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## Structural variations in RETe1.875– $\delta$ –distorted Te nets and chemical bonding

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The structures of the rare earth metal polychalcogenides  $REX_{2-\delta}$  (X = S, Se, Te;  $0 \le \delta \le 0.2$ ) share a common motive of alternating stacks of a puckered [REX] double layer and planar [X] layer, which are structurally related to the ZrSSi type. This class of compounds adopts different (super)structures, according to the chalcogen defects in their planar layers. The deficient sulfides and selenides are dominated by  $X^{2-}$  and  $X_2^{2-}$ -anions, whereas a tendency to form larger anionic entities has been observed for the tellurides.[1–3] Crystals of RETe<sub>1.875- $\delta}$ </sub> (RE = Ce, Pr, Sm, Gd; 0.005  $\leq \delta \leq 0.02$ ) have been grown by chemical transport reactions utilizing iodine and alkali halide flux reactions. All compounds crystallize in an orthorhombic unit cell, resembling a 3×4×2 supercell of the basic ZrSSi cell, with cell dimensions of about  $a \approx 13.2(2)$ ,  $b \approx 17.6(2)$ and  $c \approx 18.0(2)$ . Structure solution and subsequent refinement has been performed in space group Amm2 (No. 38), in accordance with the structures of the related sulfides and selenides.[1] The generalized motif of all compounds resembles well the motif of the  $GdSe_{1.875}$  type structure, as two stacks of a puckered [RE Te] and a planar [Te] layer are observed for all structures. Minor structural variations, i.e. slightly shifted atoms or additional vacancies, are observed for individual compounds within the planar [Te] layer, hinting towards marginally different ordered motifs, which can be understood as a result of structural frustration. The structural variety of the planar layer also manifests itself in a growing number of reflections violating the A-centering condition.

Quantum mechanical calculations based on DFT theory have been performed to investigate the bonding situation inside the planar [Te] layer by using the real space indicator ELI-D. The results justify the description of small anionic fragments constituting the [Te] layers, but also indicate long range order within a characteristic eight-membered Te ring. Unlike for the sulfides and selenides, these calculations suggest formally a  $Te_8^{8-}$ anion, as bonding interactions are expected between all neighboring atoms of the ring.

[1] T. Doert, C. J. Müller, in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Elsevier, 2016.

[2] H. Poddig, T. Donath, P. Gebauer, K. Finzel, M. Kohout, Y. Wu, P. Schmidt, T. Doert, Z. Anorg. Allg. Chem. 2018, 644, 1886–1896.

[3] K. Stöwe, Z. Kristallogr. - Cryst. Mater. 2001, 216, 215-224.

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