Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

KINETICS OF THE TRANSITION BETWEEN FERROELECTRIC AND ANTIFERROELECTRIC STATES IN LIQUID-CRYSTALLINE MIXTURES

W. Kuczyński [a] , F. Goc [a] & R. Dabrowski [b]

[a] Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179, Poznań, Poland

[b] Military University of Technology, Warszawa, Poland

Version of record first published: 24 Sep 2006

To cite this article: W. Kuczyński, F. Goc & R. Dabrowski (2001): KINETICS OF THE TRANSITION BETWEEN FERROELECTRIC AND ANTIFERROELECTRIC STATES IN LIQUID-CRYSTALLINE MIXTURES, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 366:1, 771-784

To link to this article: http://dx.doi.org/10.1080/10587250108024018

Mol. Cryst. and Liq. Cryst., 2001, Vol. 366, pp. 771-784
Reprints available directly from the publisher
Photocopying permitted by license only

Kinetics of the Transition between Ferroelectric and Antiferroelectric States in Liquid-Crystalline Mixtures

W. KUCZYŃSKI[a], F. GOC[a] and R. DĄBROWSKI[b]

[a]*Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60–179 Poznań, Poland and* [b]*Military University of Technology, Warszawa, Poland*

Investigations of a mixture with induced antiferroelectric phase are described. This mixture exhibits large thermal hysteresis of the transition between ferroelectric and antiferroelectric phases, which was demonstrated using dielectric and optical methods. The kinetics of the transition from the ferroelectric to the antiferroelectric state was extremely slow – its time constant ranged from few minutes to many hours, depending on temperature. The rate of transition formally obeys the Avrami equation describing the kinetics of phase transitions from a supercooled state. However, the remarkably small exponent suggests, that the Avrami model is not suitable for description of the investigated transition. The coexistence of ferroelectric and antiferroelectric states was noticed in a broad temperature range. In the same range the V-shaped switching was observed. The observed phenomena: hysteresis, slow kinetics and threshold-less switching are probably caused by competition of ferroelectric and antiferroelectric interactions acting between smectic layers.

Keywords: ferroelectric; antiferroelectric; chiral; smectic; kinetics; switching

1. INTRODUCTION

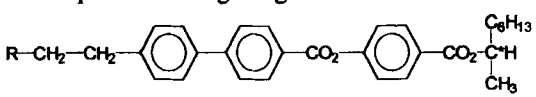
Antiferroelectric smectics belong to the currently most extensively investigated liquid crystal phases. Such a large interest is caused by both their importance in basic research and their large application potential. The variety of phases and subphases appearing in these materials is very attractive for physicists and chemists. On the other hand, the numerous application possibilities are of great interest for engineers. The most interesting is the possibility of application of antiferroelectric liquid crystals in high-resolution devices for information visualization, e.g. in TV-screens and computer monitors [1]. The recently discovered phenomenon of V-shaped switching [2] made the materials even more attractive, mainly due to the possibility of obtaining the gray scale [3].

The V-shaped „switching" consists in electric field induced threshold-less change of the intensity of light, passing the sample placed between crossed polarizers. This change produces a large contrast without hysteresis. To explain this effect, Seomun *et al.* [2] proposed a model of a "random Smectic C - like" phase. It is assumed in this model, similarly as in de Vries [4] model of SmC-phase, that the correlation between tilt directions in adjacent smectic layers are very weak. This causes lack of long - range order of the $\vec{c}$-director. Because the V-shaped switching takes place in thin samples only, one had to take the additional assumption, that the randomization of tilt direction is induced by surface interactions [2]. Gorecka *et al.* [5] have proposed another explanation. They assumed that small (nanometer size) clusters of smectic C^* and smectic C_a^* phase can exist in mixtures. The coexistence of these areas can explain the V-shaped switching. Recently, Gothenburg and Boulder groups have proposed another explanation of threshold-less behavior [5]. It is assumed, that V-shaped (analog) electrooptic response occurs in the absence of antiferroelectricity and is a consequence of the field induced switching of helical smectic C^* in its ferroelectric phase. Large extinction and high contrast observed in this case are explained by the presence of twisted structure stabilized by polar surface interactions and strong electrostatic forces in the bulk of the sample.

Up to now, the threshold-less electrooptic effect was observed only in liquid-crystalline mixtures, which exhibited antiferroelectric behavior in certain temperature range. In our earlier papers [7,8] we observed the V-shaped switching in mixtures of non-antiferroelectric materials, in which the antiferroelectric phase was induced by mixing. This suggests that the appearance of the analog electrooptic effect is indeed connected with the presence of antiferroelectric phase. We observed in these mixtures remarkable long-term effects, which will be discussed in this paper in more detail.

2. EXPERIMENTAL

The investigated materials were mixtures, composed of substances, which in their pure state do not possessed antiferroelectric C_a^*- phase. However, when mixed together, they exhibited an antiferroelectric phase in a wide temperature range [7]. The mixing induced antiferroelectric phase had the largest stability for approximately equal molar fractions of both components. In this paper we limited ourselves to description of investigations performed for binary mixture, composed of compounds having the general form:



where R is C_6F_{13} for the first component (**A**) and C_2H_5O for the second one (**B**). Pure compounds **A** and **B** have the following phase transition schemes:

A: Cr_1 81 Cr_2 99 C* 150 A 184 Is

B: Cr 102 (I* 91) A 148 Is

In this paper we report results obtained for binary mixture, containing 0.55 mole of compound **A**. Results obtained for other mixtures exhibiting induced C_a^*-phase were similar.

The mixture was introduced into measuring cell in their isotropic phase. The cells were furnished with semitransparent electrodes, coated with a polymer orienting layers and separated by

spacers which thickness was set between 2 and 27 μm. The cells were placed in a modified Mettler hot stage and their temperature was stabilized using Digi-Sense TC-9500 temperature controller with an accuracy of about 0.1 K. Prior to the experiment the samples were heated up to the isotropic phase and then slowly cooled into the Sm A phase. In most cases this procedure was sufficient for obtaining homogeneous planar alignment.

For measurements of electrooptical response the sample was placed between crossed polarizers on the stage of polarizing microscope Zeiss Axioskop. The smectic layer normal made an angle of 22.5 deg. with the light polarization direction. The AC voltage of frequency from the range 10 Hz – 100 kHz and 0.7 V amplitude was applied to the electrodes. The changes in the intensity of light, passing the system polarizer - sample - analyzer were registered with the photodetector PIN20 (FLC Electronics, Gothenburg). The output of the photodetector was put to the lock-in amplifier SR530 (Stanford Research, USA). The lock-in amplifier was controlled by a personal computer, which also performed the storage of results and temperature control. The dielectric measurements were carried out with the Hewlett-Packard HP4192A impedance analyzer. A computer controlled both the temperature and data acquisition. The measuring methods are described in papers [8-10] in more detail.

3. RESULTS AND DISCUSSION

The studied mixture, described in the former paragraph exhibited induced antiferroelectric C_a^* phase. However, the determination of the temperature range of this phase makes some problems. This range depends on the experimental conditions, first of all on the sample thickness and its thermal history. This observation is illustrated in Fig. 1, where the dependence of the electric permittivity and electrooptic response on temperature is shown.

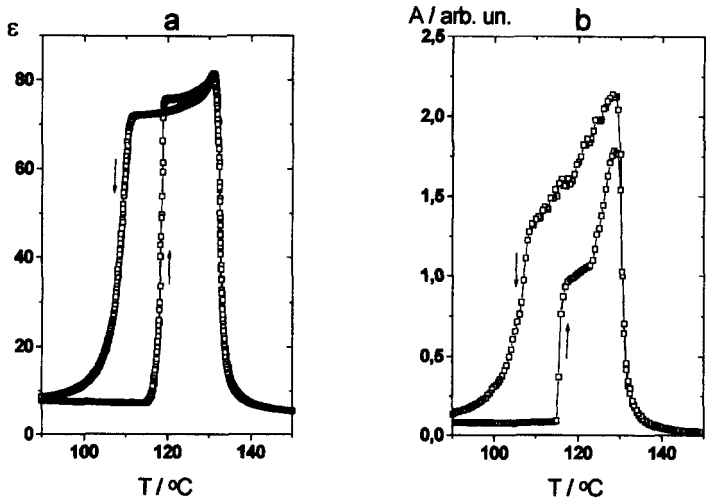


FIGURE 1 Temperature dependence of the electric permittivity (a) and the electrooptic response (b) measured at frequency 440 Hz in 5 μm thick cell. The arrows show the direction of temperature changes.

The value of the electric permittivity ε (similarly as the amplitude of electrooptic modulation [8]) can be an excellent mark of the phase transition between ferroelectric C* and antiferroelectric C_a* phases. Due to the presence of the spontaneous polarization the value of the electric permittivity in the ferroelectric C* phase is much higher than in the antiferroelectric C_a* phase, where the polarization is almost compensated due to the antiparallel orientation in adjacent layers. This large difference in permittivity is especially useful in distinguishing between C^* and C_a^* phases because the transition C* ↔ C_a* is often hardly detectable using calorimetric methods. Also the texture changes in this transition are usually very small. As it is evident from Fig. 1, the transition temperature between C_a* and C*-phases observed on heating differs considerably from that registered on cooling. This thermal hysteresis of the phase transition C_a* ↔ C* is quite large (about 10 K).

One can state on the basis of Fig. 1 that above 120°C the ferroelectric C* - phase is stable, and the antiferroelectric C_a* phase – below 110°C. The question arises, what happens between 110°C and 120°C ?

One can suspect that the observed hysteresis is connected with the kinetics of the phase transition $C_a^* \leftrightarrow C^*$. Indeed, measurements performed with different heating and cooling rates (between 6 K/min. and 0.3 K/min.) revealed distinct differences in the curve ε(T). On the other hand, it was found that the phase transition was not completed during many days, if the sample temperature was hold inside the hysteresis region. The situation is different, when the temperature is stabilized close to the border of hysteresis range (on the slope of the ε(T)-curve, registered on cooling). In this case a continuous change of electric permittivity as function of time *t* takes place: decrease in the vicinity of 110°C and increase close to 120°C (see Figure 2a). The time, when the distinct changes in ε can be observed, depends on temperature and ranges from few minutes at 107°C to same days at 115°C. The

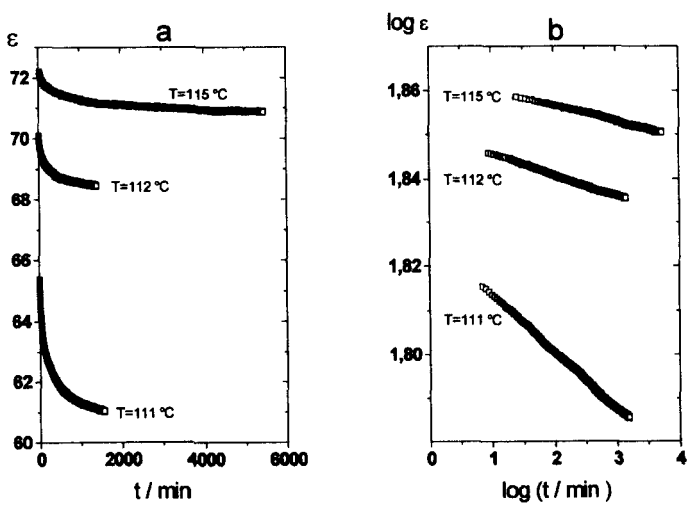


FIGURE 2 Isothermal changes in electric permittivity with time after cooling the mixture from the ferroelectric state (120°C) to the temperatures indicated in the figure. Results are plotted in linear (a) and logarithmic (b) scale.

dependence log ε = f(log *t*) is linear with great accuracy (Figure 2b). It means, that the permittivity changes can be described by the form:

$$\varepsilon(t) = A\,(t/\tau)^b \tag{1}$$

where A, τ and b are constants. This equation is a special case of Avrami [11] equation

$$V_2 = 1-\exp\{-(k\cdot t)^d\} \tag{2}$$

which describes the kinetics of transition from a metastable state to a stable one. Originally, equation (2) was derived for description of crystallization process of a supercooled liquid. In equation (2) V_2 denotes the volume fraction of the new (stable) phase, t – time, k is a constant describing transition rate and the exponent d is a constant dependent on the dimensionality of the process.

The volume fraction of the stable phase V_2 can be easily determined from dielectric measurements. Denoting ε the instantaneous permittivity of the material (measured when both phases are present between electrodes), ε_1 - electric permittivity of the old (metastable) phase and ε_2 - the permittivity of the new (stable) phase, and neglecting the thermal expansion we get

In the case of crystallization of a pure substance, the final stable state is a homogenous crystalline state. In this case the Avrami model works well. To illustrate the applicability of Avrami model for mesogenic

$$V_2 = \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 - \varepsilon_2} \tag{3}$$

materials, the changes of electric permittivity of a pure mesogenic material 4-(1-methylheptyloxycarbonyl)phenyl 4'-(octyloxy di-(phenyl-carboxylate)) have been measured as function of time. The results are presented in Figure 3.

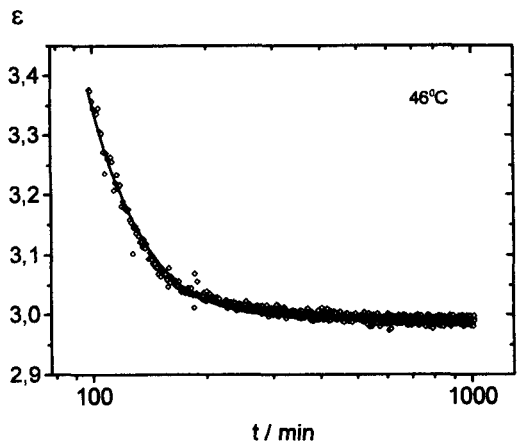


FIGURE 3 Isothermal changes of the electric permittivity of the pure mesogenic material during crystallization. Solid line presents fitting results to equation (2).

To demonstrate the agreement of data shown in Figure 3 with Avrami model, we can rewrite equation (2) in the following form:

$$\ln[-\ln(1-V_2)] = d \cdot \ln t + d \ln k \tag{4}$$

The term $\ln[-\ln(1-V_2)]$ is a linear function of $\ln t$. This result agrees well with the performed experiment, see Figure 4. The value of the exponent d determined by fitting the experimental data to equation (4) lies between 2 and 3. According to the Avrami theory, it means that the crystal growth is two-dimensional (plate-like). Microscopic observations carried out simultaneously with dielectric measurements revealed that it was two-dimensional, indeed. It occurred through a growth of circular objects in the electrode plane. Thus, the observation performed for the pure material confirmed the usefulness of the Avrami theory to the description of the crystallization process in

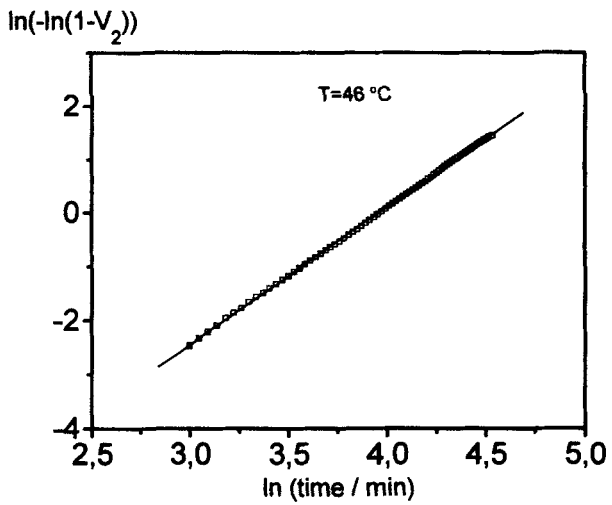


Figure 4 Fitting of dielectric data to equation (4) as a test of the Avrami model.

mesogenic materials.

Applying similar method of analysis for the case of the transition from the ferroelectric to the antiferroelectric state we obtained also an excellent agreement of the experimental results with equation (4). The fitting results are placed exactly within the experimental points in Figure 2. The fitting parameters are collected in Table 1.

As Table 1 demonstrates, the process of transformation from the ferroelectric to the antiferroelectric state can be described formally by Avrami theory. However, the value of the exponent *d* obtained for this transformation is very low (about 0.1). According to the Avrami theory, the value *d-1* describes the dimensionality of the process. As already shown, this rule works well in the case of crystallization. However, in the case of the transition from the ferroelectric to the antiferroelectric state in investigated mixtures possessing induced antiferroelectric phase the *d* value is unreasonably small. Hence, despite the formal agreement of experimental results with the theory one can not state that Avrami

TABLE 1 Fitting parameters to equation (2).

T/°C	ε_1	ε_2	d	k/min^{-1}
107	28,5	19,4	0,111	0,0694
108	31,6	24,1	0,101	0,0369
109	43,9	29,3	0,078	0,0197
110	73,1	48,7	0,190	0,5191
111	73,1	56,9	0,136	0,0071
112	74,1	67,7	0,160	0,0850
113	75,9	68,8	0,098	0,0348
115	74,9	69,9	0,149	0,0058
116	76,8	73,1	0,435	0,0013

theory describes the phenomenon of isothermal transition from the ferroelectric to the antiferroelectric state. Thus, another mechanism must be responsible for this transition.

In case of a mixture, the coexistence of solid and liquid phases may take place in a certain temperature range. Similar effect is observed in our case: the final state depends on temperature and is an equilibrium state of the ferroelectric and antiferroelectric phases. This behavior is illustrated in Fig. 5.

In this photograph taken under polarizing microscope the orange (bright) areas are antiferroelectric, which appeared from the ferroelectric state (blue, dark areas) after cooling from 120°C to 111°C. In course of time the bright areas grow on the expense of the dark areas. The growing rate decreases continuously (compare Fig. 2). In the final state, however, there is a coexistence of both areas – even after many days the transition to the bright state is not complete. The volume ratio of both states in equilibrium (after sufficiently long time) depends on temperature. The lower is the temperature, the higher the amount of antiferroelectric state is. The same conclusion can be drawn from fitting results: the permittivity in the final state ε_2 depends on temperature (see Table 1).

FIGURE 5 Microphotograph illustrating the coexistence of ferroelectric and antiferroelectric states. Vertical edge of the photograph corresponds to 370 μm. The sample was held for 7 days at 115°C.
See Color Plate XXI at the back of this issue.

The described phenomena remind crystallization process in non-homogenous systems, (e.g. in mixtures), which is associated with components separation. The investigated material is also a binary mixture and the phenomenon of phase separation could be in principle present as well. In this case, however, the effect of component separation should be visible in other phase transitions, e.g. SmC* ↔ SmA. We have never observed such a phenomenon during microscope observation. Although a kind of microseparation can not be excluded [5], we suppose that some other processes probably cause the observed kinetics.

The very slow kinetics of the transition from the ferroelectric to the antiferroelectric state (see k values in Table 1) and the phases coexistence seem to indicate that the difference in the free energy in both states is very small. In other words, the interactions leading to either ferroelectric or antiferroelectric dipole order must be of comparable strength in mixtures with induced antiferroelectric phase. The slow kinetics, hysteresis and temperature dependent equilibria are presumably connected with a competition of these interactions. Hence, even weak external factors, like surface interactions or electric fields, can stabilize one or another phase and decide which state - ferroelectric or antiferroelectric - is stable in certain conditions. This can be the cause of the thermal hysteresis of the transition C_a^* ↔ C and of the threshold-less switching, observed in investigated mixture and in other,

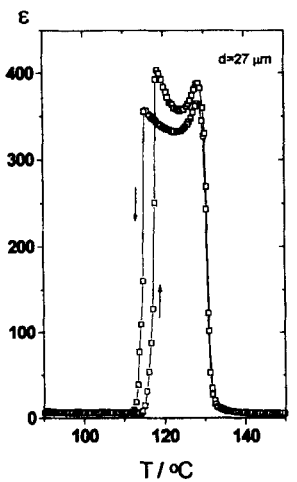


FIGURE 6 Temperature dependence of the electric permittivity measured in 27 μm thick cell.

similar systems [7,8]. This supposition is confirmed by the results of dielectric measurements, performed using cells of different thickness. These measurements revealed that the range of thermal hysteresis in thick (27 μm) cells is much lower than in thinner cells (5μm) (compare Figures 1 and 6).

As this comparison demonstrates, the cell thickness does not influence the transition temperature $C_a^* \rightarrow C^*$ on heating, but strongly influences the transition temperature $C^* \rightarrow C_a^*$ on cooling. Larger thickness results in increase of this later temperature and, consequently, in diminishing of the thermal hysteresis. The low difference of the free energy of both states can be also the reason for appearance of the so called „V-shaped switching", which we observed in the hysteresis region [7]. The dependence of the hysteresis on sample thickness explains, why the „threshold-less switching" can be observed exclusively in thin samples [2].

Similar effects can be caused by electric field. We observed that relatively weak electric fields could give rise to the transition from the antiferroelectric to the ferroelectric state. The occurrence of ferroelectric state in very weak fields can explain the "threshold-less switching" observed in studied mixtures. The V-shaped switching must be attributed to ferroelectric phase. Nevertheless, the presence of the antiferroelectric phase is needed for introducing the competition of ferroelectric and antiferroelectric interactions between smectic layers.

4. CONCLUSIONS

Our investigations revealed the existence of a distinct thermal hysteresis of the transition between ferroelectric C* and antiferroelectric C_a* phases. These effects were monitored by electric permittivity and electrooptic response. In the hysteresis region, at constant temperature, long term changes of the volume ratio of ferroelectric and antiferroelectric states were observed. This ratio tends to an equilibrium level, which depends on temperature.

The mentioned effects (hysteresis and changes with time) appear in the same temperature range, where the "V-shaped switching" is observed. This kind of switching is connected with the fact that in investigated mixtures the ferroelectric state can be induced by weak electric field. Hence, the „threshold-less switching" probably takes place in the ferroelectric state. The presence of thermal hysteresis can be an excellent mark of the threshold-less switching. All three effects (hysteresis, kinetics and threshold-less switching) are probably attributed to the competition between ferroelectric and antiferroelectric interactions, acting between neighboring smectic layers and to frustrations resulting from this competition. When these interactions are comparable, even weak external factors can decide, which state – ferroelectric or antiferroelectric – is stable under given conditions.

5. ACKNOWLEDGMENTS

The authors thank to J. Małecki for valuable discussions. This work was supported by KBN (Polish Research Committee) in the framework of the project 2PO3B09715.

References

[1] A. Fukuda, Y. Takanishi, T. Izosaki, K. Ishikawa, H. Takezoe, *J. Mater. Chem.*, **4**, 997, 1994.

[2] S.S. Seomun; Y. Takanishi; K. Ishikawa; H. Takezoe; A. Fukuda; C. Tanaka, T. Fujiyama, T. Maruyama, and S. Nishiyama, *Mol. Cryst. Liq. Cryst.*, **303**, 181 (1997).

[3] K. Takatoh, *Proc. 6-th Int. Conf. on Ferroelectric Liquid Crystals*, Brest, 20–24 July, p. 18 (1997).

[4] A. de Vries, A. Ekachai, N. Spielberg, *Mol. Cryst. Liq. Cryst.*, **49**, 143 (1979).

[5] E. Górecka, D. Pociecha, M. Głogarova, J. Mieczkowski, *Phys. Rev. Lett.*, **81**(14), 2946 (1998).

[6] P. Rudquist, J.F Lagerwall, M. Buivydas, F. Gouda, S.T. Lagerwall, N.A. Clark, J.E. Maclennan, R. Shao, D.A. Coleman, S. Bardon, T. Bellini, D.R. Link, G. Natale, M.A. Glaser, D.M. Walba, M.D. Wand, X.-H. Chen, *Mater. Chem.*, **9**, 1257 (1999).

[7] S. Gauza, K. Czupryński, R. DĄbrowski, K. Kenig, W. Kuczyński, F. Goc, *Mol. Cryst. Liq. Cryst.*, in press.

[8] W. Kuczyński, R. DĄbrowski, S. Gauza, F. Goc, J. Hoffmann, K. Czupryński, K. Kenig, *Proc. SPIE (Int. Soc. Opt. Eng.)*, **4147**, 79, (2000).
[9] F. Goc, W. Kuczyński, J. Małecki, R. DĄbrowski, J. Hoffmann, *Proc. SPIE (Int. Soc. Opt. Eng.)*, **4017**, 171 (1999).
[10] F. Goc, W. Kuczyński, R. DĄbrowski, B. Stryła, H. Gierszal, *Proc. SPIE (Int. Soc. Opt. Eng)*, **4017**, 75 (1999).
[11] M. Avrami, *J. Chem. Phys.*, **8**, 212 (1940).