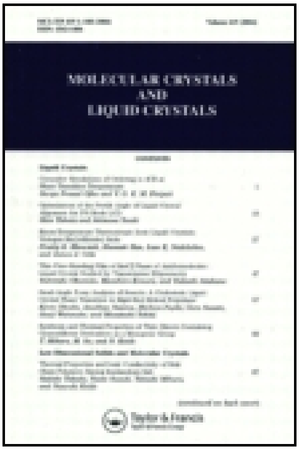

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Sergei Budakovsky [a] , Nikolai Galunov [a] & Igor Krainov [a]

[a] Institute for Single Crystals, Kharkov, Ukraine

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THE PROPERTIES OF MOLECULAR CRYSTALS GROWING FROM THE MELT CONTAINING ELECTRON-SEEKING ADDITION AGENTS

SERGEI BUDAKOVSKY, NIKOLAI GALUNOV, IGOR KRAINOV
Institute for Single Crystals, Kharkov, Ukraine

Abstract The influence of the melt centers with charge - transfer complex - like structure on the crystallization process and properties of organic materials are discussed.

INTRODUCTION

It has been shown[1-4] that doping stilbene melts with electron - seeking addition agents (ESAA) of benzene and benzophenone halogen derivatives allowed us to control the growth rate of the crystal as well as its structure perfection. It was accompanied with changes in concentration of charge carrier (≈ 1.2 ÷ 1.4 eV) as well as exciton (≈ 0.24 eV) deep traps. Doping the melt with ESAA did not cause the appearance of additional luminescence or impurity centers in the grown crystals.[1,5] The results of the X-ray fluorescence study by VRA-2 analyzer [5] for ESAA presence in the grown crystals showed that a distribution coefficient value for an addition agent did not exceed 0.01. Thus, practically, ESAA did not enter the grown crystal. Doping the melt with impurities usually results in deterioration of a crystal structure perfection and in decrease in a crystal growth rate. Doping the stilbene melt with ESAA had a rather unusual result. The increase of the ESAA concentration C in the melt for $C < 0.1$ mol% caused the "inverse" effect on the crystal structure perfection and growth rate (the latter rises two or three times), and only for $C > 0.1$ mol% a deterioration of the crystal structure perfection and decrease in the growth rate with C increase were observed.[1-5]

EXPERIMENT

The single crystals of stilbene, anthracene and p-terphenyl are grown from the melt by Bridgmann process. The ESAA were the same as those described in the previous papers.[1-5] These experiments were performed in order to verify the conclusion about the influence of charge - transfer complexes (melt molecule - molecule of ESAA) on the crystallization process of organic molecular materials made in the previous studies on the example of stilbene.[1-5] In these experiments the complexes were distributed evenly in melt volume.

The following experiments aimed to detect the "surface" effects. Growing all the aforementioned organic crystals from the melts (both with and without the ESAA) using seed inorganic crystals was carried out to study the orientation influence of electrically active point cleavage surface defects on the growth process.[6] The inorganic crystals of KCl, Al_2O_3, $CdWO_4$, as well as mica ones had been cleaved and then used to seed an organic crystal melt. Test experiments of organic crystal growth from melts (both with and without the ESAA) have been made on the surface of the previously melted down gallium as well.

The structure perfection of the crystal was determined by the value of the root-mean-square random orientation σ_c of it mosaic structure. The crystal with the least σ_c was considered as the most perfect structure one. The σ_c determination technique was reported previously.[5] Melting Q_m and crystallization Q_c heats Q and temperatures T, melting heat capacity c_p were obtained using Mettler TA-3000 thermoanalytic system, by melting a uniform mixture of powdered organic substance and ESAA with the subsequent crystallization of the resulting melt.

It allowed us to calculate the variables

$$\delta S \,/\, \delta T = c_p \,/\, T \tag{1}$$

$$dS = dW \,/\, T = dQ \,/\, T \tag{2}$$

where S is the entropy, W is the enthalpy. The process went on at constant pressure p, which determined the form of Eqs.(1) and (2).

The results were analogous to those reported for stilbene.[4] For melting, with C increase the c_p, Q_m, σ_c, $\delta S/\delta T$, dS values decreased when $C < C_R$, but when $C > C_R$ the c_p, σ_c, $\delta S/\delta T$ increased and the rates of Q_m and dS decrease slowed down. The melting temperature did not depend on C. For crystallization, with C increase the withdrawing heat Q_c and dS values decreased, structure perfection of the crystal increased (i.e. σ_c decreased) when $C < C_R$. This was accompanied by a rise in T_c that resulted in a decrease in the difference ΔT between melting temperature and that of crystallization. When $C > C_R$ with an increase in C, Q_c was practically constant, but the ΔT, dS and σ_c values increased. The growth rate of the crystal was changed as did its structure perfection.

For all the crystals $C_R \simeq 0.1$ mol%. For very high C ($C \geq 1.0$ mol%) the crystal did not grow and a few solid phases formed. The organic single crystals grew on the surface of the melted gallium only when the crystal melt contained the ESAA with $C \simeq C_R$. When the seed inorganic crystals were used as an underlying surface, the organic crystals were grown with just the same structure perfection as that for the crystals grown on orientated organic seeds.[7]

The following facts confirm the statement[5] about ESAA rejection from the solid - liquid interface back into the melt. The top of the boule had the same poor structure perfection as the crystals grown from a melt containing high C. The separation of the complexes on the boule top was observed. Thus, any processes caused by an influence of the ESAA molecules entered into crystal can't result in an improvement of the crystal structure perfection or an increase of its growth rate.

DISCUSSION

Addition agents of a high electron affinity can exist in the melt of organic aromatic substances only within charge - transfer complexes which are based on the structure: melt molecule - addition agent molecule. Such a complex can be described as an electric dipole with dipole moment d. For the substances under discussion d $\simeq$ 2.5D.[5] It is a very high value for organic molecular systems because the characteristic of their interaction energy is determined by dispersion energy, and is of the order of 10^{-3}eV. The electrostatic field which is produced by such a complex is strong enough not only to polarize the neighboring melt molecules (i.e. to induce their dipole moments and orient them), but to fix the spatial orientation of the complex and melt molecules up to some distances r_p, in spite of the existence of thermal motion in the melt. One can calculate r_p as a mean distance at which the interaction of the dipoles (with the constant dipole moment d and with the induced one) is equal to the heat energy kT, where k is the Boltzmann constant, T is the melt temperature. In much the same way, it is possible to calculate the distance r_d at which the interaction energy of two dipoles with constant dipole moments d is equal to kT. It is a distance between two or more complexes within which dipoles can be attracted to one another and form a "supercomplex" in the shape of a stack consisting of $n_{AD} > 1$ complexes. For the cases under consideration $r_p \simeq r_d \simeq 0.5$ nm.[4,5]

The analysis of the peculiarities of the stilbene single crystals growth from the melt doped with ESAA showed that the initial cause of the effects discussed is the formation of charge - transfer complexes.[4] Really, the melting is accompanied by a very effective process of complex formation. Its duration is $t_{AD} \simeq 10^{-11}s \simeq 10^{-8}\ t_c$, where t_c is the time of a single crystal layer growth. The characteristic time of the formation of orientated polarization surrounding of a complex is $t_p \simeq t_{AD} \simeq 10^{-8}$ t_c. The characteristic time of supercomplex formation is $t_s \simeq 10^{-7} \div 10^{-8}s \le 10^{-4}\ t_c$. The above results have been obtained under the conditions peculiar to chosen organic molecular substance and ESAA. Therefore, the above estimations are valid for all the cases under examination.

For $C < C_R$ the formation of single complexes is of primary importence. Their concentration $C_{AD} = C$. For $C > C_R$ when the mean distance between complexes has already become comparable with r_d, the formation of complexes with $n_{AD} > 1$ becomes the most probable, and $C_{AD} < C$. For $C_R \simeq 0.1$ mol% the mean distance between complexes $R \simeq 6$ nm, i.e. $R \simeq 10 \div 12\ r_d$.[5]

The formation of the orientated melt parts (i.e. "partial melt ordering") causes the consequences of two types. First, it may result in an increase in the growth rate and in an improvement in the structure perfection of the grown crystal due to the decrease of the withdrawing heat with the increase of the melt "ordering". It should be noted, that this process will be accompanied by a complex breakdown, and both processes are the causes of the same effect. Second, the polarized surroundings of a complex, i.e. a group of mutually orientated melt molecules, having entered into the growing crystal layer, may become a crystallization center, which will result in an increase of the growth rate. For $C > C_R$ the positive effect of those processes on the crystal growth decreases steadily with an increase in C due to an increase in the n_{AD} value, i.e. a decrease in the ratio C_{AD} / C. Entering the supercomplexes or products of their breakdown the crystal results in an increase of the number of the crystal lattice defects, and for very high C (and n_{AD}) values leads to the formation of nucleation centers, which compete with each other in the crystal growth process. The evidence of the complex electrostatic field influence on the orientated melt parts formation and on an increase in the growth rate of the perfect structure crystal has been obtained in the experiments with organic crystal growth both on seed inorganic crystals and on the surface of the metal previously melted down.

CONCLUSIONS

The described experiments and the estimations allow to draw a conclusion about the property of the centers with a charge - transfer - complex - like structure to initiate an accelerated growth of perfect structure organic crystals.

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