

**MECHANICAL AND THERMAL PROPERTIES OF BULK CUBIC  $\text{Si}_3\text{N}_4$   
PREPARED FROM SHOCK SYNTHESIZED NANOPARTICLES****Viacheslav Prokhorov<sup>1</sup>, Rustam Bagramov<sup>1</sup>, Vladimir Blank<sup>1</sup>, Andrey Deribas<sup>2</sup>, Natalia Lvova<sup>1</sup>,  
Boris Kulnitskiy<sup>1</sup>**<sup>1</sup> Technological Institute for Superhard and Novel Carbon Materials, Centralnaya st., Troitsk, Moscow Region,  
142190 Russia<sup>2</sup> Lavrentyev Institute of Hydrodynamics SB RAS, Lavrentyev Av., 15, Novosibirsk, 630090 Russia  
e-mail: pvm@ntcstm.troitsk.ru**Keywords:** Nitrides; High pressure high temperature (HTHP); Mechanical properties; Thermal properties

**Abstract:** The cubic  $\gamma\text{-Si}_3\text{N}_4$  phase was synthesized by the shock technique from the hexagonal  $\beta\text{-Si}_3\text{N}_4$  phase. The thermal stability of the  $\gamma\text{-Si}_3\text{N}_4$  was investigated during heating in vacuum up to 1773 K. An exothermal heat effect was found at 1690 K, structural investigations revealed complete transformation of  $\gamma\text{-Si}_3\text{N}_4$  to  $\beta\text{-Si}_3\text{N}_4$ . The corresponding heat effect value was estimated as  $51.3 \pm 7.7$  kJ/mol. The high-pressure-high-temperature treatment ( $P=13$  GPa,  $T=1300\text{--}2300$  K) was applied to  $\gamma\text{-Si}_3\text{N}_4$  to make bulk polycrystalline non-porous samples. It was found that temperatures below 1623 K do not change the content of the cubic  $\gamma\text{-Si}_3\text{N}_4$ , temperatures above 2273 K decrease it substantially. Mechanical properties of these bulk samples were measured by acoustic wave and nanoindentation techniques. The maximum values belong to cubic  $\gamma\text{-Si}_3\text{N}_4$ : hardness 39–44 GPa, Young's modulus 475 GPa, bulk modulus 263 GPa. Equilibrium  $\gamma\text{-}\beta$  line position in  $P\text{-}T$  phase diagram was estimated using data obtained in this work. The equilibrium pressure at  $T=300$  K was estimated as  $P_{300}=7.0 \pm 2.0$  GPa.

**1. Introduction**

In 1999 a cubic spinel-type silicon nitride  $\gamma\text{-Si}_3\text{N}_4$  phase was for the first time synthesized in diamond anvil apparatus at 15 GPa and 2000 K, bulk modulus 300 GPa and shear modulus 340 GPa of the cubic  $\gamma\text{-Si}_3\text{N}_4$  were calculated [1]. Later the same authors measured hardness values 30–43 GPa for the  $\gamma\text{-Si}_3\text{N}_4$  [2].

First shock synthesis from powder  $\beta\text{-Si}_3\text{N}_4$  yielded more than 80% of cubic  $\gamma\text{-Si}_3\text{N}_4$  [3,4]. The isentropic curve was calculated from the Hugoniot data applied to the Birch-Murnaghan equation of state of the  $\gamma\text{-Si}_3\text{N}_4$ . The bulk modulus 300 GPa and its first pressure derivative  $3.0 \pm 0.1$  were estimated [3,4].

Available data show that  $\gamma\text{-Si}_3\text{N}_4$  is promising very hard substance with low compressibility [5]. There is general difficulty to obtain sufficiently large single phase cubic  $\gamma\text{-Si}_3\text{N}_4$  sample. For example, diamond anvil or shock syntheses yield quite small pieces or very fine powder of the cubic  $\gamma\text{-Si}_3\text{N}_4$ . That is general reason why different properties of the  $\gamma\text{-Si}_3\text{N}_4$  still need precise measurements. The aim of the presented work was to create bulk samples from the cubic  $\gamma\text{-Si}_3\text{N}_4$  and investigate mechanical properties of these samples, as well as stability of the  $\gamma\text{-Si}_3\text{N}_4$  in pressure and temperature terms.

**2. Experimental details**

The cubic  $\gamma\text{-Si}_3\text{N}_4$  powder was shock synthesized as described in [6, 7] from the  $\beta\text{-Si}_3\text{N}_4$  and copper mixture. To remove copper it was rinsed in nitric acid, cleansed in distilled water and dried. The shock conditions were estimated as 53 GPa and 5370 K.

The investigations of the thermal stability of the shock-synthesized samples were carried out with the thermal analyzer TAG-24 up to 1773 K.

A series of experiments was made to establish  $\gamma\text{-Si}_3\text{N}_4$  stability under 13 GPa pressure and 1300–2300 K temperature and to create bulk material.

The sound wave velocities and the elastic moduli of the high-pressure-high-temperature-treated samples were measured with an acoustic microscopy technique. Details of the technique are described elsewhere [8]. The surface mechanical properties were investigated with the scanning

probe microscope (SPM) and Nanohardness tester “NanoScan” [9], the sclerometry technique was used for the hardness measurements, the «approach curve» [10] technique was used for the Young's modulus measurements. A contact area was  $\sim 0.01 \mu\text{m}^2$ .

The HR-transmission electron microscopy (JEM-2010 with EDS analysis) and the X-ray technique (powder diffractometer ARL X'TRA,  $\text{CuK}\alpha$ ) were used for structural investigations.

### 3. Experimental results

The cubic  $\gamma\text{-Si}_3\text{N}_4$  was synthesized from the hexagonal  $\beta\text{-Si}_3\text{N}_4$  [6]. A powder with composition 50%  $\beta\text{-Si}_3\text{N}_4$ +50% Cu was pre-pressed up to 70% density than shock loaded. The shock conditions were estimated as 53 GPa and 5370 K [6].

Typical TEM picture of the sample after shock synthesis is presented in Fig. 1. Electron transmission microscopy diffraction analysis revealed that this sample contains three different phases of  $\text{Si}_3\text{N}_4$ : hexagonal  $\alpha$  and  $\beta$ , as well as cubic  $\gamma$ .

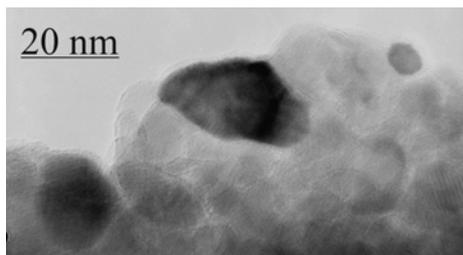


Fig.1. TEM image of the sample after shock synthesis.

X-ray diffraction analysis showed that sample after shock synthesis contains about 80 % of the cubic  $\gamma\text{-Si}_3\text{N}_4$ , about 20% of the hexagonal  $\beta\text{-Si}_3\text{N}_4$  and traces of the  $\alpha\text{-Si}_3\text{N}_4$  (specimen No. 1 in Fig. 2).

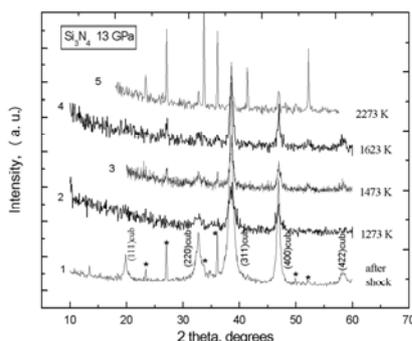


Fig. 2. X-Ray data of the  $\text{Si}_3\text{N}_4$  samples. Figures in brackets designate reflection indexes of the cubic  $\gamma$ - phase, \* - not transformed hexagonal  $\beta$ - phase.

A series of experiments was made to establish  $\gamma\text{-Si}_3\text{N}_4$  behavior under 13 GPa pressure and 1272 K, 1473 K, 1623 K and 2273 K temperatures. Diffractograms of the shock synthesized sample and the samples after high-pressure-high-temperature treatment are presented in Fig. 2. All the diffractograms contain peaks of  $\beta$ - and  $\gamma$ - phases (traces of the  $\alpha$ -phase are found only in the initial sample No. 1). TEM observation revealed  $\alpha$ -phase particles in high-pressure-high-temperature treated samples (see Fig. 3).

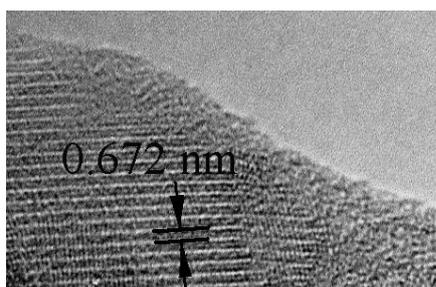


Fig. 3. TEM image of a non-perfect  $\alpha\text{-Si}_3\text{N}_4$  particle of the sample No. 2 (Table 1) after 13 GPa and 1273 K treatment.

Relative percentage of the phases, calculated X-ray density and specific weight of the samples measured with the hydrostatic weighing technique are presented in Table 1. The sample numbers in Table 1 are the same as the curve numbers in Fig. 2. The phase composition of the samples was estimated from relative intensities of the strongest lines. X-ray density of the hexagonal  $\text{Si}_3\text{N}_4$  is  $3.20 \text{ g/sm}^3$  [1], X-ray density of the  $\gamma\text{-Si}_3\text{N}_4$  is  $4.001 \text{ g/sm}^3$  (it was calculated from the cubic parameter  $a=7.75\pm 0.01\text{\AA}$ ). Best coincidence of the X-ray density and the specific weight measured with the hydrostatic weighing technique was found for the samples No. 4 and No. 5. This fact says for absence of pores in these samples.

Table 1. Results of the structural investigations of the  $\text{Si}_3\text{N}_4$  samples after 13 GPa pressure and different temperatures treatment

Sample No.	Treatment temperature (K)	% of hexagonal phase	% of cubic phase	Specific weight (X-ray) ( $\text{g/sm}^3$ )	Specific weight (hydrostatic weighing) ( $\text{g/sm}^3$ )
1	Material after shock-wave synthesis	22	78	3.83	
2	1273	24	76	3.80	3.64
3	1473	27	73	3.78	3.73
4	1623	21	78	3.79	3.83
5	2273	73	27	3.42	3.44

The experiments showed that 13 GPa and temperatures up to 1673 K do not increase content of the cubic phase. Considerable decrease of the cubic phase content takes place at 2273 K temperature due to reverse  $\gamma \rightarrow \beta$  transition.

The sound velocities measurement with an acoustic microscopy technique and results of calculations of the elastic module for the samples after high-pressure-high-temperature treatment are represented in Table 2. The data are bulk averaged. The sample numbers are the same in Tables 1 and 2. Maximum values were observed for the sample No. 4 (synthesis temperature  $T=1623 \text{ K}$ ), that is, probably, connected with the most dense structure of this sample (see Table 2).

Table 2. Results of the sound velocities measurements and the elastic moduli calculations for the samples after high-pressure-high-temperature treatment

Mechanical values	Sample No. 2	Sample No. 3	Sample No. 4
Longitudinal sound velocity (km/s)	8.58	7.31	11.70
Transversal sound velocity (km/s)	5.32	4.45	7.18
Elastic longitudinal constant (GPa)	266.2	199.1	524.0
Shear modulus (GPa)	102.9	73.9	197.5
Bulk modulus (GPa)	121.3	100.4	261.0
Young's modulus (GPa)	240.4	177.8	473.0
Poisson's ratio	0.169	0.204	0.198

The surface mechanical properties (hardness and Young's modulus) of the high-pressure-high-temperature treated samples were investigated with the SPM-Nanohardness tester "NanoScan" and are presented in Table 3. The sample numbers are the same in Tables 1, 2 and 3.

Table 3. Mechanical properties of the  $\text{Si}_3\text{N}_4$  samples after high pressure-high temperature treatment measured with SPM-Nanohardness tester "NanoScan"

Sample No.	Nano-hardness (GPa)	Young's modulus (GPa)
2	$38\pm 4$	$470\pm 60$
3	$39\pm 4$	$470\pm 60$
4	$44\pm 4$	$480\pm 60$

The pictures obtained during nanosclerometry measurements of the samples No. 2 and No. 4 are shown in Fig. 4. Pores formed during high-pressure-high-temperature treatment are well visible on the surface of the sample No. 2. At the same time surface of the sample No. 4 is more homogeneous and non-porous.

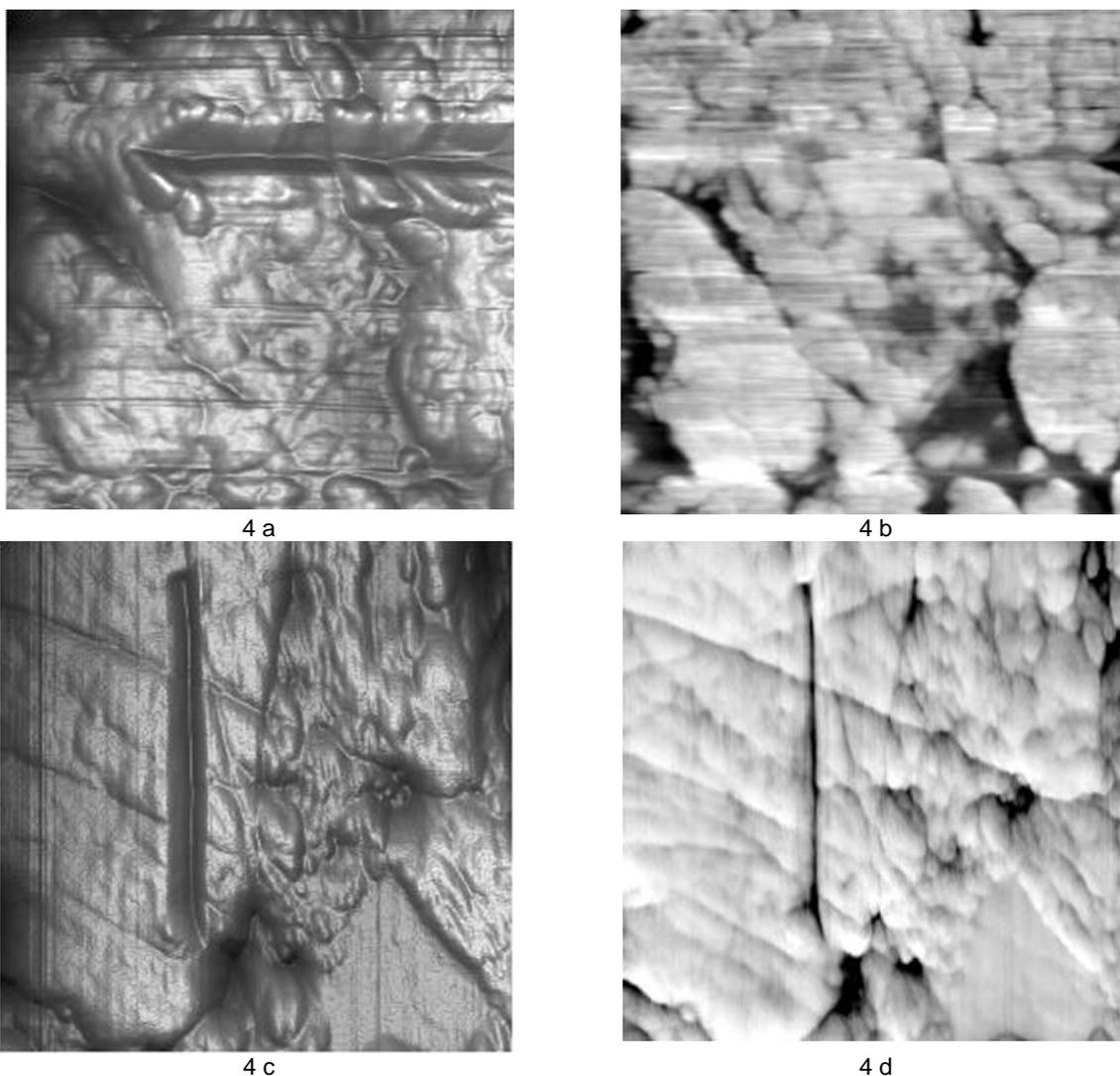


Fig. 4. Surface SPM-images of No. 2 (a,b) and No. 4 (c,d) samples; (a,c) – surface relief with scratch imprint (dimension of the images -  $5.0 \times 5.0 \times 0.3 \mu\text{m}$ ); (b,d) – corresponding elastic modulus map.

Measurements of the Young's modulus with the approaching curve technique are dependent on the surface quality and homogeneity. The hardness and the Young's modulus values of different phases are different. Only maximum measured values are presented in Table 3. We believe that these values belong to cubic phase. In this case the hardness values are in good accord with the data of work [2].

SPM-Nanohardness tester "NanoScan" measurements are local, while sound wave technique measurements are bulk (and dependent on porosity of a sample). That is why the best coincidence of the Young's modulus values obtained with the SPM-Nanohardness tester "NanoScan" and with the sound wave technique was observed for the sample No. 4 that was found non-porous.

Investigation of the thermal stability of the sample after shock wave synthesis was carried out with the thermal analyzer TAG-24 up to 1773 K.

First experiment was made up to 1473 K in helium protective environment. The heating rate was 15 K/min. An endothermal peak was found at 1360 K. Corresponding heat effect value was not estimated. X-ray diffraction studies did not reveal a difference in this sample before and after 1473 K heating. The heat effect might be assigned to a constituent that can not be revealed by X-rays (due to its low concentration or highly defective structure) or to annealing of some defects.

In second experiment the manganese was used as the reference substance. The sample and the reference were placed into small platinum crucibles, than heated in helium up to 1273 K, than vacuum pumped and dwelled at 1273 K for an hour. The following heating was in vacuum also. The heating rate was 15 K/min, maximum temperature – 1773 K. The difference thermocouple signal between the reference and the sample was recorded and is presented in Fig. 5. An exothermal effect peak in  $\text{Si}_3\text{N}_4$  was found at 1690K. It extended from 1640 K to 1750 K. Measured heat effect value was 51.3 KJ/mol.

It should be mentioned that some additional sharp heat effect appear at 1540 K if  $\gamma$ - $\text{Si}_3\text{N}_4$  is placed not into platinum but into aluminum oxide crucible.

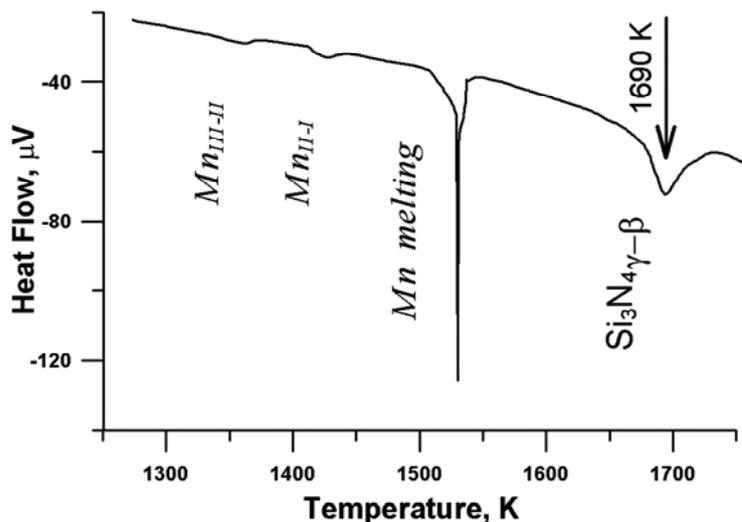


Fig. 5. Heating curve for the  $\text{Si}_3\text{N}_4$  sample (1273÷1773 K temperature interval, vacuum).

It should also be noted that manganese evaporates quickly at temperatures higher than 1633 K due to high saturation-vapor pressure but we believe this does not notably effects accuracy of the heat effect measurement that is about 15 %.

X-ray diffraction investigations revealed that after 1773 K vacuum heating  $\text{Si}_3\text{N}_4$  sample contained  $\alpha$  and  $\beta$  phases and traces of pure silicon (see Fig. 6). Amount of the  $\beta$  phase was about 80 %.

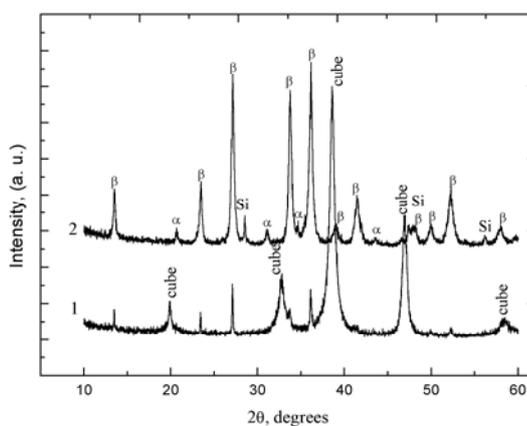


Fig. 6. Comparison of the X-ray diffractograms of the  $\text{Si}_3\text{N}_4$  sample (1) before and (2) after 1773K vacuum heating.

The result obtained confirms very high thermal stability of the cubic  $\gamma$ - $\text{Si}_3\text{N}_4$  phase that was observed previously [11]. Our results are in good agreement with [12] where small but very broad peak was observed at 1350K and another peak at 1600÷1750K.

Transmission electron microscopy investigations revealed the following. The  $\text{Si}_3\text{N}_4$  average particle size increased considerably from 30 to 150 nm (Fig. 7) during heating in vacuum up to 1773 K. Phase composition changed considerably also. Only particles with hexagonal lattice were present after heating while particles with cubic lattice were not found. High resolution TEM of a  $\beta$ - $\text{Si}_3\text{N}_4$  particle and corresponding diffraction pattern are presented in Fig. 8. Zone axis [01-1]. High resolution TEM image of a fragment of an  $\alpha$ - $\text{Si}_3\text{N}_4$  particle is presented in Fig. 9. Zone axis [11-3]. Inter-planar 0.216 nm and 0.672 nm spacing correspond to (211) and (100). The image analysis of the sample after 1773 K vacuum heating revealed much less irregularities or lattice defects than in the sample before heating.

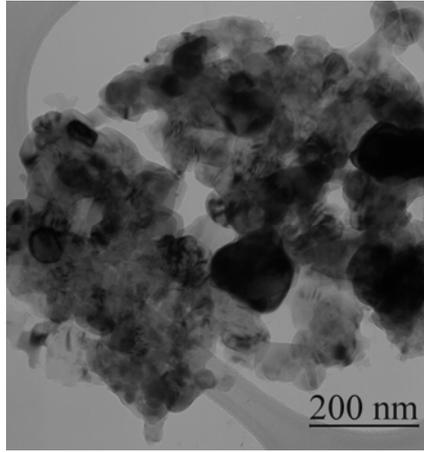


Fig. 7. TEM image of the  $\text{Si}_3\text{N}_4$  material after 1773 K vacuum heating.



Fig. 8. (a) TEM image of a fragment of a  $\beta\text{-Si}_3\text{N}_4$  particle of the sample after 1773 K vacuum heating; (b) corresponding diffraction pattern.

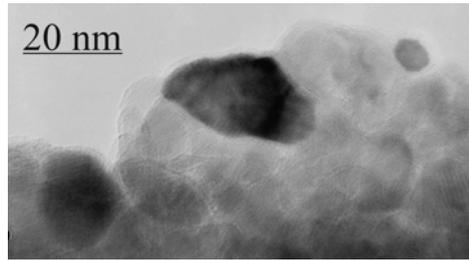


Fig. 9. High resolution TEM image of a fragment of an  $\alpha\text{-Si}_3\text{N}_4$  particle of the sample after 1773 K vacuum heating.

#### 4. Discussion

A question of the equilibrium  $\text{Si}_3\text{N}_4$  pressure-temperature phase diagram is still open. Based on available data and on the results obtained during this work we made an estimation of the equilibrium conditions for  $\beta$ - and  $\gamma$ - phases using an approach proposed in [13]. First of all we assumed that the point ( $P_Z=14\pm 1$  GPa,  $T_Z=2100\pm 100$  K) belongs to  $\beta$ - $\gamma$  equilibrium line. This assumption is based on [1] and on our high-pressure phase annealing data. So the slope of the  $\beta$ - $\gamma$  line can be calculated using values of the heat effect of the  $\gamma \rightarrow \beta$  transition at  $T=1690$  K and the volume change during this transition:

$$P_o = \frac{P_Z T_o \Delta V^{\gamma \rightarrow \beta}}{T_Z \Delta V^{\gamma \rightarrow \beta}} + \frac{\Delta H^{\gamma \rightarrow \beta} (T_Z - T_o)}{T_Z \Delta V^{\gamma \rightarrow \beta}}$$

where  $T_o$  – temperature of the transition from high-pressure  $\gamma$ -phase to low-pressure  $\beta$ -phase at  $P=0$ ;  $P_o$  – equilibrium pressure at  $T_o$ ; ( $P_Z$ ,  $T_Z$ ) – the point that was chosen belonging to  $\beta$ - $\gamma$  equilibrium line;  $\Delta V^{\gamma \rightarrow \beta}$  – volume effect of the transition;  $\Delta H^{\gamma \rightarrow \beta}$  - heat effect of the transition.

Taking into account our results and [1] data:

$$\Delta V^{\gamma \rightarrow \beta} \cong 9 \cdot 10^{-6} \text{ (m}^3/\text{mol)}$$

$$\Delta H^{\gamma \rightarrow \beta} = 51,3(\text{KJ/mol})$$

$$T_0 = 1690(\text{K})$$

$$T_Z = 2100(\text{K})$$

$$P_Z = 14(\text{GPa})$$

Hence:

$$P_0 = P_Z \frac{T_0}{T_Z} + \frac{\Delta H^{\gamma \rightarrow \beta}}{\Delta V^{\gamma \rightarrow \beta}} \frac{T_Z - T_0}{T_Z} \cong 12,4(\text{GPa}).$$

So at T=300 K the equilibrium pressure  $P_{300\text{K}}=7.0\pm 2.0$  GPa.

It should be noted that the slope of the equilibrium curve is positive  $dP/dT>0$ , and the high volume effect makes major contribution, i.e. contribution of the stored elastic energy and the correction due to different compressibility may be neglected.

## 5. Conclusion

The cubic  $\gamma\text{-Si}_3\text{N}_4$  phase that was investigated in this work was synthesized with the shock technique from the hexagonal  $\beta\text{-Si}_3\text{N}_4$  phase [6, 7].

The thermal stability of the  $\gamma\text{-Si}_3\text{N}_4$  was investigated during heating up to 1773 K. A  $51.3\pm 7.7$  KJ/mol heat effects was found at 1690 K. Structural investigations of the heated sample revealed complete reverse  $\gamma\rightarrow\beta$  transition. The  $\gamma\text{-}\beta$  equilibrium line position in P-T phase transition diagram was evaluated. Equilibrium pressure at T=300 K was estimated as  $P_{300\text{K}}=7.0\pm 2.0$  GPa

High-pressure-high-temperature quasi-hydrostatic treatment (P=13 GPa, T=1300÷2300 K) was successfully applied to make bulk polycrystalline non-porous  $\gamma\text{-Si}_3\text{N}_4$  samples. It was found that 13 GPa pressure treatment does not change cubic  $\gamma\text{-Si}_3\text{N}_4$  content if temperature is below 1623 K. Temperatures above 2273 K decrease content of the  $\gamma\text{-Si}_3\text{N}_4$  substantially. Mechanical properties of the bulk high-pressure-high-temperature treated samples were investigated. Maximum measured values were as follows: 39÷44 GPa hardness, up to 475 GPa Young's modulus, up to 263 GPa bulk modulus, 0.204 Poisson's ratio.

## Acknowledgments

Authors thank N.R.Serebryanaya, G.A. Dubitsky, V.F.Kulibaba and V.V.Aksenenkov. This work fulfilled under support of the Grant 05-03-32353 of Russian Academy of Science (RAS) and the RAS 9.4 Program.

## References:

1. Zerr A., G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fuess, P. Kroll, R. Boehler, Nature 400 (1999) 340.
2. Zerr A., M. Schwarz, R. Schmechel, R. Kolb, H. Von Seggern, R. Riedel, Acta Cryst. A58 (Supplement) (2002) C47.
3. Sekine T., Hongliang He, T. Kobayashi, Ming Zhang, Fangfan Xu, Appl. Phys. Lett. 76 (2000) 3706.
4. Hongliang He, T. Sekine, T. Kobayashi, H. Hirotsaki, Phys. Rev. 62 (2000) 11412.
5. Kroke E., M. Schwarz, Coordination Chemistry Reviews 248 (2004) 493.
6. Yunoshev A. S., Fizika Goreniya i Vzriva, 3, (2004), 132.
7. Yunoshev A. S., V. V. Silvestrov, A. A. Kalinin, and Yu. N. Pal'yanov, in: AIP Conf. Proc. 845, (2006), 1173.
8. Prokhorov V. M., V. D. Blank, S. G. Buga, V. M. Levin, Synthetic Metals 103 (1999) 2439.
9. Blank V., M. Popov, N. Lvova, K. Gogolinsky, V. Reshetov, J.Mater.Res. 12 (1997) 3109.
10. Useinov A. S. Instruments and Experimental Techniques 47 (2004) 119.
11. Jiang J. Z., F. Krag, D. J. Frost, K. Stahl and H. Lindelov, J. Phys.: Condense Matter. 13 (2001) 515.
12. Sekine T., T. Mitsuhashi, Appl. Phys. Lett. 79 (2001) 2719.
13. Blank V. D., Yu. S. Konyayev, B. M. Mogutnov, E. I. Estrin, The Physics of Metals and Metallography (USSR) 53 (1982) 402.