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Anisotropic modification of $\text{La}_2\text{NiO}_{4+\delta}$ single crystal surfaces at 1273 K. *N. Gauquelin^{a,b}, T. E. Weirich^c, J. Barthel^c, M. Schroeder^b, W. Paulus^a, M. Ceretti^a*

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The mixed conductor $\text{La}_2\text{NiO}_{4+\delta}$ is an attractive candidate for SOFC cathodes and oxygen separation membranes. For this purpose long term stability is required. Its structural as well as defect and transport properties have been extensively studied during the last decades but are still not fully understood.

$\text{La}_2\text{NiO}_{4+\delta}$ is the first member of the Ruddlesden-Popper phases $\text{La}_{2n+1}\text{Ni}_n\text{O}_{3n+1}$ where $n=1, 2, 3, \dots$ determines the stacking sequence along the *c*-axis which consists of *n* perovskite layers between any two rock-salt layers. The rock salt layer accommodates oxygen interstitial ions, providing oxygen excess δ up to 0.25 [1,2].

The aim of this study is to understand the anisotropic morphological and structural change of the near-surface region of a single crystal of $\text{La}_2\text{NiO}_{4+\delta}$ that we observed above 1273K.[3] These structural and morphological changes were studied using SEM as well as TEM (HAADF & BF) and Electron Diffraction (SAED). The studies revealed a change in the stacking sequence along the [001] direction. At surfaces perpendicular to the crystallographic (001)-plane direction we observed the growth of crystallites of $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ and $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ in a different orientation than the bulk. The phase diagram and thermodynamic studies [4-6] of the system La_2O_3 -NiO indicates that even if the $n=2$ and $n=3$ phases are stable at this temperature, they should not be present for a La/Ni ratio of 2 ; this indicates that the observed phenomenon may be linked to a Nickel enrichment or Lanthanum depletion.

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Topotactic phase transformation of $4\text{H-Cu}_y\text{Ta}_{1.10}\text{S}_2$ into $4\text{H-Ta}_{1.10}\text{S}_2$. *Bernd Harbrecht^a, Wenjie Yan^a, Otfried Lemp^a, Steffen Zörb^a, Kirsten Bohnen^b*

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Tantalum forms a series of polytypic sulfides of general composition $\text{Cu}_y\text{Ta}_{1+x}\text{S}_2$.^[1,2] The layered-type phases are good electronic and ionic conductors. The mobile Cu ions (*y*) and excess Ta (*x*) are inserted in spatially separated van der Waals gaps of a layered TaS_2 host structure. Oxidative deintercalation of Cu with iodine affords new polymorphs of $\text{Ta}_{1+x}\text{S}_2$.

They differ from known polymorphs accessible from the elements at temperatures above 1250 K by higher order staging, i.e. excess Ta (*x*) does accumulate in part of the van der Waals gaps thereby conferring lubricant-like properties to these Ta-rich disulfides. The polymorphs can be classified by a code nN; n counts the number of TaS_2 slabs in the repeat unit and N refers to the lattice symmetry, i.e., H for hexagonal, T for trigonal, R for rhombohedral. The structure of a ternary 4H polytype is presented which upon progressive deintercalation of Cu topotactically transforms into a differing 4H polymorph. The transition is reflected in the divergent X-ray diffractograms showing an offset of the reflection and a drastic change in the intensity modulation of the reflections of the h0l zone. Structural features of the two polymorphs derived from the distinctive intensity modulations are high-lighted and discussed in the light of known polymorphs. Electronic and mechanistic aspects of the transformation are discussed.

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[Pt(tht)₄](CF₃SO₃)₂ in the temperature range 202-295

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Platinum forms strong complexes with soft donors like sulphur as indicated by stability constants of the dimethyl sulphide (dms) and 1,4-thioxane (tx) complexes in aqueous solution [1]. The $[\text{Pt}(\text{dms})_4]^{2+}$ and $[\text{Pt}(\text{tx})_4]^{2+}$ complexes are square planar with Pt-S distances varying from 2.317(3) to 2.321(2) Å [2]. These are the only complexes containing monodentate neutral thioether S-donor ligands found in the CSD.

In the title compound $[\text{Pt}(\text{tht})_4](\text{CF}_3\text{SO}_3)_2$, platinum(II) is positioned at a centre of inversion with a pseudo-square planar coordination geometry with Pt-S distances in the range 2.284(13) - 2.332(2) Å at 202 K and 2.305(12) - 2.327(5) at 295 K. The ligand tetrahydrothiophene possesses a conformational flexibility, manifested by a dynamic disorder. There is a phase change at 201(1) K with the **b**-axis doubled and a third phase with the **b**-axis tripled is observed at 150 and 100 K. The checkCIF/PLATON service (IUCr) gives eight C-level alerts at 295 K which are reduced to four at 202 K. The room temperature phase has a **c**-axis showing negative expansion behaviour. Thermal expansion coefficients as well as diagonalised thermal expansion tensor elements have been calculated and the thermal behaviour as analysed in terms of intermolecular interactions.

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