JOURNAL OF SOLID STATE CHEMISTRY 65, 6–12 (1986)

Structure of a New Polymorph of Lithium Boron Nitride, Li_3BN_2*

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Received October 1, 1985; in revised form February 4, 1986

A new polymorph of lithium boron nitride, Li_3BN_2, was synthesized by slow-cooling of a mixture of Li_3N and BN from 1200 K. It has monoclinic symmetry, $P2_1/c$, $a = 5.1502(2)$, $b = 7.0824(2)$, $c = 6.7908(2)$ Å, $\beta = 112.956(2)°$, $Z = 4$, $D_m = 1.74$, $D_{calcd} = 1.737$ g cm^{-3}, $\mu = 0.082$ mm^{-1}. The structure was determined from 1352 unique X-ray reflections from a single crystal and refined to $R = 0.023$ by full-matrix least-squares method. Two kinds of layers alternate parallel to (100) in the structure. One layer includes Li and B atoms, and the other is composed of only N atoms. N(1) and N(2) are coordinated by six Li atoms and one B atom. Each Li atom is in a distorted tetrahedron of N atoms. Boron is linearly coordinated by two N atoms. The N(1)—B—N(2) bond angle is 179.12(4)°. The bond lengths of N(1)—B and N(2)—B are 1.3393(5) and 1.3361(5) Å, respectively. Bonding electrons between boron and nitrogen atoms are clearly observed. Lithium ion conductivity of 6×10^{-5} Sm^{-1} was measured at 400 K on a polycrystalline sample and an activation energy was 64 kJ/mole.

Introduction

It is necessary to find a new ionic conductor having high conductivity and both chemical and electrochemical stabilities for the development of a lithium solid state battery. The existence of a series of compounds represented by a general formula $Li_{(2n-3)}M^{n+}N_{n-1}$ where $M^{n+} = Mg^{2+}, Zn^{2+}, Al^{3+}, Si^{4+}$, has been reported (*1*). Their crystal structures were assumed to be derived from the anti-fluorite type structure, which suggests the possibility of lithium ionic conduction. Li_3AlN_2 was recently characterized as a lithium ion conductor and applied in a lithium battery (*2*).

A crystalline phase of Li_3BN_2 was first synthesized by Goubeau and Anselment (*3*). The melting point is 1143 K and infrared spectroscopy shows the presence of the $[N{=}B{=}N]^{3-}$ molecular ion in the structure. De Vries and Fleisher (*4*) reported a high-pressure phase of Li_3BN_2 in addition to the previous compound which was a low-pressure phase. They assumed the crystal structure at 1 atm to be closely related to that of Li_3AlN_2, although no crystal structure analysis was performed. We also synthesized the low-pressure phase of Li_3BN_2 by quenching the melt of a Li_3N and BN

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* The F_c–F_o table is available from NAPS. See NAPS Document No. 04389 for 26 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid.

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0022-4596/86 $3.00

mixture from 1300 K. Another new crystalline phase was obtained by slow-cooling of the melt. The phase relation between the two polymorphs and a crystal structure analysis of the former phase are under investigation (*5*).

In the present work, the crystal structure of the new Li_3BN_2 polymorph, which was not simply related to Li_3AlN_2, was studied by single-crystal X-ray diffraction.

Experimental

Lithium nitride was prepared by a reaction of nitrogen gas (Osaka Oxygen Ind. Ltd., 99.999%) with lithium (Wako Pure Chemical Ind. Ltd., 99%) in a temperature range of 373–473 K. Pulverized Li_3N was mixed with boron nitride powder (Nakarai Chem. Ltd.), compressed to a pellet and enclosed in tantalum foil. These operations were carried out in a helium-filled glovebox. The mixtures having molar ratio $Li_3N/BN = 1.0–1.2$ were heated above the melting point of the product at 1200 K, kept at this temperature for 7 hr and cooled to 1000 K at a rate of 1.5–3.0 K/hr in a stream of nitrogen.

Prismatic crystals with a size of 3.0 × 1.5 × 1.5 mm were taken from the product. They were colorless, transparent, unstable against moisture, and soluble in water. The amounts of lithium, boron, and nitrogen were determined by atomic absorption and Kjeldahl methods (obs. 34.7, 18.0, 45.8: calcd 34.9, 18.1, 47.0 in wt%). Density measured by flotation was 1.74 g cm^{-3}.

Weissenberg and precession photographs taken with Cu$K\alpha$ and Mo$K\alpha$ radiations, respectively, indicated systematic absences with $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$, which are consistent with the space group $P2_1/c$ of the monoclinic system.

A single crystal used for intensity collection was ground to an ellipsoid having dimension of 0.8 × 0.5 × 0.5 mm in an argon atmosphere. It was sealed with argon gas in a glass capillary of 0.5 mm in diameter.

Cell parameters were determined by the least-squares method using 36 reflections ($2\theta = 23–29°$, Mo$K\alpha$, $\lambda = 0.71069$ Å) measured with a four-circle diffractometer.

Mo$K\alpha$ radiation monochromatized by pyrolytic graphite was used for intensity measurements. The intensities of 2773 reflections including crystallographically equivalent reflections within the range of $0 < 2\theta < 80°$ were obtained at 293 K by 2θ–θ scan technique on a four-circle diffractometer (RIGAKU AFC-5 FOS). Three standard reflections measured after every 55 reflections showed no evidence of crystal deterioration and no instability of the detection system. All the observed reflections were summarized in 1415 unique reflections. Sixty three reflections having high standard deviations ($3\sigma_{hkl}(F_0) > |F_0|$) or unobservable intensities were eliminated from the least-squares refinement procedure, where $\sigma_{hkl}(F_0)$ is a standard deviation of each reflection obtained from counting statistics. Conventional Lorentz and polarization corrections were carried out in the process of data collection. No absorption correction was made because of the small value of μ_r (<0.04).

An appropriate structure model was obtained from Patterson synthesis diagrams. Full-matrix least-squares refinement with anisotropic temperature factors for all atoms gave final agreement factors of $R = 0.023$ ($R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$) and $R_w = 0.038$ $\{R_w = [\Sigma w(|F_c| - |F_0|)^2/\Sigma w|F_0|^2]^{1/2}\}$, where $w = 1/\sigma^2_{hkl}(F_0)$. Ratio of maximum least-squares shift to error in final refinement cycle, was 0.00. Maximum and minimum residual electron densities in the final difference-Fourier synthesis were $+0.5$ e Å^{-3} and -0.1 e Å^{-3}. Atomic scattering factors for Li, B, and N were taken from "International Tables for X-ray Crystallography" (*6*). Final positional and thermal parameters are given in Table I.

All computations for the least-squares refinements of lattice constants and structure parameters, interatomic distances and an-

TABLE I

FRACTIONAL ATOMIC COORDINATES (×10^5) AND THERMAL PARAMETERS FOR Li_3BN_2 OBTAINED FROM THE REFINEMENT

	x	y	z
Li(1)	24995(17)	48518(12)	49811(12)
Li(2)	25228(18)	1212(13)	37502(13)
Li(3)	74360(16)	20714(11)	31402(12)
B	21509(7)	31982(5)	17648(5)
N(1)	43403(6)	43735(4)	21904(5)
N(2)	99439(6)	20472(5)	13461(5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Li(1)	1267(27)	610(13)	713(15)	150(14)	179(16)	−8(10)
Li(2)	1288(27)	876(15)	671(15)	223(15)	339(16)	18(11)
Li(3)	1159(25)	466(11)	763(14)	4(13)	316(15)	14(10)
B	712(11)	332(5)	406(6)	18(5)	188(7)	−9(4)
N(1)	760(10)	335(4)	627(6)	−53(4)	171(6)	−1(3)
N(2)	817(10)	511(5)	538(6)	−160(5)	195(6)	39(4)

Note. Anisotropic temperature factors are in the form $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$. Estimated standard errors are given in parentheses.

gles, Patterson, Fourier and difference Fourier syntheses, and crystal structure drawing, were carried out using the programs *LCLSQ* (*7*), *RFINE* (*8*), *UMBADTEA* (*9*), *3DFR* (*10*), and ORTEP-II (*11*), respectively, at the Crystallographic Research Center, Institute for Protein Research, Osaka University (ACOS-700).

Results and Discussion

Stereoscopic illustrations of the structure are shown in Fig. 1. The structure of Li_3BN_2 can be explained by alternations of two kinds of layers; one is composed of only N atoms and another includes Li and B atoms. These layers are parallel to (100). Nitrogen atom layers are located at $x \approx 0$ and $x \approx \frac{1}{2}$, and layers including lithium and boron atoms are at $x \approx \frac{1}{4}$ and $x \approx \frac{3}{4}$.

Interatomic distances and angles are given in Table II.

Li(1), Li(2), and Li(3) are tetrahedrally coordinated by 2N(1) and 2N(2), and the tetrahedrons are fairly distorted. The distances between lithium and nitrogen atoms are in a wide range from 1.9 to 2.5 Å for Li(1) and Li(2) tetrahedrons, while those of Li(3)—N are in a narrow range of 2.09–2.19 Å. Bond angles deviate significantly from the tetrahedral values. Both coordination numbers around N(1) and N(2) are 7. The nitrogen atoms are coordinated by 2Li(1), 2Li(2), 2Li(3), and B.

It would be interesting to compare the bond lengths to other values. The average bond length of Li—N is 2.10 Å in $LiSi_2N_3$ (*12*). The lithium is tetrahedrally coordinated by four nitrogens. The bond lengths are in a range of 2.03 ~ 2.16 Å. The average value was compared with the Li—N bond lengths in Li_3N, Li_2NH, $LiNH_2$, LiMgN, LiZnN, and Li_2CeN_2 in the same work. The values are in a range of 1.94 ~ 2.19 Å. α-LiSiON has its lithium in LiO_3N tetrahedron where $d_{Li—N}$ = 2.25 Å (*13*).

Lithium aluminum nitride, Li_3AlN_2, has a crystal structure derived from anti-fluorite (*14*). Nitrogen atoms are in cubic closest packing and surrounded by six lithiums and two aluminums. Lithium and aluminum atoms are coordinated by four nitrogen atoms. De Vries and Fleicher (*4*) presumed that the structure of Li_3BN_2 was related

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD ERRORS IN PARENTHESES

Li(1)–N(1)	2.4508(11)
–N(1)^{vii}	2.0497(9)
–N(2)^{vi}	2.3134(10)
–N(2)^{ix}	1.9821(9)
Li(2)–N(1)^{i}	2.1809(9)
–N(1)^{ix}	2.0256(11)
–N(2)^{v}	2.1444(9)
–N(2)^{x}	2.5087(10)
Li(3)–N(1)	2.1941(8)
–N(1)^{ix}	2.0924(8)
–N(2)	2.0930(11)
–N(2)^{i}	2.1457(9)
N(1)–B	1.3393(5)
N(2)–B^{iii}	1.3361(5)
N(1)–N(2)^{v}	2.6753(5)
N(1) –Li(1)–N(1)^{vii}	110.88(4)
N(1) –Li(1)–N(2)^{ix}	97.20(4)
N(1) –Li(1)–N(2)^{vi}	132.97(2)
N(1)^{vii}–Li(1)–N(2)^{vi}	98.51(4)
N(1)^{vii}–Li(1)–N(2)^{ix}	110.33(4)
N(2)^{ix}–Li(1)–N(2)^{vi}	98.41(3)
N(1)^{i} –Li(2)–N(1)^{ix}	108.58(4)
N(1)^{i} –Li(2)–N(2)^{v}	126.21(5)
N(1)^{i} –Li(2)–N(2)^{x}	99.89(4)
N(1)^{ix}–Li(2)–N(2)^{v}	105.05(5)
N(1)^{ix}–Li(2)–N(2)^{x}	102.88(4)
N(2)^{v} –Li(2)–N(2)^{x}	112.03(4)
N(1) –Li(3)–N(1)^{ix}	114.20(4)
N(1) –Li(3)–N(2)	112.18(4)
N(1) –Li(3)–N(2)^{i}	119.43(4)
N(1)^{ix}–Li(3)–N(2)	105.86(4)
N(1)^{ix}–Li(3)–N(2)^{i}	116.07(4)
N(2) –Li(3)–N(2)^{i}	109.21(4)
N(1)–B–N(2)^{v} N(2)–B^{iii}–N(1)^{iii}	179.12(4)

Li(1) –N(1)–Li(1)^{vi}	69.12(4)
Li(1) –N(1)–Li(2)^{ii}	132.20(3)
Li(1) –N(1)–Li(2)^{viii}	143.54(3)
Li(1) –N(1)–Li(3)	109.34(3)
Li(1) –N(1)–Li(3)^{viii}	70.85(3)
Li(1) –N(1)–B	72.89(3)
Li(1)^{vi} –N(1)–Li(2)^{ii}	144.31(4)
Li(1)^{vi} –N(1)–Li(2)^{viii}	77.64(4)
Li(1)^{vi} –N(1)–Li(3)	72.72(4)
Li(1)^{vi} –N(1)–Li(3)^{viii}	90.59(3)
Li(1)^{vi} –N(1)–B	131.50(4)
Li(2)^{ii} –N(1)–Li(2)^{viii}	71.42(4)
Li(2)^{ii} –N(1)–Li(3)	113.33(4)
Li(2)^{ii} –N(1)–Li(3)^{viii}	75.41(4)
Li(2)^{ii} –N(1)–B	84.10(4)
Li(2)^{viii}–N(1)–Li(3)	73.11(4)
Li(2)^{viii}–N(1)–Li(3)^{viii}	95.54(4)
Li(2)^{viii}–N(1)–B	143.36(4)
Li(3) –N(1)–Li(3)^{viii}	161.31(3)
Li(3) –N(1)–B	93.19(3)
Li(3)^{viii}–N(1)–B	104.38(3)
Li(1)^{iii} –N(2)–Li(1)^{iv}	73.82(4)
Li(1)^{iii} –N(2)–Li(2)^{iii}	86.86(4)
Li(1)^{iii} –N(2)–Li(2)^{viii}	116.34(3)
Li(1)^{iii} –N(2)–Li(3)	81.06(4)
Li(1)^{iii} –N(2)–Li(3)^{ii}	75.09(4)
Li(1)^{iii} –N(2)–B	155.77(4)
Li(1)^{iv} –N(2)–Li(2)^{iii}	69.82(3)
Li(1)^{iv} –N(2)–Li(2)^{viii}	148.82(3)
Li(1)^{iv} –N(2)–Li(3)	144.56(3)
Li(1)^{iv} –N(2)–Li(3)^{ii}	88.51(3)
Li(1)^{iv} –N(2)–B	82.55(3)
Li(2)^{iii} –N(2)–Li(2)^{viii}	136.79(2)
Li(2)^{iii} –N(2)–Li(3)	84.36(4)
Li(2)^{iii} –N(2)–Li(3)^{ii}	155.02(4)
Li(2)^{iii} –N(2)–B	90.18(3)
Li(2)^{viii}–N(2)–Li(3)	65.60(3)
Li(2)^{viii}–N(2)–Li(3)^{ii}	67.83(3)
Li(2)^{viii}–N(2)–B	81.73(3)
Li(3) –N(2)–Li(3)^{ii}	108.92(4)
Li(3) –N(2)–B	122.55(3)
Li(3)^{ii} –N(2)–B	99.44(4)

Symmetry code

i	x	$\frac{1}{2} - y$	$z + \frac{1}{2}$	vi	$x - 1$	$\frac{1}{2} - y$	$z - \frac{1}{2}$
ii	x	$\frac{1}{2} - y$	$z - \frac{1}{2}$	vii	$1 - x$	$1 - y$	$1 - z$
iii	$x - 1$	y	z	viii	$1 - x$	$y + \frac{1}{2}$	$\frac{1}{2} - z$
iv	$x + 1$	$\frac{1}{2} - y$	$z - \frac{1}{2}$	ix	$1 - x$	$y - \frac{1}{2}$	$\frac{1}{2} - z$
v	$x + 1$	y	z	x	$1 - x$	$y - \frac{1}{2}$	$z + \frac{1}{2}$

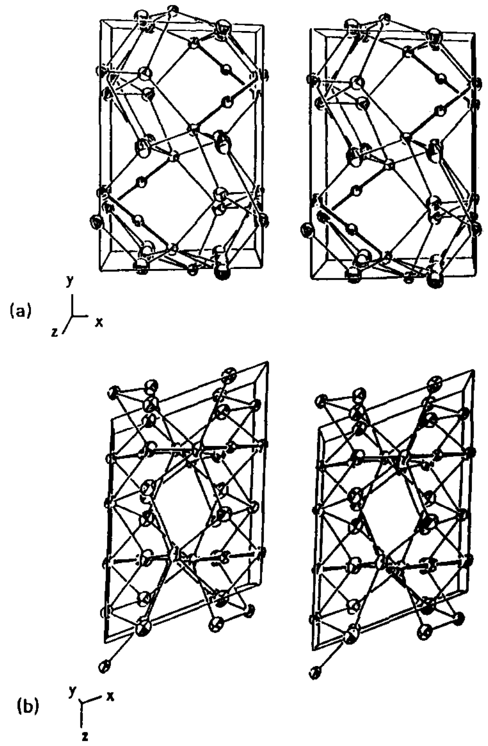

FIG. 1. Stereoscopic views down [001] (a) and [010] (b) of the Li_3BN_2 structure. The 70% probability thermal ellipsoids for all atoms are shown. No atoms are labeled, but straight N—B—N bonds are obvious because of their thicker bonds which denote covalent B—N bonds. Larger ellipsoids are Li(1) and Li(2).

to that of Li_3AlN_2. However, the crystal structure of the present Li_3BN_2 cannot be directly related to that of Li_3AlN_2 because of the linear N(1)—B—N(2) bond.

In hexagonal and cubic boron nitrides, the lengths of B—N bonds are 1.45 and 1.57 Å (*15, 16*). Those of B—N single bonds are in a range of 1.58–1.64 Å in $(CH_3)_3N—BX_3$ (X = F, Cl, I) molecules (*17, 18*). The distance of B—N bond is 1.45 Å in triangular coordination observed in $Ce_{15}B_8N_{25}$ structure (*19*). The reported lengths for B═N double bonds are 1.379 Å in $(CH_3)_2N═BCl_2$ and 1.42 Å in $(CH_3)_2N═B(CH_3)_2$ (*20, 21*). The B—N bond lengths in Li_3BN_2 are about 1.34 Å as shown in Table II. The values are a little shorter than those for the above-mentioned B═N double bond comparable to 1.333 Å for C═C double bond (*22*).

The fact that $[N═B═N]^{3-}$ is nearly linear is not surprising since it is isoelectronic with carbon dioxide. The slight distortion from a linearity is probably explained by interactions with cations in the solid state. $[N═B═N]^{3-}$ is surrounded by 12 Li^+ ions. Li—N—B angles are in a range of 73 ~ 156° as shown in Table II. The structure of the HBO_2 molecule in the vapor state has been determined by IR spectroscopy (*23*). The OBO group is linear and the H is off-axis. Similar structures have been found by electron diffraction for metaborates of lithium or sodium in the vapor phase (*24*). The $O═B—O^-$ group can be formally represented as linear $[O=B=O]^-$ group, isoelectronic with $[N═B═N]^{3-}$. The angles of <Li—O—B and <Na—O—B are 90 to 110° in vapor phase.

Figure 2 shows residual electron densities observed between nitrogen and boron atoms. We carried out difference-Fourier synthesis with coefficients $F_{obs} - F_{calcd}$, where F_{calcd} is a calculated structure factor with atomic parameters of Table I. The densities are around 0.5 e Å^{-3}. These values are equivalent to that of C═C double bond (*25*).

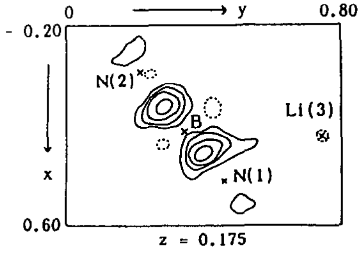

FIG. 2. Section at Z = 0.175 of the difference electron density in Li_3BN_2 synthesized using $F_{obs} - F_{calcd}$ as coefficients, where F_{calcd} is a structure factor computed with the coordinates shown in Table I. Contours begin at 0.1 e/Å^{-3}; intervals of 0.1 e/Å^{-3}; negative contours are shown as broken lines; zero contours are omitted.

The outer part of the density distribution between N(1)—B is elongated toward lithium ions as depicted in Fig. 2. B and N(1) are situated at $x = 0.22$ and $x = 0.43$, respectively. N(1)—B bond transverses a lithium atom plane of $x = 0.25$ parallel to (100). The elongations of bonding electron distributions between N(1) and B are due to electrostatic contributions of positive charge of lithium ions. This fact suggests that lithium atoms are present as cations in the crystal structure.

Lithium ion conductivity of the new polymorph of Li_3BN_2 was measured on a polycrystalline sample by the complex impedance method as a previous study (*2*). The conductivity was 4×10^{-5} S m^{-1} at 400 K and the activation energy for the ionic conduction was 64 kJ/mol. The value of conductivity was smaller by two order of magnitude than that of Li_3AlN_2 (1×10^{-3} S m^{-1} at 400 K), and the activation energy is higher than that of Li_3AlN_2 (52 kJ/mole) (*2*). The structure of Li_3AlN_2, which is derived from anti-fluorite, is basically composed of the closest packed nitrogen ions. Lithium ions can migrate through the opening of the anion packing. The unit cell volume of Li_3AlN_2 is 849.3 Å^3 and the number of formula weight (Z) equals 16 (*2, 14*). The volume of one formula weight is 57.02 Å^3 for Li_3BN_2. It is larger than the value of Li_3AlN_2 (53.08 Å^3), although boron is smaller than aluminum in ionic radius. In the more open structure of Li_3BN_2, linear $[N{=}B{=}N]^{3-}$ molecular ions are linked together by lithium ions which are in distorted tetrahedrons of nitrogen. Partial distortion or reorientation of linear $[N{=}B{=}N]^{3-}$ unit is required on the migration of lithium in Li_3BN_2. This might be a reason for the lower conductivity in comparison with Li_3AlN_2.

Acknowledgments

The authors would like to thank Dr. Y. Ito of Rigaku Denki Company Ltd. for his advice of camera work and data collections. We also thank Mr. T. Tanaka for operating the intensity collection system of MAC in ISIR. This research was partly supported by a grant from the research project in ISIR on development of new materials for energy and also by a grant from Casio Science Promotion Foundation.

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