

## **The Zintl-Klemm Concept Applied to Cations in Oxides. An Alternative Interpretation of the Structures of Silicates**

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The structures of ternary and quaternary silicates are reinterpreted on the basis of the Zintl-Klemm concept and the Pearson's generalised octet rule. The three-dimensional skeletons formed by the Si atoms can be interpreted as if the Si atoms were behaving as Zintl polyanions, adopting the structure of either main-group elements or Zintl polyanions showing the same connectivity. An example of this behaviour is the mineral pabstite BaSn[Si<sub>3</sub>O<sub>9</sub>]. In this compound, the Ba and Sn atoms donate 6 e<sup>-</sup> per formula unit to the three Si atoms, converting them into Ψ-S atoms, i.e. 2-connected atoms. Thus, the Si (Ψ-S) atoms adopt the structure of the triangular S<sub>3</sub> molecules. The O atoms are then located close to both, the hypothetical 2-electron bonds and the lone pairs, giving rise to a tetrahedral coordination. In some silicates, the Si atoms clearly show an amphoteric character so that some Si atoms act as donors (bases) adopting an octahedral coordination, whereas others behave as acceptors (acid), adopting a tetrahedral coordination. Although the octahedral coordination seems to be favoured by the application of pressure, the results reported here indicate that the coordination sphere of silicon is not a function of the assumed ionic radius of the Si<sup>4+</sup> cations but it depends on the nature of the other cations accompanying them in the structure.

**Keywords:** silicate structures, Zintl-Klemm concept, cation arrays