

# Synthesis and Crystal Structure of $\text{Sr}_2\text{ZnN}_2$ and $\text{Ba}_2\text{ZnN}_2$

Hisanori Yamane<sup>1</sup> and Francis J. DiSalvo<sup>2</sup>

*Department of Chemistry, Cornell University, Ithaca, New York 14853*

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## EXPERIMENTAL

Ternary nitrides,  $\text{Sr}_2\text{ZnN}_2$  and  $\text{Ba}_2\text{ZnN}_2$ , were prepared from Sr or Ba along with Zn metal using Na metal and  $\text{NaN}_3$  as a flux and nitrogen source, respectively. The single crystals were obtained by slow cooling from 750°C. Since these compounds hydrolyze in moist air, the crystals were isolated by washing away excess Na with liquid  $\text{NH}_3$  in an inert environment. The structures were determined by single crystal X-ray diffraction: tetragonal, space group  $I 4/mmm$  with  $Z = 2$ ,  $a = 3.8568(2)$ ,  $c = 12.935(1)$  Å, and  $R 1 = 0.049$  for  $\text{Sr}_2\text{ZnN}_2$ , and  $a = 4.152(1)$ ,  $c = 13.055(3)$  Å, and  $R 1 = 0.039$  for  $\text{Ba}_2\text{ZnN}_2$ .  $\text{Sr}_2\text{ZnN}_2$  and  $\text{Ba}_2\text{ZnN}_2$  are isostructural with  $\text{Ca}_2\text{ZnN}_2$  ( $\text{Na}_2\text{HgO}_2$  type) and contain linear  $[\text{N}=\text{Zn}=\text{N}]^{4-}$  nitridometallate anions. © 1995

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## INTRODUCTION

It is difficult to grow single crystals of many nitrides because they dissociate well before they sublime or melt (1).  $\text{Li}_3\text{N}$ , having a relatively low melting point (813°C), is an exception (2, 3). Single crystals of ternary nitrides containing lithium, such as  $\text{Li}_3\text{FeN}_2$  (4),  $\text{Li}_7\text{TaN}_4$  (5), and  $\text{Li}_7\text{NbN}_4$  (6), have been synthesized using  $\text{Li}_3\text{N}$  as a flux. Although other alkali metals do not form binary nitrides, Jacobs and Hellmann obtained single crystals of  $\text{MNbN}_2$  ( $M = \text{Na}$  and  $\text{Cs}$ ) using alkali amides ( $\text{MNH}_2$ ) as a nitrogen source (7, 8). These crystals presumably grew in the melts of alkali metals which were derived from the decomposition of the alkali amides. In the sodium-barium-nitrogen system, Simon and co-workers found single crystals of subnitrides,  $\text{NaBa}_3\text{N}$  (9),  $\text{Na}_{16}\text{Ba}_6\text{N}$  (10),  $\text{Na}_5\text{Ba}_3\text{N}$ , and  $\text{Na}_{12}\text{Ba}_7\text{N}_3$  (11).

In the present paper, we describe the synthesis of  $\text{Sr}_2\text{ZnN}_2$  and  $\text{Ba}_2\text{ZnN}_2$  single crystals using Na as a flux and  $\text{NaN}_3$  as a nitrogen source.  $\text{NaN}_3$  decomposes to Na metal and  $\text{N}_2$  gas around 300°C (12).  $\text{Sr}_2\text{ZnN}_2$  (tetragonal,  $a = 3.85$ ,  $c = 12.86$  Å, space group:  $I 4/mmm$ ) was first prepared by Kniep (13). The preparation and crystal structure of  $\text{Ba}_2\text{ZnN}_2$  have not been reported previously.

<sup>1</sup> Current address: Institute for Materials Research, Tohoku University, Sendai 980-77, Japan.

<sup>2</sup> To whom correspondence should be addressed.

All manipulations were carried out in an Ar-filled glove box. The starting materials used were Sr (Strem Chemicals, 98% purity), Ba (Aldrich, 99% purity), Zn (Alfa Aesher, shot 1-3 mm, 99.9999% purity), Na (Strem Chemicals, 99.9% purity), and  $\text{NaN}_3$  (Aldrich, 99.9% purity). Sr 88 mg (1 mmole) or Ba 137 mg (1 mmole), and Na 32 mg (1.4 mmole),  $\text{NaN}_3$  40 mg (0.6 mmole), and Zn 33 mg (0.5 mmole) were sealed in an arc furnace under 1 atm of Ar in a Nb tube (8 mm diameter, 120 mm length), which in turn was sealed in an evacuated quartz tube. The starting materials were heated to 300-750°C for 1 hr and cooled with rates of 4.5-10°C/hr.

The products prepared in the Nb tube were washed with liquid  $\text{NH}_3$  to dissolve the Na flux. The washing was performed in a glass apparatus that allowed  $\text{NH}_3$  to be distilled on to the sample, then tipped to carry away Na in liquid ammonia. The ammonia could then be redistilled back onto the sample, leaving the excess Na behind. The washing process was repeated until the solution was colorless. Some small single crystals were removed for crystallographic studies. The remainder of the sample was powdered in an agate mortar and characterized by powder X-ray diffraction (Scintag XDS 2000) using  $\text{CuK}\alpha$  radiation. The metal ratio in the single crystals was analyzed by energy dispersive X-ray spectroscopy (EDX) on a scanning electron microscope (Jeol 733).

X-ray single-crystal diffraction photographs were taken for the crystals sealed in glass capillaries with a precession camera using  $\text{MoK}\alpha$  radiation. X-ray diffraction intensity data were collected with a four circle diffractometer using graphite-monochromated  $\text{MoK}\alpha$  radiation. Lattice parameters were obtained by least-squares refinement using reflection peaks in the range  $23^\circ < 2\theta < 30^\circ$ . Parameters of the data collections and crystallographic data are summarized in Table 1.

Absorption was corrected with an empirical correction program (XEMP) (14) using psi scan data. We adopted a lamellar model since the crystals of  $\text{Sr}_2\text{ZnN}_2$  and  $\text{Ba}_2\text{ZnN}_2$  used for intensity data measurements had flat shapes in which the (001) planes were largest. Better results were

TABLE 1  
Crystal Data and Structure Refinements for Sr<sub>2</sub>ZnN<sub>2</sub> and Ba<sub>2</sub>ZnN<sub>2</sub>

Empirical formula	Sr <sub>2</sub> ZnN <sub>2</sub>	Ba <sub>2</sub> ZnN <sub>2</sub>
Formula weight	268.63	368.07
Diffractometer type	Siemens P4	Syntex P3
Monochromator	graphite	graphite
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å (MoK $\alpha$ )	0.71073 Å (MoK $\alpha$ )
Crystal system	Tetragonal	Tetragonal
Space group	<i>I</i> 4/ <i>mmm</i> (No. 139)	<i>I</i> 4/ <i>mmm</i> (No. 139)
Unit cell dimensions	<i>a</i> = 3.8568(2) Å <i>c</i> = 12.935(1) Å	<i>a</i> = 4.152(1) Å <i>c</i> = 13.055(3) Å
Volume	192.43(2) Å <sup>3</sup>	225.06(9) Å <sup>3</sup>
<i>Z</i>	2	2
Density (calculated)	4.636 Mg/m <sup>3</sup>	5.431 Mg/m <sup>3</sup>
Absorption coefficient	33.57 mm <sup>-1</sup>	22.394 mm <sup>-1</sup>
<i>F</i> (000)	240	312
Crystal size	0.09 × 0.06 × 0.03 mm	0.15 × 0.30 × 0.58 mm
$\theta$ range for data collection	5.52° to 27.48°	3.12° to 27.57°
Index ranges	-5 ≤ <i>h</i> ≤ 5, 0 ≤ <i>k</i> ≤ 5, 0 ≤ <i>l</i> ≤ 16	0 ≤ <i>h</i> ≤ 5, 0 ≤ <i>k</i> ≤ 5, 0 ≤ <i>l</i> ≤ 16
Reflections collected	233	158
Independent reflections	87 ( <i>R</i> <sub>int</sub> = 0.0546)	100 ( <i>R</i> <sub>int</sub> = 0.0743)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	87/0/10	100/0/10
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.776	0.637
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	<i>R</i> 1 = 0.0298, <i>wR</i> 2 = 0.0910	<i>R</i> 1 = 0.0390, <i>wR</i> 2 = 0.1059
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0492, <i>wR</i> 2 = 0.1107	<i>R</i> 1 = 0.0390, <i>wR</i> 2 = 0.1059
Extinction coefficient	0.004(5)	0.055(9)
Largest diff. peak and hole	1.027 and -1.497 eÅ <sup>-3</sup>	3.079 and -4.637 eÅ <sup>-3</sup>

$$^a R 1 = \sum \|F_o\| - |F_c| / \sum |F_o|; wR 2 = [\sum w (|F_o^2 - F_c^2|)^2 / \sum (w F_o^2)^2]^{1/2}; w = 1/\sigma^2.$$

obtained with a higher "take-off angle" which removes high absorption reflections along the (001) plane. In order to minimize any bias by removing reflections, take-off angles of 5° and 3° were used in the structure refinements of Sr<sub>2</sub>ZnN<sub>2</sub> and Ba<sub>2</sub>ZnN<sub>2</sub>, which remove 3 of 90 and 2 of 102 independent reflections, respectively.

Refinement was performed using SHELXL-93 (15). Extinction corrections were carried out during the refinements. The analytical forms of scattering factors for neutral atoms, as well as corrections for both real and imaginary components of anomalous dispersion, were used as given in the SHELXL-93 software.

## RESULTS AND DISCUSSION

### Preparation

Single crystals were obtained by slow cooling from 750 to 300°C at rates of 4.5°C/hr (Sr<sub>2</sub>ZnN<sub>2</sub>) and 6.4°C/hr (Ba<sub>2</sub>ZnN<sub>2</sub>). Below 300°C, the samples were more rapidly cooled to room temperature by shutting off the furnace. The size of the single crystals was below 0.1 mm for Sr<sub>2</sub>ZnN<sub>2</sub>. On the other hand, single crystals with sizes of about 1–2 mm were obtained for Ba<sub>2</sub>ZnN<sub>2</sub>. Thin platy crystals (~0.5 × 0.5 × 0.1 mm) of Ba<sub>2</sub>ZnN<sub>2</sub> grew by heating

at 500°C and by cooling to 100°C at a rate of 6.4°C/hr. When the sample mixture was heated to 300°C for 1 hr and cooled again at 6.4°C/hr, the products consisted only of a mixture of polycrystalline Ba<sub>3</sub>N<sub>2</sub> and BaZn<sub>13</sub>. Only polycrystalline Sr<sub>2</sub>ZnN<sub>2</sub> could be prepared by slow cooling from 500°C.

The single crystals of Sr<sub>2</sub>ZnN<sub>2</sub> and Ba<sub>2</sub>ZnN<sub>2</sub> had a dark metallic luster. The color of the powdered samples was dark reddish brown. They were sensitive to moisture and hydrolyzed in air to form NH<sub>3</sub>. Semiquantitative EDX analysis showed that the Ba : Zn ratio in the Ba<sub>2</sub>ZnN<sub>2</sub> crystals was 2.1 : 1, which is close to the ideal ratio of 2 : 1.

TABLE 2  
Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å<sup>2</sup> × 10<sup>3</sup>) for Sr<sub>2</sub>ZnN<sub>2</sub>

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Sr	4 <i>e</i>	0	0	0.3409(1)	7(1)
Zn	2 <i>b</i>	0	0	0	9(1)
N	4 <i>e</i>	0	0	0.1449(12)	7(3)

Note. *U*<sub>eq</sub> is defined as one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

TABLE 3  
Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for Sr<sub>2</sub>ZnN<sub>2</sub>

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23} = U_{13} = U_{12}$
Sr	7(1)	7(1)	8(1)	0
Zn	10(2)	10(2)	6(2)	0
N	10(5)	16(5)	2(6)	0

Note. The anisotropic displacement factor exponent takes the form  $-\pi^2 [(h a^*)^2 U_{11} + \dots + 2h k a^* b^* U_{12}]$ .

Hubberstey (16) and Addison *et al.* (17) mentioned that alkali-earth metals in Na solutions enhanced the solubility of N<sub>2</sub> although the solubility of nitrogen in liquid sodium was extremely low ( $7.1 \times 10^{-9}$  mole% N at 600°C). They studied the nitrogen solubility in Na-rich Na–Ba solution since barium was particularly effective in rendering N<sub>2</sub> soluble. According to their measurements, the N:Ba molar ratio in the solution is about 1:4. We assume then that barium and strontium play an important role in introducing nitrogen into the melts during the crystal growth of Sr<sub>2</sub>ZnN<sub>2</sub> and Ba<sub>2</sub>ZnN<sub>2</sub>. However, in the case of Ca, crystals of Ca<sub>2</sub>ZnN<sub>2</sub> could not be obtained by this method. This suggests that calcium does not enhance the nitrogen solubility very much in comparison with barium or strontium. We also attempted to prepare crystals of Zn<sub>3</sub>N<sub>2</sub> under the same conditions as those used in the Ba<sub>2</sub>ZnN<sub>2</sub> single-crystal growth, but with no Ba in the melt. The product obtained was the binary intermetallic NaZn<sub>13</sub>, rather than a nitride.

### Crystal Structure

Precession photographs indicated tetragonal symmetry and showed a systematic extinction of  $h + k + l = 2n + 1$ . The structure refinements of Sr<sub>2</sub>ZnN<sub>2</sub> and Ba<sub>2</sub>ZnN<sub>2</sub> were performed with a Na<sub>2</sub>HgO<sub>2</sub>-type structure model (space group:  $I 4/mmm$ ) as was reported for Ca<sub>2</sub>ZnN<sub>2</sub> (18) and Sr<sub>2</sub>ZnN<sub>2</sub> (13). Final values of  $R$  1 for all data were 4.9% for Sr<sub>2</sub>ZnN<sub>2</sub> and 3.9% for Ba<sub>2</sub>ZnN<sub>2</sub>. Atomic positions and anisotropic displacement parameters are listed in Tables 2 and 3 for Sr<sub>2</sub>ZnN<sub>2</sub> and in Tables 4 and 5 for Ba<sub>2</sub>ZnN<sub>2</sub>.

TABLE 4  
Atomic Coordinates and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for Ba<sub>2</sub>ZnN<sub>2</sub>

Atom	Site	$x$	$y$	$z$	$U_{eq}$
Ba	4e	0	0	0.3443(1)	10(1)
Zn	2b	0	0	0	9(1)
N	4e	0	0	0.1411(11)	16(4)

Note.  $U_{eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

TABLE 5  
Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for Ba<sub>2</sub>ZnN<sub>2</sub>

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23} = U_{13} = U_{12}$
Ba	12(1)	12(1)	5(1)	0
Zn	12(1)	12(1)	3(2)	0
N	16(5)	16(5)	17(10)	0

Note. The anisotropic displacement factor exponent takes the form  $-\pi^2 [(h a^*)^2 U_{11} + \dots + 2h k a^* b^* U_{12}]$ .

Selected interatomic distances for Sr<sub>2</sub>ZnN<sub>2</sub> and Ba<sub>2</sub>ZnN<sub>2</sub> are summarized in Table 6.<sup>3</sup>

Figure 1 illustrates the structure of Sr<sub>2</sub>ZnN<sub>2</sub> and Ba<sub>2</sub>ZnN<sub>2</sub>. In the structure, a Zn atom is linearly coordinated by two nitrogen atoms to form a CO<sub>2</sub>-isosteric  $[\text{N} = \text{Zn} = \text{N}]^{4-}$  “dumb-bell.” The bond distances of Zn–N in Sr<sub>2</sub>ZnN<sub>2</sub> and Ba<sub>2</sub>ZnN<sub>2</sub> are almost equal to the Zn–N distance of 1.8418 Å in Ca<sub>2</sub>ZnN<sub>2</sub> (18) and the Fe–N distance (1.86(1) Å) of  $[\text{N} = \text{Fe} = \text{N}]^{4-}$  dumb-bells in Li<sub>4</sub>[FeN<sub>2</sub>] (19). Sr and Ba atoms are coordinated by five nitrogen atoms and are close to lying in the square plane of the nitrogen square pyramid (Fig. 1). The average of the Sr–N distances in Sr<sub>2</sub>ZnN<sub>2</sub> is consistent with the Sr–N distance of 2.6118(3) Å in Sr<sub>2</sub>N (20). The Ba–N distances in Ba<sub>2</sub>ZnN<sub>2</sub> are close to the Ba–N distances (2.77–3.04 Å) in Ba<sub>3</sub>[FeN<sub>3</sub>] where Ba atoms are coordinated by five nitrogen atoms (21). The Sr–Zn and Ba–Zn distances are comparable to those in SrZn<sub>5</sub> (3.25–3.92 Å) and BaZn<sub>5</sub> (3.40–3.89 Å) (22). The Ba–Ba distance agrees well with that in BaZn<sub>5</sub> (3.85 Å) and Ba<sub>3</sub>[FeN<sub>3</sub>] (3.82–3.92 Å). The

TABLE 6  
Selected Interatomic Distances (Å) for Sr<sub>2</sub>ZnN<sub>2</sub> and Ba<sub>2</sub>ZnN<sub>2</sub>

	Sr <sub>2</sub> ZnN <sub>2</sub>		Ba <sub>2</sub> ZnN <sub>2</sub>
N–Zn	1.874(15)	N–Zn	1.842(14)
N–Sr	2.536(15)	N–Ba	2.653(14)
N–Sr <sup>a</sup>	2.733(1)	N–Ba <sup>a</sup>	2.942(1)
Sr–Sr <sup>a</sup>	3.602(2)	Ba–Ba <sup>a</sup>	3.831(2)
Sr–Zn <sup>a</sup>	3.416(1)	Ba–Zn <sup>a</sup>	3.571(1)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms:  $x + 1/2, y + 1/2, -z + 1/2$ .

<sup>3</sup> See NAPS Document 05255 for 2 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P. O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 for up to 20 pages plus \$0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15.00. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, \$1.00 for each additional 10 pages of material, and \$1.50 for postage of any microfiche orders.

distance between Sr and Sr atoms in  $\text{Sr}_2\text{ZnN}_2$  is shorter than that in  $\text{SrZn}_5$  (4.02 Å) and  $\text{Sr}_2\text{N}$  (3.8566(1) Å), but are in the range of the Sr—Sr distances observed in  $\text{Sr}_3[\text{Al}_2\text{N}_4]$  (3.368–3.772 Å) (23).

As shown in Fig. 2, the crystal structure of  $\text{Sr}_2\text{ZnN}_2$  and  $\text{Ba}_2\text{ZnN}_2$  can also be viewed as a stacking of nitrogen-centered metal octahedra. The structure consists of Sr—Sr (or Ba—Ba) edge-sharing double octahedral layers linked by sharing of the apical zinc atoms.

$\text{Sr}_2\text{ZnN}_2$  and  $\text{Ba}_2\text{ZnN}_2$ , as well as  $\text{Ca}_2\text{ZnN}_2$ , have  $\text{Na}_2\text{HgO}_2$ -type structures. The +2 ionic radii of the alkali-earth atoms (Ca, Sr, Ba) increase from 1.00 to 1.35 Å (24). Oxides having  $\text{Na}_2\text{HgO}_2$ -type structures crystallize with  $M = \text{Li, Na, K, Rb, and Cs}$  (+1 ionic radius 0.76–1.67 Å) for  $\text{M}_2\text{HgO}_2$  (25), and with  $M = \text{K, Rb, and Cs}$  (1.38–1.67 Å) for  $\text{M}_2\text{NiO}_2$  (26). It is apparent that the important structural feature is the linear anion and that the structure easily adapts to a broad range of cation sizes.

To summarize, the single crystals of  $\text{Sr}_2\text{ZnN}_2$  and  $\text{Ba}_2\text{ZnN}_2$  were synthesized by slow cooling from 750 and from 500°C, respectively, using Na as a flux. Single-crystal X-ray diffraction analysis revealed that the structures of  $\text{Sr}_2\text{ZnN}_2$  and  $\text{Ba}_2\text{ZnN}_2$  were the same  $\text{Na}_2\text{HgO}_2$  type. We expect that the single crystals of other new ternary nitrides

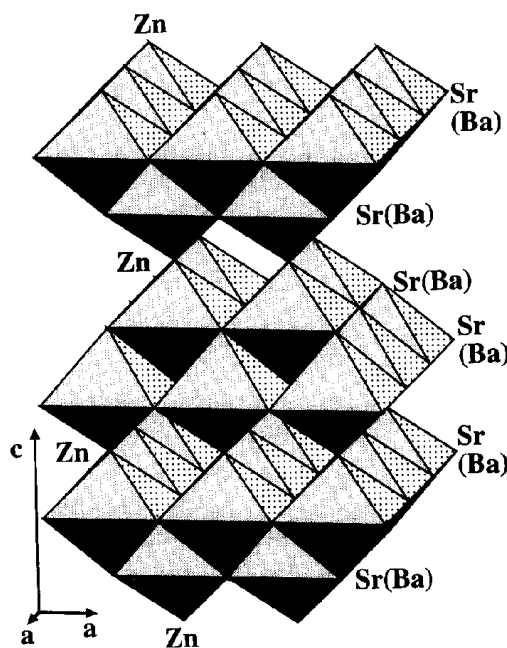


FIG. 2. Structure of  $\text{Sr}_2\text{ZnN}_2$  and  $\text{Ba}_2\text{ZnN}_2$  illustrated with nitrogen-centered edge and vertex-shared metal octahedra.

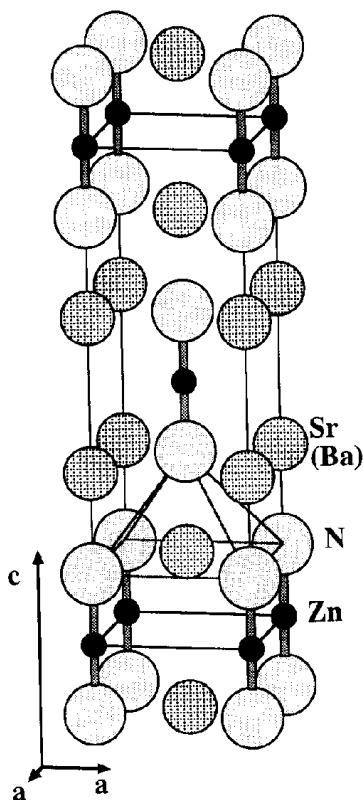


FIG. 1. Structure of  $\text{Sr}_2\text{ZnN}_2$  and  $\text{Ba}_2\text{ZnN}_2$  where the bonds in the  $[\text{N}=\text{Z}=\text{N}]^{4-}$  units are emphasized.

can be obtained using Na flux when a second alloying metal is used to solubilize N. We are testing main group metals other than Sr and Ba to see if similar behaviour is apparent.

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