**Figure captions**

**Structural description of CsTe4**

**Fig. 1.** Projection of the structure of CsTe4onto the a–c plane. The dimensions of the unit cell are given by the dashed lines. Heights are given in fractions of the b-axis. White circles represent tellurium; black circles represent cesium.

**Fig. 2.** The environment surrounding cesium cations (black circles) in the CsTe4lattice. Shaded and white circles represent tellurium atoms situated above and below the relevant alkali metal atom, respectively.

**Fig. 3.** Structure of the anion sublattice 2∞[Te4–]; view along [30]. White circles represent tellurium atoms; black circles represent tellurium atoms forming basic structural building blocks of the anion sublattice: a) isolated Te82– chains; b) Te4– units linked by covalent bridges; c) distorted (TeTe2Te2/2)– crosses. For further explanation see text.

**Structural description of NaTe3**

**Fig. 1.** Representation of the structure of NaTe3. Large circles: tellurium; small black circles: sodium. For visual clarity only a few sodium positions have been plotted. One of the Te62– chains in the lower left part of the diagram has been highlighted by shading the circles. One of the cubes resulting from bridging the Te(3) atoms of the Te62– chains has been marked by cross hatching.

**Fig. 2.** Section of the structure of NaTe3. Six Te(3) atoms form a cube whose two free vertices are occupied by sodium atoms (small black circles). Six Te(1) atoms exo-positioned at a distance of 2.98 Å mediate contact with the Te(2)–Te(2) handles, which in turn link the cube-shaped clusters into strands.

**Fig. 3.** Section of the structure of NaTe3. Dashed symbols indicate how the T-shaped building blocks (shaded) of the Te126– scaffolding build a 3D compound via contacts at 3.33 Å. When equalizing all distances (2.77 Å, 2.92 Å, 2.98 Å, 3.16 Å, 3.33 Å), the structure of NaTe3 becomes identical to that of AgTe3.