

Polytelluride Anions in Deficient $RETe_{2-\delta}$ Structures – Superstructures and Bonding Analysis

Hagen Poddig, Kati Finzel, Thomas Doert*

Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany

*thomas.doert@tu-dresden.de

The structures of the rare earth metal polychalcogenides $REX_{2-\delta}$ ($RE = \text{La-Nd, Sm; Gd-Lu; } X = \text{S, Se, Te; } 0 \leq \delta \leq 0.2$) attracted some attention due to their distorted square planar chalcogenide layer and the motives observed within these layers. All structures share a common structural motif of an alternating stacking of puckered $[REX]$ and planar $[X]$ layers (Figure 1a) and are closely related to the $ZrSSi$ structure (space group $P4/nmm$), which is regarded as their common aristotype [1]. For electronic reasons, the planar $[X]$ layer shows distortions from a perfect square net, forming dianions X_2^{2-} for the non-deficient REX_2 . By reducing the chalcogenide content vacancies are observed within the planar layer, resulting in different superstructures for the $REX_{2-\delta}$ compounds depending on the vacancy concentration. For the sulfides and selenides this results in additional X^{2-} anions along vacancies to maintain a charge balanced layer. The tellurides, however, show different ordering patterns in the planar $[\text{Te}]$ layer for the non-deficient $RETe_2$ compounds, but also a tendency to form larger anionic fragments for the deficient $RETe_{2-\delta}$ compounds, as seen for the commensurate structure of $\text{GdTe}_{1.8}$, e.g. [2].

$\text{LaTe}_{1.94}$ and $\text{LaTe}_{1.82}$ are two examples of different incommensurate crystal structures for $RETe_{2-\delta}$ compounds, separated by the number of vacancies in the planar $[\text{Te}]$ layer [3, 4]. Both compounds share an average tetragonal unit cell with $a \approx 4.50 \text{ \AA}$ and $c \approx 9.17 \text{ \AA}$, based on the structure of their aristotype (Figure 1a). The major difference of these compounds are their respective q vectors, which are compatible with tetragonal symmetry for $\text{LaTe}_{1.94}$, but indicate a loss of the fourfold rotational axis for $\text{LaTe}_{1.82}$, ending up in an orthorhombic superspace group. The $[\text{Te}]$ layer of $\text{LaTe}_{1.94}$ is mainly composed of single vacancies (point defects), isolated Te^{2-} anions and Te_2^{2-} anions. $\text{LaTe}_{1.82}$ is more Te deficient and features adjacent vacancies in addition to Te_3^{4-} anions, to compensate for the missing charges (Figure 1b). To evaluate the formation of possible larger anionic fragments, like a bent Te_3^{2-} anion and the influence of additional vacancies to the structure, DFT based ELI-D real space analysis of approximant structures were performed (Figure 1c).

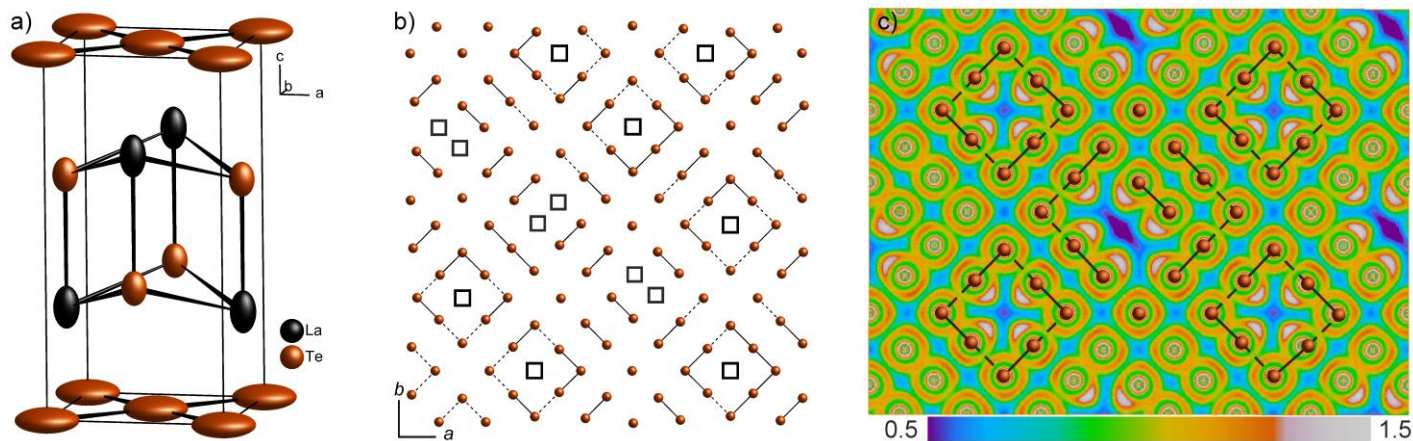


Figure 1. a) Average structure of $\text{LaTe}_{1.82}$; b) section of the modulated $[\text{Te}]$ layer of $\text{LaTe}_{1.82}$; c) orthoslices of ELI-D of the Te layer of $\text{LaTe}_{1.82}$ with isocontour lines based on a commensurate approximant.

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

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

[3] Poddig, H., Finzel, K., Doert, T. (2020) *Acta Crystallogr. Sect. C* **76**, 530–540.

[4] Poddig, H., Doert, T. (2020), *Acta Crystallogr. Sect. B*, **76**, 1092–1099.

Keywords: Polytellurides; rare earth metals; superstructures; incommensurate structures; bonding analysis