08-Inorganic and Mineralogical Crystallography

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CRYSTAL CHEMICAL NATURE OF STABILITY OF COMPLEX INORGANIC COMPOUNDS.

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The reasons for formation of complex compounds from simple ones, for instance, oxysalts from oxides, have attracted much attention for very long time. It has been shown that the stability of a complex compound increases, if the difference of acid-base properties of components increases. Besides the hypothesis of a strong anion polarization in inhomogeneous cationic surrounding has been proposed to explain the stabilization. It corresponds to the reduction of anion position symmetry.

It is not trivial that the electrostatic Madelung energy of a complex crystal is less stabilizing, as a rule, than that of sum of constituents (at constant coordination numbers). Hence, the stability of a complex crystal can be explained only by the idea of bonding character change or bond interaction effect. It is shown that the enthalpy of formation of a complex crystal is proportional to the square of cation electronegativity difference. The increase of ionicity degree of more ionic bonds and the increase of covalency of less ionic bonds is marked by bond length changes, chemical shifts in X-ray emission and electron spectra and deformation electron density distribution features. The problem of metamict behaviour of crystals is discussed on this basis.

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RESIDUAL STRESS AND MIRROR PLANES IN LEAD ANTIMONY SULPHIDES.

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The six compounds in the PbS rich part of the PbS-Sb,S3 system form three homologous series. Their structures are built of ribbons consisting of back-to-back square pyramids arranged in three different tilings. The -4Å repeat in the ribbons results in common feature, a short crystallographic axis, usually taken as g. A mirror plane normal to g is another common feature of these compounds. However, recently synthetized Pb,Sb,S3, a higher homolog of boulangerite, has the space group P212121, i.e., no mirror plane normal to g.

The loss of the mirror plane can be attributed to internal stresses (detected by the bond valence sums) that arise when crystal packing prevents the ribbons from curling in the way that the distribution of Pb and Sb atoms requires. The stress is larger in wider ribbons and is relieved, in part, by the Sb atoms moving off the mirror plane to give them a distorted coordination environment.