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Study of temperature conditions of organic DAST single crystals growth from solution

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Considered are the temperature conditions of the solution growth of organic DAST single crystals by means of an electric contact thermometer or a thermocouple as a temperature regulator. It is shown that in the former case the accuracy of temperature control does not exceed ±0.1°C. The synthesis of the parameters of the temperature controller of a thermostat with a crystallizer as a control object with a delay has been carried out. A microprocessor-based program logic unit has been built, where the thermocouple signal is digitized and programmatically filtered by an exponential moving average filter in order to determine the tendency of the measured value to change and in order to form a regulating effect on the heater. The control accuracy is ±0.01°C. The absence of surface and internal defects in crystals grown without fluctuations in the cooling rate of the solution using a type K thermocouple is shown.

Keywords: organic single crystal, thermocouple, regulator parameters, exponential filter, control accuracy.

Дослідження температурних умов вирощування органічних монокристалів DAST із розчину. *О.П.Воронов, В.С.Задорожній, І.М.Притула, І.І.Тавровський, І.С.Терзін, R.Galbadrakh, L.Enkhtor*

Розглянуто температурні умови вирощування органічних монокристалів DAST з розчину при використанні в якості регулятора температури електроконтактного термометра або термопари. Показано, що при регулюванні температури електроконтактним термометром точність регулювання не перевищує ±0.1°C. Проведено синтез параметрів регулятора температури термостата з кристалізатором як об'єкта управління з запізненням. Побудований мікропроцесорний програмно-логічний блок, де сигнал термопари оцифровується і програмно фільтрується експоненціальним фільтром змінного середнього з метою визначення тенденції зміни вимірюваної величини і формування регулюючого впливу на нагрівач. Точність регулювання становить ±0.01°C. Показано відсутність поверхневих і внутрішніх дефектів у кристалах, вирощених без флуктуацій швидкості охолодження розчину із застосуванням термопари К-типу.

Рассмотрены температурные условия выращивания органических монокристаллов DAST из раствора при использовании в качестве регулятора температуры электроконтактного термометра или термопары. Показано, что при регулировании температуры электроконтактным термометром точность регулирования не превышает ±0.1°C. Определены параметры регулятора температуры термостата с кристаллизатором, как объекта управления с запаздыванием, при использовании в качестве датчика температуры термопары. С целью определения тенденции изменения измеряемой температуры и формирования регулирующего воздействия на нагреватель построен микропроцессорный программно-логический блок, где сигнал термопары оцифровывается и програмно фильтруется экспоненциальным фильтром скользящего среднего. Точность регулирования составляет ±0.01°C. Показано отсутствие поверхностных и внутренних дефектов в кристаллах, выращенных без флуктуаций скорости охлаждения раствора с применением термопары К-типа.

1. Introduction

Organic molecular structures characterized by high nonlinear optical coefficients are considered promising materials to be used in different photonic applications including light frequency conversion, electrooptical modulation, generation and registration of terahertz waves [1–3]. Such structures are based on nonlinear optical molecules (chromophores) with high molecular nonlinearity, mostly dipolar ones [4]. In order to obtain macroscopic nonlinear optical response, in the process of crystallization, such molecular structures must form a noncentrosymmetric structure from molecules with high dipole moment [5]. This can be achieved e.g. by incorporation of chromophores into polymer matrices with subsequent polarization by electric field, molecular self-assembling with subsequent formation of an amorphous acentric structure, or the growth of noncentrosymmetric nonlinear optical single crystals [6].

Organic molecular structures possess high thermal and photochemical stability, steady packing of chromophores in comparison with polymer composites that makes them promising for the obtaining of electrooptical and nonlinear optical materials. However, the problem of the growth of high-perfection bulk and thin-film crystals has not been solved so far. Molecular crystals are obtained by different, sometimes rather complex, methods and growth equipment. The most traditional growth technologies include the method of slow cooling, or slow isothermal evaporation which may be combined with temperature gradients at the crystallization front [7].

Many nonlinear bulk organic crystals with high optical quality such as DAST (4N,N-dimethylamino-4′-N′-methylstilbazolium tosylate), DSTMS (4-N,N-dimethylamino-4′-N′-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate), HMQ-TMS 2-[(4-hydroxy-3-methoxystyryl)]-1-methylquinolinium 4-(trifluoromethyl) trimethylbenzenesulfonate), OH1 (2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene) malononitrile) etc. are grown from the solution [5, 6, 8]. Thereat, the most promising among them is DAST. Optimization of the solution growth of such crystals with high optical quality is described in [9]. Nevertheless, the obtaining of perfect DAST crystals still remains a topical problem. As a rule, the growth of high-quality bulk (DAST) crystals lasts from one to two months, thereat during this period it is necessary to provide high accuracy of temperature stabilization that is caused by physicochemical features of the growth of DAST from the solution in methanol.

During the growth of crystals by the method of lowering the solution temperature, an abrupt change of the temperature gives rise to the corresponding change of the solution supersaturation in the vicinity of the growing crystal. This inevitably affects the composition, real structure and, finally, optical properties of the grown crystal. So, there arises the necessity of a smooth change of the temperature in order to maintain the constant motive force of the process or its normal change.

Smooth temperature changes are especially necessary for the substances which growth rate and structure imperfection strongly depend on the solution supersaturation. Such a temperature control can be realized only by means of automated devices.

In the present paper we analyze the temperature conditions of the solution growth of DAST single crystals at different systems of temperature control using electric contact thermometer or thermoelectric temperature transducer — type K thermocouple (chromel-alumel).

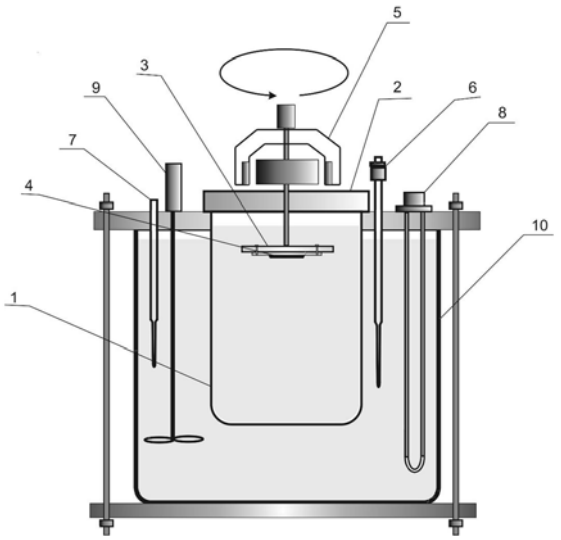

Fig.1. Setup for single crystals growth from solution.

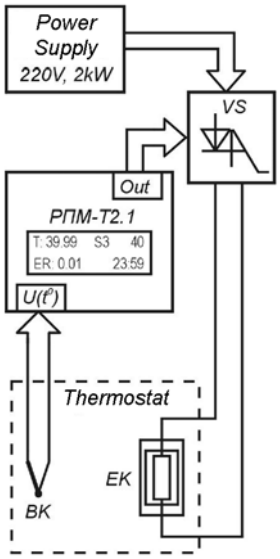

Fig. 2. Block diagram of the temperature control system for DAST single crystals growth from solution using type K thermocouple as a temperature sensor of the thermoregulator.

2. Experimental

To study the temperature conditions for growing DAST crystals, both in the case of temperature control with an electric contact mercury thermometer and a type K thermocouple, we used the setup shown in Fig. 1.

The setup used contains a liquid thermostat — a cylindrical thick-walled glass jar filled with water which plays the role of heat carrier. To provide uniformity of the temperature field, the water contained in the thermostat is to be mixed. The crystallizer **1** made in the form of cylindrical glass jar is placed in the cylindrical glass thermostat **10** containing supersaturated solution. The crystallizer **1** is hermetically sealed with the lid **2**. The thermostat **10** is supplied with two stirrers **9** for uniform mixing of the water (heat carrier). The temperature conditions in the thermostat are maintained by means of two heaters **8** and the electric contact thermometer **6** which is the temperature sensor of the heat regulator. Temperature control is realized using the thermometer **7**. The seed **4** placed into the solution is fixed to the crystal holder **3** which is also a reversible agitator for creation of motion of the solution in the process of crystal growth.

The volume of the thermostat depends on the dimensions of the crystallizer placed in it, as well as on the requirements to the accuracy of maintenance of the temperature. The larger the thermostat volume, the less temperature fluctuations in the crystallizer.

Temperature control by means of electric contact thermometer is realized as follows. The crystallizer placed into the thermostat heated up to the growth temperature is filled with filtered DAST solution. The automated system which controls the temperature conditions during the growth has a two-position temperature control and includes the power block of the heaters, the electric contact thermometer-heat regulator, and the generator of pulses controlling the step motor for rotation of the magnetic head of the electric contact thermometer. The generator provides different speeds of rotation of the magnetic head and, as a consequence, different rates of temperature change at different stages of crystal growth. If necessary, the crystal growth conditions can be changed by the operator.

Shown in Fig. 2 is the block diagram of the regulation system with the type K thermocouple used as a sensor of the thermoregulator. The system comprises: 1 — control object EK: the heater in the thermostat; 2 — the temperature sensor BK (type K thermocouple); 3 — program logic block (controller): microprocessor-based programmable temperature controller RPM-T2.1; 4 — triac power module VS.

Temperature control by means of thermocouple is realized as follows. The program logic block — microprocessor-based programmable temperature controller RPM-T2.1 — is programmed with temperature

values linearized at each subsection and the temperature value that must be maintained in the thermostat with an accuracy of ±0.01°C is set in advance. The signal from the temperature sensor BK (type K thermocouple) with a frequency of 120 Hz is fed to the input U (t°C) of the RPM — T2.1 regulator, where it is digitized in the ADC and programmatically filtered by an exponential moving average filter, implemented as:

$$x_n = x_{n-1} - \frac{x_{meas} - x_{n-1}}{n}, \quad (1)$$

The exponential filter is a sequential series of values with exponential coefficients, where x_n is the new value of the smoothed series; x_{n-1}, the preceding value of the said series; x_{meas}, the last measured value.

The exponential filter is calculated for finding out the tendency of changes in the measured value. The logical unit of the microprocessor compares the preset temperature value with the deviation of the measured temperature from the mean value and creates a two-position regulating action on the heater EK via triac power module VS.

The influence of the temperature conditions on the growth of DAST crystals during temperature control using either an electric contact mercury thermometer or a thermoelectric temperature transducer — a type K thermocouple as a temperature sensor, was observed on micrographs of the crystal surface using a Zeiss Axioskop 40 A POL microscope with access to the computer.

3. Results and discussion

It is well known that the motive force of solution crystallization is supersaturation of the solution. The greater the supersaturation, the higher the crystal growth rate. Supersaturation of solutions depends on their temperature, and this dependence is well approximated within a narrow temperature interval by a linear function [10]. The degree of supersaturation is limited by the value of metastable solution zone and controlled by changes in the temperature.

According to the literature data [9, 11, 12], for the growth of DAST crystals the optimum concentration of the solution DAST/methanol is 3.7 g of DAST/100 g of methanol. If to approximate the temperature dependence of solubility by the relation

$$C_0^{DAST} = -0.044 + 0.0016 \cdot T_0, \quad (2)$$

it can be easily shown that the concentration C_0^{DAST} is equal to 0.0232 g/ml solution at the saturation temperature T_0 = 42°C. The width of the solution metastable zone is ~ 8°C, while the relative supersaturation at the edge of the metastable zone (~ 34°C) will be $\sigma = C - C_0/C_0 = 55.17$ %. For comparison, the corresponding value for KDP (KH_2PO_4) water solution at similar temperature conditions is $\sigma = 10.6$ %, for phosphate LDP (LiH_2PO_4) solution σ = 3.6 %.

As shown in [13], the value of supersaturation is defined by the corresponding solution supercooling, and also depends on the growth temperature and the solution concentration. High-concentration solutions such as KH_2PO_4 require more essential supercooling to obtain a desired supersaturation than low-concentration solutions, e.g. DAST. In particular, the relative supersaturation $\sigma = 10.6$ % for KH_2PO_4 is achieved at a supercooling of ~ 8°C with respect to the supersaturation temperature T_0 = 42°C, for DAST with $\sigma = 11.5$ % it is enough to obtain a supercooling of ~ 1.7°C.

According to [14], the normal rate R of solution crystal growth is proportional to σ and expressed as:

$$R \sim \beta\Omega C_0\sigma, \quad (3)$$

where β is the kinetic coefficient, Ω is the volume of the dissolved substance molecule, C_0 is the equilibrium concentration.

As is seen, the same values of supersaturation in high-concentration and low-concentration solutions provide different growth rates — 10 mm/day and 0.4 mm/day for KDP [14] and DAST [9], respectively. So, it follows that the growth of DAST crystals is effective enough even at insignificant supercooling values, that gives rise to rather stringent requirements to precision of temperature control in the process of crystal growth.

Control of the temperature conditions of crystal growth must provide the required heating of the solution, stable maintenance of the temperature and the possibility to smoothly change it. Smooth control of the temperature can be achieved by means of standard electric contact thermometers. In the latter electric contacts are arranged along the capillaries at different heights. One of them made in the form of metal tungsten hair can move through the capil-

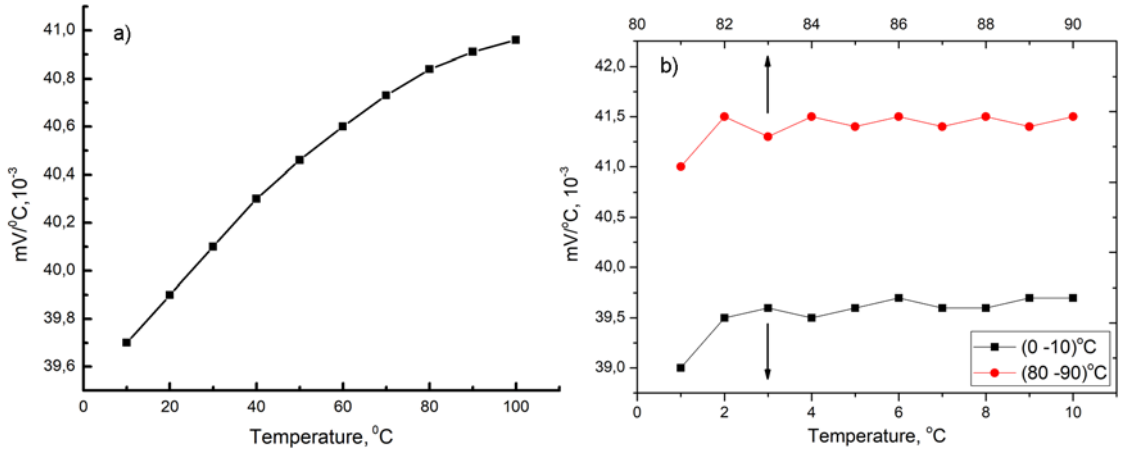

Fig. 3. Changes in thermo-EMF values of type K thermocouple in mV/°C: a) when going from (0–10)°C to (0–100)°C (the absolute temperature measurement error increases by $\delta = 1.26 \cdot 10^{-3}$ mV/°C); when going from (0–10)°C to (80–90)°C (the absolute temperature measurement error for each fragment is $\delta = 0.2 \cdot 10^{-3}$ mV/°C).

lary by means of a micrometric screw with magnetic head.

At heating above the normal value set by the position of the upper contact mercury moves through the capillary and closes the contacts. Until the contacts in the thermometer are not closed, the power block conducts current through the heater. After the heater has raised the temperature up to the value at which the contacts are closed, in the power block there appears a control signal which opens the contacts to start cooling. The error of temperature maintenance for the given thermostat with two-position temperature control is ±0.1°C.

The described system has an essential drawback, since the tungsten hair in the thermometer is in contact with mercury. During circuit breaking a spark jumps across the contacts, and the temperature of the mercury meniscus sharply rises. This leads to oxidation of mercury followed by wetting of the capillary and distortion of the meniscus. Thereat, in the course of time the moments of chain closure and breaking will not exactly correspond to the preset temperature. Errors associated with the "sticking" of the mercury-tungsten filament contact during opening, as well as errors associated with the mechanical maintenance of a given uniform temperature change (rotation of the magnetic head) are also added, which further reduces the accuracy of temperature control.

In view of the mentioned drawbacks, the system which controls the temperature conditions of the solution growth of DAST crystals is to be improved.

One of the methods for solving the above-said problem is to substitute the electric contact thermometer by a thermoelectric temperature sensor, e.g. type K thermocouple. However, the latter has an essential nonlinearity of the characteristic curve within the interval which includes the growth and annealing temperatures of organic single crystals (0–100°C).

To provide the lowest measurement error and temperature stabilization while using the thermocouple in the capacity of the sensor, it is convenient to divide the nonlinear part of its characteristic curve into equal fragments corresponding to 1°C and to linearize each of them by the function $y = ax$. Here x takes on discrete values not exceeding 0.001°C, whereas the coefficient a corresponds to the tangent of the inclination angle of the linearized curve for each 1°C fragment of the characteristic thermocouple curve.

If to divide the mentioned curve into equal non-linearized fragments, the error of temperature stabilization will be defined by non-linearity of the thermo-EMF values of the thermocouple on each portion of the non-linearized section. For instance, the comparison of the segments (0–10)°C and (0–100)°C shows that the absolute error of temperature measurement rises by the value $\delta = 1.26 \cdot 10^{-3}$ mV/°C, Fig. 3a.

Meanwhile, when the characteristic curve of the thermocouple is divided into 1°C portions linearized as shown above, the error of temperature stabilization will be also defined by non-linearity of the thermo-EMF values of the thermocouple which arises on

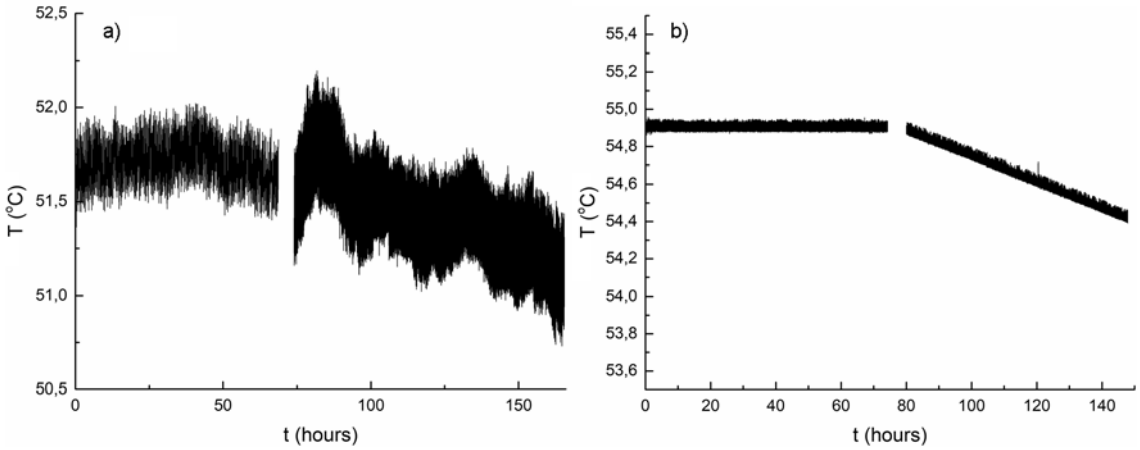

Fig. 4. Temperature changes in the thermostat of the setup for single crystals growth from solution by means of: a) electric contact thermometer; b) type K thermocouple.

each linearized segment of the characteristic curve. However, in this case the comparison of the segments (0–10)°C and (80–90)°C testifies that the absolute error of temperature measurement on each segment is $\delta = 0.2 \cdot 10^{-3}$ mV/°C, that is almost by an order less than the one for the nonlinearized characteristic curve (Fig. 3b).

The thermostat with the crystallizer for the solution growth of the crystals is a time delay control system [15, 16]. The required control precision was achieved due to the study of the control object characteristics, parametric modelling/simulation, synthesis of the regulator parameters, that allowed to obtain the transient function for a time delay system:

$$W_H(p) = \frac{0.5}{4p^2 + 8p + 1} e^{-3p}. \quad (4)$$

Then there was proposed the transient function of the regulator in the form:

$$W_p(p) = \frac{b_1 p + b_0}{p(a_1 p + 1)}. \quad (5)$$

Here p is the Laplace operator.

Formulated were the following synthesis criteria: $\delta_z = 5$ % and the condition $\delta - \Delta\delta_z \leq \delta \leq \delta + \Delta\delta_z$, $\Delta\delta_z = 1$ %, where δ_z is the preset overcontrol; $t_v \to \min$, t_v is the overcontrol time.

The synthesis was realized using the numerical method [12, 13] in MATLAB medium, and there was chosen digital filtration by exponential filter of moving average.

The use of two-position control is caused by the fact that the control object has a very large delay time that makes the use of the PID control ineffective. Additional investigations show that the range of time steps of the regulated action on control object is 1–10 s.

To provide temperature control accurate up to ±0.01°C, it is necessary to ensure a maximal accuracy and a minimal error of temperature measurement.

In the discussed case the maximal measurement accuracy can be achieved by means of an analog-digital converter with a capacity of 24 bit, a rate up to 470 samples per second and digital signal filtration. Based on the established range of time regulation steps, there was chosen the minimal regulation step equal to 1 sec, that allowed to realize 120 measurements per sec. Such a high measurement frequency was achieved due to digital filtration between the regulation steps in the form of exponential filter of moving average. The main criteria of the choice of analog-digital converter and exponential filter of moving average were minimization of the microprocessor resources and simplicity of realization. The least significant 8 digits of the 24 digits of the measured value digitized by the ADC are discarded. The remaining 16 digits give 65535 gradations of the measured value, which provides a measurement accuracy of 100°/65535 = 0.0015°C.

As mentioned above, to provide the minimal error of temperature measurement, the nonlinear section of the characteristic curve of the thermocouple was divided into equal fractions corresponding to 1°C with subsequent linearization of each of them.

Fig. 4 presents the curves of changes of the temperature in the thermostat of the crystal growth setup for the solution

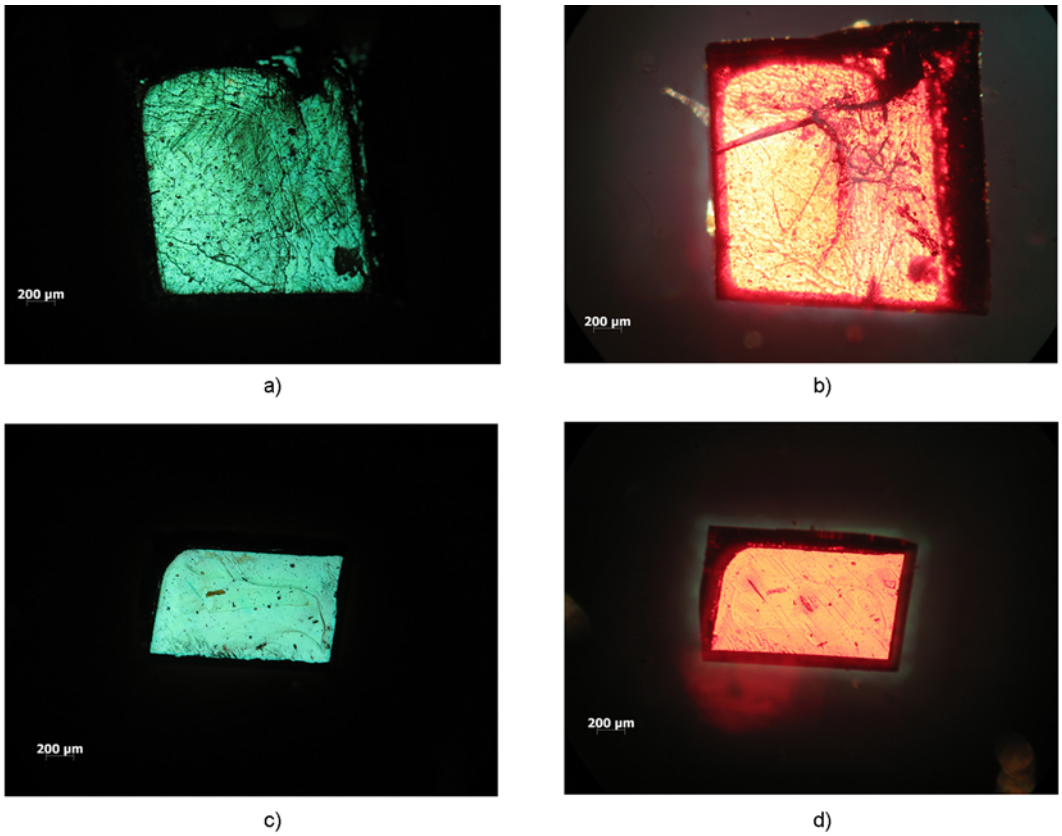

Fig. 5. Micrographs of the surface of DAST crystals grown under temperature control using an electric contact thermometer (a,b), and using a type K thermocouple (c,d). Micrographs (a), (c) show (001) plane in reflected light, (b), (d) show $(00\bar{1})$ plane in transmitted light. ×50.

growth of crystals with temperature control by means of the electric contact thermometer (Fig. 4a) and the type K thermocouple (Fig. 4b). The analysis of the dependences of stabilization and decrease of the temperature testifies that the efficiency of temperature control by the thermocouple is noticeably higher than the one realized using the thermometer. The accuracy of temperature stabilization is ±0.01°C and ±0.2°C, respectively.

The influence of temperature fluctuations of the supersaturated solution cooling on the growth of DAST crystals is clearly observed in the micrographs of the crystal surface obtained in the process of temperature control by means of the electric contact thermometer (Fig. 5a,b) and the thermocouple with the above-mentioned approximation of the nonlinear part of the characteristic curve (Fig. 5c,d).

As is seen, there arise parasitic crystals on the surface (001) plane (Fig. 5a) and characteristic defects (cracks) in the crystal bulk which do not reach the surface (Fig. 5b).

In the crystals grown in the absence of fluctuations of the solution cooling rate using the thermocouple the mentioned defects are not observed (Fig. 5c,d).

The formation of the cracks may be connected with the fact that fluctuations of the cooling rate of the solution during the growth disturb homogeneity of its composition. Inhomogeneous solution of DAST in methanol favors the formation of a larger number of active growth centers on the surface of the growing crystal in comparison with the one of the homogeneous solution. During the growth of additional crystallization nuclei the neighboring domains compress each other that results in the appearance of internal stresses in the crystal and its cracking.

4. Conclusions

As established while studying the temperature conditions of the solution growth of organic DAST single crystals, the developed system of precision temperature control using type K thermocouple as a temperature sensor of the thermoelectric temperature transducer may be used within the range (0–100)°C which includes the tem-

peratures of the growth and annealing of organic single crystals.

It is shown that the division of the non-linear part of the characteristic thermocouple curve into equal fragments and linearization of each of them makes it possible to minimize the temperature measurement error, the absolute measurement error being almost by an order less than that in the case of the non-linearized characteristic curve.

It is established that to ensure temperature control in the thermostat with an accuracy of ±0.01°C, a prerequisite is the use of a microprocessor-based program-logic unit, in which the thermocouple signal is digitized by an ADC with a 24-bit resolution and a rate of up to 470 samples per second and programmed with an exponential moving average filter in order to determine the trend of the measured value change. The logic device of the microprocessor compares the set temperature value with the deviation of the measured temperature from the average in the exponential filter, and forms a two-position control on the heater.

In the crystals grown without fluctuations of the solution cooling rate using the type K thermocouple, there were not observed surface and internal defects.

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