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Nitride tuning of lanthanide chromites

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LnCrO_{3-x}N_x perovskites with Ln = La, Pr and Nd and nitrogen contents up to x = 0.59 have been synthesised through ammonolysis of LnCrO₄ precursors. These new materials represent one of the few examples of chromium oxynitrides. Hole-doping through O²⁻/N³⁻ anion substitution suppresses the magnetic transition far less drastically than Ln³⁺/M²⁺ (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,¹ for example, TiO₂:N photocatalysis,² (Sr,Ca,Ba)Si₂O₂N₂ luminescence³ and Ca_{1-x}La_xTaO_{3-x}N_x colour,⁴ BaTiO_{3-x}N_{2x/3} ferroelectrics⁵ and BaTaO₂N-SrTaO₂N dielectrics,⁶ and EuNbO₂N, EuWO_{1+x}N_{2-x} CMR.^{7,8} Lanthanum chromite (LaCrO₃) 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 CH₄ combustion.¹⁰ Magnetism in LnCrO₃ perovskites (Ln = La-Lu, Y) is also of fundamental interest as antiferromagnetic order of Cr³⁺ spins varies with the size and 4fⁿ moments of the Ln³⁺ cations.¹¹ Although chemical tuning through substitutions of A = Ca, Sr in Ln_{1-x}A_xCrO₃ 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)¹⁴, antiferroite Li₁₀CrN₄O₂¹⁵ or Li₁₄CrN₂O₈¹⁶ and apatite Sm₈Cr₂Si₆N₂O₂₄.¹⁷ Here we show that ammonolysis of LnCrO₄ precursors produces new LnCrO_{3-x}N_x perovskites for Ln = La, Pr and Nd, with nitrogen contents up to x = 0.59. Nitride substitution induces

oxidation of Cr³⁺ to Cr⁴⁺ as the mechanism of charge compensation and the consequences of this on magnetic ordering transitions have also been determined.

LnCrO_{3-x}N_x perovskites with Ln = La, Pr and Nd were synthesised by heating the corresponding LnCrO₄ precursors under flowing ammonia gas for several 10 hour cycles at 700 - 800 °C with intermediate regrinding. The Cr⁵⁺ precursors were obtained at 540 °C in air using the Pechini method. The reaction in NH₃ proceeds through the initial reduction of LnCrO₄ to give poorly nitrated LnCrO_{3-x}N_x perovskites with chromium mainly in the Cr³⁺ state. Nitrogen content x increases with concomitant oxidation of Cr³⁺ to Cr⁴⁺ during subsequent ammonia treatments. The kinetics of nitrating were found to be slow; using low ammonia flow rates (below 600 cm³/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 Ln₂O₃. Prolonged reactions in NH₃ of small samples with high surface areas at 700 -800 °C gave the most nitrated products.

LnCrO_{3-x}N_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 Ln³⁺ size decreases. All of the LnCrO_{3-x}N_x products were found to adopt the orthorhombic GdFeO₃-type perovskite superstructure which was refined in space group Pbnm using powder synchrotron and neutron diffraction data, as shown in Figure 1 for LaCrO_{2.72}N_{0.28}. O/N anion order has been observed in neutron diffraction studies of several stoichiometric ABO₂N and ABON₂ perovskites,^{18,19,20} including LnVO_{3-x}N_x analogues of the present materials.^{21,22} However, no O/N order was detected in the LnCrO_{3-x}N_x neutron refinements, in keeping with their relatively small nitrogen contents (x < 0.42). Fits for PrCrO_{2.81}N_{0.19} and NdCrO_{2.58}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_{2.72}N_{0.28}, PrCrO_{3-x}N_x (x=0.19, 0.36) and NdCrO_{2.59}N_{0.41}. See DOI: 10.1039/x0xx00000x

Fig. 1. Rietveld fits to (a) synchrotron X-ray and (b) neutron powder diffraction patterns for $\text{LaCr}_{0.72}\text{N}_{0.28}$ in space group Pbnm.

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^{4+} which is smaller than Cr^{3+} (0.55 Å for Cr^{4+} vs. 0.62 Å for Cr^{3+}).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 ,²⁴ but NdCrO_3 has a complex low temperature behaviour, with Nd–Cr interactions driving a Cr spin reorientation transition at $T_{\text{SR}} = 34$ K and Nd^{3+} spin ordering below 11 K.²⁵

Susceptibility measurements for $\text{LnCrO}_{3-x}\text{N}_x$ 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 $\text{LaCrO}_{3-x}\text{N}_x$ 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 μ_B and negative Weiss temperatures showing that antiferromagnetic interactions between localised $\text{Cr}^{3+}/\text{Cr}^{4+}$ 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

Fig. 2. Reduced cell parameters for $\text{Ln} = \text{Nd}$ and volumes for $R = \text{La, Pr and Nd}$ as a function of nitrogen content x in $\text{LnCrO}_{3-x}\text{N}_x$ perovskites.

Fig. 3. Magnetic susceptibility data for selected $\text{LnCrO}_{3-x}\text{N}_x$ samples with (a) $\text{Ln} = \text{La}$, (b) $\text{Ln} = \text{Pr}$, and (c) $\text{Ln} = \text{Nd}$, and nitrogen contents x as shown. Inset in (b) shows the enlarged region around T_C .

observed in the $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ system.¹² However, the spin reorientation transition temperature in $\text{NdCrO}_{3-x}\text{N}_x$, 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 nitrated $x = 0.59$ sample.

The variations of T_C with Cr^{4+} content x in our $\text{LnCrO}_{3-x}\text{N}_x$ samples and literature values for $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ ¹² and $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ ²⁶ systems are shown in Fig. 4(a). In the pure LnCrO_3 perovskites, T_C falls from 293 K for $\text{Ln} = \text{La}$ 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 σ^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;

$$T_C^0 = T_C + A \langle (1 - d_{\text{AX}}/d_{\text{AX}}^0)^2 \rangle$$

where A is a constant, $\langle \rangle$ denotes an average, and d_{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 $d_{\text{AX}}^0 = \sqrt{2} \langle d_{\text{MX}} \rangle$ is calculated from the average M-X distance, here using standard 6-coordinate ionic radii for $\text{Cr}^{3+}/\text{Cr}^{4+}$ cations and $\text{O}^{2-}/\text{N}^{3-}$ anions.²³

Systematic studies of multiple doped LaCrO_3 systems would be needed to extract an accurate value of the constant A . Here $A = 3.0 \times 10^4$ 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 $T_C^0 \approx 320$ 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 nitrated $\text{NdCrO}_{2.41}\text{N}_{0.59}$ 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 's 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 $\text{LaCrO}_{2.72}\text{N}_{0.28}$, $\text{PrCrO}_{2.64}\text{N}_{0.36}$ and $\text{NdCrO}_{2.58}\text{N}_{0.42}$ 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 $\text{NdCrO}_{2.58}\text{N}_{0.42}$ at low temperatures, and magnetic peaks were fit using the model published for $\text{Nd}_{1-x}\text{Sr}_x\text{CrO}_3$,³¹ as shown in Figure 5. Plots for

Fig. 4. Cr spin ordering temperatures for doped LnCrO_3 materials ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$), $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$, and $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$) as a function of Cr^{4+} content x ; (a) measured T_C 's, and (b) T_C^0 values corrected for lattice effects as described in the text. The shaded regions show the different T_C^0 variations for nitride and cation doped samples.

Fig. 5. Powder neutron diffraction pattern of $\text{NdCrO}_{2.58}\text{N}_{0.42}$ at 1.5 K, with magnetic diffraction peaks from Cr and Nd spins labelled accordingly ($\lambda = 2.524$ Å). Inset shows temperature variations of the Nd and Cr moments.

$\text{LaCrO}_{2.72}\text{N}_{0.28}$ and $\text{PrCrO}_{2.64}\text{N}_{0.36}$ are in SI. The saturated Cr moment values of 2.6–2.7 μ_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 $\text{NdCrO}_{2.58}\text{N}_{0.42}$ is only 1.3 μ_B , showing that these moments are not fully ordered. It is

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 NdCrO_{3-x}N_x samples most likely through the presence of more covalent Nd-N-Cr connections.

AB(O,N)₃ 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 LnCrO_{3-x}N_x compositions with x up to 0.59 for Ln = Nd. This is in keeping with a previous study of LnVO_{3-x}N_x samples where higher nitrogen contents up to x = 1 were obtained for the smallest (Nd³⁺) cation used.²¹ Stabilisation of Cr⁴⁺ perovskite oxides such as SrCrO₃ requires high pressure, so it may be possible to obtain stoichiometric LnCrO₂N 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⁺/M²⁺ (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-oxide enhances magnetic interaction strengths, almost completely compensating for the intrinsic reduction in T_c 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 La_{1-x}Sr_xCrO₃ 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.

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