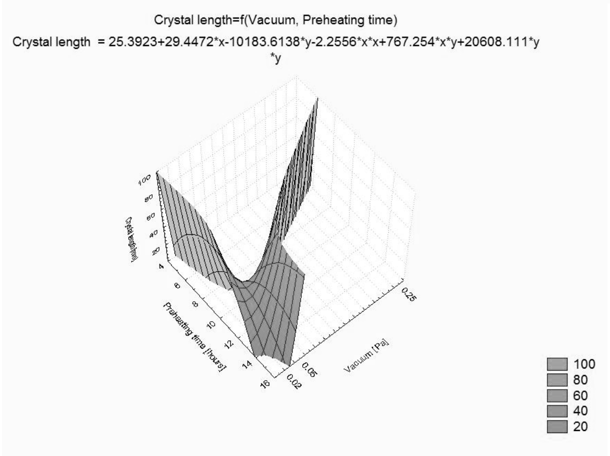


Fig. 10 - Relationships and graphs for the dependent variable and independent variables / *Relații şi grafice pentru variabila dependentă şi variabile independente.*

length as a function of independent variables obtained in previous graphs indicates the lower values of crystal length than the experimental data from Table 1.

In order to obtain a better correlations we generated relationships between two independent variables and the single crystals length as dependent variable using STATISTICA 10 (trial version 10.0.1011.0) software; different relationships and appropriate graphs can be obtained (Figure 10). A deeper analysis reveals that these results are not able to indicate with accuracy the best value of variables which control the growth process. Some of them can be accessed when the optimization model will be designed.

We assume that the single crystals length obtained through the growth process is a function of the zone temperatures created in Bridgman-Stockbarger furnace, vacuum value in the growing chamber, preheating time, speed of crucible and procedure time.

Relation 1 shows the resulting function.

$$L=f(p,t,v,w,s,i) \text{ or } y=f(x_1,x_2,x_3,x_4,x_5,x_6). \quad (1)$$

We have used multiple regression in order to get a function with six variables. The function obtained using STATISTICA software is presented in relation 2.

$$L=1120.902+0.53558p-0.26913t-0.01361v-18.0414w-1.03453s-0.16464i, \quad (2)$$

where:

L = single crystals length;
t = translation time [h];
p = preheating time [h];
v = chamber pressure [Pa];
w = translation speed [mm/h];
s = high temperature zone [^oC];
i = low temperature zone [^oC].

The function defined above can be used as objective function for the crystal growth optimization. The optimization model, based on mathematical programming, can be represented with system (3).

$$b_j<g_j(x_1, x_2,\ldots,x_n)<a_j, \quad j=1,m$$
$$x_i\geq 0, \quad i=1,n \quad (3)$$

(optimal) $y_k=(\min/\max)y_k(x_1,x_2,\ldots x_n)$, k=1,p,

where:

a_j, b_j = values imposed by the technological and quality conditions;

g_j = functions which correlate x_i independent variables;

y_k = objective functions which must be optimized.

Our optimization problem solved with MATHCAD software has the form displayed in following model:

Relation (2)
p≥0; t≥0;
v≥; w≥0;
s≥0; i≥0;
maximize L=f(t,p,v,w,s,i).

The variables values obtained by solving the problem can be as follow:

L=49.9 mm; t=45; p=8; v=208; w=2.4; s=871; i=706.

The result is situated in the experimental data range and promises the best quality for the grown single crystals.

4.Conclusions

The advantages of prediction and optimization functions used in LiF single crystals growth are:

- establishing of correlations between the installation parameters and one important property of the single crystals;
- obtaining of one regression equation for each variable;
- prediction of possible system evolutions;
- possibility to find out one major characteristic of the single crystals without experiments.
- process optimization using objective functions obtained by multiple regression and restriction conditions for every variable;
- optimal growth parameters solving a linear programming problem.

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