Structural principles for minerals and inorganic compounds containing anion-centered tetrahedra

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ABSTRACT

Several minerals and inorganic compounds contain (XA_4) tetrahedra, with anions, X (O^{2-}, N^{3-}, and F^-), as central atoms and cations, A (Cu^{2+}, Zn^{2+}, Pb^{2+}, Bi^{3+}, REE^{3+}, etc.), as ligands. These tetrahedra are well defined in these crystal structures because the bond valences between A and X are essentially higher than the bond valences between A and atoms from other structural units. According to their size, anion-centered tetrahedra may be subdivided into large and small tetrahedra, formed from cations with ionic radii near to 1.0 Å (e.g., Pb^{2+}, Bi^{3+}, and REE^{3+}) and 0.5–0.7 Å (e.g., Cu^{2+} and Zn^{2+}), respectively. The small anion-centered tetrahedra prefer to link through corners, whereas the large tetrahedra prefer to link through edges. When the tetrahedra are built from both "small" and "large" cations, "small" cations prefer to be corners shared between lesser numbers of tetrahedra and not involved in linking tetrahedra via edges. The general crystal-chemical formula of minerals and compounds containing anion-centered tetrahedra may be written as $A'_k[X_nA_m][A_pX_q]X'_l$, where $[X_nA_m]$ (usually $n \leq m$) is a structural unit based on anion-centered tetrahedra (ACT) and $[A_pX_q]$ ($p < q$) is a structural unit based on cation-centered polyhedra (CCP). A' is a cation that does not belong to anion- or cation-centered polyhedra; it is usually an interstitial cation such as an alkali metal; X' is an interstitial anion such as halide or S^{2-}. Structures containing both ACT and CCP units may be ordered according to the values of their dimensionality. In structures without CCP units, an important role is played by large interstitial anions that link finite ACT units, chains, or layers into three-dimensional structures or fill cavities in ACT frameworks.