

# $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ (Ln = Nd, Pr, Sm): a novel series of defective Ruddlesden–Popper phases

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The reaction of  $\text{Nd}_2\text{S}_2\text{O}$ ,  $\text{TiS}_2$  and S at 1000 °C and subsequent chemical transport with  $\text{I}_2$  yields the new crystalline layered oxysulfide  $\text{Nd}_2\text{Ti}_2\text{S}_2\text{O}_5$  that possesses a defective  $\text{Sr}_3\text{Ti}_2\text{O}_7$  structure whose cuboctahedral sites within the double-perovskite layers are empty;  $\text{Nd}_2\text{Ti}_2\text{S}_2\text{O}_5$  is paramagnetic and semiconducting; the synthesis of the isostructural compounds  $\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$  and  $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$  is also reported.

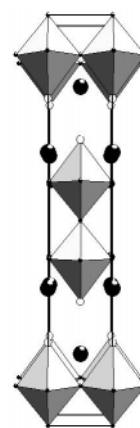
Layered materials represent an active area of research owing to their interesting physical properties that include superconductivity<sup>1</sup> and charge density waves.<sup>2</sup> Important groups of layered compounds are bronzes  $\text{A}_x\text{M}_y\text{O}_z$  (A = alkali, alkaline earth metals, lanthanides; M = Ti, V, Nb, Mo)<sup>3</sup> or early transition metal chalcogenides.<sup>4</sup> Surprisingly, chalcogenide analogues of bronzes are unknown; partial replacement of oxygen by chalcogen atoms leads to metal oxychalcogenides, a family of compounds that have received comparatively little attention so far. A number of rare-earth representatives have been reported, the simplest of them having compositions  $\text{M}_2\text{O}_2\text{Q}$  or  $\text{M}_2\text{O}_2(\text{Q}_2)$  and  $\text{M}_4\text{O}_4\text{Q}(\text{Q}_2)$  (Q = S, Se).<sup>5</sup> Most of them crystallize in layer structures where the oxide and chalcogenide ions form individual layers. We are generally interested in metallic layered materials close to the metal–semiconductor boundary that are composed of transition-metal oxide and/or transition-metal chalcogenide layers, where one of the components can act as a charge reservoir and the second electronically active component dictates the physical properties.<sup>6</sup> There is both experimental and theoretical evidence that a combination of the electronic properties of the individual layers may lead to materials with interesting electronic and magnetic properties;<sup>7</sup> therefore, a structural integration of these two types of layers represents a promising route to new electronic materials. The key problem in the design of new layered oxychalcogenides/oxypnictides is to achieve a large enough difference in the oxophilicity and chalcophilicity of the layer components that one metal is bonded to only one anion type and segregated layers (or stacks) with partial charge transfer are obtained. A combination of two metals with too similar oxo/chalcophilicity often leads to phase separation and the formation of ternary oxide and chalcogenide phases.

In the quest for new compounds with these properties we have investigated the quaternary Ln–M–O–Q phase systems (M = Ti, Nb, Mo, Mn, Fe; Q = S, Se); among others, we obtained the new layer compound  $\text{Nd}_2\text{Ti}_2\text{S}_2\text{O}_5$  **1** whose synthesis, structure and properties are reported here. **1** was made by heating  $\text{Nd}_2\text{S}_2\text{O}$ ,  $\text{TiS}_2$  and S in a 1 : 1 : 1 ratio at 1000 °C. Single phase material was prepared using the following procedure:  $\text{Nd}_2\text{S}_2\text{O}$ ,  $\text{TiS}_2$  and S were mixed in a ratio 1 : 1 : 1, sealed in an evacuated quartz tube and fired at 1000 °C for one week. The corresponding Pr compound,  $\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$  **2**, may be synthesized from the starting materials  $\text{Pr}_6\text{O}_{11}$ ,  $\text{TiS}_2$ , Ti and S in a 1 : 2 : 2 : 3 ratio,  $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$  **3** was obtained by heating a 1 : 1 : 1 mixture of  $\text{Sm}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{TiS}_2$  at 1000 °C for 1 week in a sealed quartz tube. The resulting powders are contaminated with small amounts of  $\text{TiS}_2$  and rare earth oxysulfides. Single crystals of **1–3** were grown from the resulting powders by chemical transport (950 → 850 °C, 4 weeks) using iodine (3 mg cm<sup>-3</sup>) as

a transport agent. Red rectangular crystals of **1**, reddish brown crystals of **2** and brown–yellow platelets of **3** formed at the cold end of the tube.

A microprobe analysis by energy dispersive X-ray spectroscopy (EDX) performed in a Zeiss DSM 962/Philipps PSEM 500 scanning electron microscope (accelerating voltage 20 kV, accumulation time 1 min) equipped with a KEVEX energy dispersive spectroscopy detector indicated the presence of the elements Nd (Pr, Sm), Ti, S and O in an approximate 1 : 1 : 1 : 2 ratio in satisfactory agreement with the results of the structure determination.† The parent compound  $\text{Nd}_2\text{Ti}_2\text{S}_2\text{O}_5$  (Fig. 1) crystallizes in a defect Ruddlesden–Popper structure  $\text{Nd}_2\text{Ti}_2(\text{Q})_7$  of the  $\text{Sr}_3\text{Ti}_2\text{O}_7$  type<sup>8</sup> and is structurally closely related to the high- $T_c$  superconductors of the  $\text{La}_2\text{CaCu}_2\text{O}_6$  type.<sup>9</sup> It is characterized by distorted double NdS rocksalt layers and defective double perovskite  $\text{Ti}_2\text{O}_{10/2}\text{S}_2$  (=  $\text{Ti}_2\text{S}_2\text{O}_5$ ) blocks intergrown along the *c* axis of the lattice. The perovskite  $\text{TiSO}_2$  blocks contain the  $\text{TiSO}_2$  octahedra linked at their corners with the twelve-coordinate site being empty. The Nd atoms in the NdS layers are eight-coordinate. The Nd–S bond length of 3.022(2) Å parallel to the *c* axis is significantly longer than the Nd–S distances of 2.855(1) Å in the *ab* plane. Furthermore, the Ti–S bond which is proximal to the NdS layer is, at 2.896(3) Å, extremely elongated and much longer than a typical Ti–S bond length, whereas the opposite Ti–O distance of 1.790(2) Å indicates significant double bond character and points to an effective 5 + 1 coordination of Ti. The Ti–O bond distances of 1.975(1) Å in the *ab* plane are in the expected distance range.

The magnetic behavior of **1** is determined by the  $f^3$  configuration of the Nd atoms. The results of temperature dependent magnetic susceptibility measurements (Fig. 2) are



**Fig. 1** Polyhedral view of the  $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$  structure along the *b* axis. The polyhedra represent the  $\text{TiSO}_2$ , large black circles the Ln atoms, open circles the S atoms, and small black circles the O atoms (selected distances [Å]: (Ln = Nd, Pr, Sm): Ln–O 2.496(3), 2.505(4), 2.474(3); Ln–S 2.855(1), 2.869(1), 2.834(1); 3.022(2), 3.025(3), 2.986(2), Ti–O(1) 1.975(2), 1.983(1), 1.961(1); Ti–O(2) 1.790(2), 1.796(2), 1.790(1); Ti–S 2.896(3), 2.881(3), 2.887(2)).

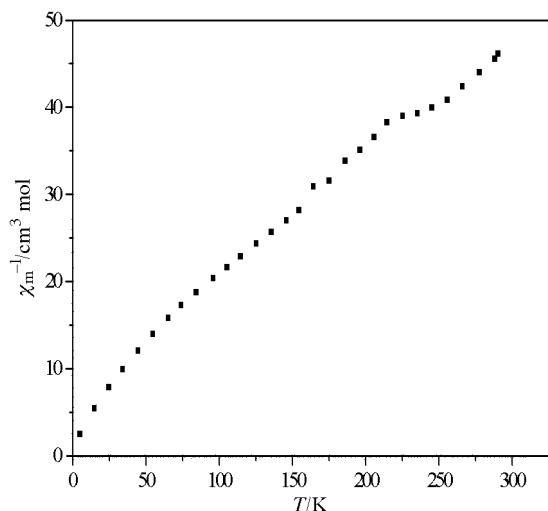


Fig. 2 Magnetic susceptibility  $\chi_M$  vs. temperature plot for  $\text{Nd}_2\text{Ti}_2\text{S}_2\text{O}_5$ .

compatible with antiferromagnetically coupled  $\text{Nd}^{3+}$  centers with  $f^3$  configuration as apparent from a room temperature magnetic moment of  $10.04 \mu_B$  (compared to a theoretical value of  $14.48 \mu_B$  for four independent  $\text{Nd}^{3+}$  centers). Above 260 K and below 175 K Curie–Weiss-type behavior is observed. The red color of  $\text{Nd}_2\text{Ti}_2\text{S}_2\text{O}_5$  points to semiconducting behavior. This is in agreement with the results of LMTO-ASA calculations. The optical (diffuse reflectance) spectrum is characterized by a number of narrow bands that fall into the energy gap of 1.82 eV and can be assigned to transitions from the  $^4I_{9/2}$  ground state to the excited  $^4I_{11/2}$ ,  $^4I_{13/2}$ ,  $^4I_{15/2}$  (or  $^4G_{5/2}$ ,  $^4G_{7/2}$ ,  $^2K_{13/2}$ ) states of the  $\text{Nd}^{3+}$  chromophore. The gap between filled and empty states in the LMTO-DOS is in reasonable agreement with the measured optical band gap obtained from the diffuse reflectance spectrum. In a similar fashion, it is possible to rationalize the diffuse reflectance spectra of **2** ( $^3H_4$  ground state) and **3** ( $^6H_{5/2}$  ground state).

The title compounds have several intriguing features, which are currently explored synthetically: (i) the R–P phases are the compounds for many high  $T_c$  superconductors and the layered manganites  $\text{Ln}_{3-x}\text{Sr}_x\text{Mn}_2\text{O}_7$ <sup>10</sup> that exhibit large negative magnetoresistance effects. (ii) A series of presumably isostructural defective R–P phases  $\text{Ln}_2\text{Ti}_2\text{O}_7$  (Ln = La, Nd, Sm, Gd) was reported recently by Gopalakrishnan and coworkers.<sup>11</sup> The materials were prepared by topotactic dehydration of  $\text{HLnTiO}_4$ <sup>12</sup> and considered metastable whereas the title compound was obtained from a high temperature reaction and should be therefore a thermodynamically stable phase. (iii) The replacement of oxide by sulfide ions in the LnS layers is counterintuitive as Ln is more chalcophilic than titanium. The sulfur substitution pattern can be rationalized by the amount of space accessible to the sulfide (compared to the oxide) anions through the less dense packing in the interlayer region. (iv) Electronic variation of the title compounds might be possible by cation intercalation into the unfilled voids in the LnS slab or metal substitution (e.g. group 5 metals for Ti).

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## Notes and references

† Crystal data:  $\text{Nd}_2\text{Ti}_2\text{S}_2\text{O}_5$  **1**:  $T = 25^\circ\text{C}$ ; tetragonal, space group  $I4/mmm$  (no. 139),  $a = 3.849(1)$ ,  $c = 23.064(5)$  Å,  $V = 341.7(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\lambda = 0.71073$  Å,  $D_c = 5.136$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 17.76$  mm<sup>-1</sup>, crystal block-like, dimensions  $0.3 \times 0.3 \times 0.5$  mm<sup>3</sup>,  $2\theta_{\text{max}} = 50^\circ$ , data collected on a Nicolet P2<sub>1</sub> four circle diffractometer, number of reflections, 1902, unique data with  $I > 4\sigma(I)$ , 124, number of variables, 17. Structure solved and refined using the SHELX93 program system. A numerical absorption correction was applied to the data (min., max. transmission = 0.31, 0.49). Final  $R$ ,  $R_w = 0.016, 0.042$ .

$\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$  **2**:  $T = 25^\circ\text{C}$ ; tetragonal, space group  $I4/mmm$  (no. 139),  $a = 3.871(1)$ ,  $c = 23.036(5)$  Å,  $V = 345.2(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\lambda = 0.71073$  Å,  $D_c = 5.020$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 16.66$  mm<sup>-1</sup>, crystal plate-like, dimensions  $0.3 \times 0.3 \times 0.1$  mm<sup>3</sup>,  $2\theta_{\text{max}} = 70^\circ$ , data collected on a Nicolet P2<sub>1</sub> four circle diffractometer, number of reflections, 1782, unique data with  $I > 4\sigma(I)$ , 232, number of variables, 17. Structure solved and refined using the SHELXTL program system. A numerical absorption correction was applied to the data (min., max. transmission = 0.52, 0.99). Final  $R$ ,  $R_w = 0.031, 0.070$ .

$\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$  **3**:  $T = 25^\circ\text{C}$ , tetragonal, space group  $I4/mmm$  (no. 139),  $a = 3.818(1)$ ,  $c = 22.952(5)$  Å,  $V = 334.6(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\lambda = 0.71073$  Å,  $D_c = 5.366$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 20.17$  mm<sup>-1</sup>, crystal rod-like, dimensions  $0.2 \times 0.2 \times 0.3$  mm<sup>3</sup>,  $2\theta_{\text{max}} = 54^\circ$ , data collected at  $25^\circ$  on a Nicolet P2<sub>1</sub> four circle diffractometer, number of reflections, 1066, unique data with  $I > 4\sigma(I)$ , 129, number of variables, 17. Structure solved and refined using the SHELXTL program system. A numerical absorption correction was applied to the data (min., max. transmission = 0.53, 0.78). Final  $R_1$ ,  $wR_2 = 0.015, 0.035$ . CCDC 182/1191. See <http://www.rsc.org/suppdata/cc/1999/979/> for crystallographic files in .cif format.

Note added in proof: After submission of this manuscript a paper describing the structure of  $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$  appeared; C. Boyer, C. Dendon and A. Meerschaut, *C. R. Acad. Sci. Ser. 2*, 1999, 93.

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