Journal of Crystal Growth 621 (2023) 127381

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

On the solubility of boron nitride in supercritical ammonia-sodium solutions

Jacob Dooley [a], Nathan Stoddard [a], Kai Landskron [b], Siddha Pimputkar [a,*]

[a] Department of Materials Science and Engineering, Lehigh University, PA 18015 USA
[b] Department of Chemistry, Lehigh University Bethlehem, PA 18015 USA

ARTICLE INFO

Communicated by Matthias Bickermann

Keywords:
A1 Solubility
A2 Ammonothermal
B1 Nitrides
B1 Boron nitride
B2 Wide band gap semiconductor

ABSTRACT

Cubic boron nitride (cBN) is considered to be one of the leading candidates for next generation electronic devices yet has no current synthesis route for single crystals greater than a few mm in size leading to a lack of suitable substrates. New synthesis methods need to be explored, with the ammonothermal method being a potential candidate for synthesis of large area, thick cBN and hexagonal BN (hBN) single crystals. This paper investigates the solubility of BN in supercritical ammonia using sodium amide ($NaNH_2$) as a mineralizer and cBN crystals as feedstock. Solubilities were measured based on mass loss of the feedstock at temperatures from 450—600 deg. C, with pressures of 150–190 MPa, using durations from 24—96 h and with varying amounts of Na. A positive solubility trend is demonstrated with respect to temperature with solubility varying from 0.017—0.050% mol_{BN}/mol_{NH3}. Solubilities did not vary as a function of time or when>0.07 mol_{Na}/L mineralizer content was used suggesting both that equilibrium was reached and the solutions were saturated. These values are high enough to motivate further investigation for solution-based growth of BN.

1. Introduction

Wide bandgap semiconductors are an important class of materials for developing higher efficiency power electronics used in communications, energy conversion and power transmission. [1] In determining the best material for these applications there are several combinatory metrics for critical electronic material properties used to compare different semiconducting materials. Two of the principal figures of merit (FOM) are the Baliga FOM and Johnson FOM. The Baliga FOM combines electronic bandgap, electron mobility, and relative dielectric constant to predict device power efficiency, whereas the Johnson FOM, used to quantify high frequency performance, simply multiplies saturation velocity and breakdown electric field.

In the current field of (ultra-)wide bandgap semiconductors that can be grown to large single crystals (i.e. > 5 cm diameter), these FOMs have been used to justify pursuing GaN as a desirable material for electronic applications, having Baliga and Johnson FOMs over 20 times higher than Silicon. [2] Other materials have been identified that have potentially superior power efficiency and high frequency performance, but face technological barriers. One of the materials of highest interest is cubic boron nitride (cBN). This material has promising mechanical, thermal, electrical, and optical applications, with estimated Baliga and Johnson FOMs 3.3 and 2.4, respectively, times higher than GaN.[3] However, a lack of a demonstrated scalable synthesis process for growing wafer-scale bulk single crystals acts as a significant barrier. [4].

Within the BN material family there are several allotropes that exist with the most readily and commonly synthesized allotrope being the hexagonal phase (hBN). Thermodynamically, cBN has been determined to be the stable phase at temperatures below ~ 1700 K at 1 atm in an oxygen-free environment. [5] In the absence of a native seed crystal, synthesis proceeds with the formation of a small nucleus and at this length scale, computational studies suggest that the hexagonal allotrope becomes thermodynamically more stable and high pressures (>1 GPa) are required to stabilize the cubic phase at this length scale. [6] This has led to high pressure high temperature (HPHT) anvil systems being the dominant method for production of cBN. [7,8] While critical to demonstrating the extreme material properties of cBN [9], the method lacks a clear path to scalability and controlled, well-formed, continuous growth from a seed crystal without parasitic, spontaneous nucleation and growth. [5,10,11] As with many other nitrides, and especially Group III nitrides, melting of the material can only be achieved under extreme, typically unattainable, pressures, leading the field to look for

* Corresponding author.
E-mail address: sip516@lehigh.edu (S. Pimputkar).

https://doi.org/10.1016/j.jcrysgro.2023.127381
Received 24 June 2023; Received in revised form 28 July 2023; Accepted 30 July 2023
Available online 31 July 2023

alternative pathways involving dissolution of the material into another medium and precipitating the material therefrom (solution growth). [12] This has been successfully demonstrated for a few nitrides, with gallium nitride (GaN) having received the greatest attention thus far leading to successful demonstrations of > 2-inch diameter boules when using the ammonothermal method. [13–16] The ammonothermal method is a solvothermal process for which supercritical ammonia is the solvent and a nitride-forming cation is the solute. [14-19] Additional materials, termed mineralizers, are added to the system to aid in promoting the precursor into solution via chemical intermediate formation. [17–19].

Application of the ammonothermal method to synthesis of BN is limited with only one report found in literature demonstrating the conversion of hBN into rhombohedral BN (rBN) using barium and magnesium nitrides as mineralizers in an isothermal system. [20] They speculated, based on their results, that dissolution of hBN into solution occurred, though did not further investigate.

The successful application of the ammonothermal method to grow larger crystals requires both a solubility gradient within the autoclave between the zone containing the feedstock and the zone of the seed crystal as well as continuous mass transport between the two zones. Literature does not currently describe the solubility of BN in supercritical ammonia solutions—a prerequisite for properly configuring a system for crystal growth.

The solubility of BN in pure ammonia is expected to be negligibly small, but alkalis and halides have been widely used as solubility-enhancing mineralizers in ammonothermal processes. [14] Sodium (Na) is known to react with ammonia to form sodium amide ($NaNH_2$), a soluble specie in supercritical ammonia. Based on studies of other ammonothermal nitrides, it is plausible that sodium amide will react with the BN to form an intermediate chemical specie that is orders of magnitude more soluble in the ammonia than BN in pure ammonia. [21].

This study is a first effort to map out the process space for Na-enabled BN dissolution in an ammonothermal environment with respect to temperature, time, and mineralizer amount. The procedure and experimental conditions of this study were informed by previous studies of the solubility of GaN when $NaNH_2$ was used as the mineralizer. [21] Establishing a usable solubility gradient opens the door to attempts at single crystal bulk growth for BN.

2. Methods and materials

2.1. Materials and autoclave

To achieve the target temperature ranges of 400–600 °C and pressures of 150–200 MPa, Ni-Cr superalloy autoclaves with an inner diameter of 25 mm and internal free volume of 150 mL were used. The autoclave systems used in this study are identical to those used in previous ammonothermal studies and details can be found in [22].

Materials for this study included ammonia (99.99994% semiconductor grade NH_3, from Airgas), cBN (99.99% pure, 50 mesh crystals, from MSE supplies), and Na metal (99.8% pure, cubes coated with mineral oil, from Fisher Scientific).

In addition to the Ni-Cr alloy autoclave walls, other wetted materials include pure nickel and molybdenum.

2.2. Procedure

The procedure used to load an autoclave is as follows. All the autoclave and internal components were removed from an oven and placed inside a nitrogen-atmosphere MBRAUN glovebox. Oxygen gas and water vapor were monitored and continuously maintained at levels less than 5 ppm.

While in the glovebox, the six surfaces of the Na cubes were shaved to remove any surface oxides and other contaminants. Na and cBN masses were measured on a A&D GX-324A mass balance (measurement error +/- 0.1 mg). Prior to and after weighing the masses, a calibration weight was used to measure the error of the system. The cBN feedstock was placed within a molybdenum (Mo) crucible and covered with a 100 mesh nickel (Ni) wire cloth. The Na was dropped to the bottom of the autoclave body, followed by placement of a Ni stand in the autoclave and the cBN-containing crucible on top of that. The final position of the crucible was approximately mid-height of the autoclave. The autoclave was then closed, sealed, and removed from the glove box.

Ammonia is added to the system through the needle valve (see Fig. 1 for details). The autoclave was cooled using liquid nitrogen and gaseous ammonia was flown into the autoclave and condensed until the desired density of ammonia was obtained (17.7–24.6 mol/L). Verification of the ammonia fill occurred via feedback from a mass flow controller (Bronkhorst 201CM-2, measurement accuracy of +/- 0.2 slm), and via a mass measurement of the autoclave assembly before and after filling using a Hogentogler MC-30KS scale (measurement accuracy +/- 1.5 g). A calibration weight was used to determine the offset/drift of the scale prior to and after measurement of the autoclave.

The fully loaded autoclave was then placed within a resistive heater stack. The temperature of the external walls of the autoclave was measured longitudinally on two opposing sides of the autoclave using Type-K thermocouples (TCs) with special limits of error (SLE) (Omega Engineering, greater value of +/- 1.1 °C absolute error or 0.4% relative error). The internal fluid pressure was monitored using a Honeywell BP521EP pressure transducer (measurement accuracy +/- 1.8 MPa). Further details of the heater setup and design can also be found in [22]. A schematic of the entire experimental setup is presented in Fig. 1.

The run commenced by initiating and controlling the heater temperature using a PID controller and monitoring the total system pressure to verify leak-tightness of the system and verify target pressures were reached. Upon conclusion of the run (after holding the autoclave at the dwell temperature for the specified time ranging from 24—96 h) the autoclaves were allowed to naturally cool back to room temperature over the course of 6–8 h.

The gases in the autoclave (ammonia, nitrogen, hydrogen) were exhausted and the mass of the autoclave was measured using the same procedure. The autoclave was opened under ambient conditions and the mesh-covered crucible was removed in a fume hood. The remaining cBN was emptied into a filter paper-lined funnel through which it is rinsed with water multiple times. The autoclave and all of the internal components were cleaned using deionized water/ isopropyl alcohol mixtures to safely dissolve the residual sodium amide formed during the experiment and the waste stream was run through a filter and inspected for any residual cBN. Across all experiments the only deposits observed were a uniform white powder that had a volatile reaction with water, forming a

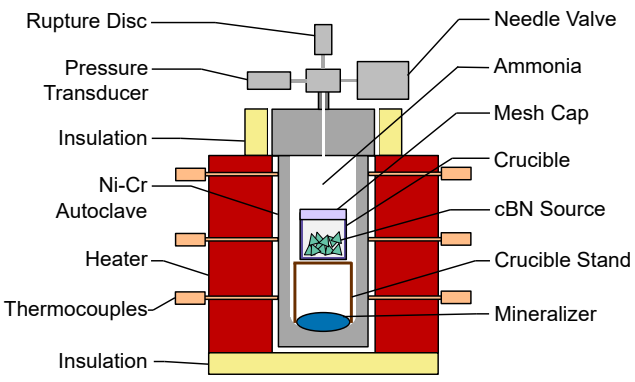

Fig. 1. Autoclave design used for all ammonothermal experiments in this study. Identified external components are the rupture disc, pressure transducer, needle valve, thermal insulation, the Ni-Cr autoclave, the ceramic heaters, type-K thermocouples. Identified internal components are the ammonia, the crucible mesh cap, the crucible, cBN source, the crucible stand, and the mineralizer.

basic solution. This was treated as $NaNH_2$. Due to volatility, it was not characterized as part of this study. No unique, unreacted deposits of BN were observed during any cleaning step of the autoclaves. As a final cleaning step the autoclaves and internal components were sonicated in deionized water. All autoclave and internal components were then placed in an oven and dried.

The cBN was dried on the filter paper in a vacuum oven and then transferred to a clean container. The mass of the cBN was measured using the same scale from the loading procedure and the same calibration weight procedure was used to correct for any long-term drift errors. The mass loss from the remaining cBN materials in the autoclave were considered the amount of cBN that went into solution and reacted with the mineralizer.

2.3. Experimental study parameter space

This study investigates how autoclave temperature, dwell time at peak temperature, and Na density (i.e. the mass of sodium divided into the autoclave free volume) affects the solubility of BN in a supercritical ammonia-Na solution. Concerning the sodium density, it was not possible to measure exactly how much sodium was transformed to sodium amide nor how much sodium amide was dissolved in the ammonia. Therefore, for the purposes of the experiment, sodium density is the known value that can be reported in the attempt to vary mineralizer quantity, while further studies will be needed to assess the variation of actual dissolved mineralizer. The experimental parameters that were chosen for each of these studies are summarized in Table 1.

3. Results

Measured outputs from a total of 19 individual ammonothermal runs are presented in Fig. 2, Fig. 3, and Fig. 4. The BN solubility, normalized as the ratio of BN molar loss relative to the initial molar ammonia fill amount, is plotted in relationship to changes in temperature, experimental duration, and dwell time. Each data point represents a single autoclave run with a callout indicating the peak pressure of the autoclave in MPa achieved at the end of the run, just prior to cooling of the autoclave. Error bars represent the total of estimated and known measurement errors.

3.1. Solubility dependency on temperature

Fig. 2 summarizes 12 runs with the solubility measured at temperatures ranging from 450 °C to 600 °C in 50 °C intervals. The dwell time of 48 h and a 0.13 mol/L density were held constant for all runs. To target similar peak pressure the fill densities at each temperature (450, 500, 550, and 600 °C) were 24.6, 22.8, 20.8, and 17.7 mol/L, respectively.

Table 1
Targeted experimental parameters for each of the BN-solubility studies that compare the BN solubility at different temperatures, Na densities, and autoclave dwell times.

Study	Ammonia Fill (mol/L)	Na Fill (mol/L)	cBN Feedstock (mol)	Temperature (°C)	Dwell Time (hr)
Temperature	24.6, 22.8, 20.8, 17.7	0.13	0.20	450, 500, 550, 600	48
Dwell Time	22.8	0.13	0.20	500	24, 48, 96
Na Density	22.8	0.00, 0.07, 0.13, 0.27, 0.53	0.20	500	48

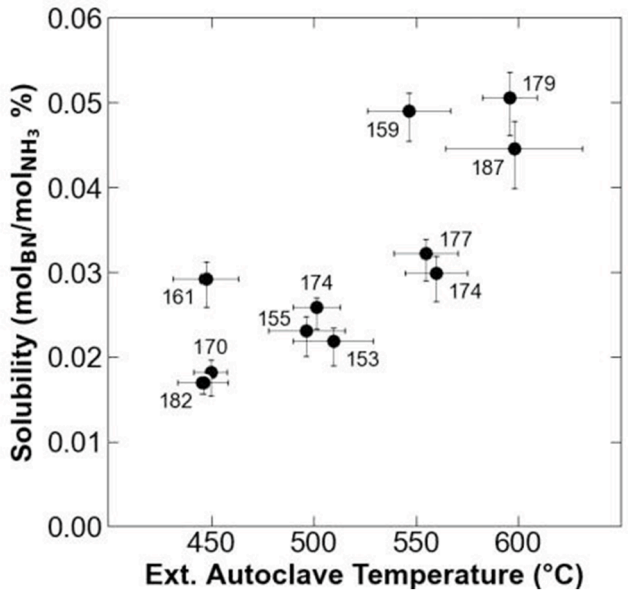

Fig. 2. Measured solubility of BN normalized to the quantity of ammonia in the system as a function of the external (ext.) autoclave temperature. Each data point is labeled with the maximum pressure in MPa reached during the run. All runs had a hold duration of 48 h at the target temperature and had 0.13 mol/L of added Na to the autoclave.

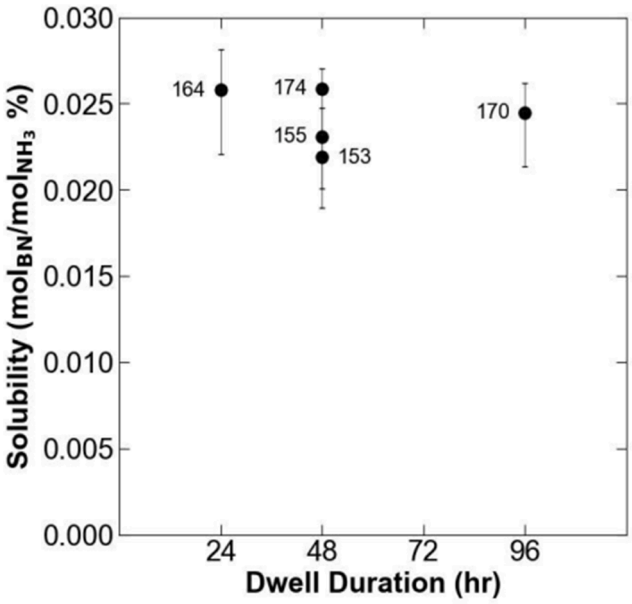

Fig. 3. Measured solubility of BN normalized to molar quantity of ammonia as a function of time of dwell at temperature. The temperature for all data points was 500 °C and the Na density was 0.13 mol/L. The pressures in MPa are labeled next to the data points.

3.2. Solubility dependency on dwell time

The dwell duration time is presented as the independent variable in Fig. 3. With times ranging from 24—96 h, the temperatures was held at 500 °C, ammonia fill and density was fixed at 22.8 mol/L and 0.13 mol/L, respectively.

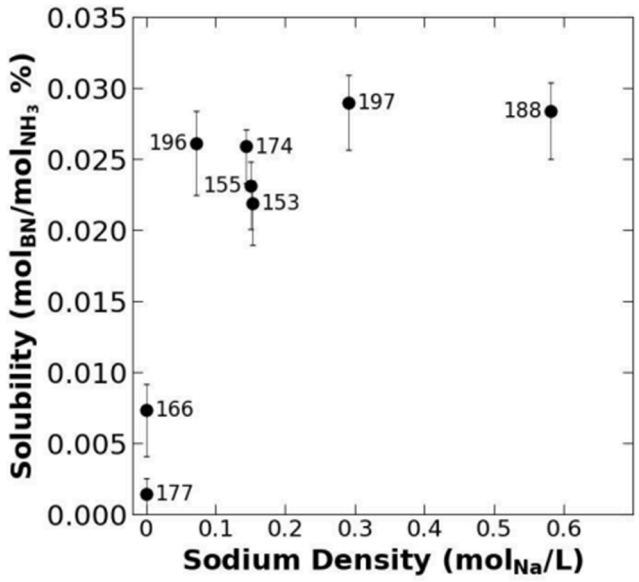

Fig. 4. Measured solubility of BN normalized to molar quantity of ammonia as a function of Na density in the system. The dwell temperature for all data points was 500 °C and dwell time was 48 h. The pressures in MPa are labeled next to the data points.

3.3. Solubility dependency on Na density

In Fig. 4, data from 8 individual ammonothermal experiments is presented. Dwell temperature was held constant at 500 °C, with an ammonia fill density at 22.8 mol/L, and dwell time of 48 h for all cases. Na content in the autoclave varied from 0.0 to 0.6 mol/L.

4. Discussion

4.1. Overall observations

Collectively, the data clearly demonstrates a consistent mass loss of cBN feedstock and hence solubility in a solution of supercritical ammonia and Na. With each Na-containing experiment, regardless of conditions, there was a measured mass loss of the supplied BN that resulted from the exposure to the soluble ammonothermal environment. This is reasonably consistent with previous ammonothermal results for other group III nitrides, specifically GaN. [21].

While there is an initial understanding of the thermodynamic equilibrium state of a pure ammonia system under these operating conditions, the actual amount of ammonia present in the Na-NH_3 system during the run could not be determined as it was still evolving and the impact of Na to the total system pressure has yet to been clarified. [23] As such, no correction to the data was performed for the actual amount of ammonia present in the system at temperature and fill densities were used instead.

It should be noted that while external wall temperatures are reported, it has been established that the internal fluid temperature is typically lower (due to heat sinking from the ends of the autoclave) and actual fluid temperatures vary; in comparable systems these temperature differences were measured to be lower by up to 80 °C. [22 23,24] For these experiments, the temperature profile was consistent in shape with the body measuring a linear profile from the bottom up until the top ~ 15% of the heated/internal fluid exposed autoclave portion. In the upper portion the temperature, the external wall temperature of the autoclave body dropped by a few tens of degrees (typically less than 50 °C) due to heatsinking from the unheated nozzle and head assembly. TCs were positioned in pairs and in the same elevation on opposite poles in the radial direction of the autoclave body. Temperature variations between two TC pairs was typically less than 15 °C, though increased slightly on higher temperature runs. Significant outliers to the commonly observed spread can be attributed to poor contact between the TC and the autoclave body. Slight changes in, for example, the autoclave centering alignment or the quality of contact of the heater control TCs can affect the actual autoclave temperature, giving rise to systematic, minor deviations in temperature between runs. The data points in Fig. 2 report the average autoclave temperature along the measured profile with a horizontal error bar representing the standard deviation of all TC measurements excluding outliers>50 °C which can confidently be attributed to poor contact and hence not actually measuring the autoclave temperature.

Each data point plotted in the figures is labeled with the peak pressure that the autoclave achieved during the experiment. This pressure varies in a range from 153 MPa to 197 MPa, with some pressure variations for autoclaves that had the same nominal amount of BN, Na, ammonia and temperature. These pressure differences can be attributed to small differences in the autoclave average temperature, a differing rate of decomposition of ammonia to nitrogen and hydrogen gas depending on slight differences in the initial autoclave state, and catalytically active sites, but there does not appear to be a discernible trend in pressure within this window. There was no evidence of leaks in any of the ammonothermal runs presented in this study.

One potential source of error in the measurements relates to the lack of removal of the solution while hot and allowing the system to cool to room temperature, thereby allowing for redeposition of the dissolved BN as it proceeds into a lower solubility regime. This error would show up as an *under*estimation of the solubility as the redeposition of the BN material can occur on the source material. Given that the amount of surface area of cBN feedstock to all other internal wetted surfaces is less than 1% and that the autoclave cools at a rapid rate (~300 K/h) relative to the experiment duration, it can be speculated that the large majority of BN in solution would precipitate elsewhere in the autoclave. It can be concluded that this error is minor and will not significantly affect the results of the study.

While exceptional care was taken to ensure complete retention of any small cBN crystallites in the system outside the crucible, it cannot be guaranteed and an estimated uncertainty was added relative to the largest amount one could conceivable not capture in the filters without noticing it, thereby contributing to an *over*estimation of the solubility.

When comparing unused cBN crystals with those that have been through the process a few times, features observed in an electron microscope were observed consistent with both surface erosion of the crystals in the solution and some areas of redeposition of small islands, platelets and clusters. These behaviors are consistent with the measured mass loss and the presence of dissolved boron nitride in the system coming out of solution quickly during the rapid cool-down.

4.2. Temperature effect on solubility

A positive correlation is evident between the BN solubility and the temperature of supercritical ammonia with solubilities in the range of 0.017–0.050% mol$_{BN}$/mol$_{NH3}$. The level of solubility is low, but significantly above the estimated error bars in the measurements with reasonable consistency in repeated runs at the same conditions.

The biggest exception to this consistency is one data point at 550 °C and another at 450 °C that each have much higher solubility than the other points within 50 °C. On examination of the pressure traces and the post-run autoclave there was nothing to suggest a difference in environment that would affect the solubility to this degree. There potentially could have been chemical sinking of the boron in the autoclave or $NaNH_2$ resulting in larger mass differences, but the equipment was consistent throughout all of the experiments. Despite the two noisy data points, there is still a strong argument for positive temperature dependent solubility.

Comparing this solubility data to a previous study of GaN

ammonothermal solubility reported that used similar chemistry, equipment, and experimental processes, both the GaN and BN system demonstrate a similar degree of solubility, with the highest solubility GaN conditions being only double the highest measured solubility of BN. [21] An interesting comparison is that the BN data seems to have a more well-defined relationship between solubility and temperature. Ranging between 0.017 and 0.050% mol_{BN}/mol_{NH3} the solubilities are low relative to the total nitride, but as demonstrated with GaN even a low solubility can result in significant ammonothermal growth rates of 30–200 μm/day. [15,25].

4.3. Time effect on solubility

For dwell time there is no discernible time relationship, shown in Fig. 3. Whatever dissolution is occurring happens within the first 24 h and stops once the solubility limit is reached. The range of solubilities is relatively narrow, varying from 0.022—0.026% mol_{BN}/mol_{NH3} offering good confidence in the data.

Some conclusions can be drawn about the kinetics of the system. First, since the amount of BN loss is constant from 24—96 h without any discernable trend, there are evidently no significant boron chemical sinks within the autoclave, unlike the case for GaN. Were the autoclave walls, the internal crucible stand, monitoring devices, or crucible composed such that dissolved boron transported to those regions and reacted there to form a solid compound there would be a net driving force to dissolve more BN into solution to replenish the sunken BN, thereby increasing the apparent solubility of BN into solution. This is not the case, so it can be concluded that the measured mass loss likely corresponds closely to the dissolved BN at saturation.

Second, the constant behavior with time indicates that the dissolution process is not kinetically limited by the availability of feedstock in the crucible or the relatively small surface-to-volume ratio of the cBN feedstock. If available surface area were the limitation, then we would expect to see a slow rise in dissolved material over time. Since this is not the case, both the form factor of the feedstock and the exposure of the feedstock in the mesh-covered crucible to naturally convecting ammonia are evidently sufficient to reach the solubility limit within the first 24 h.

4.4. Na density effect on solubility

For variations in Na density there is a remarkably flat and consistent behavior in the data, shown in Fig. 4. In a conventional system, it is a fair assumption that by adding more of a reactant (Na) there will be a corresponding increase in dissolved species (soluble BN intermediate), at least to within some range. That is not what is being observed here.

To verify that $NaNH_2$ was required for dissolution of BN and was actively participating in the reaction, two runs were performed back-to-back in the same autoclave without any deliberate addition of Na to the system. The measured solubility data points were significantly lower than those in which Na was deliberately added to the system. The second solubility measurement point was lower (possibly zero to within the error of the measurements) as compared to the first solubility point for the Na-free runs, suggesting that it is possible that the autoclaves could have had minor residual traces of Na compounds in them from prior runs and the cleaning procedure did not completely remove it. This result demonstrates that not only is $NaNH_2$ critical to ammonothermal BN solubility, but also that the threshold amount of required $NaNH_2$ to influence solubility is lower than the amount of $NaNH_2$ used in any of the experiments with intentional Na additive in this study.

Combining this observation with the lack of increase in BN solubility relative to increased added amounts of Na suggests the solution reaches its $NaNH_2$ saturation limit using only a small amount of Na. Further evidence to back this hypothesis is that for experiments performed with excess amounts of Na in the system, the bottom of the stands used to hold the crucible had a distinctly different coloration along the length of the stand legs when compared to areas further up the stand. This would suggest that the lower portion of the legs were submersed in a molten bath of sodium amide, preventing equivalent exposure to the nitriding environment, leading to differences in surface nitridation which would then appear as differences in surface coloration. The presence of a sodium amide pool at the bottom of the autoclave that increases with increasing amounts of Na metal in the system would explain the insensitivity of BN solubility to increasing amounts of added Na.

5. Conclusion

In this work the Na-assisted ammonia solubility of BN was explored, utilizing the ammonothermal technique. The process space was mapped using temperatures ranging from 450—600 °C, and times from 24—96 h under supercritical ammonia pressures above 150 MPa. Solubility was also measured as a function of Na added to the autoclave.

It was demonstrated that increases in the temperature of the ammonothermal solution were positively correlated with the amount of BN dissolved into solution in the range from 450—600 °C. Absolute solubility ranged between 0.017 and 0.050% mol_{BN}/mol_{NH3}. Full solubility was achieved within 24 h and no further dissolution was measured up to 96 h, while Na additions of 0.08 mol/L were sufficient to achieve maximum solubility and a nominally Na-free ammonothermal system was shown to have nearly zero solubility.

The levels of BN solubility represent a promising first milestone in a potential pathway towards crystal growth. More study is called for, and the GaN process development history points to the need to investigate different mineralizing agents (including halides) as well as a wider range of temperatures and pressures in order to maximize the useful solubility gradient.

CRediT authorship contribution statement

Jacob Dooley: Conceptualization, Writing – original draft, Methodology, Investigation. **Nathan Stoddard:** Conceptualization, Writing – review & editing, Methodology, Investigation. **Kai Landskron:** Conceptualization, Funding acquisition, Supervision. **Siddha Pimputkar:** Conceptualization, Writing – review & editing, Project administration, Funding acquisition, Methodology, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors acknowledge the support from NSF under Award No. 1832824 and S.P.&N.S. also acknowledge the Lehigh New Faculty Startup Funds. Additionally, the authors wish to acknowledge Itzel Esparza for her assistance in graphically representing the data.

References

[1] J.Y. Tsao, et al., Ultrawide-Bandgap Semiconductors: Research Opportunities and Challenges, Adv. Electron. Mater. 4 (1) (Jan. 2018) 1600501, https://doi.org/10.1002/AELM.201600501.

[2] H. Amano, et al., The 2018 GaN power electronics roadmap, J. Phys. D Appl. Phys. 51 (16) (Apr. 2018), 163001, https://doi.org/10.1088/1361-6463/aaaf9d.

[3] J. Chilleri, P. Siddiqua, M.S. Shur, S.K. O'Leary, Cubic boron nitride as a material for future electron device applications: A comparative analysis, Appl. Phys. Lett. 120 (12) (Mar. 2022), https://doi.org/10.1063/5.0084360.

[4] X. Zhang, J. Meng, Recent progress of boron nitrides. (2019), https://doi.org/10.1016/b978-0-12-815468-7.00004-4.
[5] V.Z. Turkevich, Phase diagrams and synthesis of cubic boron nitride, J. Phys. Condens. Matter 14 (44) (Nov. 2002) 10963–10968, https://doi.org/10.1088/0953-8984/14/44/410.
[6] X. F. Guo, B. Xu, W. Zhang, M. Z. Lv, H. M. Yang, and X. H. Fan, "Thermodynamic Analysis about Nucleation and Growth of Cubic Boron Nitride Crystals in the hBN-Li3N System under High Pressure and High Temperature," *Entropy 2015, Vol. 17, Pages 755-762*, vol. 17, no. 2, pp. 755–762, Feb. 2015, doi: 10.3390/E17020755.
[7] O.O. Kurakevych, V.L. Solozhenko, High-pressure design of advanced bn-based materials, Molecules 21 (10) (2016) 1–16, https://doi.org/10.3390/molecules21101399.
[8] T. Taniguchi, S. Yamaoka, Spontaneous nucleation of cubic boron nitride single crystal by temperature gradient method under high pressure, J. Cryst. Growth 222 (3) (Jan. 2001) 549–557, https://doi.org/10.1016/S0022-0248(00)00907-6.
[9] T. Taniguchi, S. Koizumi, K. Watanabe, I. Sakaguchi, T. Sekiguchi, S. Yamaoka, High pressure synthesis of UV-light emitting cubic boron nitride single crystals, Diam. Relat. Mater. 12 (3–7) (2003) 1098–1102, https://doi.org/10.1016/S0925-9635(02)00330-8.
[10] A.E. Naclerio, P.R. Kidambi, A Review of Scalable Hexagonal Boron Nitride (h-BN) Synthesis for Present and Future Applications, Adv. Mater. 35 (6) (2023) 1–38, https://doi.org/10.1002/adma.202207374.
[11] T. Taniguchi, K. Watanabe, Synthesis of high-purity boron nitride single crystals under high pressure by using Ba–BN solvent, J. Cryst. Growth 303 (2) (May 2007) 525–529, https://doi.org/10.1016/J.JCRYSGRO.2006.12.061.
[12] O. Ambacher, Growth and applications of group III-nitrides, J. Phys. D Appl. Phys. 31 (20) (1998) 2653–2710, https://doi.org/10.1088/0022-3727/31/20/001.
[13] S. Pimputkar, *Gallium nitride*. Elsevier Ltd (2018), https://doi.org/10.1016/B978-0-08-102096-8.00011-2.
[14] E. M. and M. B. D. Ehrentraut, Technology of Gallium Nitride Crystal Growth Vol 133 2010 Springer-Verlag Berlin, Heidelberg.
[15] D. Tomida, et al., Ammonothermal growth of 2 inch long GaN single crystals using an acidic NH4F mineralizer in a Ag-lined autoclave, Appl. Phys Express 13 (5) (2020) pp, https://doi.org/10.35848/1882-0786/ab8722.
[16] R. Dwiliński, et al., "Properties of truly bulk GaN monocrystals grown by ammonothermal method", *Physica Status Solidi (C) Current Topics*, Solid State Physics 6 (12) (2009) 2661–2664, https://doi.org/10.1002/pssc.200982582.
[17] S. Zhang, N.S.A. Alt, E. Schlücker, R. Niewa, Novel alkali metal amidogallates as intermediates in ammonothermal GaN crystal growth, J. Cryst. Growth 403 (2014) 22–28, https://doi.org/10.1016/j.jcrysgro.2014.06.015.
[18] J. Hertrampf, E. Schlücker, D. Gudat, R. Niewa, Dissolved Intermediates in Ammonothermal Crystal Growth: Stepwise Condensation of [Ga(NH2)4]- toward GaN, Cryst. Growth Des. 17 (9) (Sep. 2017) 4855–4863, https://doi.org/10.1021/acs.cgd.7b00815.
[19] T. Richter, R. Niewa, Chemistry of Ammonothermal Synthesis, Inorganics (Basel) 2 (1) (Feb. 2014) 29–78, https://doi.org/10.3390/inorganics2010029.
[20] Y. Maruyama, T. Kurozumi, K. Omori, H. Otsubo, T. Sato, T. Watanabe, Ammonothermal synthesis of rhombohedral boron nitride, Mater. Lett. 232 (August) (Dec. 2018) 110–112, https://doi.org/10.1016/j.matlet.2018.08.092.
[21] S. Griffiths, S. Pimputkar, J.S. Speck, S. Nakamura, On the solubility of gallium nitride in supercritical ammonia–sodium solutions, J. Cryst. Growth 456 (2016) 5–14, https://doi.org/10.1016/j.jcrysgro.2016.08.041.
[22] S. Pimputkar, S. Kawabata, J.S. Speck, S. Nakamura, Improved growth rates and purity of basic ammonothermal GaN, J. Cryst. Growth 403 (2014) 7–17, https://doi.org/10.1016/j.jcrysgro.2014.06.017.
[23] S. Pimputkar, S. Nakamura, Decomposition of supercritical ammonia and modeling of supercritical ammonia-nitrogen-hydrogen solutions with applicability toward ammonothermal conditions, J. Supercrit. Fluids (2016), https://doi.org/10.1016/j.supflu.2015.07.032.
[24] S. Griffiths, et al., Growth kinetics of basic ammonothermal gallium nitride crystals, J. Cryst. Growth 501 (August) (2018) 74–80, https://doi.org/10.1016/j.jcrysgro.2018.08.028.
[25] K. Grabianska, R. Kucharski, A. Puchalski, T. Sochacki, M. Bockowski, Recent progress in basic ammonothermal GaN crystal growth, J. Cryst. Growth 547 (July) (2020), 125804, https://doi.org/10.1016/j.jcrysgro.2020.125804.