



Contents lists available at ScienceDirect

## Progress in Solid State Chemistry

journal homepage: [www.elsevier.com/locate/pssc](http://www.elsevier.com/locate/pssc)

## Sodium flux synthesis of nitrides

Hisanori Yamane <sup>a,\*</sup>, Francis J. DiSalvo <sup>b</sup><sup>a</sup> Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Aoba-ku, Sendai, 980-8577, Japan<sup>b</sup> Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

## ARTICLE INFO

Article history:  
Available online xxx

Keywords:  
Nitrides  
Single crystals  
Sodium flux  
X-ray diffraction  
Zintl polyanions

## ABSTRACT

Studies of the synthesis of solid state nitrides using a Na flux are reviewed. The role and effect of Na is to solubilize polyatomic species containing nitrogen, and to lower the crystal growth temperature below the decomposition temperature of the obtained product(s). Many new ternary and quaternary nitrides have been synthesized in single crystal forms with sizes at least large enough (or larger) than is needed for structure analysis by X-ray diffraction. Isolated and extended anionic groups typically containing N and Si, Ge, Ga, and/or some transition metal elements are typical. These are usually surrounded by alkaline-earth atoms and are the most common of such nitrides. Compounds composed of nitridometallate anions and Zintl polyanions are also obtained. The structural features of each of these compounds are described.

© 2017 Elsevier Ltd. All rights reserved.

## Contents

1. Introduction .....	00
2. Na flux and crystal growth conditions .....	00
2.1. Solubility of nitrogen in Na .....	00
2.2. Formation of some binary nitrides .....	00
3. Na flux growth and crystal structures of ternary and multinary nitrides .....	00
3.1. Synthetic methods .....	00
3.2. Synthesis and crystal structures .....	00
4. Ternary and multinary compounds containing nitridometallate anions and Zintl polyanions .....	00
5. Conclusions .....	00
Acknowledgments .....	00
References .....	00

## 1. Introduction

The study of extended structure inorganic solid-state materials has expanded from the well-known oxides, sulfides, halides, etc. Most of these are stable in air at least under ambient conditions and include many minerals. There are also a growing and sizeable number of compounds that so far have only been synthesized under controlled laboratory conditions. The number of the constituent elements has also been extended from binary to ternary and to

multinary [1,2].

Nitrides are compounds in which N is formally anionic  $N^{3-}$ . In the case of solid state extended structure nitrides, some nitrides such as osbornite (TiN) [3], carlsbergite (CrN) [4], roaldite ((Fe,Ni)<sub>4</sub>N) [5], nierite (Si<sub>3</sub>N<sub>4</sub>) [6] and qingsongite (BN) [7], are found in the natural earth environment and meteorites. However, in many terrestrial compounds, N is found bound to C, O, H, etc, and usually in oxidation states higher than  $N^{3-}$ . These substances include nitrates, nitrites, etc. Interestingly, many novel nitrides and nitride-related compounds have been synthesized in the laboratory [8–36]. These include the simple binary nitrides, of compositions  $M_xN_y$ . Almost all of these binaries contain only M–N bonds, with

\* Corresponding author.

E-mail address: [yamane@tagen.tohoku.ac.jp](mailto:yamane@tagen.tohoku.ac.jp) (H. Yamane).

very few containing any residual N–N bonding, such as in pernitride,  $(\text{N}=\text{N}^{2-})$  [37,38]. Some of the nitrides are useful in a variety of applications (structural, electronic, optical etc.) [30,33,39–43]. In the studies of new compounds, crystal structure analysis is crucial and X-ray diffraction (XRD) techniques are widely applied. XRD structure analysis from single crystals is much easier than from powder or polycrystalline samples, especially when the unit cell dimensions are large and when the cell has high symmetry (which results in degenerate reflections of non-symmetry related d-spacings). The size of the single crystals required for common laboratory XRD measurements is several tens of micrometers up to perhaps a few tenths of millimeters.

$\text{Li}_3\text{N}$  and  $\text{Li}_3\text{BN}_2$  melt at 813 °C and 916 °C, respectively, under atmospheric pressure of nitrogen gas [44,45], and single crystals of these nitrides can be grown from their respective melt [46,47]. However, most nitrides sublime or decompose at high temperature, and melt growth of single crystals cannot be performed at ambient  $\text{N}_2$  pressure. For example, GaN decomposes above 900 °C under atmospheric pressure of  $\text{N}_2$ . Using a high-temperature high-pressure apparatus, the melting point of GaN has been reported to be 2220 °C. An  $\text{N}_2$  pressure of 6.0 GPa is needed to maintain a steady state of solid GaN in contact with liquid Ga–N [48].

The solution (flux) method is a widely used method of crystal growth. A suitable solvent/flux dissolves the desired product at one temperature and precipitates crystals of the same from the melt at another, usually cooler, temperature. Water is a common solvent for the growth of oxides, halides, etc. especially under hydrothermal conditions (modest temperature and pressures). Such aqueous conditions have been widely exploited. In contrast, virtually all nitrides are quite chemically unstable under aqueous conditions, especially under acidic or alkaline conditions, undergoing hydrolysis and forming  $\text{NH}_3$  or  $\text{NH}_4\text{OH}$ . Consequently, liquid ammonia and supercritical ammonia (ammonothermal) solvents were explored for single crystal growth of some nitrides [49–51]. In parallel developments, single crystals of a large number of intermetallic compounds have been grown in fluxes with low melting point metals [52]. Na metal has a low melting point of 98 °C. But Na has been little studied as a flux, since it is highly reactive with the moisture in air and water, and since many other metals, especially the transition metals, are not soluble in liquid Na.

Beginning with the early experiments of Juza and his coworkers on the synthesis of ternary nitrides, many ternary nitrides, in particular, those containing Li, have been synthesized [9,33]. The first ternary nitride containing Na recorded in the inorganic crystal structure data base (ICSD), is  $\text{NaGe}_2\text{N}_3$  reported by the group of Laurent in 1984 [53]. A polycrystalline sample of  $\text{NaGe}_2\text{N}_3$  was prepared by heating  $\text{Na}_2\text{GeO}_3$  at 750–820 °C in  $\text{NH}_3$ . The second report was on the synthesis of microcrystalline  $\text{NaTa}_2\text{N}_2$  by Jacobs and Pinkowski in 1989 [54]. They heated  $\text{Ta}_3\text{N}_5$  and  $\text{NaNH}_2$  at 400 °C in an autoclave.  $\text{NaTa}_2\text{N}_2$  was also prepared at ambient  $\text{NH}_3$  pressure by heating a mixture of  $\text{Ta}_3\text{N}_5$  and Na under flowing ammonia [55]. The mixture was first heated to 350 °C and Na reacted with ammonia gas, forming sodium amide, and then the temperature was raised to 500 °C to form  $\text{NaTa}_2\text{N}_2$  by reaction of  $\text{Ta}_3\text{N}_5$  and  $\text{NaNH}_2$ . Polycrystalline  $\text{Na}_3\text{WN}_3$  and  $\text{Na}_3\text{MoN}_3$  were also prepared with  $\text{W}_2\text{N}$  and  $\text{Mo}_2\text{N}$  and Na metal heated in  $\text{NH}_3$  flow via formation of  $\text{NaNH}_2$  [56]. The interactions of nitrogen dissolved in liquid sodium with metals and alloys for use in both fast reactors and fusion reactor systems were also investigated [57].

After the report of on the synthesis of microcrystalline  $\text{NaTa}_2\text{N}_2$  [54], single crystals of  $\text{NaNbN}_2$ ,  $\text{Na}_3\text{MoN}_3$ , and  $\text{Na}_3\text{WN}_3$  were obtained by reaction of NbN, Mo, and W with an excess  $\text{NaNH}_3$  at 450–900 °C in high-pressure autoclaves [58–60]. It was assumed that  $\text{NaNH}_3$  decomposes to  $\text{Na} + 1/2 \text{N}_2 + \text{H}_2$  during heating. The single crystals of these ternary nitrides would be grown in a Na

melt. Quaternary nitrides of alkali metals and tungsten, e.g.  $\text{Na}_2\text{KWN}_3$  [61],  $\text{Na}_5\text{RbW}_2\text{N}_6$  [62], and  $\text{Na}_5\text{CsW}_2\text{N}_6$  [62], were also prepared with excess  $\text{NaNH}_2$  and alkali metal amides ( $\text{ANH}_2$ : A = K, Rb, Cs). The hydrogen generated by thermal decomposition of the amides was released from the autoclaves through a Ni membrane and  $\text{N}_2$  pressure rose up to about 1 kbar. Single crystals of these nitrides were obtained with alkali metals from the excess amides. Rauch and Simon reported that needle-shaped black single crystals (>1 mm) of a subnitride,  $\text{NaBa}_3\text{N}$ , could be separated from the soft solidified “flux” of Ba and Na [63].

Since the earliest work on nitrides several decades ago, various new nitrides and nitrogen containing compounds have been synthesized in single crystal forms by using a melt of Na as a flux. The present paper reviews the single crystal synthesis of novel ternary and multinary nitrides and nitride-related compounds by the Na flux method and their crystal structures.

## 2. Na flux and crystal growth conditions

### 2.1. Solubility of nitrogen in Na

Na metal is a group I element, melts at 98 °C and boils at 883 °C [64]. While Na is quite reactive with  $\text{H}_2\text{O}$  and  $\text{O}_2$ , it does not react with  $\text{N}_2$  gas. Nonetheless,  $\text{Na}_3\text{N}$  can be prepared as a metastable phase by crystallization from the gas phase in plasma activated nitrogen [65]. Single crystals of  $\text{Na}_3\text{N}$  were isolated from the products prepared by the reaction of Na or a liquid Na–K alloy with plasma-activated nitrogen at low pressure [66].  $\text{Na}_3\text{N}$  decomposes above 104 °C with  $\Delta H$  at +64 kJ/mol [65,66]. In contrast, Li (melting point 180 °C, boiling point 1317 °C) reacts readily with  $\text{N}_2$  gas at room temperature to form  $\text{Li}_3\text{N}$  [67].

1.35 mol% of N can be dissolved in a Li melt at 346 °C, and it was determined that the solubility of nitrogen in Li is greater than that in Na by factors of approximately  $10^7$  [68]. Veleckis et al. measured the solubility of  $\text{N}_2$  in Na for the temperature range of 450–600 °C, and presented the following equation,

$$\log S = -7.18 - 2780 T^{-1},$$

where  $S$  is solubility in grams of nitrogen gas ( $\text{N}_2$ ) per gram of sodium,  $T$  is temperature in degrees Kelvin [69]. They carried out nitrogen isotope tracer experiment and showed that most of the nitrogen dissolved in the molecular form  $\text{N}_2$ . The solubility of  $\text{N}_2$  in Na measured at 450 °C was  $10 \times 10^{-12}$  g/g, which is converted into  $1.6 \times 10^{-9}$  at % of N in Na [69,70]. The solubility of nitrogen in sodium is extremely small, but the solubility increases dramatically with the addition of Ba. The solubility of N in a 4.24 or 4.4 mol% solution of Ba in sodium is 1.02 or 1.08 mol% at 300 °C [70,71]. The Ba:N ratio in the sodium melt was close to 4:1 which also persisted throughout precipitation of  $\text{Ba}_2\text{N}$  by addition of more nitrogen. The increase of the N solubility was attributed to a soluble barium-nitrogen species of ‘ $\text{Ba}_4\text{N}$ ’ which was assumed from the Ba:N ratio but the structure and bonding of the species in the solution has not been clarified [64,70,71].

In the process of single crystal growth of nitrogen containing compounds by the Na flux method, a second metal which can hold (solvate) N and form soluble species in the Na flux is usually necessary. In section 3, many N-containing ternary and multinary compounds prepared by the Na flux method are presented, and most of them contained the alkaline-earth elements Ca, Sr, and Ba. These elements increase the N concentration in the Na flux by forming soluble species. The driving force for nucleation and subsequent single crystal growth is supersaturation of the soluble species, which is usually attained by cooling, or by Na (solvent) evaporation, by  $\text{N}_2$  addition.

Download English Version:

<https://daneshyari.com/en/article/8961410>

Download Persian Version:

<https://daneshyari.com/article/8961410>

[Daneshyari.com](https://daneshyari.com)