200 years after discovery of the general phenomena of crystal chemistry by Eilhard Mitscherlich: iso- and polymorphism, highly anisotropic and negative thermal expansion

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The great German chemist EilhardMitscherlich was one of the first to be at the forefront of crystal chemistry about 200 years ago. He discovered and generalized the phenomena of isomorphism, polymorphism, anisotropy of thermal expansion and negative thermal expansion. Brief information on the discovery of these phenomena and its development to date is given below.

Isomorphism was first introduced by Mitscherlich in 1819 (Abhandl. Berlin. Akad.Wissensch.)as a term meant an equality of formsof a solid matter and he formulated a law [1]: *crystals composed of the same number of similar elements tend to demonstrate isomorphism*. Later it was determined as a substitution of some fragments of a crystal structure by other (atoms, ions, vacancies, molecules, atomicgroups) to form an isomorphic mixture (solid solution). A reverse process, i.e. discontinuation of an existence of the solid solution is reached by an ordering of the atoms by positions in the original crystal structure(*factor of structural diversity*[2, p. 182]). If a number of such positions is insufficient, then the problem can be solved by the solid solution's decomposition, formation of superstructures, incommensurate modulations, splitting of atomic positions*etc*[2, p. 190].

Polymorphism.A doctrine of mineral's dimorphism created by Mitscherlich[3] raised a doubt of*R. J. Haüy*and other chemists due to a presence of impurities in minerals. In response, Mitscherlich was the first scientist to conduct experiments on the synthesis of various crystals from pure synthetic compounds, in particular, fromthe sulfur, and provedthe phenomenon of dimorphism (polymorphism generally). In the mid-twentieth century, M.J. Buerger created a unified theory of polymorphism as transformations of I (coordination polyhedron, *c.p.*) and II (local environment of the *c.p.*) coordination spheres (*c.s.*) with and without a break of chemical bonds [4]. S.K. Filatov and P. Paufler introduced zero *c.s.* (atom, ion) and an intermediate (local) break of bonds [5].

Anisotropy of thermal expansion and negative thermal expansion.E. Mitscherlich made an optical tube for the Wollaston's reflective goniometer in order to fix a position of an eye when registering a luster of a crystal's face. This allowed him to find the difference of values of angles between the faces of calcite crystal at different time of a day as a function of temperature, i.e. to discover the anisotropy of the thermal expansion. Moreover,Mitscherlichdiscovered the negative thermal expansion of calcite crystals. Later this led to the understanding of reasons causing a thermal cracking ofrocksand metasomathosisprocesses as well as of a deposition of ores in the Earth's crust[2, p. 246].

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