Synthesis, Crystal Structure, Electric and Magnetic Properties of LaVO$_{2.78}$N$_{0.10}$


Dedicated to Professor Reinhard Nesper on the Occasion of His 65th Birthday

Keywords: Lanthanum vanadium oxynitride; Electrical conductivity; Thermoelectricity; Perovskites; Oxynitrides

Abstract. Perovskite-type LaVO$_{2.78}$N$_{0.10}$ powder was synthesized by thermal ammonolysis of the oxide precursor LaVO$_4$. By X-ray, neutron, and electron diffraction an orthorhombic crystal structure with space group $Pnma$ was identified. XANES spectra showed that the oxidation state of vanadium changes from 5+ in LaVO$_4$ to approximately 3+ in LaVO$_{2.78}$N$_{0.10}$. The temperature dependence of the electrical conductivity revealed an Arrhenius-type behavior with an activation energy of 0.103 eV in the temperature range of 119–302 K indicating that the conduction process is thermally activated band transition. Based on the positive Seebeck coefficient, holes were identified as the dominant charge carriers in the temperature range of 100–302 K. Both the Seebeck coefficient and the thermal conductivity showed an anomaly at 138 K, which is attributed to the Néel temperature for antiferromagnetic ordering according to magnetic susceptibility measurements.

Introduction

Since the first investigations of the perovskite crystal structure by X-ray diffraction in the 1940’s,[1] perovskite-type oxides have been the most widely studied materials among all ternary oxides. Perovskites have attracted much research interest due to their substantial physical and chemical properties including high-$T_c$ superconductivity,[2] colossal magnetoresistance (CMR),[3] dielectric, ferroelectric, piezoelectric, and multiferroic properties,[4] thermoelectricity,[5] and nonlinear optical properties[6] and photocatalytic activity.[7] The general chemical formula of perovskite-type oxides is $ABO_3$, where $A$ and $B$ are different-sized cations with $A$ typically being alkali, alkaline earth, or rare earth cations, and $B$ transition metal cations.

Due to its structural and compositional flexibilities, the perovskite structure is sustained even with extensive substitutions aimed at modulating the electronic structure, charge carrier concentration and thus fine-tuning of physical and chemical properties.[8] So far cationic substitution has been the most common way to tailor perovskite-type materials. Partial anionic substitution of nitrogen for oxygen offers an alternative to cationic substitution, producing a number of interesting physical properties for technical applications.[9] By partially replacing oxygen with nitrogen the valence band is formed of a mixture of oxygen and nitrogen 2p orbitals resulting in narrowing the energy bandgap. Thus, proper control of the nitrogen content enables modulation of the electronic structure, charge carrier concentration and thus fine-tuning of physical and chemical properties.[8]

* Prof. Dr. A. Weidenkaff
Fax: +41-58-765-4019
E-Mail: weidenkaff@imw.uni-stuttgart.de
[a] Laboratory for Solid State Chemistry and Catalysis
Empa - Swiss Federal Laboratories for Materials Science and Technology
Überlandstrasse 129
8600 Dübendorf, Switzerland
[b] Department of Chemistry and Biochemistry
University of Berne
Freiestrasse 3
3012 Berne, Switzerland
[c] Institut für Energie und Klimaforschung IEK-9
Forschungszentrum Jülich
Wilhelm-Johnen-Straße
52428 Jülich, Germany
[d] Institut für Chemie
Martin-Luther-Universität Halle-Wittenberg
Kurt-Mothes-Straße 2
06120 Halle/Saale, Germany
[e] Institute for Materials Science
University of Stuttgart
Heisenbergstr. 3
70569 Stuttgart, Germany

colossal magnetoresistance have been discovered in EuNbO$_2$N and EuWON$_2$. The electrical conductivity of SrMoO$_2$N$_{0.4}$ and SrMoO$_2$N have been investigated. Lie et al. reported that metallic behavior for SrMoO$_2$N$_{0.4}$ in the temperature range of 5–290 K and Logvinovich et al. presented that semiconductor-like electrical resistivity for SrMoO$_2$N in the temperature range of 3–300 K also showed semiconducting electrical transport properties. However, comparatively few studies have been carried out concerning the synthesis, crystal structure, electric, and magnetic properties of perovskite-type vanadium oxynitrides. Possible short- and long-range ordering in the crystal structures and thermal stability are not fully described, and the mechanism of the electrical transport is not well understood yet. In this study, we report the synthesis for a lanthanum vanadium oxynitride sample with the composition of LaVO$_2$N$_{0.10}$. The changes in long- and short-range order of the crystal structure were thoroughly investigated by powder X-ray diffraction (XRD), powder neutron diffraction (ND), electron diffraction (ED), and X-ray absorption near edge structure (XANES) spectroscopy. Furthermore, electrical and magnetic properties are described in detail.

Results and Discussion

The anionic composition of the synthesized oxynitride was determined by hot-gas extraction and the obtained stoichiometric composition was LaVO$_2$N$_{0.10}$ (in the following the sample is referred to as LaVO$_2$N$_{0.10}$). At temperatures higher than 600 °C ammonia undergoes significant decomposition and partial decomposition of NH$_3$ is also reported to produce active nitriding species (NH, NH$_2$) along with molecular hydrogen. The formed hydrogen can reduce the precursor LaVO$_4$ to LaVO$_2$N$_{0.10}$ and the active nitriding species reacts with the reduced lanthanum vanadium oxide resulting in LaVO$_2$N$_{0.10}$. Thus NH$_3$ can act as a reducing and a nitriding agent during thermal ammonolysis inducing oxygen deficiencies in the perovskite structure. Reportedly nitridation kinetics are such that the nitrogen content still increases even after several days of thermal ammonolysis. However, as the ammonolysis conditions including temperature, interaction time, and NH$_3$ flow rate are not precisely given in the literature, the nitrogen content in this study cannot be directly compared to the reported data. In our work, NH$_3$ mainly provides a reducing atmosphere and only partly a nitriding agent and consequently, a nitrogen-poor oxynitride was obtained. With a prolonged ammonolysis of 19 h at 1123 K under flowing NH$_3$ (100 mL·min$^{-1}$), a secondary phase La$_2$O$_x$N$_y$ was detected by XRD (data not shown). Therefore, long ammonolysis times that might be beneficial for an enhanced incorporation of nitrogen also give rise to secondary phases.

Figure 1(a) shows the XRD pattern and Le Bail fit of LaVO$_2$N$_{0.10}$. All peaks were indexed to the perovskite-type orthorhombic crystal structure (space group Pnma) and details of the structure refinement are listed in Table 1. As the X-ray atomic scattering factors of oxygen and nitrogen are nearly identical, the two elements cannot be distinguished by XRD.

Furthermore, XRD patterns of perovskite-type oxynitrides are usually dominated by the contribution of the heavier cations making it difficult to obtain detailed and correct structural information (i.e. the atomic positions, atomic displacement parameters, and site-occupation factors) of the anions. Therefore, ND is the method of choice for the determination of the crystal structure of perovskite oxynitrides. Figure 1(b) shows the powder ND pattern and Rietveld refinement profile of LaVO$_2$N$_{0.10}$. The refined structural parameters and agreement factors from the ND data are summarized in Table 1. The structural parameters of orthorhombic LaVO$_2$N$_{0.10}$ are listed in Table 2. From the refined site-occupancy factors, mole fractions of oxygen and nitrogen of 2.88 and 0.10, respectively, were calculated. Together with the presence of anion vacancies, the amount of nitrogen is small. The refined nitrogen/oxygen occupancies are therefore less accurate, as it is shown by the observed differences between refined oxygen content 2.88 and analyzed oxygen content 2.78. Lattice parameters and unit-cell volume of LaVO$_2$N$_{0.10}$ are larger than those of LaVO$_3$ presented in previous papers.

Furthermore, LaVO$_2$N$_{0.10}$ crystallites were studied by HR-TEM and SAED in order to gain a deeper insight into the local microstructure. A representative HR-TEM image is given in Figure 2(a). It shows lattice fringes oriented in the [101] zone axis according to the orthorhombic crystal structure. The image proves good crystallinity without defects or dislocations. The corresponding SAED pattern of the crystallite in the same orientation supports the orthorhombic crystal structure with the tilt system a0b–b– in Glazer’s notation as it was determined by XRD and ND. Yang et al. claimed that the presence of weak satellite reflections indexed as (0kl) and (h0l) (h or k = odd) in electron diffraction patterns of SrNbO$_2$N and SrTaO$_2$N are attributed to symmetry lowering due to the anion ordering. Oró-Solé et al. observed anion ordering in the perovskite oxynitride NdVO$_2$N. Our results did not show weak satellite reflections.

The pre-edge region of the normalized V K-edge XANES spectra of LaVO$_2$N$_{0.10}$, LaVO$_3$, and LaVO$_4$ are shown in Figure 3. XANES is an excellent probe for the oxidation state and chemical environment of the elements and it is highly sensitive to the local structure such as bond angles and bond lengths around the X-ray absorbing element. In this study, an intense pre-edge feature at 5.4696 keV uniquely distinguishes the V K-edge XANES spectrum of LaVO$_3$ indicating that vanadium is coordinated tetrahedrally and is in the oxidation state V$^{4+}$. This pre-edge peak is drastically diminished in the XANES spectrum of LaVO$_2$N$_{0.10}$ implying that the local structure around the vanadium ion in LaVO$_2$N$_{0.10}$ is entirely different from that of the precursor LaVO$_4$. The pre-edge feature of LaVO$_2$N$_{0.10}$ is, in contrast, almost identical to that of LaVO$_3$ indicating that with the conversion of LaVO$_4$ to LaVO$_2$N$_{0.10}$ the coordination environment of the vanadium ion changes from tetrahedral (VO$_4$) to octahedral [V(O,N)$_6$]. This is consistent with the long range order of the crystal structure evident from XRD, ND, and SAED patterns. Moreover, XANES spectra indirectly reveal that the oxidation state of vanadium changes from V$^{4+}$ in LaVO$_3$ to V$^{3+}$ in
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LaVO$_{2.78}$N$_{0.10}$. However, we cannot rule out the existence of a small amount of vanadium ions in different oxidation states. The thermal stability and re-oxidation behavior was investigated by TGA. Figure 4(a) illustrates the weight change upon heating the oxynitride powder in O$_2$. LaVO$_{2.78}$N$_{0.10}$ is thermally stable up to about 573 K. Above this temperature, the oxygen uptake leads to a mass increase up to about 900 K followed by a gradual mass loss ($\Delta m \approx 6.17\%$) commonly observed in oxynitrides during the re-oxidation process.[23] The re-oxidized powder was identified by XRD as LaVO$_4$. The evolved gases were determined by mass spectrometry [Figure 4(b)].

The gradual mass decrease above 900 K is also accompanied by a small hump in the MS signal at 1273 K, which is caused by the complete release of the remaining N$_2$.

The temperature dependence of the electrical conductivity in the temperature range of 119–302 K is presented in Figure 5(a). From the Arrhenius plot shown in Figure 5(b) the following relationship can be deduced:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

where $E_a$ is the activation energy of electrical conduction, $k_B$ the Boltzmann constant, $T$ the absolute temperature, and $\sigma_0$ the pre-exponential factor. By means of the best-fit line an activation energy of conduction ($E_a$) was determined to be 0.103 eV. This is in good agreement to the activation energy of 0.11 eV, which was reported for LaVO$_{2.91}$N$_{0.09}$.[15]

Figure 6(a) shows the temperature dependence of the Seebeck coefficient ($S$) in the temperature range of 100–302 K. A positive Seebeck coefficient indicates holes are the dominant charge carriers. Down to 166 K, $S$ slightly decreases with decreasing temperature followed by an increase to a maximum at 138 K. In previous publications, the Néel temperature ($T_N$) of LaVO$_3$, below which antiferromagnetic ordering occurs, was reported to be 137 K.[24] Likewise, Antoine et al. observed antiferromagnetic ordering in LaVO$_3$–$x$N$_x$ at 140 K,[15] which is very close to the temperature of the maximum Seebeck coefficient of LaVO$_{2.78}$N$_{0.10}$ in this study. Figure 6(b) shows the temperature dependence of the thermal conductivity ($\kappa$). A very low thermal conductivity was observed over the whole measurement range, which can be attributed to the low density of the pellet. $\kappa$ gradually decreases with decreasing temperature showing an anomalous peak at 138 K. From here $\kappa$ remains almost constant down to 62 K, again gradually decreasing at lower temperatures. However, the origin of the transition at 62 K is not yet understood.

The magnetic structural change was further investigated by measuring the magnetic susceptibility ($\chi$). Figure 7(a) shows that $\chi$ increases with decreasing temperature. The maximum susceptibility appears at 138 K, which $Nguyen$ and

### Table 1. Crystallographic and structural refinement data a).

<table>
<thead>
<tr>
<th>Chemical formular</th>
<th>LaVO$<em>{2.78}$N$</em>{0.10}$</th>
<th>LaVO$<em>{2.78}$N$</em>{0.10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>X-ray (Cu-K$_\alpha$)</td>
<td>Neutron</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
<td>Pnma</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Lattice parameter $a$/Å</td>
<td>5.5526(1)</td>
<td>5.5516(2)</td>
</tr>
<tr>
<td>Lattice parameter $b$/Å</td>
<td>7.8496(1)</td>
<td>7.8469(2)</td>
</tr>
<tr>
<td>Lattice parameter $c$/Å</td>
<td>5.5574(1)</td>
<td>5.5620(2)</td>
</tr>
<tr>
<td>$V$/Å$^3$</td>
<td>242.222</td>
<td>242.294</td>
</tr>
<tr>
<td>$R_p$/%</td>
<td>4.39</td>
<td>2.85</td>
</tr>
<tr>
<td>$R_{wp}$/%</td>
<td>5.64</td>
<td>3.57</td>
</tr>
<tr>
<td>$R_{exp}$/%</td>
<td>3.78</td>
<td>2.67</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.23</td>
<td>2.17</td>
</tr>
<tr>
<td>Wavelength /Å</td>
<td>1.5406</td>
<td>1.155</td>
</tr>
<tr>
<td>$2\theta$ range /°</td>
<td>20–100</td>
<td>3.95–164.90</td>
</tr>
<tr>
<td>$2\theta$ step width /°</td>
<td>0.0167</td>
<td>0.05</td>
</tr>
</tbody>
</table>

a) Numbers in parentheses are standard deviations; $R_p$, $R_{wp}$, $R_{exp}$, and $\chi^2$ are the reliability factors and goodness-of-fit, respectively.

Figure 1. (a) Powder X-ray diffraction pattern (X-ray wavelength: 1.5406 Å) and Le Bail fitting plot and (b) powder neutron diffraction pattern (neutron wavelength: 1.155 Å) and Rietveld refinement plot of LaVO$_{2.78}$N$_{0.10}$ obtained at room temperature. The difference plot of observed and calculated diffraction profiles is shown beneath and the Bragg positions are given by short vertical tick markers.
Table 2. Crystal structural parameters of LaVO$_{2.78}$N$_{0.10}$ determined by the Rietveld refinement of the powder neutron diffraction pattern.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{iso}$ /Å$^2$</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.0286(2)</td>
<td>¼</td>
<td>0.4937(4)</td>
<td>0.374(17)</td>
<td>0.5</td>
</tr>
<tr>
<td>V</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.4$^{a)}$</td>
<td>0.5</td>
</tr>
<tr>
<td>O1/N1</td>
<td>0.4909(4)</td>
<td>¼</td>
<td>0.5706(5)</td>
<td>0.447(2)</td>
<td>0.468/0.032 $^{b)}$</td>
</tr>
<tr>
<td>O2/N2</td>
<td>0.2818(3)</td>
<td>0.0369(2)</td>
<td>0.2186(3)</td>
<td>0.648(2)</td>
<td>0.972/0.018 $^{c)}$</td>
</tr>
</tbody>
</table>

$^{a)}$ Isotropic thermal factor ($B_{iso}$) for V is fixed during the refinement otherwise the refinement have not converged. $^{b)}$ Linear constrain: O1 + N1 = 0.5. $^{c)}$ Linear constrain: O2 + N2 = 1.0.

Goodenough have explained with the presence of a canted-spin ferromagnetism as a result of the Dzialoshinskii antisymmetric exchange in LaVO$_3$$^{[19a]}$ and is also in good agreement with the Seebeck coefficient measurement. After a drastic decrease in the range of 138 K to 84 K, the susceptibility increases again with decreasing temperature. The second transition temperature (84 K) was found to be slightly increased compared to the transition temperature (62 K) obtained from thermal conductivity measurements. At present, it is difficult to conclude what can be the origin of increased magnetic susceptibility below 84 K. It might be related to the existence of a small amount of paramagnetic secondary phases formed during the thermal ammonolysis or to the presence of intrinsic electronic point defects with varying vanadium oxidation states. Above the Néel temperature, the susceptibility is inversely proportional to the temperature [Figure 7(b)], correspondent to the Curie-Weiss law

$$\chi = \frac{C}{T - \theta}$$

where $\chi$ is the susceptibility, $C$ the Curie constant, $T$ the absolute temperature, and $\theta$ the Weiss constant. $C = 1320.76$ kg K m$^{-3}$ and $\theta = -1018.2$ K were obtained by fitting in the temperature range of 160 to 300 K. The Weiss constant $\theta = -670$ K was reported for LaVO$_3$$^{[19a]}$ which is smaller than that of LaVO$_{2.78}$N$_{0.10}$ in this study. The temperature-dependent Figure of merit

$$ZT = \frac{S^2\sigma}{\kappa}T$$

is a measure of the quality of a thermoelectric material.$^{[25]}$ The maximum ZT value of LaVO$_{2.78}$N$_{0.10}$ was calculated to be $7.27 \times 10^{-6}$ at 302 K. This ZT is too low for efficient thermoelectric applications but it might be increased by cation substitutions and/or advanced sintering techniques such as spark plasma sintering (SPS) to enhance grain boundary connectivity.

Figure 8(a) shows the normalized X-band Electron paramagnetic resonance (EPR) spectra of LaVO$_{2.78}$N$_{0.10}$ as a function of temperature between 5 K and 297 K. A signal with $g =$
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2.00(1) can be observed at 297 K with $\Delta B_{pp} = 27$ mT. This signal might be attributed to a defect signal like a singly charged oxygen vacancy (V$_{\text{O}}^-$), but it may as well be the superposition of well-resolved EPR spectrum ending up with the broad signal. Upon cooling down to 5 K the g-value is changing from $g = 2.00(1)$ to $g = 1.94(1)$. At 5 K a half-field signal was still observed and only for spin systems with $S > 1/2$ can be the origin of it. Therefore, the observed EPR signal can be attributed to V$^{3+}$ with $S = 1$, while V$^{4+}$ with $S = 1/2$ can be ruled out. The lineshape of the EPR signal at $g = 1.94$ was fitted by a Lorentzian function. The linewidth at 5 K is reduced to 17 mT compared to 26 mT at room temperature. The narrowing of the signal and the Lorentzian lineshape can be attributed to an exchange coupled system. Temperature dependence of the inverse susceptibility and the g-value of LaVO$_{2.78}$N$_{0.10}$ are shown in Figure 8(b). From room temperature to 150 K the reciprocal susceptibility is linearly decreasing. Extrapolation of the fit gives a Néel temperature of 137 K, which is in good agreement with the values from the Seebeck coefficient ($S$) and the magnetic susceptibility ($\chi$) measurements. In the region between 150 K and 90 K, a plateau is observed where a significant change occurred in the Seebeck coefficient measurement. Below 90 K down to 5 K a non-expected paramagnetic behavior was observed. The g-value decreases from room temperature down to 110 K and the g-value remains constant from 110 K down to 5 K.

Normally electrical conduction in a transition metal oxynitride involves a complicated conduction mechanism due to the presence of narrow 3d bands. The electrical conduction may either originate from thermally activated band transition and/or variable range hopping process.$^{[26]}$ From the Arrhenius plot of the electrical conductivity [Figure 5(b)], it is clearly seen that the conduction process is thermally activated band transition in the temperature range of 119–302 K. This result indi-

Figure 4. (a) Thermogravimetric analysis (TGA) and (b) mass spectrometry (MS) carried out during the thermal reoxidation of LaVO$_{2.78}$N$_{0.10}$.

Figure 5. (a) Temperature dependence of the electrical conductivity of LaVO$_{2.78}$N$_{0.10}$ and (b) Arrhenius plot of $\ln \sigma$ vs. $T^{-1}$.
Figure 6. Temperature dependence of (a) Seebeck coefficient and (b) thermal conductivity of LaVO$_{2.78}$N$_{0.10}$. Arrows indicate the anomalous transition points.

cicates that the conduction mechanism of LaVO$_{2.78}$N$_{0.10}$ is not entirely different from that of LaVO$_3$[24b,27] and is also in good agreement with the previous report in LaVO$_3$–xN$_x$.[15]

Conclusions

Perovskite-type oxynitride LaVO$_{2.78}$N$_{0.10}$ was synthesized by thermal ammonolysis of LaVO$_4$. The crystal structure, electrical transport, and magnetic properties were investigated. X-ray, neutron, and electron diffraction studies reveal an orthorhombic crystal structure with $Pnma$ space group. LaVO$_{2.78}$N$_{0.10}$ shows an Arrhenius-type electrical conductivity with activation energy of 0.103 eV. Investigations of the temperature dependence of the Seebeck coefficient, the thermal conductivity, and the magnetic susceptibility reveal an anomaly at 138 K due to the antiferromagnetic ordering.

Experimental Section

Lanthanum vanadium oxynitride powder was synthesized via thermal ammonolysis of LaVO$_4$ prepared by solid-state reaction. Stoichiometric amounts of La$_2$O$_3$ (Alfa Aesar, 99.99 %) and V$_2$O$_5$ (Alfa Aesar, 99.6 %) were thoroughly ground using an agate mortar. The mixture was calcined in air at 1273 K for 12 h and at 1473 K for 12 h with intermediate grinding. Phase purity of the LaVO$_4$ powder was confirmed with powder X-ray diffraction (XRD) (not shown here). The ammonolysis reaction was performed in a rotating cavity reactor. LaVO$_4$ (about 3 g) was heated at 1123 K for 6 h in a NH$_3$ flow (Messer, 99.99 %) of 100 mL·min$^{-1}$. Subsequently, the oxynitride samples were quenched to room temperature under flowing NH$_3$.

Oxygen and nitrogen content of the ammonolyzed powder was determined by hot-gas extraction using a Horiba EMGA 820 analyzer. About 10 mg of sample together with a Ni-flux was placed in a graphite crucible and rapidly heated up to 3000 °C using an electrode impulse furnace. The oxygen generated during the sample decomposition...
reacted with the graphite crucible forming CO and finally CO₂, which was detected quantitatively using an infrared detector. The evolved nitrogen was detected in its molecular form with a thermal conductivity detector. Y₂O₃ and Si₃N₄ were used as calibration standards for the thermal neutron diffraction measurement.

Figure 8. (a) Normalized X-band EPR spectra of LaVO₂.78N₀.10 in the temperature range of 5 to 297 K and (b) temperature dependence of the g-value and inverse susceptibility (χ–¹).

Powder XRD patterns were obtained with a PANalytical X’Pert PRO 0–20 scan system equipped with a Johansson monochromator (Cu-Kα₁ radiation, 1.5406 Å) and an X’Celerator linear detector. The diffraction patterns were recorded from 20° to 100° in 2θ with an angular step interval of 0.0167°. XRD pattern of the oxynitride was analyzed by the Le Bail method[28] incorporated in the Rietveld refinement program, FullProf[29] to determine the space group and lattice parameters. The instrumental contribution for peak broadening was adjusted using a Si(111) double crystal monochromator. Higher order harmonics were suppressed by detuning the second monochromator crystal to 50% of the maximum energy. The samples were mixed with polyethylene and pressed into pellets of 13 mm diameter. The spectra were collected in transmission mode at room temperature and processed using the program WinXAS.[31] The background was corrected in the energy range of 5.3500–5.4450 keV by subtraction of a linear function. Subsequently, the XAS spectrum was normalized in the energy range of 5.4880–5.4960 keV. The photon energy was calibrated to the first inflection point in the spectrum of a vanadium metal foil and assigned to 5.4658 keV.

The thermal re-oxidation study by thermogravimetric analysis (TGA) was carried out with a NETZSCH STA 409 CD thermobalance. Oxynitride powder (about 120 mg) was heated in an alumina crucible in O₂ (50 mL·min⁻¹) to 1573 K at a heating rate of 10 K·min⁻¹. Gas analysis was done with a connected mass spectrometer (MS).

Physical properties measurements were performed in the temperature range of 6–302 K with a PPMS (Quantum Design, Inc.). Transport properties were measured on a bar (10 mm × 3 mm × 2 mm) obtained by applying a uniaxial pressure of 20 bar on oxynitride powder followed by cold isostatic pressing at 2000 bar.

Magnetic susceptibility measurement was carried out with a superconducting quantum interference device (SQUID) magnetometer (SHE905). The field strength was 500 Oe (5 × 10⁵/4π (A/m)) and the data was collected upon cooling in the temperature range of 2–300 K.

Electron paramagnetic resonance (EPR) experiments were performed at X-Band (9.5 GHz) frequency with a BRUKER EMX spectrometer with a rectangular resonator. The magnetic field was calibrated with a standard field marker (DPPH) with g = 2.0036. A helium-flow cryostat (Oxford Instruments) was used for low temperature measurements. The spin-concentration was determined by numerical double integration of the continuous-wave (c.w.) EPR spectrum.

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