ANALYSIS OF THE RELATIONSHIP BETWEEN CHANGES IN THE STRUCTURE AND MORPHOLOGY OF MOLECULAR CRYSTALS FOR ENERGETIC MATERIALS UNDER THERMAL INFLUENCE

A. V. Stankevich

FSUE «RFNC – VNIITF named after Academ. E. I. Zababakhin», Snezhinsk, Russia

Kazan National Research Technological University, Kazan, Russia

Postovsky Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Ekaterinburg, Russia

Under thermal influence on molecular crystals, processes of anisotropic thermal deformation and polymorphic transitions occur. Each point of a crystalline solid moves relative to its initial position by a certain amount, which is determined not only by a change in the parameters of the unit cell, but also by a change in the independent coordinates of atoms, i. e. by the tensor of the distribution of electron density and the potential of chemical activity. In turn, at certain values of ambient temperature and pressure, crystalline bodies form various types of equilibrium crystal facets and habitus. In case of deviation from the set parameters of the crystal's existence, internal stresses accumulate in proportion to the displacement of the deformation field inside the crystal, which can lead to a loss of equilibrium morphology.

In this paper, we analyze the relationship between changes in the characteristics of the crystal structure (unit cell parameters, packing density, independent atomic coordinates and bond lengths in molecules) and micromorphological characteristics (habitus, equilibrium faceting, surface area of the facets, rate of deformation of the facets). The analysis was performed for seventeen molecular crystals of energy materials in an ultrapure state: α-, β-, β′-DNAN, α-TNT, α-, β-, γ-, δ-HMX, α-, β-, γ-FOX-7, α-NTO, α-RDX, PETN-I, BTF and TATB. Experimental data on the state of solid crystals at a specific temperature were obtained by powder X-ray diffraction and Raman spectroscopy. Data processing was performed using full-profile analysis methods with an integrated refinement cycle of the quantum topological model using various semi-empirical methods of quantum chemistry [1–5]. Experimental crystal cutting data were obtained by electron and optical microscopy. Data processing was performed using dichotomy and Monte Carlo methods according to the Bravais-Friedel-Donnelly-Harker (BFDH) growth rate rule and the Gibbs thermodynamic minimum surface energy (EM).

As a result, diagrams of the strain tensor of the morphology of molecular crystals were constructed along all crystallographic planes of face growth. The relationship between the main crystallographic axes in the equilibrium morphology and the unit cell of the studied molecular crystals has been established.

References

1. **Stankevich, A. V.** Anisotropic thermal expansion of HE crystals under atmospheric pressure [Text] / A. V. Stankevich, et al. // XXXII International Conference on Interaction of Intense Energy Fluxes with Matter, Book of Abstracts. – March 1–6, 2017, Elbrus, Russia – P. 292.

2. **Stankevich, A. V.** Thermal strain tensors for benzotrifuroxane and pentaerythritol tetranitrate molecular crystals [Text] / A. V. Stankevich, et al. // J. Phys.: Conf. Ser. – 2019. – Vol. 1147. – P. 012009.

3. **Stankevich, A. V.** Polymorphism and thermal deformation of 1,1-diamino-2,2-dinitroethylene in the temperature range from 145 to 473 K [Text] / A. V. Stankevich, et al. // J. Phys.: Conf. Ser. – 2021. – Vol. 1787. – P. 012006.

4. **Stankevich, A. V.** Anisotropic thermal expansion for molecular crystal of 1,3,5-triamino 2,4,6-trinitrobenzene at normal pressure [Text] / A. V. Stankevich, E. B. Smirnov, O. V. Kostitsyn et al. // School for the training of young specialists "The use of synchrotron and terahertz radiation for the study of high-energetic materials" September 15–20, 2015. – Book of Abstracts, Novosibirsk, P. 46–49.

5. **Stankevich, A. V.** Tensors of thermal deformation for various polymorphic modifications of 2,4-dinitroanisole [Text] / A. V. Stankevich, N. A. Rasputin, A. Kh. Rudina et al. // Energetic Materials Frontiers. – 2024. – Vol. 5. – P. 257–266.