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Citation for published version:

Digital Object Identifier (DOI):
10.1039/c6cc00744a

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Chemical Communications

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Nitride tuning of lanthanide chromites

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Received 06th January 20xx, Accepted 06th January 20xx
DOI: 10.1039/x0xx00000x

www.rsc.org/

LaCrO$_3$$_x$N$_3$$_x$ perovskites with Ln = La, Pr and Nd and nitrogen contents up to $x = 0.59$ have been synthesised through ammonolysis of LnCrO$_3$ precursors. These new materials represent one of the few examples of chromium oxynitrides. Hole-doping through O$^2/$N$^-$ anion substitution suppresses the magnetic transition far less drastically than Ln$^{3+}$/M$^{3+}$ (M = Ca, Sr) cation substitutions because of the greater covalency of metal-nitride bonds. Hence, nitride doping is a more benign method for doping metal oxides without suppressing electronic transitions.

Substitution of nitride for oxide anions is an important method for tuning many materials properties, for example, TiO$_2$:N photocatalysis,$^7$ (Sr,Ca)BaSi$_2$O$_6$N$_2$ luminescence$^3$ and Ca$_{1-x}$La$_x$TaO$_{3.5}$N$_y$ colour,$^6$ BaTiO$_3$:N$_{3y/5}$ ferroelectrics$^5$ and BaTaO$_2$:SrTaO$_2$:N$_N$ dielectrics,$^8$ and EuNbO$_3$, EuWO$_4$, EuO$_2$N$_2$$_x$ and LnCrO$_2$$_x$$_N$$_x$ CMR.$^{1,8}$

Lanthanum chromite (LaCrO$_3$) is an important ceramic material with applications as a mixed (electronic and ionic) conductor in fuel cells and heating elements,$^9$ and as an oxidation catalyst for CO or CH$_4$ combustion.$^{10}$ Magnetism in LnCrO$_3$, perovskites (Ln = La$_{1-x}$Lu$_x$) is also of fundamental interest as antiferromagnetic order of Cr$^{3+}$ spins varies with the size and 4f$^0$ moments of the Ln$^{3+}$ cations.$^{11}$ Although chemical tuning through substitutions of A = Ca, Sr in Ln$_1$A$_x$CrO$_3$ perovskites is much studied,$^{12,13}$ nitride substitution has not been reported before, and chromium oxynitrides have been reported only for three structure types: NaCl type Cr$_{1-x}$(O,N)$_x$, antifluorite Li$_{1-x}$Cr$_x$N$_{2-x}$, or Li$_{1-x}$Cr$_x$N$_{3-x}$ and apatite Sm$_{1-x}$Cr$_x$Si$_2$N$_2$O$_{24}$.$^{14-17}$ Here we show that ammonolysis of LnCrO$_3$ precursors produces new LnCrO$_3$:N$_3$$_x$, perovskites for Ln = La, Pr and Nd, with nitrogen contents up to $x = 0.59$. Nitride substitution induces oxidation of Cr$^{3+}$ to Cr$^{4+}$ as the mechanism of charge compensation and the consequences of this on magnetic ordering transitions have also been determined.

LnCrO$_3$$_x$N$_3$$_x$ perovskites with Ln = La, Pr and Nd were synthesised by heating the corresponding LnCrO$_3$ precursors under flowing ammonia gas for several 10 hour cycles at 700 - 800 °C with intermediate regrinding. The Cr$^{3+}$ precursors were obtained at 540 °C in air using the Pechini method. The reaction in NH$_3$ proceeds through the initial reduction of LnCrO$_3$ to give poorly nitrided LnCrO$_3$$_x$$_N$$_x$ perovskites with chromium mainly in the Cr$^{3+}$ state. Nitrogen content x increases with concomitant oxidation of Cr$^{3+}$ to Cr$^{4+}$ during subsequent ammonia treatments. The kinetics of nitriding were found to be slow; using low ammonia flow rates (below 600 cm$^3$/min), large samples, temperatures below 700 °C or short treatment times gave low nitrogen contents, while treatments above 800 °C lead to partial decomposition of the perovskite and formation of LnO$_3$. Prolonged reactions in NH$_3$ of small samples with high surface areas at 700 - 800 °C gave the most nitried products.

LnCrO$_3$$_x$N$_3$$_x$ products have been characterised by chemical analysis, laboratory and synchrotron X-ray and neutron diffraction, and magnetisation measurements. Experimental details are in Supporting Information. The maximum analysed nitrogen contents were $x = 0.28$, 0.36 and 0.59 for R = La, Pr and Nd respectively, showing that N content increases as Ln$^{3+}$ size decreases. All of the LnCrO$_3$$_x$$_N$$_x$ products were found to adopt the orthorhombic GdFeO$_3$-type perovskite superstructure which was refined in space group Pbmn using powder synchrotron and neutron diffraction data, as shown in Figure 1 for LaCrO$_3$:N$_{0.28}$O$_{0.28}$. O/N anion order has been observed in neutron diffraction studies of several stoichiometric ABO$_3$N and ABO$_3$$_x$$_N$$_x$ perovskites,$^{18,19,20}$ including LnVO$_3$:N$_3$$_x$ analogues of the present materials.$^{21,22}$ However, no O/N order was detected in the LnCrO$_3$:N$_3$$_x$ neutron refinements, in keeping with their relatively small nitrogen contents ($x < 0.42$). Fits for PrCrO$_3$:N$_{0.19}$ and NdCrO$_3$:N$_{0.42}$ and refinement results are in Supporting Information. Variations of lattice parameter with N-content based on laboratory X-ray fits are shown in Figure 2.

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Electronic Supplementary Information (ESI) available: Experimental conditions, Rietveld refinement information from powder X-ray and neutron diffraction and crystallographic data of LaCrO$_3$:N$_{0.28}$, PrCrO$_3$:N$_3$$_x$ (x=0.19, 0.36) and NdCrO$_3$:N$_{0.41}$. See DOI: 10.1039/x0xx00000x

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The unit cell expands with $x$ showing that the larger ionic radius of nitride with respect to oxide (1.48 vs 1.40 Å) outweighs the increasing proportion of Cr$^{3+}$ which is smaller than Cr$^{4+}$ (0.55 Å for Cr$^{4+}$ vs. 0.62 Å for Cr$^{3+}$).\textsuperscript{23}

LnCrO$_3$ perovskites are magnetic insulators with ordering transitions at 200-300 K due to antiferromagnetic coupling of localised $S = 3/2$ Cr$^{3+}$ spins, although canting of moments leads to weak ferromagnetism. No further transitions are observed down to 4 K for PrCrO$_3$.\textsuperscript{24} but NdCrO$_3$ has a complex low temperature behaviour, with Nd-Cr interactions driving a Cr spin reorientation transition at $T_{SR} = 34$ K and Nd$^{3+}$ spin ordering below 11 K.\textsuperscript{25}

Susceptibility measurements for LnCrO$_3$-$N_x$ perovskites (Figure 3) show the magnetic ordering temperature $T_C$ is reduced as $x$ increases, for example from 293 to 285 to 281 K for LaCrO$_3$-$N_x$ samples with $x = 0$, 0.11 and 0.28 respectively in Figure 3(a). There is also a decrease in the weak ferromagnetic component below $T_C$, as evidenced by the decline in low temperature susceptibility with $x$. Values of Curie temperatures and other magnetic parameters from Curie-Weiss fits to data above $T_C$ are shown in Supplementary Information. All samples have substantial localised Cr paramagnetic moments of 3-4 $\mu_B$ and negative Weiss temperatures showing that antiferromagnetic interactions between localised Cr$^{3+}$/Cr$^{4+}$ moments are dominant. The Weiss temperature and effective moment per Cr ion both fall in magnitude with increasing $x$ as Cr$^{3+}$ is oxidised to Cr$^{4+}$, as observed in the La$_{3-x}$Sr$_x$CrO$_3$ system.\textsuperscript{12} However, the spin reorientation transition temperature in NdCrO$_3$-$N_x$, shown by the inflection in the data in Fig 3(c), increases on going from $x = 0$ to $x = 0.35$, although the transition is no longer evident for the highly nitrided $x = 0.59$ sample.
The variations of \( T_c \) with Cr\(^{4+} \) content \( x \) in our LnCrO\(_3\)-N\(_x\) samples and literature values for La\(_1\)-Sr,CrO\(_3\) \(^{12}\) and La\(_1\)-Ca,CrO\(_3\) \(^{20}\) systems are shown in Fig. 4(a). In the pure LnCrO\(_3\) perovskites, \( T_c \) falls from 293 K for Ln = La to 226 K for Nd, as smaller Ln\(^{3+}\) cations lead to greater bending of Cr-O-Cr bridges and hence weakening of the magnetic superexchange interactions. The different \( T_c \) variations with \( x \) in the doped series are also in part because of lattice effects reflecting the different influences of N\(^{3-}\), Sr\(^{2+}\) and Ca\(^{2+}\) as dopants. Previous studies of \( T_c \) variations in cation-doped LnMnO\(_3\) and other perovskites showed that A-site cation size (equivalent to tolerance factor \( t \)) and disorder (variance \( \sigma^2 \)) are important, and an approximate single-parameter correction for these effects was proposed.\(^{27,28}\) This can be extended to include anion-disorder in AMX\(_3\) perovskites through the equation;

\[
T_c^0 = T_c + A\langle 1 - d_{\text{ax}}/d_{\text{ax}}^0 \rangle^2
\]

where \( A \) is a constant, \( \langle \cdot \rangle \) denotes an average, and \( d_{\text{ax}} \) is A-cation to anion distance. An ideal perovskite (with \( t = 1 \) and no disorder) at a given doping level \( x \) has transition temperature \( T_c^0 \) and \( d_{\text{ax}}^0 \) is calculated from the average M-X distance, here using standard 6-coordinate ionic radii for Cr\(^{3+}/Cr^{4+}\) cations and O\(^2-\)/N\(^3-\) anions.\(^{23}\)

Systematic studies of multiple doped LaCrO\(_3\) systems would be needed to extract an accurate value of the constant \( A \). Here \( A = 3.0 \times 10^6 \) K is estimated as this gives fair agreement between \( T_c^0 \) values for the three LnCrO\(_3\) materials as shown in Fig. 4(b). In this analysis, the Curie transition for an ideal LnCrO\(_3\) perovskite with \( t = 1 \) is \( T_c^0 = 320 \) K. \( T_c^0 \) falls rapidly with \( x \) for Sr or Ca doping, however, the decrease with nitride doping is much less steep. This demonstrates that nitride doping has another important electronic influence (which lies outside the above analysis of lattice effects); Cr-N-Cr superexchange interactions are evidently stronger than Cr-O-Cr interactions due to greater covalency and these partly offset the suppression of magnetic order \( T_c^0 \) due to doping so that \( T_c^0 \) remains relatively high even in the most highly nitrided NdCrO\(_{3.41}\)N\(_{0.59}\) sample. The stronger covalent character of metal-nitride bonds is a consequence of the lower electronegativity of nitrogen compared to oxygen and has been demonstrated by first principles calculations for several metal oxynitrides including perovskites.\(^{29,30}\) In LnCrO\(_3\) perovskites the influence of the Cr-O-Cr angle on \( T_c^0 \) for different lanthanides has been widely established. However in the present study it is difficult to determine the effect of nitride on Cr-(O,N)-Cr angles because neutron diffraction data are available only for one O/N ratio for each rare earth cation.

Magnetic order was also characterised by variable temperature powder neutron diffraction of LaCrO\(_{3.72}\)N\(_{0.28}\), PrCrO\(_{3.64}\)N\(_{0.36}\) and NdCrO\(_{3.58}\)N\(_{0.42}\) samples. G-type antiferromagnetic order, in which each Cr moment is antiparallel to nearest neighbours in \( x \), \( y \) and \( z \) directions, was observed below the \( T_c \)’s in all cases. Antiferromagnetic Nd\(^{3+}\) spin order is also observed for NdCrO\(_{3.58}\)N\(_{0.42}\) at low temperatures, and magnetic peaks were fit using the model published for Nd\(_{1.4}\)Sr,CrO\(_5\),\(^{31}\) as shown in Figure 5. Plots for

\begin{itemize}
  \item LaCrO\(_{3.72}\)N\(_{0.28}\) and PrCrO\(_{3.64}\)N\(_{0.36}\) are in Si.
  \item The saturated Cr moment values of 2.6-2.7 \( \mu_B \) are in agreement with theoretical values for these mixed Cr\(^{3+}\)(S = 3/2)/Cr\(^{4+}\)(S = 1) phases, but the saturated Nd\(^{3+}\) moment in NdCrO\(_{3.58}\)N\(_{0.42}\) is only 1.3 \( \mu_B \), showing that these moments are not fully ordered. It is
\end{itemize}
notable that the Nd ordering temperature of 25 K is substantially higher than the 11 K transition reported for NdCrO₃. This, and the enhancement of the spin reorientation transition temperature noted above, show that Nd-Cr spin-spin interactions are enhanced in the insulating NdCrO₃:Nₓ samples most likely through the presence of more covariant Nd-N-Cr connections.

AB(O,N)ₓ oxynitride perovskites for early transition metals B = Ti, V; Zr, Nb, Mo; Ta, W have been studied extensively. This study shows that careful ammonolysis of suitable precursors can extend the range to later 3d transition metals such as Cr for which oxynitride perovskites have not previously been reported. The present reactions have led to LnCrO₃:Nₓ compositions with x up to 0.59 for Ln = Nd. This is in keeping with a previous study of LnVO₃:Nₓ samples where higher nitrogen contents up to x = 1 were obtained for the smallest (Nd³⁺) cation used. Stabilisation of Cr⁺⁺ perovskite oxides such as SrCrO₃ requires high pressure, so it may be possible to obtain stoichiometric LnCrO₃:Nₓ perovskites by using smaller Ln cations under strongly nitriding conditions.

This study also demonstrates that hole-doping of LnCrO₃ perovskites through O²⁻/N³⁻ anion substitution suppresses magnetic order far less drastically than Ln³⁺/M⁺⁺ (M = Ca, Sr) cation substitutions do, and Nd spin-order is enhanced up to at least x = 0.4. The greater covalency of metal-nitride bonds compared to metal-oxygen enhances magnetic interaction strengths, almost completely compensating for the intrinsic reduction in Tₑ due to hole-doping. Hence, nitride-doping may be viewed as a more benign method for doping holes into metal oxides without suppressing electronic transition temperatures than traditional cation-substitution approaches. An insulator to metal transition is reported in La₁₋ₓSrₓCrO₃ materials at high Sr contents, and it will be useful to discover whether the same change can be driven by nitridation. Doped-LaCrO₃ is also important as a mixed conductor in fuel cells and as an oxidation catalyst for gas combustion, and the effects of nitride substitution on these properties will also be of interest.

This work was supported by the Spanish Ministerio de Economía y Competitividad (MINECO), Spain (Projects MAT2014-53500-R and MAT2015-71664-R), EPSRC and STFC, and it has been developed under the Materials Science PhD program of the Universitat Autònoma de Barcelona. Fellowship support to AB from Ministerio de Economía, Spain (FPI, project MAT2011-24757) is gratefully acknowledged. ICMM acknowledges the Severo Ochoa Program (MINECO, SEV-2015-0496). We thank the Institut Laue Langévin (ILL) and Alba synchrotron for the provision of beamtime; we also thank Dr. F. Fauth (Alba) for assistance during data collection.

Notes and references
