

Structural variations induced by difference of the inert pair effect in the stibnite-bismuthinite solid solution series (Sb,Bi)₂S₃

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ABSTRACT

Structural refinements of single crystal X-ray diffraction data for synthetic (Sb,Bi)₂S₃ solid solutions revealed structural variations in the stibnite (Sb₂S₃)-bismuthinite (Bi₂S₃) series. Coordination environments of the M cations are (3 + 4)-fold for the M1 site and (5 + 2)-fold for the M2 site. For the M1 and M2 polyhedra, the short M-S bond lengths increase constantly with increasing Bi concentration, whereas the long M-S bond lengths decrease continuously. The S-M-S interatomic angles interposing lone-pair electrons increase continuously from stibnite to bismuthinite. Stereochemical activity of the lone-pair electrons induces configurational changes of ligands around the M cations from elongated ellipsoidal coordinations to spheroidal ones. Substitution of Bi³⁺ for Sb³⁺ in the solid solution expands the basic building block, which causes linear increase of the *b* lattice parameter with slight positive deviation from Vegard's law. This feature is ascribed to order-disorder with concentration of Sb at the M1 site and Bi at the smaller M2 site. Furthermore, increased Bi content engenders both expansion of the basic building block and contraction of intervals between these blocks, contributing to smaller changes in the *a* and *c* lattice parameters than in the *b* lattice parameter. The M2 polyhedra expand relative to the M1 polyhedra with increasing Bi content because the large Bi cation is concentrated at the smaller M2 site. One striking characteristic of (Sb,Bi)₂S₃ crystal structures is that geometries of central M cation and ligand atoms can be adapted flexibly to transformation of stereochemical activity from 5s² lone-pair electrons to Bi 6s² lone-pair electrons by altering the centroid-central atom distance and by changing angles of the centroid-central atom to the *a* axis.