

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 $S'(\text{Bi}_{2k}\text{X}_3) \cdot L'[\text{Bi}_{2(k+1)}\text{X}_3]$ (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) $\mathbf{q} = \gamma \mathbf{c}_{\text{sub}}^*$ ($q \sim$ homoatomic interval; $\gamma = 1.8$ – 1.64 for analytical range; $c_{\text{sub}} \sim 3d_1$), based on displacive modulation between chalcogen and Bi atoms; and (2) $\mathbf{q}_F = \gamma_F \mathbf{c}_{\text{sub}}^*$; $q_F = (i/N)d_1^* = id_N^*$, $i = S' + L'$, 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 $n\text{Bi}_2 \cdot m\text{Bi}_2\text{X}_3$, 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