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# Feasibility of density and viscosity measurements under ammonothermal conditions

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ABSTRACT

With an eye on numerical simulations of ammonothermal growth of group III–V bulk single crystals, precise data for viscosity and density are strongly needed. In this work, changes in viscosity depending on temperature and pressure are traced in the developed ball viscometer. There, the falling time is detected by acquiring the acoustic signal of the ball using a high temperature borne-noise acceleration sensor. The results for the viscosity of pure ammonia at ammonothermal conditions already show good accuracy. The apparatus is designed to measure the density in addition to the viscosity, by the substitution of the rolling ball material in later experiments. This is important because the density of the flowing fluid is not constant due to the solubility change of GaN in ammonia by the mineralizers obligatory in ammonothermal process.



## 1. Introduction

The ammonothermal synthesis is a promising route for the growth of different group III nitride bulk materials, like GaN. But even ternary or higher nitrides like nitridosilicates or nitridogallates can be synthesized. To enhance the efficiency of the growth process with an increased growth rate and to achieve high quality crystals, a broad knowledge regarding the thermodynamic properties of the fluid and the formed intermediates is required.

Chen et al. are one of the major group that are currently working on the simulation of ammonothermal processes [1,2]. They were the first to describe the model of a modified Peng–Robinson-Equation-of-state (EOS) in order to extrapolate the values of pure ammonia to ammonothermal conditions, which are given in literature up to 426.9 °C [3]. Masuda et al. use only fluid property data of pure ammonia, too [4]. In the author's opinion the lack of realistic data leads to a significant error if the mineralizers, which are essential for ammonothermal crystal growth, are present. In Fig. 1 experimental pressure and temperature data of a typical mixture in ammonothermal processes (here gallium nitride/ammonium chloride/ammonia) are displayed. The curve represents the Peng–Robinson-EOS. Up to 550 K the Peng–Robinson-EOS fits quite well with the measured values. With rising temperature the measured values deviate from the EOS increasingly while the measurement precision decreases. At 650 K the error decreases, but an offset remains between the measured values and the EOS.

Ehrentraut et al. showed that the solubility of the mineralizers changes in the temperature range between 570 K and 680 K [5]. In addition, this effect was observed by Alt et al. with the use of UV/vis-spectroscopy [6]. Therefore, the system is in an unsteady state in this temperature range, which leads to the remarkable error. In summary, it is imprecise to simplify the simulations by using the fluid properties of pure ammonia. The arising error can be compensated only by considering the measured data of the mixture. As result processes can be simulated with a higher accuracy the more influencing factors are known.

One important variable is the viscosity, as it appears in many characteristic dimensionless numbers such as Reynolds or Stokes number. Not only flow characteristics, but also the supersaturation of the mixture, are affected by the viscosity. Finally the crystallization in high-pressure ammonothermal-synthesis is influenced. In addition, the convection is affected by the viscosity, playing an important role in mass transport. Knowledge of the viscosity in the process is decisive for a successful re-crystallization in the ammonothermal-synthesis.

## 2. A suitable viscometer for ammonothermal conditions

Since the viscosity can be measured in several ways, there all sorts of viscometer types. The rheological measurement method of choice primarily depends on the present process conditions and

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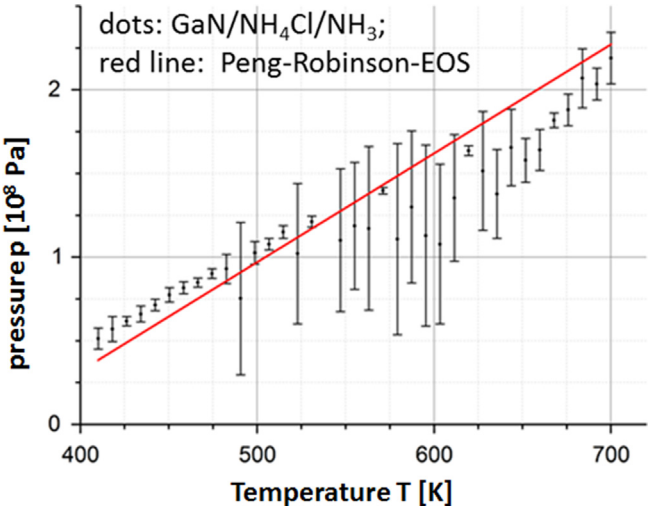


**Fig. 1.** Pressure–temperature-curve of a typical mixture in ammonothermal process.

the physical properties of the substance to be measured. In the last decade various viscometers where applied at high temperature and high pressure. These types are divided in four different main groups: capillary viscometers, oscillatory systems (e.g. vibration and ultrasonic viscometer), rotational viscometer or concentric cylinder rheometers and falling body/rolling ball viscometers. A review of some high-pressure applications is given elsewhere by Kulisiewicz [7]. Below the different main groups are discussed briefly and reasons for choosing a rolling ball viscometer suitable to the process conditions, like 600 °C and 300 MPa maximum, are shown.

Capillary viscometers are only applicable on flowing media [8]. Especially at low viscosities large inaccuracies appear, why very large spiral capillaries are used [9]. For ammonothermal conditions a flowing apparatus is hardly feasible and capillaries will soon be jammed, due to crystallization. As a consequence of this, an application of the capillary viscometers is not favorable.

Rotational viscometer or concentric cylinder rheometers with the advantages of an increased flexibility of the apparatus are mainly used for ex situ measurement because of difficulties with sealing. Nevertheless pressures up to 900 MPa at 120 °C where realized by Galvin et al. [10] and Semjonow published an apparatus with maximum operation conditions at 300 °C and 220 MPa [11]. Finally Murphy patented a method which should work up to 371 °C and 138 MPa [12], but the feasibility was not found. Still, the maximum temperature where this kind of viscometer works is far below the target operating temperature. Due to this limits, the rotational viscometer will hardly be practicable under ammonothermal conditions.

Oscillatory systems are widely used in high-pressure applications and temperature can be handled quite well, too. Nevertheless, the strong dependence of the medium used and the high frequency dependence associated are disadvantageous for the determination of viscosity [13–15]. It cannot be estimated how solutes affect the viscosity, the resonators work like a cooling device where crystallization may occur. For first measurements of the viscosity this method is less useful, but it is not completely excluded for future experiments.

A rolling ball viscometer is a rather simple and robust apparatus, but with proper calibration and accurate fabrication it can be quite precise. An apparatus for elevated temperature and high pressure was developed by Hersey [16] which is similar to the viscometer of Höppler [17]. This apparatus was already applied by Carmichael [18] for the measurement of the viscosity of liquid ammonia between 4 °C and 104 °C. Rolling ball viscometers are already used for high pressure [19] or high temperature applications [20]. Funakoshi et al. could determine with the use of X-ray detection, the viscosity even in extreme conditions like pressures between 5 GPa to 20 GPa and temperatures over 1500 °C or even 2000 °C may be feasible [21–23]. With rising temperature and decreasing viscosity the simple working Eq. (1) has to be adjusted. Hubbard and Brown showed the influence parameters like the diameter ratio or the Reynolds number [24]. These parameters will be discussed in detail later. In general, the rolling ball viscometer satisfies the needs for the application to the ammonothermal process.

Still two major challenges have to be solved. First, how bringing back the ball to the starting position, which can easily be solved with a rocking autoclave. And second, how to determine the velocity of the rolling ball. Typically the time at two measuring positions at a known distance is ascertained. The timekeeping however is not so easy to solve, because under ammonothermal conditions electrical devices are hardly usable, due to complicated electrical isolation and the external heating. Also magnetic systems cannot be applied, due to the vanishing of magnetism with rising temperatures. Even high temperature magnets like AlNiCo or $SmCo_5$ with Curie-Points at 850 °C or 800 °C have no influence through the thick autoclave walls. A visible method may be feasible with Sapphire windows, but radial weakening and local temperature drops would be the results. X-ray detection systems can be applied, like shown by Schimmel et al. lately [25], but it would not be manageable in this context, because of the large dimension needed.

So a new type of high-temperature borne-noise sensor with no active cooling is used. The rolling time is detected by acquiring the acoustic signal of the ball. This provides an insight into the autoclave without influencing the temperature profile too much.

## 3. Materials and methods

The experiments were carried out in a temperature range between room temperature and 588 °C and pressures up to 100 MPa verifying the function of the device, although the apparatus is designed and tested for maximum temperature of 600 °C and maximum pressures of 300 MPa. The viscometer is made of nickel-based superalloy (Alloy 718) and is sealed with metal c-ring gaskets (Type MCI, GFD mbH). It was heated by three heating sleeves (HORST GmbH) which guarantee a uniform temperature distribution over the length of the viscometer. If not specified otherwise, temperatures given refer to the fluid temperature inside the apparatus, which is measured continuously by a type K thermocouple (TC direct). The pressure was constantly monitored during reaction using a digital high-pressure transmitter (P2VA1/5000 bar, HBM). For determination of the run duration a high temperature borne-noise sensor (Typ3316M3, disynet GmbH) applicable up to 550 °C was applied. To optimize the results and for density measurements three different types of balls were used, made of $Al_2O_3$ (grade 28) with a density of 3.94 g/cm³, SiN (grade 10) with a density of 3.44 g/cm³ or titanium (grade 100) with a density of 4.54 g/cm³.

For calibration and determination of the instrument constant fluids with known physical properties in the supposed range of the ammonothermal mixtures were used. Calibration was done with demineralized water, ethanol (99.9% Carl Roth) carbon dioxide (4.3, Linde Gas) and nitrogen (5.0, Linde Gas). For validating the instrument, pure ammonia (5.0 Linde Gas) was used. The device is filled using a high pressure pump MSF-111L (MAXIMATOR GmbH) to vary the density of the fluid. For vacuum a venturi tube with a minimum pressure of 3000 Pa absolute is used.