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# Synthesis, crystal structure and electronic structure of $\text{La}_3\text{Cr}_2\text{N}_6$ .

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## Keywords

Chemical synthesis; Crystal growth; Crystal and structure symmetry

## Abstract

The rare earth – transition metal ternary nitride  $\text{La}_3\text{Cr}_2\text{N}_6$  was synthesized from the elements and an excess of sodium and gallium at 900°C in a sealed niobium tube. This compound crystallizes in the tetragonal space group  $I4/mmm$  (No. 139) with  $a = 3.8525(5)$  Å and  $c = 20.508(4)$  Å. It is isostructural with the recently discovered ternary nitride  $\text{R}_3\text{M}_2\text{N}_6$  (R = La, Ce or Pr; M = V, Nb or Ta) and with the high  $T_c$  superconducting copper oxide  $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$ . Band structure calculations using density functional theory show that  $\text{La}_3\text{Cr}_2\text{N}_6$  contains  $\text{CrN}_2$  conducting layers.

## 1. Introduction

Among the numerous ternary or quaternary nitrides synthesized over the past 30 years, only a few compounds containing rare earth metals have been described [1], [2], [3], [4], [5], [6], [7], [8], [9] and [10]. Recently, we have reported the first rare earth nitridogallate compound,  $\text{La}_2\text{GaN}_3$  that contains infinite chains of corner-sharing  $[\text{GaN}_2\text{N}_{2/2}]^{6-}$  tetrahedra [10]. Of the known rare earth transition metal ternary nitrides, most exhibit structures related to the perovskite-type, especially of the Ruddlesden–Popper series.  $\text{TaThN}_3$  [6] has the perovskite structure while the  $\text{R}_2\text{MN}_3$  nitrides ( $\text{R}=\text{U}$ ,  $\text{Th}$  or  $\text{Ce}$ ;  $\text{M}=\text{Cr}$  or  $\text{Mn}$ ) adopt a defect  $\text{K}_2\text{NiF}_4$  structure [4], [5] and [7]. More recently, the  $\text{R}_3\text{M}_2\text{N}_6$  compounds ( $\text{R}=\text{La}$ ,  $\text{Ce}$  or  $\text{Pr}$ ;  $\text{M}=\text{Nb}$  or  $\text{Ta}$ ) [9] and  $\text{La}_3\text{V}_2\text{N}_6$  [10] have been found to crystallize in a defect  $\text{Sr}_3\text{Ti}_2\text{O}_7$  type structure. Here we report the synthesis and both the crystal and electronic structures of a new member of the above mentioned  $\text{R}_3\text{M}_2\text{N}_6$  series with  $\text{R}=\text{La}$  and  $\text{M}=\text{Cr}$ .

## 2. Experimental

Two different types of crystals—a few black metallic plates of  $\text{La}_3\text{Cr}_2\text{N}_6$  and a large amount of black silvery octahedral crystals of  $\text{La}_3\text{Cr}_{10-x}\text{N}_{11}$  [4]—were obtained from the same reaction using the following procedure. Due to the air sensitivity of the reagents, all manipulations were carried out in an argon-filled glove box. Na, Ga, La, Cr and  $\text{NaN}_3$  were placed into a niobium tube ( $\text{OD}\approx 1$  cm,  $\text{length}\approx 12$  cm) such as the atomic ratios of  $\text{Na}:\text{Ga}:\text{La}:\text{Cr}:\text{N}_2$  were 6:4:1:1:3. The corresponding masses are Na (Aldrich, A.C.S reagent grade) 83 mg, Ga (99.99%) 200 mg, La (filled from rod, Jonhson Matthey Company) 100 mg, Cr (99.9%) 37 mg and  $\text{NaN}_3$  (99.9%) 47 mg. The niobium container was sealed under argon in a Centorr Associates arc furnace and then

itself sealed under vacuum in a fused silica tube in order to be protected from subsequent oxidation during heating. The silicon tube was then placed into a muffle furnace, heated up to 900 °C over 15 h, and held at temperature for 36 h. Then the furnace was cooled to RT in 100 h. Following the reaction, unreacted sodium was removed by evaporation from the products by heating the niobium tube to 350 °C under a vacuum of  $\sim 10^{-6}$  bar for 8 h. In order to increase the amount and the sizes of the  $\text{La}_3\text{Cr}_2\text{N}_6$  crystals, several reactions with different elemental ratios and different experimental conditions (temperature and times) have been carried out, but all were unsuccessful at producing a significantly larger mole fraction of the desired product or larger crystal sizes. The products of the reaction were analyzed with powder X-ray diffraction using a Scintag 2000  $\theta$ – $\theta$ – $\theta$  diffractometer with  $\text{CuK}\alpha$  radiation. The X-ray sample was prepared in an argon-filled glove box and covered with Mylar film to prevent aerial oxidation. Single crystal X-ray diffraction data were obtained using a Bruker X8 Apex II diffractometer equipped with 4K CCD detector and graphite monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.07107 \text{ \AA}$ ,  $\lambda = 0.07107 \text{ \AA}$ ). The Bruker software package SAINT [11] was used to integrate the data, an empirical absorption correction was applied using SADABS [12] and the initial input files for solving the structure prepared by XPREP [13]. The integrated data were analyzed with the SHELX97 [14] suite of programs within WinGX [15]. The La:Cr ratio of the both lanthanum chromium nitrides were determined by electron microprobe analysis, performed with a JEOL 8900 electron microprobe.

GGA-PW91 [16] and [17] DFT-based periodic calculations were carried out in a PAW [18] and [19] basis using the VASP [20] package. The plane wave cut-off energy was fixed at 450 eV. A  $10 \times 10 \times 2$  Monkhorst Pack [21] grid of KK points was

used. The optimized geometry used to calculate the band structure and density of states varied less than 1% from the experimental values (optimized lattice parameters:  $a = b = 3.821 \text{ \AA}$ ,  $c = 20.341 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ). The Wigner Seitz radii used to calculate projected densities of states were 1.535 Å for La, 1.323 Å for Cr and 0.741 Å for N. All electronic iterations were converged within  $10^{-5} \text{ eV}$ .

### 3. Results and Discussion

After the sodium was removed from the sample, the tube was moved back into the argon-filled glove box. The remaining product was a dark gray, silvery mass in which small crystals were apparent by tilting the collection of solids. A fraction of the product was ground in an agate mortar for powder X-ray diffraction analysis, and the powder pattern revealed many peaks that were assigned to known phases  $\text{Na}_x\text{Ga}_y$ ,  $\text{La}_x\text{Ga}_y$  and  $\text{Cr}_x\text{Ga}_y$  and to the nitrides  $\text{LaN}$  and  $\text{La}_3\text{Cr}_{10-x}\text{N}_{11}$  [4]. Another sample of the reaction product was placed into polybutene oil for inspection under an optical microscope. Two different types of crystals were observed: a few thin black metallic plates and numerous well-shaped black silvery octahedral crystals. The latter were found to be the known  $\text{La}_3\text{Cr}_{10-x}\text{N}_{11}$  nitride by XRD. Several of the black metallic plates were analyzed and all were consistent with a tetragonal symmetry. A suitable crystal with approximate  $100 \times 60 \times 20 \text{ }\mu\text{m}^3$  dimensions was chosen for long data collection. Its structure was solved in  $I4/mmm$  (No. 139). Details of the refinement are shown in Table 1. No extra symmetry was found by ADDSYM [22]. The atomic coordinates were standardized with STRUCTURE TIDY [23] and are shown in Table 2. Some relevant bond lengths and the anisotropic displacement factors are detailed in Table 3 and Table 4, respectively. In order to verify the elemental

composition found by the single crystal XRD solution, semi-quantitative electron microprobe spectroscopy measurement was carried out and revealed a La:Cr ratio of 1.7:1. The difference from the theoretical 1.5:1 ratio is due to the fact that no standards were used for internal calibration. No signal corresponding to sodium, gallium or niobium was observed. The presence of nitrogen was confirmed by wavelength dispersive spectroscopy.

$\text{La}_3\text{Cr}_2\text{N}_6$  is isostructural with the ternary nitrides  $\text{R}_3\text{M}_2\text{N}_6$  ( $\text{R}=\text{La, Ce or Pr}$ ;  $\text{M}=\text{V, Nb or Ta}$ ) [8] and [9] and with the double layer superconducting copper oxides  $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$  [24]. Fig. 1 gives a perspective view of the structure that is related to the one of the Ruddlesden–Popper phase  $\text{Sr}_3\text{Ti}_2\text{O}_7$ , i.e.  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  with  $n=2$  [25]. Compared to the oxo-titanate, one nitrogen position is vacant in the perovskite double-layers of  $\text{La}_3\text{Cr}_2\text{N}_6$ . While in  $\text{Sr}_3\text{Ti}_2\text{O}_7$  the titanium atoms are located in the center of an octahedron, the chromium atoms in  $\text{La}_3\text{Cr}_2\text{N}_6$  are located slightly above the basal plane of a nitrogen square pyramid. These pyramids form extended  $2\text{D } \frac{2}{\infty}[\text{CrN}_{4/2}\text{N}]$  layers via corner sharing. The average rare earth-nitrogen distance  $\text{La}-\text{N} \approx 2.67 \text{ \AA}$  in  $\text{La}_3\text{Cr}_2\text{N}_6$  is similar to that found in the binary nitrides  $\text{LaN}$  ( $\text{La}-\text{N} \approx 2.65 \text{ \AA}$ ) or the ternary nitride  $\text{La}_2\text{GaN}_3$  [10]. But the average chromium–nitrogen distance  $\text{Cr}-\text{N} \approx 1.94 \text{ \AA}$  is slightly shorter than what is reported for  $\text{CrN}$  ( $\text{Cr}-\text{N} \approx 2.07 \text{ \AA}$ ) and can be compared to those found in another rare earth chromium nitride,  $\text{Ce}_2\text{CrN}_3$ , a structure that is related to another member of the Ruddlesden–Popper phases,  $\text{Sr}_2\text{TiO}_4$  ( $n=1$ ) with a defective  $\text{K}_2\text{NiF}_4$  structure:  $\text{Cr}-\text{N} \approx 1.99 \text{ \AA}$  [4].

The total and projected densities of states calculated for  $\text{La}_3\text{Cr}_2\text{N}_6$  are shown in Fig. 2. The La d-bands lie well above the Fermi level, i.e.  $\text{La}^{3+}$ , which cuts through the Cr d-bands, predicting metallic behavior, i.e. formally  $\text{Cr}^{4.5+}$ . Around the Fermi level,

the important features of the band structure of  $\text{La}_3\text{Cr}_2\text{N}_6$  are determined by the nitrogen chromium interactions within the  $\frac{2}{\infty}[\text{CrN}_{4/2}\text{N}]$  layer.

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## Figures and tables captions

Figure 1: Structure of  $\text{La}_3\text{Cr}_2\text{N}_6$  shown in perspective along aa axis. The chromium and the lanthanum coordination environments are shown on the right of the figure with the main inter-atomic distances.

Figure 2: Total and projected densities of states (DOS) calculated for  $\text{La}_3\text{Cr}_2\text{N}_6$  with DFT.

Table 1: Crystal data and structure refinement for  $\text{La}_3\text{Cr}_2\text{N}_6$ .

Table 2: Atomic coordinates and values of  $U_{\text{eq}}U_{\text{eq}}$ , the equivalent isotropic displacement parameter ( $\text{\AA}^2 \times 10^3$ ), for  $\text{La}_3\text{Cr}_2\text{N}_6$ .

Table 3: Selected bond lengths for  $\text{La}_3\text{Cr}_2\text{N}_6$  ( $\text{\AA}$ ) .

Table 4: Anisotropic displacement factors for  $\text{La}_3\text{Cr}_2\text{N}_6$ .

Figure 1

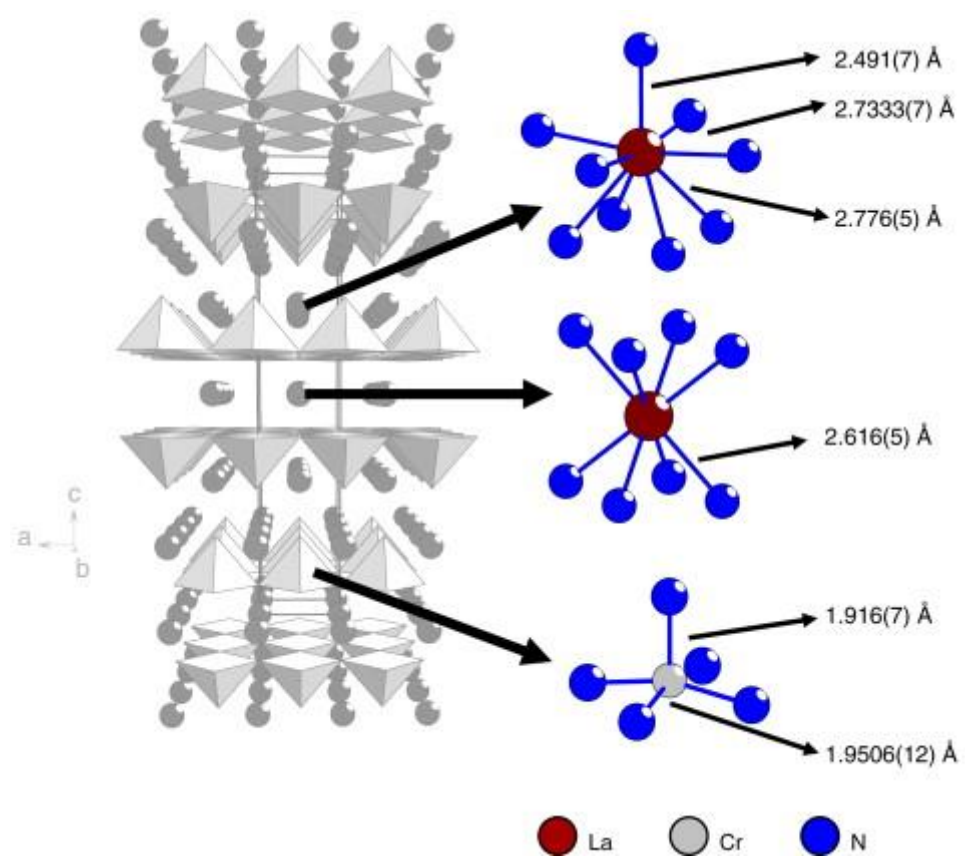


Figure 2

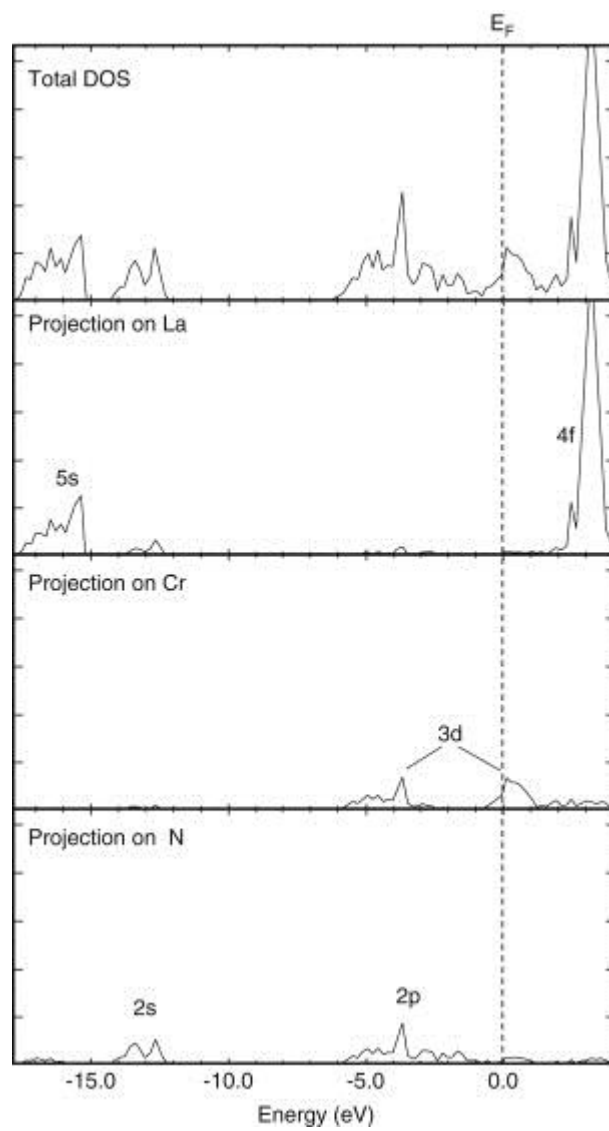


Table 1

Empirical formula	La <sub>3</sub> Cr <sub>2</sub> N <sub>6</sub>
Formula weight ( <i>M</i> )	604.79
Temperature (K)	167(2)
Crystal system	Tetragonal
Space group	<i>I</i> 4/mmm
<i>a</i> (Å)	3.8525(5)
<i>b</i> (Å)	3.8525(5)
<i>c</i> (Å)	20.508(4)
Volume (Å <sup>3</sup> )	304.38(8)
<i>Z</i>	2
Density (calculated) (Mg m <sup>-3</sup> )	6.599
Absorption coefficient ( $\mu$ ) (mm <sup>-1</sup> )	23.969
F(000)F(000)	522
Crystal size (mm <sup>3</sup> )	0.10×0.06×0.02
Theta range for data collection (°)	1.99–40.64
Index ranges	–5≤ <i>h</i> ≤6 –5≤ <i>h</i> ≤6 –7≤ <i>k</i> ≤6 –7≤ <i>k</i> ≤6 –36≤ <i>l</i> ≤356–
Reflections collected	3361
Independent reflections	339 [ <i>R</i> <sub>int</sub> = 0.0352]
Completeness to theta=40.64°	98.8%
Max. and min. transmission	0.6457 and 0.3824
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup> <i>F</i> <sup>2</sup>
Data / restraints / parameters	339 / 0 / 16
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.120
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0302 <i>wR</i> 2 = 0.0746
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0321 <i>wR</i> 2 = 0.0752
Largest diff. peak and hole (e Å <sup>-3</sup> )	3.124 and –4.286

Table 2

Atom	Wyckoff position	$x$	$y$	$z$	$U_{\text{eq}}$
Cr	$4e$	0	0	0.3987(1)	25(1)
La1	$2a$	0	0	0	14(1)
La2	$4e$	0	0	0.1838(1)	9(1)
N1	$4e$	0	0	0.3053(3)	10(1)
N2	$8g$	0	0.5	0.0863(3)	33(2)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

Table 3

Cr—N1 x 1	1.916(7)
Cr—N2 x 4	1.9505(12)
La1—N2 x 8	2.616(5)
La2—N1 x 1	2.491(7)
La2—N1 x 4	2.7333(7)
La2—N2 x 4	2.776(5)

Table 4

Atom	Wyckoff position	$x$	$y$	$z$	$U_{\text{eq}}$
Cr	$4e$	0	0	0.3987(1)	25(1)
La1	$2a$	0	0	0	14(1)
La2	$4e$	0	0	0.1838(1)	9(1)
N1	$4e$	0	0	0.3053(3)	10(1)
N2	$8g$	0	0.5	0.0863(3)	33(2)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.