

## Ab initio calculations and crystal structure simulations for mixed layer compounds from the tetradymite series

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### ABSTRACT

Density functional theory (DFT) is used to obtain structural information of seven members of the tetradymite homologous series:  $\text{Bi}_2\text{Te}_3$  (tellurobismuthite),  $\text{BiTe}$  (tsUMOite),  $\text{Bi}_4\text{Te}_3$  (pilsenite),  $\text{Bi}_5\text{Te}_3$ ,  $\text{Bi}_2\text{Te}$ ,  $\text{Bi}_7\text{Te}_3$  (hedleyite), and  $\text{Bi}_8\text{Te}_3$ . We use the formula  $\text{S}(\text{Bi}_{2k}\text{Te}_3) \cdot \text{L}[\text{Bi}_{2(k+1)}\text{Te}_3]$  as a working model ( $k = 1-4$ ) where S and L are short and long modules in the structures. The relaxed structures show an increase in the  $a$  parameter and decrease in the interlayer distance ( $d_{\text{sub}}$ ) from  $\text{Bi}_2\text{Te}_3$  (2.029 Å) to  $\text{Bi}_8\text{Te}_3$  (1.975 Å). DFT-derived formation energy for each phase indicates that they are all thermodynamically stable. Scanning transmission electron microscopy (STEM) simulations for each of the relaxed structures show an excellent match with atom models. Simulated electron diffractions and reflection modulation along  $c^*$  are concordant with published data, where they exist, and with the theory underpinning mixed-layer compounds. Two modulation vectors,  $\mathbf{q} = \gamma \cdot c_{\text{sub}}^*$  ( $\gamma = 1.800-1.640$ ) and  $\mathbf{q}_F = \gamma_F \cdot d_{\text{sub}}^*$  ( $\gamma_F = 0.200-0.091$ ), describe the distribution of reflections and their intensity variation along  $d_{\text{sub}}^* = 1/d_{\text{sub}}$ . The  $\gamma_F$  parameter reinforces the concept of  $\text{Bi}_{2k}\text{Te}_3$  and  $\text{Bi}_{2(k+1)}\text{Te}_3$  blocks in the double module structures, and  $\gamma$  relates to  $d_{\text{sub}}$  variation. Our model describing the relationship between  $\gamma$  and  $d_{\text{sub}}$  allows prediction of  $d_{\text{sub}}$  beyond the compositional range considered in this study, showing that phases with  $k > 5$  have values  $d_{\text{sub}}$  within the analytical range of interlayer distance in bismuth. This, in turn, allows us to constrain the tetradymite homologous series between  $\gamma$  values of 1.800 ( $\text{Bi}_2\text{Te}_3$ ) and 1.588 ( $\text{Bi}_{14}\text{Te}_3$ ). Phase compositions with higher Bi/Te should be considered as disordered alloys of bismuth. These results have implications for mineral systematics and classification as they underpin predictive models for all intermediate structures in the group and can be equally applied to other mixed-layer series. Our structural models will also assist in understanding variation in the thermoelectric and topological insulating properties of new compounds in the broader tetradymite group and can support experimental work targeting a refined phase diagram for the system Bi-Te.

**Keywords:** Tetradymite series, mixed layer compounds, crystal structure, density functional theory, STEM simulations