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Tetragonal LaN and Its New La–B–N Ternary Reaction Product Prepared Under High Pressure

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Abstract

Two kinds of new nitrides related to rocksalt LaN were obtained. One is a tetragonal LaN prepared by nitriding of La metal after heating at 1223K in vacuum. It has lattice parameters of $a = 0{\cdot}5284\,nm$, $c = 0{\cdot}5357\,nm$ and $c/a = 1{\cdot}014$. The other is an La–B–N ternary compound obtained under high pressure of 2·5GPa at 1773K. Its X-ray diffraction pattern could be indexed with an orthorhombic lattice having lattice parameters of $a = 0{\cdot}3756\,nm$, $b = 1{\cdot}3037\,nm$ and $c = 1{\cdot}6327\,nm$. The crystal structure was assumed to be a composite of LaN layers with interleaving boron atoms. © 1997 Elsevier Science Limited.

1 Introduction

Lanthanide metal nitrides (LnN) are hard materials with high melting points in a range of 2773 to 3273K, depending on the kind of Ln metal. They are hygroscopic to decompose to their hydroxides and ammonia. They have been reported to be mostly stoichiometric with a cubic rocksalt structure where nitrogen atoms are located in interstitial sites of fcc packing of Ln metal atoms.[1] Most lanthanides also form oxynitrides with rocksalt-derived structure. There has been no report on lanthanide metal nitride with a different structure from the rocksalt LnN. Some kinds of multinary LnN-based compounds have been reported. Their crystal chemistry has been reviewed together with nitrides of other kinds of metal.[1]

Some nitrides with transition or lanthanide metal are attractive magnetic materials. Double metal nitrides containing both of them are very interesting. $Sm_2Fe_{17}N_x$ has a giant magnetism larger than that of $Nd_2Fe_{14}B$.[2] It has a high Curie temperature of around 750K and large coercivity. There is a series of $Ln_2Fe_{17}N_x$ where Ln = Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm. A small amount of nitrogen is distributed in interstitial sites of Ln_2Fe_{17} alloy with Th_2Zn_{17}- or Th_2Ni_{17}-type crystal structure to expand interatomic distance between Fe atoms.[3] The nitrides are thermally unstable to decompose releasing nitrogen. Another double metal nitride $La_6Cr_{21}N_{23}$ was prepared by a reaction between LaN and CrN in a nitrogen atmosphere in a temperature range between 1523 and 1573K, although La and chromium metals do not form any solid solution.[4] $La_6Cr_{21}N_{23}$ has an NaCl-related crystal structure and showed superconductivity below 2·7K. Superconductivity of Tc = 12–13K was reported on $La_3Ni_2B_2N_3$ prepared by arc-melting of their element mixture in nitrogen atmosphere.[5] Its crystal structure consists of three rocksalt LaN layers alternating with tetrahedral Ni_2B_2 layers. The structure was completely different from several kinds of lanthanide boron nitride with direct bond between B and N. $Ce_{15}B_8N_{15}$ was obtained by a reaction between CeN and h-BN at above 2000K. Its crystal structure consists of three-dimensional packing of NCe_6 octahedra linked together by planar BN_3 units.[6] Both $Ln_3B_2N_2$ and Ln_BN_2 were prepared by direct reaction in a mixture of h-BN and lanthanide metal under nitrogen at above 1473K. Boron and nitrogen atoms are directly bonded with covalent bond nature in these lanthanide boron nitrides. There are $B_2N_4^{9-}$ anion in $Ln_3B_2N_4$ (Ln = La, Ce, Pr, Nd)[7] and BN_2^{3-} anion in $LnBN_2$ (Ln = Nd, Sm, Gd).[8]

In the present investigation, lanthanum metal was nitrided by an unusual procedure to obtain a different kind of nitride. High temperature and pressure synthesis was also applied to obtain new compounds in La-B-N ternary and in La–Ni–B–N quaternary systems.

2 Experimental

Rocksalt LaN has been prepared by nitriding lanthanum metal powder in nitrogen atmosphere at 1173K.[9] In the present study, lanthanum metal granule with a diameter of 5–10 mm (Kojundo Chemical Laboratory Co.) was reacted in alumina boat for 10 h at 1223K in N_2 gas (6N) flow after annealing in vacuum at the same temperature. The product was pressed to a pellet of 5 mm in diameter and 7–10 mm in height. It was heated in nitrogen or in argon atmosphere at 1273K for 50 h to study their phase relation. Hot isostatic pressing was also applied to the pellet under 100MPa of nitrogen at 1573K for 1 h. Both nitrogen and oxygen contents in the products were determined by reducing the samples in Horiba EMGA-2800.

High pressure synthesis was performed using cubic-type high pressure equipment. The above LaN powder product was mixed with nickel metal powder (Aldrich Chem. Co., 99·8%) and boron powder (Kojundo Chemical Laboratory Co., 5N) in appropriate ratios. The mixture was subjected to high pressure (2·5GPa) and temperature (1773–1823K) conditions for 1 h in an h-BN cell loaded in a pyrophyllite cube. The mixing ratio (m,n) in $(LaN)_m(NiB)_n$ was varied in a range of (m,n) = (1,4), (1,2), (2,3), (1,1), (3,2), (2,1), (4,1), (6,1), (8,1). Surface texture was observed by SEM (Hitachi S-2150). Chemical analysis was performed by XMA (Horiba EMAX-2770) installed on the SEM. A transmission electron microscope (Hitachi H-600) was used to obtain electron diffraction with chemical analysis. Auger spectroscopy (VG Microlab. Mark III) was also applied to analyze chemical composition. The chemical bond nature was investigated by XPS for nitrogen and boron using AlKα X-ray. The sample was supported on conductive carbon tape and etched with Kr for 15 min if necessary.

All procedures were performed in an Ar-filled glove box to prevent direct air exposure. All samples were kept in a glove box until each experiment. Powder X-ray diffraction was taken using Rigaku RAD-RB system with monochromatized Cu-Kα radiation. The sample was mounted on a slide glass and then loaded in a special holder filled with dry Ar.

3 Results and Discussion

3.1 Tetragonal LaN

Nitriding of lanthanum metal was exothermic and proceeded very rapidly at 1223K after nitrogen was introduced into the evacuated reaction chamber. The product was successively annealed in a N_2 flow for 10 h as it was in order to improve its homogeneity after the self-combustion reaction. It had a tetragonal lattice with a = 0·5284 nm, c = 0·5354 nm and c/a = 1·014, as shown both in Fig. 1(a) and in Table 1. X-ray diffraction of cubic LaN is also represented in Fig. 1(b) as a reference. Chemical composition of the tetragonal product was estimated to be $LaN_{0.926}O_{0.062}$ (N: 8·429 wt%, O: 0·747 wt%) by chemical analysis assuming 0·622 wt% of La_2O_3 impurity present estimated by an excess La_2O_3 addition method. It can be assumed to be an almost stoichiometric LaN composition because of the small oxygen content. The tetragonal LaN transformed gradually to its cubic form by its heating in N_2 or in Ar flow at 1273K for 50 h. The transformation was also quickly completed in high pressure nitrogen atmosphere of 100MPa at 1573K for 1 h. The high pressure

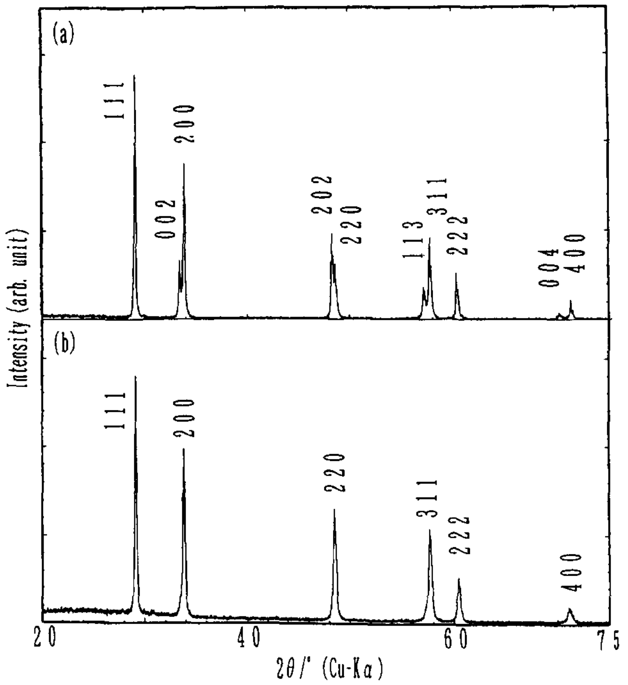

Fig. 1. X-ray diffraction patterns for LaN obtained by (a) nitriding at 1223K for 10 h in nitrogen flow after elevation of temperature in vacuum, and (b) nitriding at 1173K for 20 h after elevation of temperature in nitrogen flow.

Table 1. Powder X-ray diffraction data for tetragonal LaN[a]

hkl	d_{obs}.nm^{-1}	d_{calc}.nm^{-1}	$I\,I_0^{-1}$
111	0·3068	0·3065	100
002	0·2681	0·2679	24
200	0·2644	0·2642	64
202	0·1882	0·1881	39
220	0·1870	0·1868	20
113	0·1612	0·1611	15
311	0·1596	0·1595	37
222	0·1533	0·1532	21
004	0·1339	0·1339	4
400	0·1321	0·1321	8
313	0·1220	0·1220	13
331	0·1213	0·1213	7
204	0·1195	0·1195	6

[a] a = 0·5284 nm, c = 0·5357 nm, c/a = 1·014.

product had a cubic lattice with a = 0·5302 nm. The value is comparable to the reported one of 0·5303 nm.[10]

There have been some reports on tetragonal crystal lattice of transition metal nitride. Tetragonal θ-Mn_6N_5 ($MnN_{0\cdot833}$) transforms to a cubic lattice with random distribution of nitrogen atom.[11] There is a tetragonal niobium nitride in a compositional range of $NbN_{0\cdot751}$–$NbN_{0\cdot780}$ as well as a cubic form in a range of $NbN_{0\cdot800}$–$NbN_{0\cdot942}$.[12] The molar ratio of N/La in the present tetragonal LaN is much larger than the values of N/M in these tetragonal transition metal (M) nitrides. The present tetragonal lattice seems not to be induced by the ordering of nitrogen defect. Its nitrogen content is much larger in comparison to values in the transition metal nitrides. Several kinds of oxynitride of rare earth metal have been reported; LaN_xO_y ($10 < y/(x+y) < 50$) has a cubic rocksalt lattice[13] and both 2 × 1 × 1 and 4 × 2 × 1 superlattices have been observed in cerium oxynitrides by electron diffraction.[14] There has been no tetragonal lattice on these oxynitrides.

HIP-treated LaN had a composition of N: 8·627wt% and O: 0·445wt% with a cubic crystal lattice. These values are practically the same with values for the above-mentioned tetragonal phase. There are two polymorphs: low temperature α- and high temperature β- in La metal. La atoms pack in hcp and in fcc, respectively. Nitrogen might be very rapidly absorbed into the fcc lattice of β-La metal at around melting point to induce a tetragonally distorted lattice of rocksalt LaN where La metal pack in fcc.

3.2 Lanthanum boron nitride

High pressure products obtained from various starting compositions of LaN–Ni–B ternary were mixtures of several kinds of compounds, as shown in Fig. 2. Presence of superconducting $La_3Ni_2B_2N_3$ was not observed on these products.[5] There are several common diffraction lines for the products obtained from the starting compositions of (4,1) to (2,3) such as a strong peak at around 2Θ = 28°. The product at (4,1) gave the simplest X-ray diffraction pattern with the sharpest diffraction lines among the products. The diffraction pattern changed with air exposure as represented in Fig. 3. The main phase was hygroscopic and gradually decomposed over the duration. There remained only several lines related to h-BN and some minor impurity after long air exposure. The disappeared diffraction lines with the air exposure may be assigned to a new compound. They are marked with stars in Fig. 3(i) and can be indexed with an orthorhombic lattice with a = 0·3756 nm, b = 1·3037 nm and c = 1·6327 nm as depicted in Table 2. The high pressure product was a polycrystalline brown mass with white grain boundary. It could be crushed to small brown pieces of several mm in diameter. The crushed surface was smooth and most of the pieces

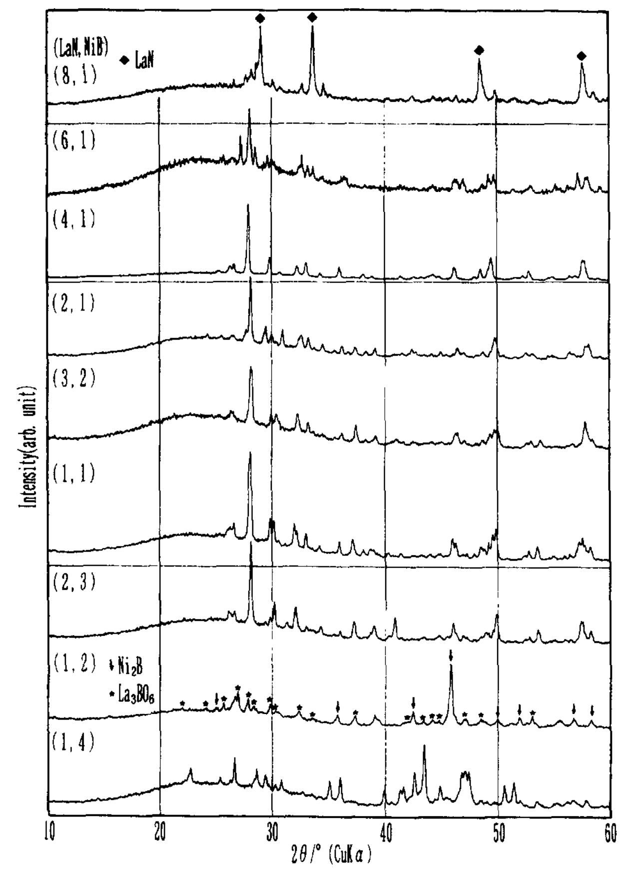

Fig. 2. X-ray diffraction patterns for the high pressure products obtained from starting composition of various mixing ratios (m,n) in $(LaN)_m(NiB)_n$. Assignments for cubic LaN, Ni_2B and La_3BO_6 impurities only were given for the products from only two starting compositions to get rid of a complexity in representation. These impurities are also present in some other products.

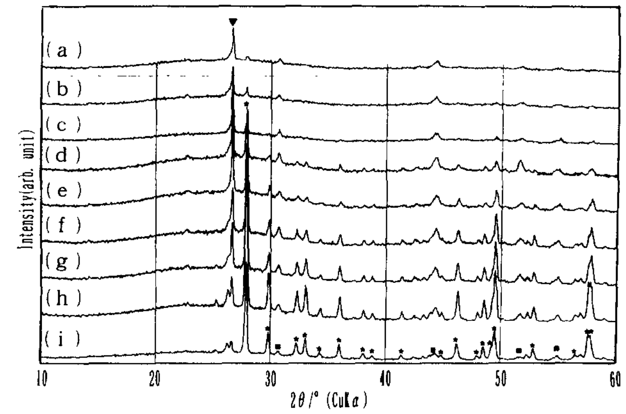

Fig. 3. Variation of X-ray diffraction pattern for the high pressure product obtained from $(LaN)_4(NiB)$ starting mixture with the following durations of air exposure: (a) 21 days; (b) 19 days; (c) 16 days; (d) 10 days; (e) 7 days; (f) 5 days; (g) 3 days; (h) 1 day; (i) as-prepared. Diffraction lines with star marks which correspond to the present new compound disappeared with air exposure. Those with square marks were still observed even after the long air exposure with a line for h-BN marked with a triangle.

Table 2. Powder X-ray diffraction data for new La–B–N ternary compound[a]

hkl	$d_{obs.}$ nm^{-1}	$d_{calc.}$ nm^{-1}	$I\ I_0^{-1}$
033	0·3377	0·3396	11
	0·3334		6
041	0·3184	0·3196	100
121		0·3192	
034	0·2983	0·2975	30
025	0·2900	0·2920	6
104	0·2765	0·2764	17
114	0·2700	0·2704	21
050	0·2603	0·2607	8
052	0·2487	0·2484	16
142	0·2356	0·2357	8
045	0·2311	0·2307	6
116	0·2176	0·2173	7
	0·2120		4
126	0·2086	0·2088	5
037	0·2059	0·2055	5
018	0·2015	0·2017	7
117	0·1959	0·1959	16
127	0·1892	0·1896	7
200	0·1872	0·1878	13
211	0·1846	0·1847	16
162	0·1837	0·1833	27
	0·1745		6
048	0·1728	0·1730	11
128		0·1729	
170	0·1668	0·1669	4
240	0·1627	0·1628	6
215	0·1614	0·1615	6
242	0·1596	0·1596	22
173		0·1595	
067	0·1591	0·1590	16

[a]orthorhombic: a = 0·3756 nm, b = 1·3037 nm, c = 1·6327 nm.

were covered with white lustrous h-BN film. The white cover can be easily removed by a needle. Chemical analysis with EDX showed that the brown product contained mostly La with only 1–3 at % of Ni. The compound having the same diffraction pattern was also obtained as a mixture with some impurities on high pressure products from starting mixtures between LaN and B. It was observed in the products either from $(LaN)_2B$ or $(LaN)_4B$ under the same preparation conditions of $(LaN)_m(NiB)_n$, respectively. These results suggest that the main chemical components in the new compound are La, B and N. Nickel seems just to enhance its crystallization.

Auger spectrum of the brown pieces showed presence of La, O, N, C, B on their surface. Surface etching showed that both O and C were due to oxide and hydrocarbon contamination from the atmosphere. The brown compound has a ternary composition of La–B–N. X-ray photoelectron spectroscopy showed two B1s spectra at 188·3eV and at 190·7eV. The former can be assumed to correspond to B in the product because it still remained after etching. The binding energy is equivalent to the value of B1s peak in LaB_6 and some other borides (*ca.*188eV).[15] The latter is the same with that of h-BN and could be removed by etching. The present product may be a compound with boride-like bond nature covered with h-BN skin. There were two N1s peaks at 395·2eV and 398·3eV before etching. The latter corresponds again to a value for h–BN and is removed by the etching. The spectrum after etching could be resolved to two peaks at 396·8eV and at 394·5eV with *ca.* 30% relative intensity against the former peak. They can also be observed on LaN. These XPS spectra suggest that the product has both lanthanum nitride- and boride-like bond nature simultaneously. There have been no available XPS data for the previous Ln-B-N ternary compounds with direct B–N bond. We can compare the present XPS peak position with those for h–BN. The present compound shows the maximum peak intensity at 188·3eV for B1s and at 396·8eV for N1s after etching. The values are smaller than those of 190·7eV for B1s and 398·3eV for N1s in h–BN, respectively. The difference suggests that both boron and nitrogen are more ionized to anion in the present product than those in h–BN, forming both boride- and nitride-like chemical bond simultaneously. There may be no direct bond between B and N in the present new compound. The situation may also be different from planar BN_3 units in $Ce_{15}B_8N_{25}$,[6] $B_2N_4^{9-}$ anion in $Ln_3B_2N_4$ (Ln = La, Ce, Pr, Nd),[7] BN_2^{3-} anion in $LnBN_2$ (Ln = Nd, Sm, Gd)[8] and linear BN_2^{3-} anion in Li_3BN_2.[16]

A rectangular array of diffraction spots was often observed on electron diffraction of the brown product. Their spacings of 0·375 nm and 1·33 nm almost correspond to the a- and b-lattice parameters observed on X-ray diffraction: a = 0·3756 nm and b = 1·3037 nm. They can be understood assuming the closest packing of La metal in the ab-plane. The atomic radius of La metal has been reported to be 0·18 7nm.[17] Metal atoms of La form fcc-packing in the rocksalt LaN lattice. Lattice parameters of a- and b- in the present product are almost the same with an La–La bond distance (0·37 nm) and its $3^{1/2}$x2 times (1·30 nm), as represented in Fig. 4, respectively. A value of 1·65 nm can be calculated for c-lattice parameter assuming an ABABAA-type stacking of the La close-packed layers. X-ray photoelectron spectroscopy showed that the present compound has nitrogen similar to that in LaN together with boron in boride. Nitrogen atoms are incorporated in the interstitial sites of the closest packing of La metal. Boron atoms are in trigonal prismatic sites of AA-type packing of La metals. Lanthanum nitride layers are separated from the interlayered boron. There is no B–N direct bond observed in $Ce_{15}B_8N_{15}$, $Ln_3B_2N_2$ and $LnBN_2$. The present type of La–B–N ternary compound may be stabilized with an application of high pressure.

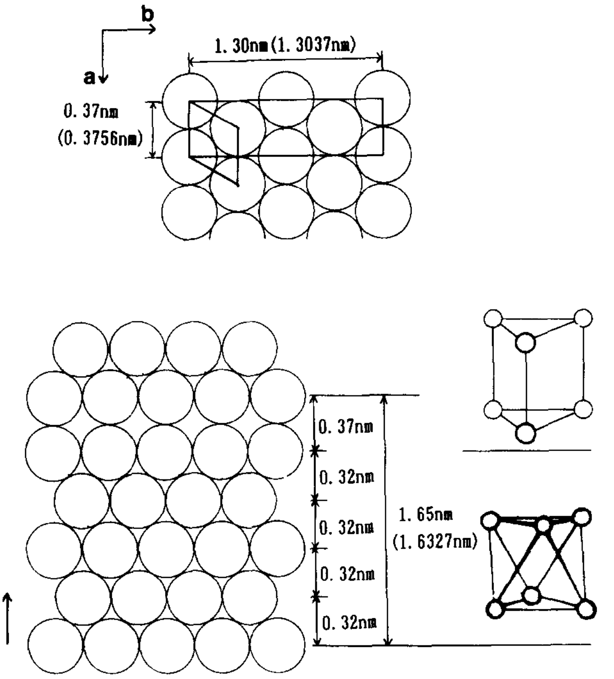

Fig. 4. Schematic crystal structure of the new La–B–N ternary high pressure compound. The lengths were estimated from atomic radius of La metal (0·187 nm). Values in parenthesis are the observed lattice parameters.

4 Conclusion

In summary, tetragonal LaN with a = 0·5284 nm and c = 0·5357 nm could be prepared by nitriding of La metal after evacuation at high temperature. It transformed to the normal cubic form by HIP annealing in nitrogen atmosphere. A new ternary La–B–N compound could also be obtained applying high pressure synthesis. It has an orthorhombic lattice with a = 0·3756 nm, b = 1·3037 nm and c = 1·6327 nm. The crystal structure may be formed with a closest packing of La metal where lanthanum nitride layers stack each other with some amount of boron in their interlayer forming a boride-like chemical bond.

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