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Chemical-structural modularity in the tetradymite group: A HRTEM study

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Abstract

Mixed-layer compounds from the tetradymite group, in the range Bi_2Te_3-Bi_8Te_3, were studied by HRTEM. The formula $S'(Bi_{2k}X_3)\cdot L'[Bi_{2(k+1)}X_3]$ (X = chalcogen; S′, L′ = number of short and long modules, respectively) was introduced as a working model. Diffraction patterns show that all phases are N-fold (N = layers in the stacking sequence) superstructures of a rhombohedral subcell with $c/3 = d_1 \sim 0.2$ nm. The patterns, with two brightest reflections about the middle of d_1^*, are described by monotonic decrease of two modulations with increase in Bi: (1) $\mathbf{q} = \gamma\mathbf{c_{sub}}^*$ ($q \sim$ homoatomic interval; $\gamma = 1.8$–1.64 for analytical range; $c_{sub} \sim 3d_1$), based on displacive modulation between chalcogen and Bi atoms; and (2) $\mathbf{q_F} = \gamma_F\mathbf{c_{sub}}^*$; $q_F = (i/N)d_1^* = id_N^*$, i = S′ + L′, relating changes in module size and number to displacements in a basic substructure.

The $\mathbf{q_F}$ model, besides underpinning the stacking sequences, was adapted to incorporate the homology for S′, L′ modules related by k. The displacements are quantifiable by fractional shifts between reflections in the derived and basic structures. The condition for "the brightest two reflections about the middle of d_1^* to be separated by id_N^*" is fulfilled only if the shift at this position is minimal (equal to $1/N_b$; N_b = layers in the basic structure). This model and accompanying program compiled to find suitable N_b and simulate intensity pattern(s) can be used to (1) constrain stacking sequences estimated from observation; (2) predict polysomes as larger building blocks; and (3) discriminate single-phases from random polysomes.

The formula $nBi_2\cdot mBi_2X_3$ describing the configuration for $Bi_{2k}X_3$ modules by $n/m = k - 1$ is proven by lattice fringes, but is not underpinned by $\mathbf{q_F}$ and does not constrain assumed homology.

Keywords: HRTEM, tetradymite group, chemical-structural modularity, minimal shift condition, polysomatism