

Solid Solutions between LaN and Ca₃N₂: Defect Rock Salt Nitrides La_{1-x}Ca_xN_{1-x/3}

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La_{1-x}Ca_xN_{1-x/3} (0 < x < 0.7) has been prepared by reacting LaN with Ca₃N₂ at temperatures between 1200 and 1300°C. All the phases have the LaN-like rock-salt structure with no evidence for ordering between La and Ca or of the x/3 N vacancies. The lattice parameters of materials with different compositions lie between those of the isostructural LaN and CaNH according to Vegard law. Ca adopts octahedral coordination in the title compound, in contrast to its tetrahedral coordination geometry in Ca₃N₂. The materials are poorly conducting. © 1997 Academic Press

INTRODUCTION

The recent surge in the interest in ternary nitride materials (1–3) has been fueled by the search for materials with novel structures and useful electronic properties. Some binary nitrides are used as, and in, ceramics (e.g., AlN and Si₃N₄), others are currently being exploited as semiconductors (e.g., GaN and InN), and some are superconductors at low temperatures (e.g., TaN, NbN). All nitrides are thermodynamically less stable than oxides due to the strength of the triple bond in N₂ (941 kJ·mol⁻¹ compared to 500 kJ·mol⁻¹ in O₂). However, most transition metal binary nitrides and some of those in the main group such as AlN, GaN, and Si₃N₄ are kinetically stable in air and inert in many chemical environments. Binary nitrides of more electropositive metals such as the alkaline and rare earths are invariably very air-sensitive, particularly when moisture is present. Most known ternary transition metal and main group nitrides contain large mole fractions of alkaline earth metals. This confers stability on the nitride ion by the inductive donation of the electrons from the electropositive metal (4), but causes most of these nitrides to be very air-sensitive. A second energetic consideration is that the large energy required to form N³⁻ from N (2300 kJ·mol⁻¹

compared with 700 kJ·mol⁻¹ for O²⁻ from O) results in highly covalent M–N bonding (M = transition metal), whereas some ionic contribution is important in oxides. Routes to the synthesis of ternary nitrides have been developed over the past few years and these are summarized in recent reviews (2, 3). Although the known ternary nitrides are currently relatively few, it is clear that they adopt dramatically different structures to the corresponding oxide systems, and their covalent nature means they often have more in common with sulfides or carbides than with oxides. Apart from the rock-salt binaries, LnN, very few nitrides containing rare earth metals are known. Here we report the synthesis of members of the partial solid solution between LaN and antifluorite type Ca₃N₂.

EXPERIMENTAL DETAILS

Starting materials and products were all handled in an argon-filled MBraun MB 150M dry box which had had its combined oxygen and water content reduced to below 1 ppm by means of circulation through molecular sieves and a Dow Q-5 reagent copper catalyzer.

La metal (99.9% from Aldrich Chemical Co.) had its oxide coating removed by means of drip-melting under vacuum in a Ta container. About 2 g of clean La pieces was placed in an alumina boat. This boat was placed in a quartz tube through which ammonia gas, cleaned as the liquid with Na, flowed at a rate of about 100 cm³·min⁻¹. The temperature was raised to 600°C over 5 h, the furnace was allowed to cool quickly, and the now brittle gray-black charge was removed and ground. The powder was then heated in an alumina crucible at 1000°C under 1 atm of clean N₂ for 12 h to ensure full conversion to the charcoal gray LaN; this was confirmed by measuring the increase in mass and by powder X-ray diffraction (PXRD) carried out using a Scintag XDS 2000 diffractometer operating in Bragg–Brentano geometry.

Chestnut-colored Ca₃N₂ was prepared by reacting clean chunks of Ca metal (99% from Aldrich Chemical Co.) with N₂ at 1000°C in a flow furnace for 24 h. The N₂ had been cleaned by passing over a Ti getter at 800°C.

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Mixtures of LaN and Ca_3N_2 with a combined mass of about 0.5 g were ground together for about 5 min., cold pressed in 5/16-in. (7.9-mm) dies with a force of 2000 kg, and placed in a cylindrical Ta crucible 30 mm long and 12.5 mm wide. The crucible was suspended using a Mo wire in a vertical quartz tube 25 mm in diameter and this was inserted inside the 25-mm induction coil of an Ameritherm Inc. 2.5-kW radio frequency induction furnace. N_2 gas which had been purified using molecular sieves, a copper catalyzer, and a Ti getter at 800°C was passed over the sample. The Ta crucible was heated to a temperature of approximately 1200°C as measured using an optical pyrometer. The temperature was maintained for 1–5 h, during which time a small amount of Ca sublimed out of the crucible onto the walls of the quartz tube. When the temperature exceeded 1250°C , the loss of Ca was quite severe. The sublimate was confirmed to be Ca metal by PXRD and presumably rose from the decomposition of Ca_3N_2 during the reaction. The composition of the resulting material was determined by the loss of mass of the pellet assuming that only Ca_3N_2 was lost, i.e., assuming no La was lost from the pellet and the oxidation states of the metals did not change. The product of the reaction was a black powder which could be easily ground. The samples investigated are summarized in Table 1.

RESULTS AND DISCUSSION

A pellet of a material with an initial La:Ca ratio of 0.343:1 was prepared by heating at 1250°C for 5 h. The mass loss in this case indicated that 28% of the Ca_3N_2 had been lost. PXRD indicated that the sample was single-phase, which implies the composition $\text{La}_{0.34}\text{Ca}_{0.66}\text{N}_{0.78}$. This is very close to the limiting composition: when the reaction was repeated so that the product was much richer in Ca, excess Ca_3N_2 was observed by PXRD. This sample was analyzed for nitrogen content using a modified Kjeldahl method (5). About 70 mg of powder was digested in molten KOH under an atmosphere of moist Ar until the melt,

TABLE 1
Synthesis, Composition and Lattice Information for
 $\text{La}_{1-x}\text{Ca}_x\text{N}_{1-x/3}$ Phases

| Initial La:Ca | Conditions | Final composition ^a | $a/\text{\AA}$ |
|---------------|--|---|----------------|
| 0.667:1 | 1200°C 72 h ^b | $\text{La}_{0.75}\text{Ca}_{0.25}\text{N}_{0.92}$ | 5.2319(2) |
| 1.000:1 | 1250°C 1 h | $\text{La}_{0.52}\text{Ca}_{0.48}\text{N}_{0.84}$ | 5.1860(10) |
| 0.343:1 | 1250°C 5 h | $\text{La}_{0.34}\text{Ca}_{0.66}\text{N}_{0.78}^c$ | 5.1732(5) |
| 0.362:1 | 1300°C 1.5 h | $\text{La}_{0.28}\text{Ca}_{0.72}\text{N}_{0.76}$ | 5.1459(1) |

^a Final compositions are inferred from the mass loss of the pellets unless stated otherwise.

^b Contained in sealed Ta tube.

^c N content confirmed by chemical analysis.

contained in a Pt crucible, was completely colorless and clear (approximately 2 h). The ammonia produced was driven into an aqueous solution of H_3BO_3 and the resulting basic solution was titrated against HCl to determine the nitrogen content. The nitrogen content in this case was determined to be 1.5% less than that inferred from the mass loss of the pellet. This small difference is probably due to incomplete sweeping of the ammonia into the H_3BO_3 solution, as observed with N-containing standards. Thus we conclude that the formal oxidation states of +2 for Ca and +3 for La are attained as expected.

Immediately after removal from the furnace, this pellet was placed between the probes of an electrical multimeter. The resistance across the pellet was on the order of $1.0 \times 10^6 \Omega$. However, the pellet was mechanically easy to grind, so we can do no more than say that the material is poorly conducting at this composition. More detailed conductivity measurements on well-sintered pellets have not been carried out.

PXRD indicated that the products of the reactions listed in Table 1 were single-phase materials with the rock-salt structure, but with lattice parameters intermediate between those of the isostructural LaN and CaNH . There was no indication of any extra peaks, so there is no evidence of La/Ca or N-vacancy ordering. The diffraction peaks were similar in width to those of LaN treated under the same conditions. The lattice parameters were refined using a least-squares routine, and the results for the different compositions are shown graphically in Fig. 1.

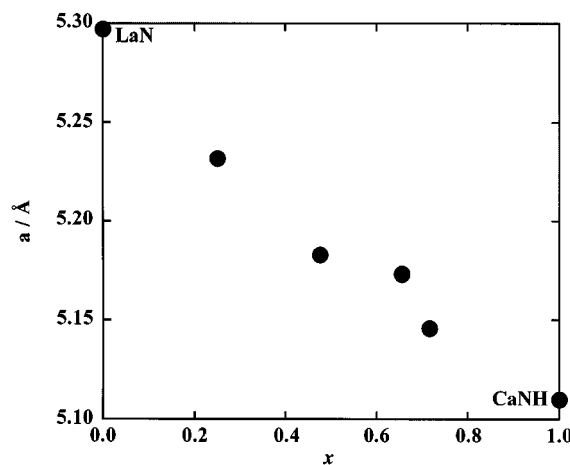


FIG. 1. A graph showing the variation of lattice parameters of $\text{La}_{1-x}\text{Ca}_x\text{N}_{1-x/3}$ as a function of x . The variation of the lattice parameter of the rock-salt phases is close to linear between the isostructural limiting phases LaN and CaNH ; the latter is used because Ca_3N_2 does not adopt this structure, although the lattice parameter of CaNH may be larger than that of hypothetical rock-salt Ca_3N_2 . The uncertainties in composition are about the size of the points on the graph.

SUMMARY

We have prepared a solid solution of the form $\text{La}_{1-x}\text{Ca}_x\text{N}_{1-x/3}$ in the range $0 < x < 0.7$. There is some evidence that the materials are conducting but have a much higher resistivity than LaN , which is a semimetal. There was no indication of any superstructure reflections in the diffraction pattern which would suggest ordering of La and Ca. In nondefect rock-salt, the metal site is 6-coordinate by N, which contrasts with antibixbyite Ca_3N_2 in which Ca is 4-coordinate. Since the tetrahedral holes in the rock-salt structure are too small to admit Ca, the structure must be deficient in N, so the average coordination around each metal ion is less than 6. However, N is 6-coordinate, which is by far the most common coordination geometry in both binary and ternary nitrides (3).

We presume that the inability to make samples which are more Ca-rich than the sample discussed is that the structure cannot support the necessary number of N vacancies, and so phase separation results. There was no evidence for substitution of La into the Ca_3N_2 structure, which would require La to adopt 4-coordination.

Ca^{2+} and La^{3+} are similar in size (1.00 Å for Ca and 1.03 Å for La in 6-coordination), but in nitride chemistry

even metals with very different radii and formal oxidation states can occupy the same site. Li-Ta-N (6), Mg-Ta-N (6), Ca-Ta-N (7) and Na-Ta-N (8) all form disordered rock-salt phases.

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