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

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ABSTRACT

Several minerals and inorganic compounds contain (XA4) tetrahedra, with anions, X (O2–, N3–, and F–), as central atoms and cations, A (Cu2+, Zn2+, Pb2+, Bi3+, REE3+, 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., Pb2+, Bi3+, and REE3+) and 0.5–0.7 Å (e.g., Cu2+ and Zn2+), 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][XnAm][ApXq]X', where [XnAm] (usually n ≤ m) is a structural unit based on anion-centered tetrahedra (ACT) and [ApXq] (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 S2–. 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.

INTRODUCTION

Minerals are commonly viewed in terms of cation polyhedra; yet, many simple important oxide mineral types are composed entirely of O-centered tetrahedra (alumina-hematite; fluorite-related oxides such as cerianite, thorianite, and bixbyite; copper oxides such as cuprite, tenorite, and paramecaonite; lead oxides such as litharge and massicot; wurtzite-structure oxides such as bromellite and zincite, etc.; O’Keeffe and Bovin 1978; O’Keeffe and Hyde 1985, 1996; Hyde and Andersson 1989; Krivovichev et al. 1998a). Structural units based on (XA4) anion-centered tetrahedra differ from those based on (AX4) cation-centered ones (e.g., silicates) in that they may link through edges as well as through corners. This possibility gives rise to many polyions that may be classified on the basis of extended systematics of silicates proposed by Liebau (1982, 1985). Using the arguments by Krivovichev (1997) and Krivovichev et al. (1997), oxocentered tetrahedral polyions were subdivided into 63 structurally distinct types (Krivovichev et al. 1998a), at least one-half of which occur in minerals. Schleid (1996) described seven structural units consisting of N-centered tetrahedra, and two additional units may be added to this list from work of Lulei and Corbett (1995) and Braun et al. (1996). However, these reviews focused on only the linkage topology of anion-centered tetrahedral units, and not on their relations with other units in a structure. A description of crystal structures in terms of anion coordination based on purely geometric aspects was developed by O’Keeffe and Hyde (1985) with emphasis on the arrangement of cations and by Brese and O’Keeffe (1995) for the description of inorganic nitrides. The primary motivation of the present paper is to use bond-valence theory to examine the rules of construction of structures with (XA4) tetrahedra. The second motivation is that oxocentered metal polycations play a role in the transport processes of metals in gases and aqueous solutions (Hilpert 1990; Boldyrev et al. 1995; Henry et al. 1991; Rouse and Peacor 1994; Grimes et al. 1995), and it is possible that condensation of these polycations results in minerals with crystal structures containing well-defined oxocentered tetrahedra.

ANION-CENTERED TETRAHEDRA AS INDEPENDENT STRUCTURAL SUBUNITS

Consideration from the viewpoint of bond-valence theory

The strength of X-A bonds in anion-centered (XA4) tetrahedra can be understood in terms of bond-valence theory (Brown 1981; Brese and O’Keeffe 1991). Table 1 gives the bond-length and bond-valence analysis of minerals containing O atoms belonging to oxyanions (TOq) (T = Se, S, Cr, V, As; q = 3, 4) and additional O atoms; these O atoms are designated

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