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Neutron diffraction study of nitride perovskite LaReN₃

Simon D. Kloß,^[a] Clemens Ritter,^[b] and John Paul Attfield*^[c]Dedicated to Prof. Dr. Wolfgang Schnick on the occasion of his 65th birthday

Nitride perovskites ABN₃ are extremely rare with only two known instances of bulk-phase materials, ThTaN₃ and LaReN₃. Here, we present a powder neutron diffraction study of the recently-reported nitride perovskite LaReN₃. A full structural model of LaReN₃ at 300 K (*I* $\bar{1}$, *a* = 5.58523(5), *b* = 5.59297(5), *c* = 7.90419(6) Å, α = 89.9170(8), β = 90.1729(7), γ = 90.1709(7)°) has been refined simultaneously against powder neutron and previously-collected synchrotron X-ray diffraction data. This

indicates that the triclinic distortion is due to cooperative electronic distortions of ReN₆ octahedra, and also demonstrates that all nitrogen positions are fully occupied so the sample is stoichiometric LaReN₃. Lattice strains derived from fits to variable temperature powder neutron data from 5 to 300 K indicate that LaReN₃ undergoes structural transitions to higher symmetry perovskite tilt structures between 300 and 350 K.

Introduction

Nitride materials have important applications such as β -Si₃N₄ in high-temperature ceramics, GaN as a semiconductor for optical materials, and main group nitrides like nitridosilicates and nitridophosphates as phosphors for solid-state lighting.^[1–6] Nitride perovskites ABN₃ have recently gained much attention as theoretical studies have suggested stable compositions based on early heavy transition metals as B-cations with rare-earths (R) occupying the A-sites.^[7,8] Moreover, prediction of properties such as ferroelectricity in LaWN₃, suitable bandgaps for photovoltaics in CeMN₃ (M = Ta, Nb), as well as hard ferromagnetism in RReN₃, sparked interest in these materials.^[8–10] However, synthesized nitride perovskites ABN₃ are scarce and to date only three materials are reported: bulk-phase ThTaN₃ from 1995, thin-film LaWN₃ with a polar structure from 2021, and bulk-phase LaReN₃ from 2021.^[11–13]

These few reports reflect synthetic challenges rooted in the low formation energies of transition metal nitrides. The stable N≡N triple bond (947 kJ/mol) impedes oxidation of metals and

often leads to nitrogen-poor materials with low oxidation states.^[14,15] Nitride perovskites ABN₃ however require highly oxidized metals to balance the nine negative charges of the three nitride anions, which necessitates A/B charge combinations such as II/VII, III/VI, and IV/V. ThTaN₃ was prepared from high-temperature reaction of binary nitrides, but oxygen impurities were suggested owing to impure starting materials.^[11,16] Thin-film LaWN₃ was prepared with a physical vapor deposition method using a nitrogen plasma source, but chemical analysis suggested a high amount of nitrogen vacancies resulting in LaWN_{3-x} with $x \approx 0.5$.^[12]

We recently prepared LaReN₃ under high-pressure high-temperature conditions (8 GPa, 1200 °C) generated with a multianvil large volume press using sodium azide as a solid-state nitrogen source.^[13] Although the compound has a Goldschmidt tolerance factor $t = 0.99$, high-resolution synchrotron powder diffraction revealed an intricate octahedra tilt structure resulting in a triclinic metric. The metric distortion is very small (space group *I* $\bar{1}$, *a* = 5.58532(6), *b* = 5.59484(6), *c* = 7.90587(8) Å, α = 89.9325(11), β = 90.1703(9), γ = 90.1536(8)°, *Z* = 4) leading to significant peak overlap of inequivalent reflections. Moreover, the strong X-ray scattering by heavy atoms La and Re limited determination of reliable N atom positions and occupancies. Free refinement of a triclinic model with nine independent coordinates for three inequivalent N sites was not possible and symmetry constraints from space group *I2/c* were used. Refinement of nitrogen positions suggested cooperative distortions of ReN₆ octahedra, which were attributed to spin-orbit coupling or orbital ordering through Jahn-Teller distortion.

In this contribution, we present a powder neutron diffraction study of LaReN₃ that has been used to refine unconstrained nitrogen positions in *I* $\bar{1}$ as well their occupancies. Moreover, we have carried out a temperature-dependent study using powder neutron diffraction data from 5 to 300 K to follow the thermal evolution of the structure of LaReN₃.

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Results and Discussion

300 K Neutron and X-ray Co-refinement

The previously reported synchrotron X-ray data provide high $\Delta Q/Q$ resolution to high- Q but are insensitive to N in the presence of heavy La and Re atoms, whereas the neutron data have lower resolution and Q -range but give excellent sensitivity to nitrogen atoms (neutron coherent scattering lengths are La=8.27, Re=9.2 and N=9.36 fm). The crystal structure was therefore co-refined against both datasets simultaneously and this permitted full refinement in $\bar{1}$ without use of $I2/c$ symmetry constraints. Initial refinement of the three anion site occupancies (constrained to be equal) gave 100.1(4)% N occupancy showing that no significant oxygen substitution or vacancy formation occurs. Previous reports of nitride perovskites have suggested oxygen impurities in ThTaN_3 ^[11,16] and a high level of vacancies in LaWN_{3-x} prepared by physical vapor deposition,^[12] so the present study is significant in demonstrating that LaReN_3 is a stoichiometric nitride perovskite. N site occupancies were fixed in the final refinement giving results shown in Figure 1 and Table S1.

The refined cell parameters from the co-refinement are $a = 5.58523(5)$, $b = 5.59297(5)$, $c = 7.90419(6)$ Å, $\alpha = 89.9170(8)$, $\beta = 90.1729(7)$, $\gamma = 90.1709(7)^\circ$. Re–N distances and Re–N–Re angles

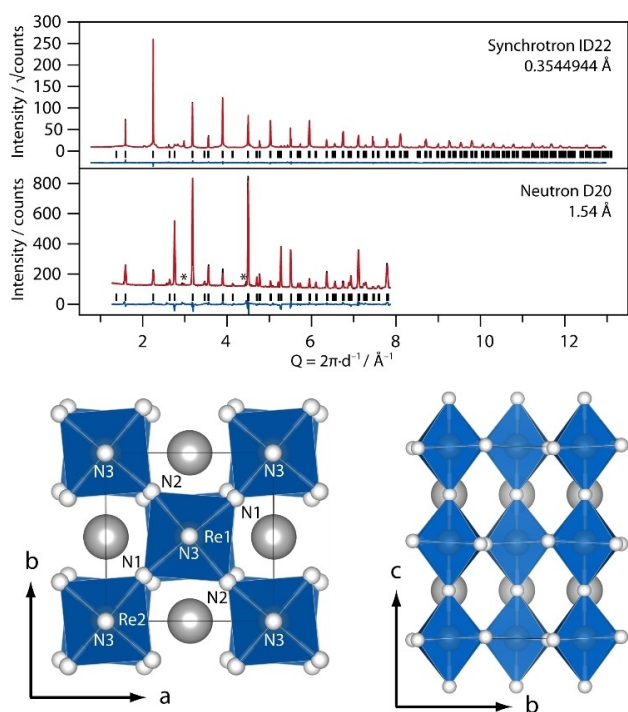


Figure 1. (top) Synchrotron X-ray and neutron co-refinement of LaReN_3 with powder data obtained at 300 K. Black line indicates observed data, red line Rietveld fit, and grey line difference plot. Impurity lines from unreacted Re (~1 wt-%) are marked with asterisks. (bottom) Two views of the crystal structure of LaReN_3 with La as grey spheres and ReN_6 octahedra in blue with N as white spheres.

from the co-refinement have very similar values to those from the previously reported synchrotron X-ray refinement^[13] (Table 1), although uncertainties for Re–N3 distances are much smaller in the latter due to the use of $I2/c$ constraints. The $\bar{1}$ refinement thus confirms the previously reported pattern of ReN_6 octahedral distortions and justifies the use of $I2/c$ constraints in fitting the structure of LaReN_3 . Re1/2–N1/3 distances are all very similar, but Re1/2–N2 distances are shorter/longer corresponding to a cooperative order of tetragonally compressed/elongated $\text{Re1N}_6/\text{Re2N}_6$ octahedra, likely due to spin-orbit or orbital ordering effects as reported previously.^[13]

Variable Temperature Neutron Study

Powder neutron diffraction data from LaReN_3 were collected at 5, 60, 120, 180, 240 and 300 K. No magnetic diffraction peaks were observed down to 5 K confirming the previous report that LaReN_3 remains metallic and paramagnetic without spin order down to low temperatures.^[13] As the neutron data do not have sufficiently high resolution for refinement of the small triclinic distortion of the unit cell, the cell angles were fixed at the values from the 300 K co-refinement and $I2/c$ symmetry constraints were applied to the N positions during refinements. Results are in Figures 2 and 3, and Tables S3 and S4.

Variation of unit cell lengths with temperature are plotted in Figure 2. The cell parameters and volume show typical thermal expansion behavior between 5 and 300 K with no evidence for any phase transitions below room temperature. However, the cell lengths do display a notable convergence at the higher temperatures suggesting that structural transitions probably occur not far above 300 K. To estimate possible structural transition temperatures assuming continuous transitions, lattice strains $s_{ab} = 2(b-a)/(b+a)$ and $s_{ac} = 2(c/\sqrt{2}-a)/(c/\sqrt{2}+a)$ were calculated and were fitted by the critical expression $s = s_0(1-T/T_c)^\beta$ with fixed $\beta = 0.5$ for mean-field behavior. This gives good fits as shown in Figure 2 although these strains are only approximate order parameters as they neglect changes in the cell angles α , β and γ . Estimated transition temperatures T_c from fits to s_{ab} and s_{ac} are 349 and

Table 1. Comparison of 300 K Re–N distances and Re–N–Re angles obtained from the previous powder synchrotron X-ray refinement with $I2/c$ constraints^[13] and unconstrained $\bar{1}$ co-refinement using the synchrotron X-ray and neutron datasets.

	N1/Å,°	N/Å,°	N3/Å,°
Synchrotron ($I2/c$ constraints)			
Re1	2.021(14)	1.953(15)	1.979(1)
Re2	1.950(15)	2.024(14)	1.979(1)
Re1–N–Re2	167.7(7)	169.0(8)	174.2(13)
Co-refinement ($\bar{1}$)			
Re1	1.988(17)	1.968(11)	1.98(2)
Re2	1.973(17)	2.007(11)	1.97(2)
Re1–N–Re2	170.1(9)	169.3(6)	178.8(5)

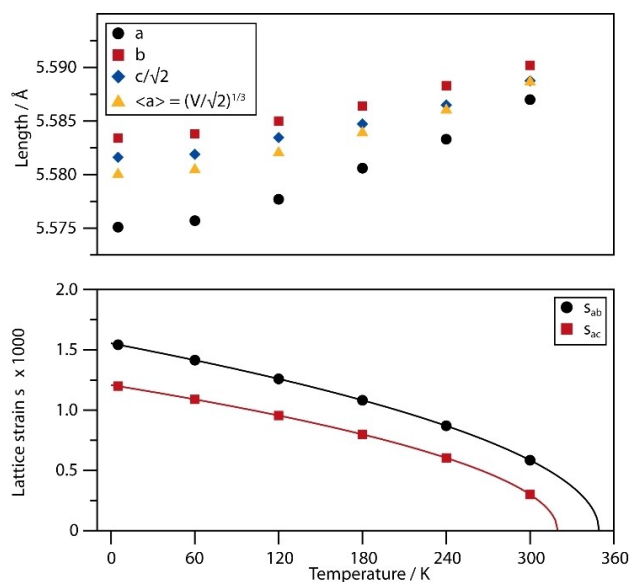


Figure 2. (top) Variation of cell parameters and the pseudocubic average with temperature from Rietveld fits to neutron powder diffraction data. (bottom) Lattice strains plotted against temperature with critical fits as described in the text.

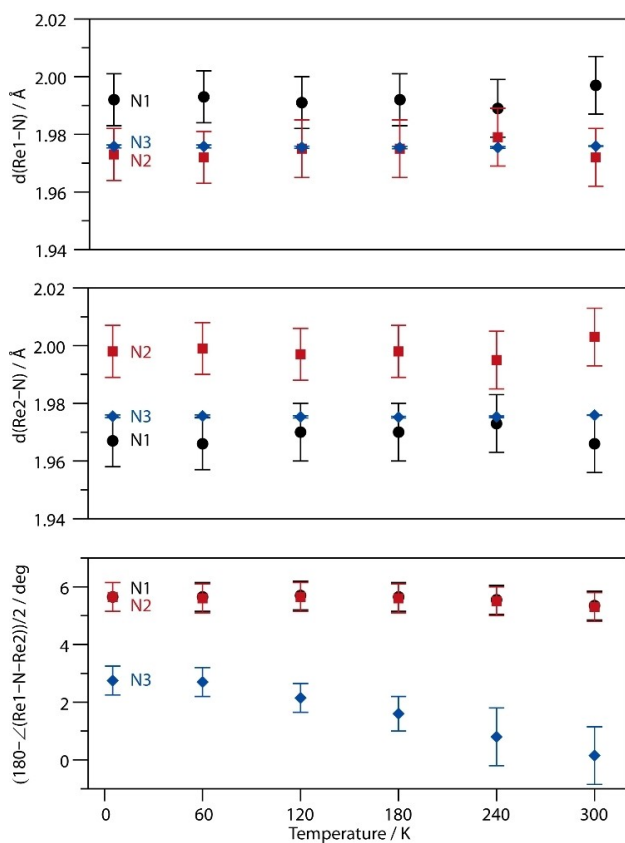


Figure 3. Temperature dependence of bond distances (top) Re1–N, (middle) Re2–N, and tilt angles Re–N–Re (bottom). Different nitrogen positions are marked with colour.

320 K respectively, revealing that one or more structural phase transitions are expected not far above room temperature.

The temperature dependence of the Re–N interatomic distances as well as octahedral tilt or rotation angles, calculated as $(180 - \angle(\text{Re1}-\text{N}-\text{Re2}))/2$ are plotted in Figure 3. The interatomic distances remain constant within error, indicating that the octahedral distortions are robust over the measured temperature range. The $I2/c$ symmetry constraints used in these refinements describe an $a^-b^-b^-$ pattern of out-of-phase octahedral tilts in Glazer notation.^[17] The equivalent N1 and N2 tilt angles measure octahedral rotation in the ab plane, and this shows little thermal change with a value of $\sim 5.5^\circ$ throughout. However, the N3 angle which quantifies the tilt from the c -axis decreases from $\sim 3^\circ$ at 5 K to near zero at 300 K. This suggests that the initial structural transition is to an orthorhombic $Imma$ structure (where the tilting pattern is $a^0b^-b^-$).^[18] High temperature laboratory X-ray diffraction data were previously reported but these did not have sufficient resolution to follow the lattice strains.^[13] Further high resolution diffraction studies of LaReN_3 above 300 K will be needed to discover the expected structural transitions and higher symmetry structures.

Conclusions

Co-refinement against powder neutron and previously collected synchrotron X-ray powder diffraction data permits full refinement of the triclinic $\bar{1}$ structure of LaReN_3 at 300 K, as the high-resolution synchrotron data are sensitive to the slight metric distortions and neutron data are sensitive to the nitrogen atoms. The refinement confirms the octahedral distortions obtained previously from a synchrotron refinement with $I2/c$ symmetry constraints, justifying the use of this approach. Refinement of the anion site occupancies demonstrate that LaReN_3 is a fully stoichiometric nitride perovskite whereas prior nitride perovskites likely had vacancies or oxygen substituents. Variable temperature neutron data show that no magnetic or structural transitions occur between 5 and 300 K, but the thermal variations of lattice strains and one of the Re–N–Re angles suggest that one or more structural transitions occur in the 300 to 350 K region.

Experimental Section

Preparation of LaReN_3 . The samples used for the neutron diffraction study of LaReN_3 were the same as used for the initial report on LaReN_3 .^[13] Several samples obtained from high-pressure high-temperature experiments were combined to obtain 100 mg of sample, sufficient for neutron diffraction.

Powder diffraction. Powder neutron diffraction experiments were performed at the D20 beamline of the Institut Laue-Langevin (ILL), Grenoble, France.^[19] Powder diffraction data were obtained with a constant-wavelength neutron beam with wavelength $\lambda = 1.5437 \text{ \AA}$ at temperatures of 5, 60, 120, 180, 240 and 300 K. Synchrotron powder diffraction data were collected at the ID22 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble, France with wavelength $\lambda = 0.3544944 \text{ \AA}$ at a temperature of 300 K.^[13] Rietveld refinements against powder data was carried out with

Topas Academic V6.^[20] For the co-refinement of synchrotron and neutron powder data, cell metric for the neutron data was constrained to the refined values of the synchrotron data and neutron wavelength refined.

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Conflict of Interest

The authors declare no conflict of interest.

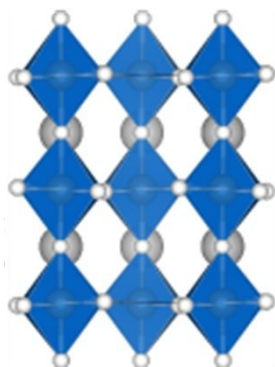
Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Perovskite phases · Nitrides · Neutron diffraction · High-pressure chemistry · Structure elucidation

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