



High-pressure high-temperature behavior of nitrogen-doped zirconia

T. Locherer^{a,*}, D. Frost^b, H. Fuess^a

^a Darmstadt University of Technology, Institute for Materials Science, Structure Research, Petersenstr. 23, D-64287 Darmstadt, Germany

^b University of Bayreuth, Bayerisches Geoinstitut, D-95440 Bayreuth, Germany

ARTICLE INFO

Article history:

Received 11 December 2007

Received in revised form

18 July 2008

Accepted 23 July 2008

Available online 3 August 2008

PACS:

61.10.Eq

62.20.Dc

62.50.+p

64

64.30.+t

Keywords:

Zirconium oxonitride

Zirconium oxide

Zirconium nitride

High pressure

Phase diagram

ABSTRACT

The stability of nitrogen-doped zirconia/zirconium oxonitride $Zr_7O_{11}N_2$ has been studied at pressures up to 20 GPa and temperatures up to 2273 K using a multi-anvil press and X-ray powder diffraction. Depending on pressure and temperature it was found to decompose into the respective stable oxides and nitrides. Therefore the critical influence of temperature, pressure and consequently mechanical tension on doped materials have been revealed. The transition pressures of some oxidic and nitridic high-pressure modifications have been confirmed. The coefficient of thermal expansion of $Zr_7O_{11}N_2$ was determined to $\alpha(T) = 17.94(20) \times 10^{-6} K^{-1} + 6.35(14) \times 10^{-9} K^{-2} \times T$.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

Ceramics composed of or containing zirconium oxide are some of the most important modern materials. They offer properties such as low thermal conductivity, solid state ionic conduction in oxygen sensors or act as toughening agents in ceramic composites. The various high-temperature polymorphs have been widely investigated due to these valuable properties [1–4]. Aliovalent cationic dopants such as Y_2O_3 , MgO or CaO are well known to stabilize these modifications to room temperature. A supplementary effect has been reported for the usage of nitrogen as an additional dopant [5,6]. The high-pressure behavior has been subject of many investigations [7–18], since the toughening mechanism of zirconium oxide ceramics is explained by a phase transformation induced by a stress field [19,20]. However, only little is known about doped zirconia at high pressures [7].

Nitrogen-doped zirconia, i.e. zirconium oxonitrides were first reported by Gilles et al. [21,22]. Recent investigations by Lerch et al. [23–26] aimed at enhanced oxygen and nitrogen transport capacity within the Zr–O–N system. They also yielded a detailed

description of the structure and the high-temperature properties of these materials. In oxygen-rich zirconium oxonitrides the cubic phase with fluorite structure is stable above ~ 1243 K. Below this temperature an ordering of anion vacancies occurs, which subsequently leads to a rhombohedral distortion of the fluorite lattice. Depending on the nitrogen content, several of these so-called β -type phases are known. The major difference of these rhombohedral phases is the stacking order of the two building units, the Bevan cluster and the Zr_7O_{14} -unit [23–27].

Since our recent investigations on the compressibility of the β' -zirconium oxonitride resulted in the comparably high isothermal bulk modulus of $B_0 = 254$ GPa, $Zr_7O_{11}N_2$ can be considered as a potential hard material. In the present work the general high-pressure high-temperature behavior of nitrogen-doped zirconia has been studied up to 20 GPa and 2273 K in order to judge the restrictions of this material for the potential application as toughening agent or hard material in cutting tools.

2. Experimental

Zirconia powder (unstabilized, monoclinic; Alfa, Karlsruhe, Germany) was heated under constant ammonia flow in a sealed quartz tube at 1423 K for 12 h. To prevent the formation of

* Corresponding author.

E-mail address: locherer@st.tu-darmstadt.de (T. Locherer).

compounds with higher nitrogen content on the particle surface, the sample was ground in 2-propanol before further nitridation. After grinding, XRD measurements were carried out for phase analysis. This procedure was repeated until only a negligible residual amount of monoclinic zirconia could be detected. With the synthesis conditions described above $Zr_7O_{11}N_2$ with a mean grain size of about 270 nm was obtained. In zirconia ceramics no particle size-dependent influence on pressure-induced phase transformation exists above 100 nm grain size [29]. The amount of residual monoclinic zirconia in the oxonitride was below 4%.

The HP/HT experiments have been carried out mainly at the Bayerisches Geoinstitut using a 6–8 multi-anvil press apparatus with tungsten carbide cubes, Cr_2O_3 -doped MgO octahedra and a $LaCrO_3$ furnace. The sample container was made of zirconium foil to prevent sample contamination from the other oxide materials used in the experimental setup. The reaction time in the high-pressure high-temperature experiments was ~30 min. On account of the lower reaction kinetics for experiments below 1000 K the reaction time was raised to 60 min. The experimental uncertainties are estimated to be approximately 1 GPa for pressure and 50 K for temperature. Some HP modifications of zirconia have also been identified as potential hard materials [17]. It is possible, therefore, that grinding could lead to sample contamination as a result of abrasion of the mortar material. In order to investigate the quenched and recovered experimental run products, thin slices of about 150 μm thickness were prepared from the samples using a diamond wire saw. However, samples originating from experiments at pressures higher than ~15 GPa were too small for this kind of preparation. These samples were only ground in an agate mortar.

Subsequent to preparation, XRD investigations for phase analysis were carried out with a STOE Stadi-P powder diffractometer using $MoK\alpha_1$ radiation ($\lambda = 0.70926 \text{ \AA}$), a curved Ge-(111)-monochromator and a linear position-sensitive detector with an aperture of 6° . For the investigation of the high-pressure samples phase analysis and least-squares structural refinements were carried out with the WinPlotr software package [30]. Since for the β -type zirconium oxonitrides nitrogen cannot be localized on particular atomic sites, only oxygen was placed in the anion positions in the Rietveld refinement. Additional qualitative elemental analysis was performed by electron energy loss spectroscopy (EELS) using a Jeol JEM 3010 transmission electron microscope with GIF 200 Gatan image filter. To determine the thermal expansion of pure $Zr_7O_{11}N_2$ additional temperature-dependant XRD measurements were performed using rotating quartz capillaries placed in a electrically heated graphite furnace.

3. Results

3.1. High-pressure high-temperature experiments

In our first experimental series the respective samples have been compressed up to 7 GPa and heated to 1023 K to probe the pressure stability of the rhombohedral zirconium oxonitride. Since no structural change could be detected for the quenched samples, the experiments were repeated at 1973 K, where the cubic modification is the thermodynamically stable phase at ambient pressure. Again, in this second experimental series there was no evidence for a phase transformation and no cubic phases were observed. The recovered samples consisted of rhombohedral zirconium oxonitride and the monoclinic polymorph. The amount of ZrO_2 was determined to stay below 4%, as in the starting material.

In our previous study [28], we found evidence for a potential phase transition of $Zr_7O_{11}N_2$ at pressures of approximately 10 GPa. To investigate the existence of further high-pressure polymorphs we conducted HP/HT experiments up to 20 GPa and 2273 °C. The diffraction patterns of the recovered samples obtained under the various pressure regimes are shown in a separate appendix. In these regimes different behaviors/reactions can be detected.

Up to 7–7.5 GPa $Zr_7O_{11}N_2$ is stable without any changes in structure or chemistry. At pressures above 8 GPa the zirconium oxonitride starts to decompose into several different oxidic and nitridic compounds. From about 8 to 12 GPa the decomposition reaction leads to the formation of zirconium mononitride ZrN with rock salt structure and monoclinic ZrO_2 (m- ZrO_2). In some samples some additional residual oxonitride was found. The appearance of this material is related to incomplete decomposition as a result of insufficient reaction time or experimental conditions near a potential decomposition phase boundary. The general composition of the samples was found to be close to 48% ZrN and 52% m- ZrO_2 . At pressures above 12–12.5 GPa different products have formed as a function of temperature. Below ~1373 K the formation of a recently discovered high-pressure modification of Zr_3N_4 with the thorium phosphide structure was confirmed [31–33]. In addition to the monoclinic phase of zirconium oxide a certain amount of ~5% $ZrO_{0.27}$, a suboxide with trigonal symmetry (space group $P3c1$), was found. In samples heated to 1473 K or above neither Zr_3N_4 nor $ZrO_{0.27}$ were present. The composition was determined again to 48% ZrN and 52% m- ZrO_2 . Increasing the pressure above ~14 GPa leads to the formation of cotunite-type ZrO_2 with orthorhombic symmetry (oII- ZrO_2) and nine-fold coordinated zirconium. Again the nitridic product was cubic Zr_3N_4 at lower temperatures and ZrN at temperatures of 1473 K or above.

Due to the nature of cubic Zr_3N_4 and cotunite-type ZrO_2 and the sample size necessary to fit into the experimental setup, grinding in an agate mortar was the only way to prepare them for XRD measurement. Therefore the respective diffraction pattern also shows reflections originating from abrasion of the mortar material. However, the presence of the suboxide $ZrO_{0.27}$ could not be determined.

3.2. Thermal expansion

To determine the thermal expansion of pure $Zr_7O_{11}N_2$ temperature-dependent XRD measurements were performed

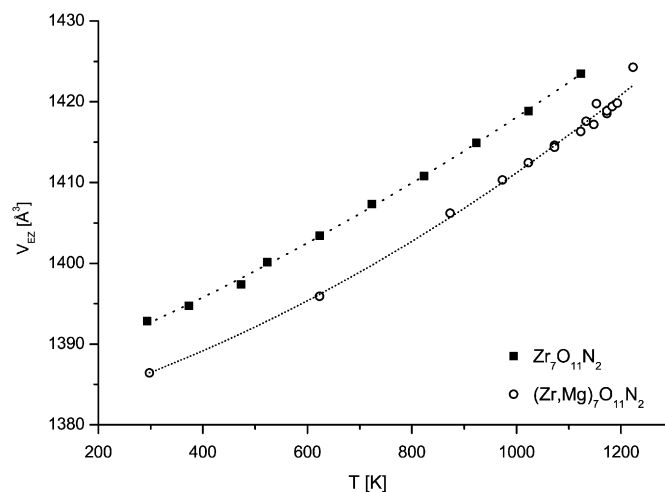


Fig. 1. Unit cell volume vs. temperature plotted for pure (■) and Mg-doped $Zr_7O_{11}N_2$ (○).

Table 1
Molar volumes, bulk moduli and coefficients of thermal expansion used for calculations

Compound	V_0 (Å ³) per atom	K_0 (GPa)	K'_0	α_0 (10 ⁻⁶ K ⁻¹)	α_1 (10 ⁻⁹ K ⁻²)	Refs.
(Zr,Mg) ₇ O ₁₁ N ₂	11.502	–	–	12.07	7.25	[36]
Zr ₇ O ₁₁ N ₂	11.509	254	14	17.94	6.35	[28], this work
c-ZrO ₂	10.923	267	4.42	12.83	13.56	[36,37]
ZrN	11.961	248	4	3.73	14.64	[38,39]
Cubic Zr ₃ N ₄	11.008	219	4.4	–	–	[34]
m-ZrO ₂	11.722	212	8	24.58	–	[40,41]
t-ZrO ₂	11.2049	172	8.5	34.85	–	[41,42]
ol-ZrO ₂	11.028	243	7	–	–	[9,40]
oII-ZrO ₂	9.998	278	3.7	20.52	–	[43]

between 300 and 1123 K. The unit cell volumes at the respective temperatures were evaluated by Rietveld refinement of the powder patterns. From the volume vs. temperature data in Fig. 1 the coefficient of the volumetric thermal expansion was calculated according to:

$$\alpha_V = 1/V * \delta V / \delta T = a_0 + a_1 * T \quad (1)$$

Also shown in Fig. 1 are the unit cell volumes of Mg-doped β' -zirconium oxonitride (Zr,Mg)₇O₁₁N₂ obtained from high-temperature data published by Lerch [31]. For both compounds the calculated values of the a_0 and a_1 are given in Table 1.

4. Discussion

Materials usually respond to pressure through either elastic compression or through phase transformations to form compounds with a higher coordination of the respective atoms. The mode of response at a particular pressure will in general be dictated by the path leading to the lowest molar volume. For the discussion of the decomposition reaction observed for Zr₇O₁₁N₂, its compressibility has to be compared to that of the reaction products after decomposition. In addition, as these experiments take place at high-temperature the thermal expansion of the different compounds has to be considered. Thus using the known values of the bulk moduli and thermal expansion (Table 1) preliminary thermodynamical calculations have been performed in order to provide a better understanding of the HP/HT behavior of the zirconium oxonitride.

For the calculations bulk moduli B_0 and their first pressure derivatives B'_0 have been employed with the third-order Birch–Murnaghan equation of states [32] of the form:

$$P = \frac{3}{2} B_0 [(V/V_0)^{-7/3} + (V/V_0)^{-5/3}] [1 + \frac{3}{4} (B'_0 - 4) (V/V_0)^{-2/3} - 1] \quad (2)$$

The thermal expansion of the compounds was taken into account according to Eq. (1).

Since the experimental errors are about 1 GPa in pressure and 50 K in temperature, mixed derivatives have been neglected. Compressions have been calculated from an initial high-temperature state, i.e. the material was first raised to high temperature and then compressed isothermally. Due to the differences in chemistry of the observed oxides, nitrides and oxonitrides, i.e. 1.27–20 atoms per formula unit, the molar volume per atom was used to provide a better comparability of the compounds. No temperature-related phase transitions are known for ZrN below the melting temperature of ~3223 K. In the pressure and temperature regimes which have been experimentally probed and which are found to be relevant for the decomposition, only the tetragonal modification of ZrO₂ (t-ZrO₂) is thermodynamically stable according to the most recent published partial HP/HT phase diagram [18].

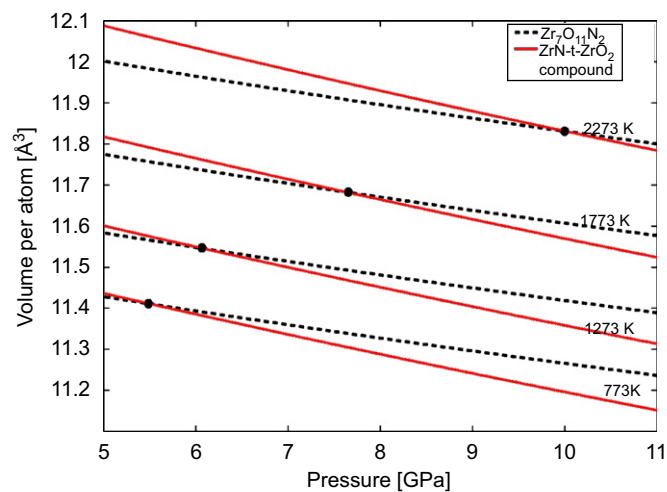


Fig. 2. Decomposition phase boundary of pure Zr₇O₁₁N₂ calculated by comparison of compressibility and thermal expansion of the oxonitride (black line) and the decomposition product of 48% ZrN and 52% t-ZrO₂ (red line). The pressures where the volumes are equal to each other at the given temperature are marked with full circles. Calculations were performed between 500 and 2500 K. For better clarity only four temperatures are shown.

A phase transformation of the zirconium oxonitride to its cubic modification during HP/HT experiments was not expected for two reasons: the first is the preferred compression of the rhombohedral modification along its *c*-axis, which we published in our recent work [28]. At high pressures the anions and cations diverge more from their ideal cubic fluorite-type structure arrangement than at ambient pressure. The second reason is, that preliminary calculation showed that for a cubic zirconium oxonitride decomposition was not favorable. The corresponding calculations have been performed up to a pressure of 175 GPa. Thus, only the comparison between the molar volumes of rhombohedral Zr₇O₁₁N₂ and a 48:52 mixture of ZrN and t-ZrO₂ was considered in the main calculations according to the observed ratio of the respective decomposition products. The results of the calculations are displayed in Fig. 2. Due to the difference in thermal expansion between pure Zr₇O₁₁N₂ and (Zr,Mg)₇O₁₁N₂ a different course of the proposed decomposition phase boundary is obtained (see Fig. 3).

The pressures where the molar volumes of the oxonitride and the 48:52 mixture are equal at the respective temperatures are marked full circles. The calculation clearly indicates that the zirconium oxonitride decomposes because the assemblage of ZrN and tetragonal zirconia has a lower molar volume. The calculation reproduces almost exactly the experimental conditions of the decomposition reaction. Fig. 4 shows the experimental results combined with the calculated phase boundary. Beyond the decomposition pressure the behavior of Zr₇O₁₁N₂ can be described

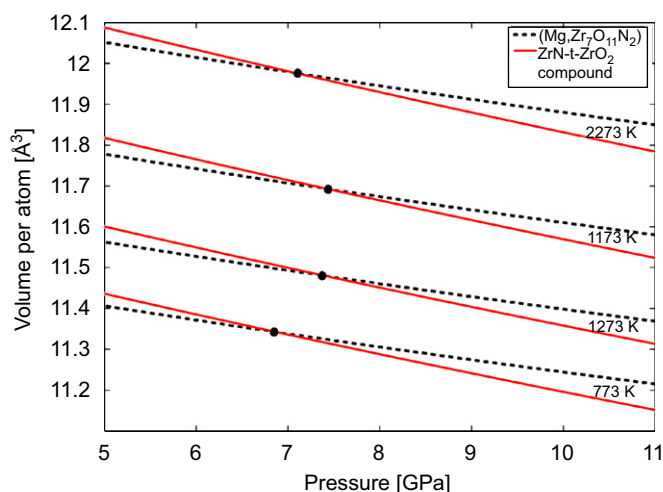


Fig. 3. A modified course for the decomposition phase boundary arises for Mg-doped $(\text{Zr,Mg})_7\text{O}_{11}\text{N}_2$ due to its different thermal expansion calculated from the data available in Ref. [31].

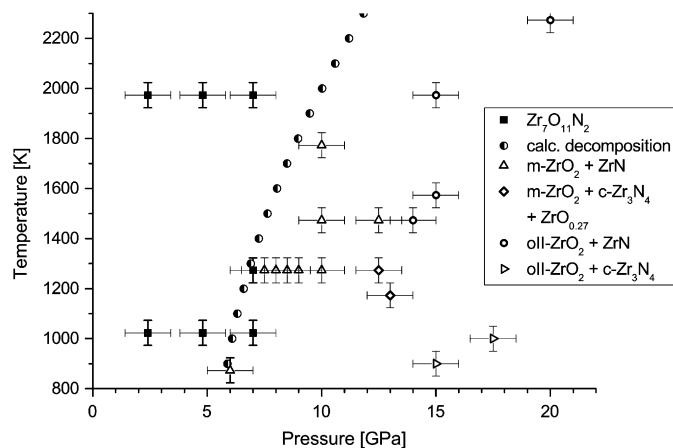


Fig. 4. The calculated phase boundary (●) fits to the results obtained in multi-anvil press experiments with fair agreement.

by a superposition of the temperature vs. pressure diagrams of ZrO_2 and the zirconium nitrides. Since neither tetragonal nor orthorhombic-I zirconia can be quenched from high-pressure experiments only monoclinic zirconia is obtained from the respective conditions.

To draw a draft for a decomposition phase diagram some additions nevertheless had to be made with respect to the temperature stability of cubic Zr_3N_4 . Despite a recent publication [35] on the synthesis of this high-pressure phase at 12 GPa and 1873 K in a multi-anvil press, we cannot confirm its formation for temperatures higher than ~ 1373 K. For some reason the formation of the stoichiometric zirconium nitride does not occur at the synthesis conditions reported in Ref. [35]. Due to this observation further investigations were performed using EELS for the determination of the elemental composition of phases observed. These investigations revealed that in all samples synthesized at pressures above 12 GPa and 1373 K the ZrN formed also includes oxygen. This leads to the conclusion, that the cubic Zr_3N_4 reacts with the Zirconium suboxide $\text{ZrO}_{0.27}$ to form a compound ZrN(O) with rocksalt structure. For this compound no aberration from the lattice constants of ZrN could be found and no oxygen-related superstructure reflections have been

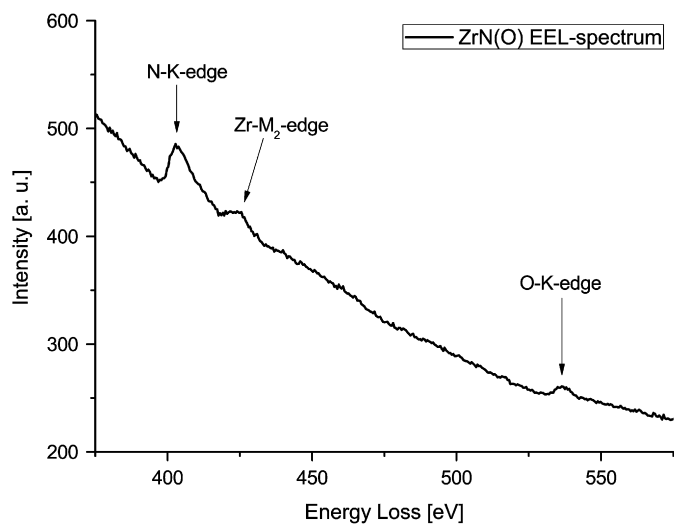


Fig. 5. Electron energy loss spectrum of the sample obtained from HP/HT experiments at 12.5 GPa and 1200 °C. Oxygen is dissolved in the zirconium mononitride.

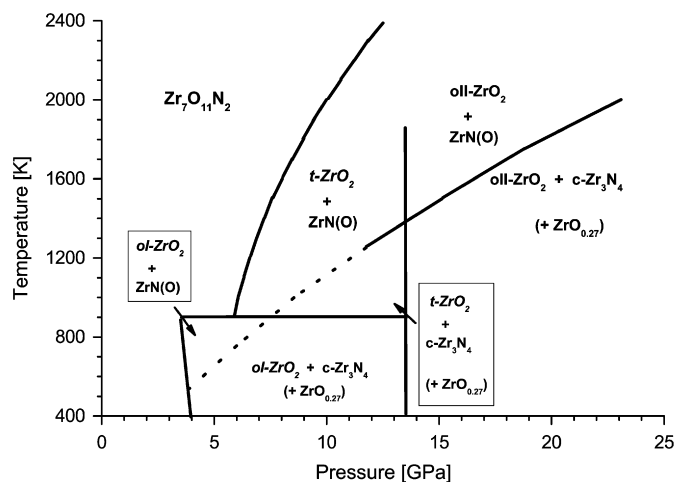


Fig. 6. Draft for the decomposition phase diagram of $\text{Zr}_7\text{O}_{11}\text{N}_2$. Non-quenchable phases are denoted in italics. See text for further information.

found in XRD measurements. The EEL spectrum of the sample prepared at 12.5 GPa and 1473 K is shown in Fig. 5. Due to high absorption no reasonable quantification of nitrogen and oxygen was possible.

In another publication the pressure and temperature stability of cubic Zr_3N_4 vs. $\text{ZrN}+\text{N}_2$ and nitrogen was calculated by Kroll [44]. The phase boundary between the nitrides shown in this publication fits well to the observations done in our experiments. For further discussion the data presented in Kroll's work were taken into account. Yet additional changes were made according to the fact that the formation of cubic Zr_3N_4 never was observed below 12 GPa, as confirmed by literature [34,35].

A combination of the calculations performed in this work with the known phase diagram of zirconia and Kroll's work leads to the draft for the decomposition reaction diagram of $\text{Zr}_7\text{O}_{11}\text{N}_2$ shown in Fig. 6.

Within the generally accepted experimental errors of 1 GPa and 50 K our experiments confirm the diagram with fair agreement. Since both tetragonal and orthorhombic zirconia cannot be quenched from high-pressure experiments we rely on the well-known phase boundaries reported in literature over the past decades.

Parts of the phase boundary between cubic Zr_3N_4 and ZrN are depicted with dots due to the fact that it is not yet experimentally proven for pressures below 12 GPa.

5. Conclusion

The HP/HT stability of $Zr_7O_{11}N_2$ was studied using the multi-anvil press technique and *ex situ* X-ray powder diffraction. Depending on pressure and temperature conditions the material was found to decompose into various combinations of binary and quasi-binary Zr–N and Zr–O compounds. Below ~ 800 – 900 K the decomposition starts at about 4 GPa and is dominated by the more favorable sample volume obtained from the formation of *o*- ZrO_2 . Above this temperature *t*- ZrO_2 is the stable zirconia modification. Our calculations showed that a decomposition of $Zr_7O_{11}N_2$ into tetragonal zirconia and zirconium mononitride is clearly temperature dependent. The minimum decomposition pressure is 5–6 GPa at 1000 K, and it increases with temperature. Excess oxygen is incorporated into the zirconium mononitride which therefore has to be considered as $ZrN(O)$. At pressures above 12 GPa and temperatures below ~ 1473 K, cubic Zr_3N_4 and $ZrO_{0.27}$ are formed instead of $ZrN(O)$.

No new high-pressure or high-temperature modifications of $Zr_7O_{11}N_2$ were found. The critical effects of temperature, pressure and consequently also mechanical tension on nitrogen-doped zirconia were revealed. We highly suggest further high-pressure high-temperature experiments, using cationic dopants to determine the potential critical influence on the stability of the industrially used zirconia ceramics.

Acknowledgements

The authors are grateful to Prof. M. Lerch of the TU Berlin for fruitful discussions and the Deutsche Forschungsgemeinschaft (FU 125/39) and FAME Network of Excellence for financial support.

Appendix

See Figs. A1–A6 for XRD diffractograms of experimental samples mentioned in the text.

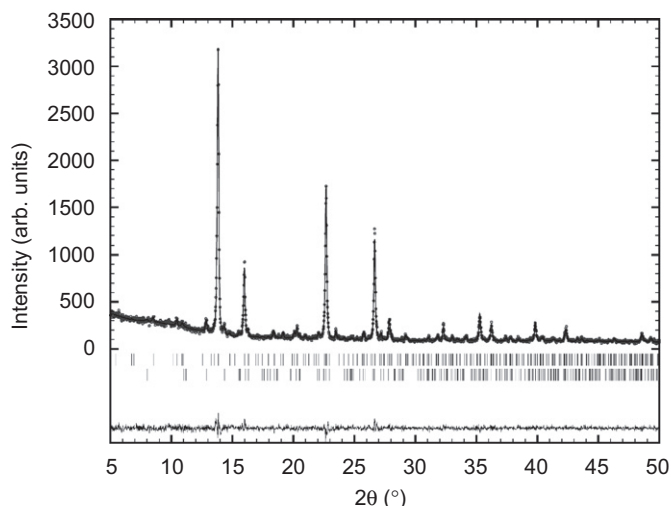


Fig. A1. X-ray diffractogram of a sample obtained from 7 GPa and 1973 K. The composition stayed unaltered in comparison to the starting material of $Zr_7O_{11}N_2$ and $<4\%$ monoclinic ZrO_2 .

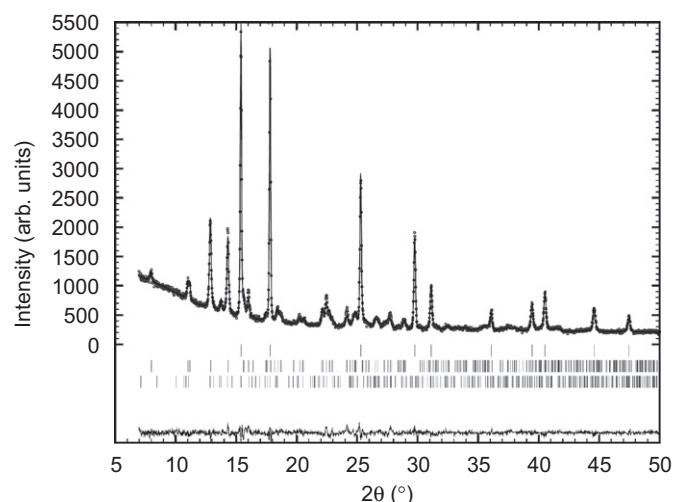


Fig. A2. Zirconium mononitride and monoclinic zirconia (first and second row of reflection markers) and a small amount of $\sim 4\%$ residual oxonitride (lower reflection markers) were received at 10 GPa and 1273 K.

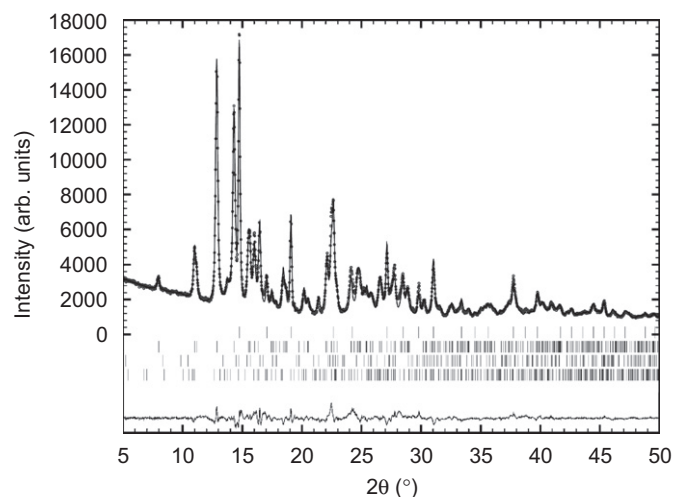


Fig. A3. At 12.5 GPa and 1273 K the cubic high-pressure modification of Zr_3N_4 and the zirconium suboxide $ZrO_{0.27}$ (first and third row of reflection markers) form instead of ZrN . Also monoclinic zirconia and $\sim 2.5\%$ of residual oxonitride (second and lower row of reflection markers) were formed.

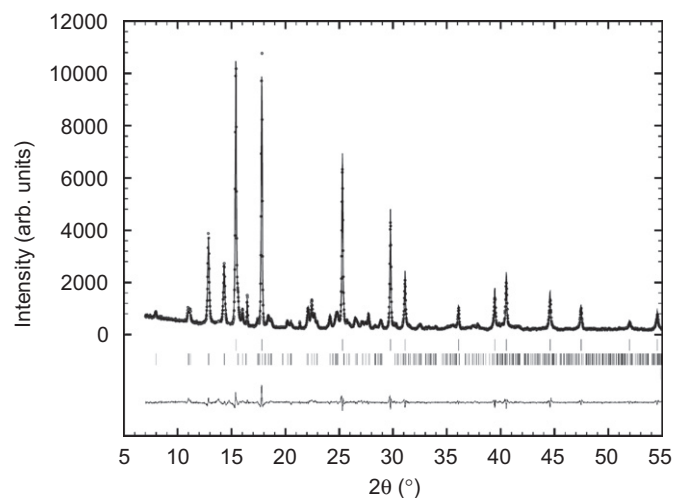


Fig. A4. Only ZrN and monoclinic zirconia were obtained at 12.5 GPa and 1473 K.

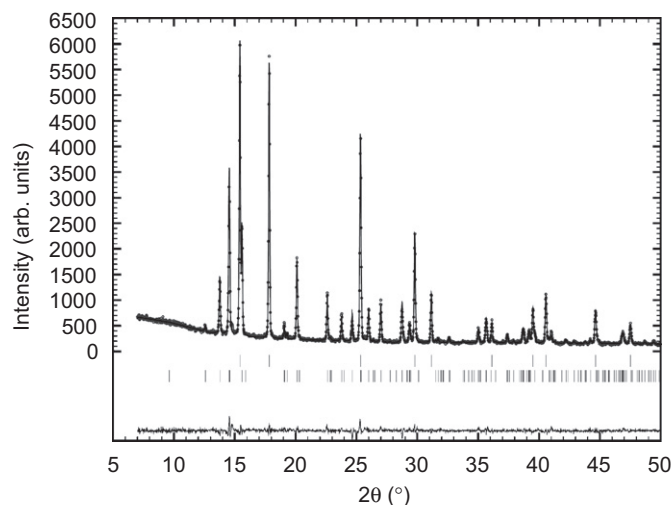


Fig. A5. From experiments at 14 GPa and 1573 K only samples consisting of ZrN and cotunite-type zirconia were obtained.

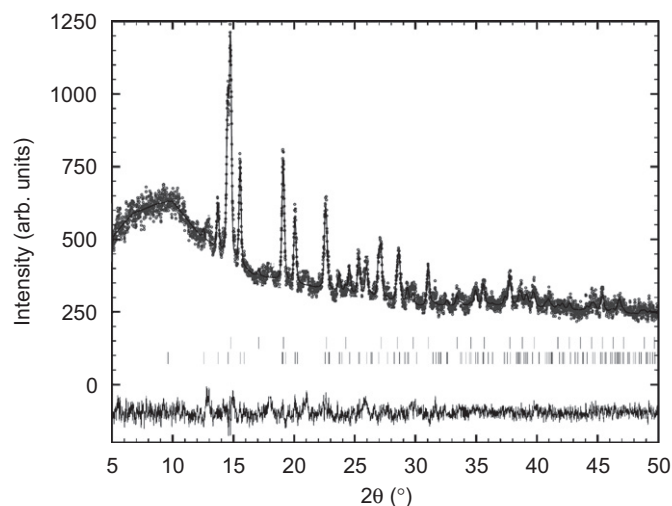


Fig. A6. Samples obtained at 17.5 GPa and 1173 K consisted solely of the two high-pressure phases cubic Zr_3N_4 and cotunite-type zirconia.

References

- [1] C.J. Howard, R.J. Hill, et al., *Acta Crystallogr. B* 44 (1988) 116.
- [2] J.D. McCullough, K.N. Trueblood, *Acta Crystallogr.* 12 (1959) 507.
- [3] G. Teufer, *Acta Crystallogr.* 15 (1962) 1187.
- [4] D.K. Smith, C.F. Cline, *J. Am. Ceram. Soc.* 45 (5) (1962) 249.
- [5] Y.-B. Cheng, D.P. Thompson, *J. Am. Ceram. Soc.* 76 (3) (1993) 683.
- [6] M. Lerch, J. Wrba, et al., *J. Solid State Chem.* 125 (1996) 153.
- [7] E.H. Kisi, C.J. Howard, et al., *J. Am. Ceram. Soc.* 72 (9) (1989) 1757.
- [8] J.M. Léger, P.E. Tomaszewski, *Phys. Rev. B* 47 (21) (1993) 14075.
- [9] Y. Kudoh, H. Takeda, et al., *Phys. Chem. Miner.* 13 (1986) 233.
- [10] A.H. Heuer, V. Lanteri, et al., *J. Mater. Sci.* 24 (1989) 124.
- [11] O. Ohtaka, H. Fukui, et al., *J. Am. Ceram. Soc.* 84 (6) (2001) 1369.
- [12] C.J. Howard, E.H. Kisi, et al., *J. Am. Ceram. Soc.* 74 (9) (1991) 2321.
- [13] S. Block, J.A.H. Dajornada, et al., *J. Am. Ceram. Soc.* 68 (9) (1985) 497.
- [14] L.G. Liu, *J. Phys. Chem. Solids* 41 (4) (1980) 331.
- [15] J. Haines, J.M. Léger, et al., *J. Am. Ceram. Soc.* 78 (2) (1995) 445.
- [16] H. Arashi, T. Yagi, et al., *Phys. Rev. B* 41 (7) (1990) 4309.
- [17] J. Haines, J.M. Léger, *J. Am. Ceram. Soc.* 80 (7) (1997) 1910.
- [18] O. Ohtaka, D. Andraut, et al., *J. Appl. Crystallogr.* 38 (2005) 727.
- [19] T.K. Gupta, F.F. Lange, et al., *J. Mater. Sci.* 13 (7) (1978) 1464.
- [20] W.M. Kriven, *J. Am. Ceram. Soc.* 71 (12) (1988) 1021.
- [21] R. Collongues, J.C. Gilles, et al., *Mater. Res. Bull.* 2 (9) (1967) 837.
- [22] J.C. Gilles, *Bull. Soc. Chim. Fr.* 11 (1) (1962) 218–2122.
- [23] M. Lerch, F. Krumeich, et al., *Solid State Ionics* 95 (1–2) (1997) 87.
- [24] M. Lerch, O. Rahausser, *J. Mater. Sci.* 32 (5) (1997) 1357.
- [25] M. Lerch, J. Lerch, et al., *J. Solid State Chem.* 128 (2) (1997) 282.
- [26] M. Lerch, H. Boysen, et al., *J. Phys. Chem. Solids* 58 (10) (1997) 1557.
- [27] M.R. Thornber, D.J.M. Bevan, et al., *Acta Crystallogr. B* 24 (1968) 1183.
- [28] T. Locherer, L. Dubrovinsky, H. Fuess, *Solid State Commun.* 143 (8–9) (2007) 408.
- [29] S. Kawasaki, T. Yamanaka, S. Kume, T. Ashida, *Solid State Commun.* 76 (4) (1990) 527–530.
- [30] T. Roisnel, J. Rodriguez-Carvajalel, *EPDIC 7: European Powder Diffraction, Parts 1 and 2*, vol. 378–3, 2001, p. 118.
- [31] M. Lerch, *Habilitationsschrift*, Universität Würzburg, 1997.
- [32] F. Birch, *Phys. Rev.* 71 (1947) 809–824.
- [33] A. Zerr, G. Miehe, R. Riedel, *Nat. Mater.* 2 (2003) 185.
- [34] D.A. Dzivenko, A. Zerr, et al., *Appl. Phys. Lett.* 90 (2007) 191910.
- [35] D.A. Dzivenko, A. Zerr, et al., *Adv. Mater.* 19 (2007) 1869.
- [36] Calculated from data provided in [31].
- [37] J.E. Lowther, J.K. Dewhurst, *Phys. Rev. B* 60 (21) (1999) 14485.
- [38] T.W. Baker, *Acta Crystallogr.* 11 (1958) 300.
- [39] X.J. Chen, et al., *Proc. Natl. Acad. Sci. USA* 102 (9) (2005) 3198.
- [40] S. Desgreniers, K. Lagarec, *Phys. Rev. B* 59 (13) (1999) 8467.
- [41] H. Boysen, F. Frey, T. Vogt, *Acta Crystallogr. B* 47 (1991) 881.
- [42] P. Bouvier, E. Djurado, et al., *Phys. Rev. B* 62 (13) (2000) 8731.
- [43] O. Ohtaka, H. Fukui, et al., *Phys. Rev. B* 63 (17) (2001) 1741081.
- [44] P. Kroll, *J. Phys.: Condens. Matter* 16 (14) (2004) S1235.