PARTIALLY IONIC / PARTIALLY COVALENT CRYSTALS OF |AB AND ABO_3 TYPES: DEPENDENCIES BETWEEN CHEMICAL COMPOSITION, STRUCTURE, NATURE OF CHEMICAL BONDS AND CHOSEN PROPERTIES

Summary

Partially ionic / partially covalent crystals form a family of materials that are very divers in their chemical composition, structure and usable parameters. This is why it is important to increase knowledge about relations between a constitution and properties of these materials. A research reported in the present monograph is contained in this area.

It has been an author's purpose to discuss some examples of such interrelationships. A role of the chemical bond as a basis for classifying materials to proper positions in the bond triangle and bond tetrahedron is underlined. It is shown, for a series of AB-type crystals, that ionic/covalent character of the bond depends on properties of atomic cores (their effective charges). The respective relation has been discussed in the light of structural aspects.

The knowledge of the ionic character of a chemical bond allows estimating an amount of charge transfer between cation and anion in the crystal. This in turn influences a shape of a potential energy curve – as given by spectroscopic constants: bond energy, bond length, force constants and Sutherland scaling parameter.

According to a simplified picture, a stability of an ionic crystal may be described with a reference to five Pauling's rules. It is proved in this work that a co-ordination number of an ion can be determined by fractional net ionic charges in covalent/ionic crystal. One may use an appropriate graph to present the formulated dependence. For the crystals in which the bonds between the same atoms may have various lengths, a bond valence idea appears to be useful. It can be successfully applied in the description of structural phase transitions. In particular, the bond valence may serve as a crucial parameter to characterise ferroelectric phase transitions in perovskite-type crystals. Performed calculations have confirmed that the valences relate to the covalent character of the respective bonds. It is underlined, within the present context, that the bond valence may be used instead of a bond order defined within Pauling's molecular resonance. On the other hand, it gives an alternative for Goldschmidt's tolerance factor, originally proposed for ideal ionic crystals.

The results presented in this monograph show that the description of a diversity of the ionic/covalent crystals needs a general attitude including both geometric and electron structure models. The expected results may be achieved with application of the ideas described herewith: ionic / covalent character of the bond, its length, energy and force constant as well as ionic net charges, ionic radii, the bond strength, valence and order.