

Microstructure and luminescence properties of the high pressure high temperature sintered AlN–TiN ceramics

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ABSTRACT

Composite ceramics of titanium nitride grains incorporated in an aluminium nitride matrix have been synthesized by high pressure high temperature treatment of a mechanical mixture of AlN–TiN (3 mol % TiN) powders. The microstructure of the samples analysed by means of electron beam microanalysis and Raman spectroscopy shows that the formation of cubic AlN in the composite begins near titanium nitride grains. The areas of mixed chemical composition, which can be assigned to the formation of the solid solutions $Al_{1-x}Ti_xN$, have been observed at the phase interfaces. The luminescence properties of AlN–TiN ceramics have been considered focusing on the choice of high pressure and high temperature treatment conditions. Three main components at 2.0 eV, 2.4 eV and 3.1 eV are revealed in the cathodoluminescence spectra analysed quantitatively. The observed emission originates from the radiative transitions with participation of valence band states, oxygen-vacancy centres ($V_{Al}-O_N$), nitrogen vacancies V_N , and shallow donors which form a complex system of energy levels in the bandgap of the wurtzite-type AlN.

1. Introduction

Owing to a valuable combination of physical and chemical properties, aluminium nitride has a wide application in micro- and optoelectronics [1–3] and is considered to be an effective material for highly sensitive β -, γ - and UV-irradiation detectors [4–8]. AlN is a widegap semiconductor with good thermal conductivity up to 320 W/(m²K) for its single crystals, and 180–258 W/(m²K) in the form of sintered powders [9,10]. This allows for using AlN-based materials as insulators which are insensitive to spontaneous heating and as holders for LED equipment, ceramic wafers, and thermal conductive gaskets for electron lasers, without the risk of electrical breakdown [11,12]. Moreover, having the widest bandgap (6.2 eV for the hexagonal phase) amongst group-III nitrides, AlN attracts much attention in the semiconductor industry as a functional media for a blue light emitting diode and high frequency laser [13].

Several crystal modifications of aluminium nitride are known: the most stable (and well-studied) modification has a hexagonal wurtzite-type lattice (w-AlN) [14], and familiar phases have cubic zinc blende

(zb-AlN) [15,16] and rock-salt type (rs-AlN) structures [17–19], for which larger values of thermal conductivity, and mechanical and electrical strength are predicted due to a higher crystal structure symmetry [19]. Among few approaches to the production of rs-AlN [20], the implementation of the polymorphic transition w-AlN $\rightarrow$ rs-AlN can be distinguished, which is possible owing to the fact that the rs-AlN modification becomes thermodynamically stable under elevated pressures (above 13 GPa), and the cubic structure remains stable when the pressure is removed [21–25]. According to the simulated p–T diagram and experimental data, the minimal pressure for stabilising the rs-AlN phase decreases with a rise in temperature. This is likely to be due to atomic mobility enhancement in the aluminum nitride structure [17]. At temperatures of 1773–1873 K, the phase transition is observed under a pressure of 16.5 GPa [23]. The phase transition from hexagonal to cubic phase was first observed from the colour shift: an initially white sample abruptly turned black at 16.6 GPa [21]. Further development of equipment allowed detection of phase transitions using in situ X-ray diffraction (XRD). Therefore, the colour of the sample was shown to change from white to black at 18–20 GPa, while the rs-AlN phase was

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found to appear only at 22.9 GPa [22].

The other method of rs-AlN synthesis is the isostructural spinodal decomposition of metastable solid solutions with the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ composition, into aluminium and titanium cubic nitrides [26–28].

Since NaCl-type titanium nitride has a lattice parameter $a = 4.23 \text{ \AA}$ that is only 4.8% smaller than that of rs-AlN ($a = 4.38 \text{ \AA}$), and the heats of formation of AlN and TiN are quite similar ($\approx 318\text{--}338 \text{ kJ mol}^{-1}$), these materials form extended solid solutions with a rock salt structure in a wide concentration range [29–32]. Solid solutions of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ have been intensively studied as hard cutting, scratch-resistant and protective coatings [33–36], and the most investigated concentration range is $x < 0.7$, while the composition region near pure AlN has been poorly investigated. In our previous work [24] we tried to fill this gap and it was found that when TiN was added to AlN, the stabilising effect is promoted in the formation of the cubic aluminium nitride phase by high pressure high temperature (HPHT) treatment. Inclusion of 3 mol % TiN in the high pressure Al–Ti–N system leads to a polymorphic transition from w-AlN to rs-AlN at $T = 1773 \text{ K}$ and 12 GPa, which is 25% lower than the earlier theoretical and experimental data [17] for undoped aluminium nitride. AlN/TiN ceramic composite materials, obtained by HPHT treatment, have intermediate physical and mechanical properties as compared to the pure w-AlN and $\text{Ti}_x\text{Al}_{1-x}\text{N}$ solid solutions. It is extremely hard (up to 31.9 GPa) and thermally conducting (up to 100 W (m K)^{-1} at 298 K), which is of interest for applications requiring a combination of wear resistance and efficient heat removal. A colour shift from white to black was also observed for composite nitrides samples, as was previously found for undoped AlN [21,22].

The increase in microhardness and pronounced darkening are known to be indicative of the variation in the electronic structure of materials. The latter often originates from defects formation and consequently the growth of concentration of colour centres under the influence of high pressure and high temperature. In this study, a combination of diffraction and optical spectroscopy methods were used for closer inspection of the microstructure of AlN- and TiN-based materials to explain the changes in properties after HPHT treatment. The possibilities of Raman spectroscopy and pulsed cathodoluminescence methods for examination of microstructure changes in nitride-based composite materials were investigated.

2. Materials and methods

The samples were produced using HPHT treatment of a mechanical mixture of high-purity aluminium nitride and titanium nitride. A detailed description of the experiment is presented in Ref. [24]. The conditions of HPHT treatment and chemical composition of the samples are presented in Table 1. The density of the as-prepared samples was measured by the Archimedes method.

Raman spectral mapping was performed on a Horiba LabRam HR800 Evolution spectrometer using a He–Ne laser with 632.8 nm excitation ($\sim 10 \text{ mW}$ at the sample surface) with a 600 gr/mm grating. The dispersive system was equipped with an Olympus BX-FM series optical microscope, $100 \times$ Olympus objective lens (n.a. 0.9) and a Peltier-cooled charge-coupled device (CCD) detector. Additional Raman spectra were recorded on a Renishaw inVia Reflex Raman microscope equipped with a confocal Leica DML microscope, $50 \times$ Olympus objective lens with a numerical aperture of 0.5, a notch filter, and a cooled charge-coupled device detector. A Nd:YAG laser operating at 532.1 nm and $\sim 0.2 \text{ mW}$ power at the sample was employed as an excitation

source. Typical spectral acquisition time was 300 s, and the resolution was 1 cm^{-1} . The Raman spectrum of a silicon wafer (520.6 cm^{-1}) was used for spectral calibration.

Pulsed cathodoluminescence (PCL) was analysed using a compact RADAN-EXPERT electron accelerator [25] and an Andor Shamrock 303i spectrograph with a Newton EMCCD DU970P detector. The spectra were measured by pulses with the following parameters: duration 2 ns, frequency 1 Hz, average electron energy $155 \pm 5 \text{ keV}$, current density 150 A/cm^2 , and pulse number 44. The PCL spectra were recorded in the range 200–1100 nm, the acquisition time was 5 ms, and signal-to-noise ratio was >100 for all intensity measurements within the spectral range. The above listed spectroscopic measurements were carried out at room temperature.

The study of the internal texture (structure of phase inhomogeneity) and chemical composition at the surface of the samples with micron size locality was performed using a scanning electron microscope Jeol JSM 6390LV equipped with an Oxford INCA module for energy-dispersive X-ray spectroscopy analysis (EDX).

3. Results and discussion

3.1. Microstructure

The image of sample 1 before and after HPHT treatment shows a typical colour shift from white-grey to black (Fig. 1). The colour of sample 2 changes in a similar way. The observed darkening can be associated with an enhanced concentration of point and extensive defects. The other reason of this variation of colour of the samples is the appearance of new interphase boundaries.

The results of XRD analysis of the samples after HPHT treatment and the BSE images of their surfaces proves that the samples are composite ceramic materials with an aluminium nitride matrix in which titanium nitride grains are incorporated, and areas of a mixed chemical composition can be seen at the phase interfaces which can be attributed to the formation of a solid solution [24]. This confirms the results of chemical microanalysis (Fig. 2) since both signals of X-ray lines Al-K_α and Ti-K_α are observed at the interphase boundary. The XRD pattern of sample 2 also includes peaks of the cubic phase of aluminium nitride rs-AlN (ca. 3 mol %) formed as a result of polymorphic transition. The broadening of diffraction peaks reveals an increase in intrinsic stress due to micro strains. The density of the ceramics is within experimental error, and equal to the AlN theoretical density of 3.27 g cm^{-3} .

The Raman mapping study of the sample 1 region with the phase boundary of TiN and AlN is illustrated in Fig. 3. The Raman band of TiN (Fig. 3c) and AlN (Fig. 3d) correlate well with the data of BSE and optical microscopy. The Raman spectra of the TiN, AlN phases and boundary (points 1, 2, 3 on Fig. 3b) are shown in Fig. 4.

The profile of the Raman spectrum recorded at point 1 definitely comprises typical peaks of the w-AlN phase. In their turn, Raman peaks in the spectrum of point 3 correspond to titanium nitride. Besides TiN peaks, the spectrum contains 2 peaks with maxima at 440 cm^{-1} and 800 cm^{-1} . The latter are related to the wavenumbers of the Raman lines in the spectrum of rs-AlN [37]. The Raman spectrum of point 3 includes the typical lines of both TiN and cubic and hexagonal AlN phases. The positions of the Raman lines are practically unchanged. The spectrum of one phase changes to the spectrum of the other one. However, the profile of the Raman spectrum is averaged in the region in which it is measured. Since the laser beam is focused to a point with a cross-section dimension of about one micron, the absence of signals from the solid solution at the interface can be related to the fact that its width is much smaller. This observation agrees with the BSE images of the sample's surfaces.

No significant differences are observed in the Raman spectra of aluminium nitride in the initial powder samples 1 and 2 (Fig. 5a). New peaks with the position corresponding to rs-AlN appear in the Raman spectra of titanium nitride in samples 1 and 2. However, no considerable effects of peak shifting, and broadening occur (Fig. 5b). Therefore, it is

Table 1
Chemical composition of samples and experiment conditions.

Sample	x in $\text{Al}_{1-x}\text{Ti}_x\text{N}$	Temperature, K	Pressure, GPa	Duration of treatment, minutes
1	0.03	1473	12	3
2	0.03	1773	12	3

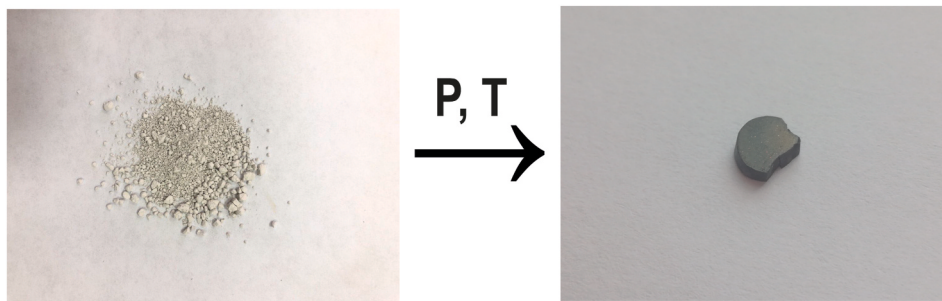


Fig. 1. The image of samples before and after HPHT treatment.

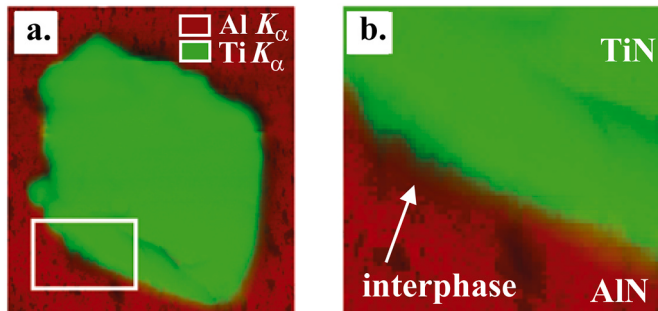


Fig. 2. X-ray map in the region with a TiN particle surrounded by AlN. a. Distribution of Al- K_{α} (red) and Ti- K_{α} (green) intensities. b. Magnification of the phase boundary area from a., where the arrow shows an additional phase different from AlN and TiN. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

supposed that the formation of the cubic phase begins near titanium nitride grains in the system under consideration. Since the Raman spectra were selected pointwise, they characterize the local microstructure and do not reflect the change in the macroscopic properties of

the samples. As a result, negligible differences were found in the Raman spectra of samples before and after HPHT treatment. Therefore, the cathodoluminescence method was employed to allow spectrum selection from the whole surface of the samples for the study of their macroscopic properties.

3.2. Pulsed cathodoluminescence

Fig. 6a represents the PCL spectra of the initial aluminium nitride and titanium nitride powders measured at room temperature. The AlN spectrum is characterised by a wide luminescence band with a maximum at about 400 nm in the short-wavelength region, and a narrower band with a maximum at about 600 nm in the red region. Note that the considered luminescence bands are typical of hexagonal aluminium nitride and have been previously observed in its different structural modifications [4,8,38,39]. No cathodoluminescence response was observed for TiN powder.

The profiles of PCL spectra of the initial powder mixture, as well as samples 1 and 2, are analogous to the luminescence of initial aluminium nitride with respect to spectral composition (Fig. 6b). Meanwhile, the ratios of intensities of emission bands are different for all three samples. In the initial powder AlN + TiN, the luminescence in the region of 400 nm is almost 2.5 times more intensive than in the region of 600 nm,

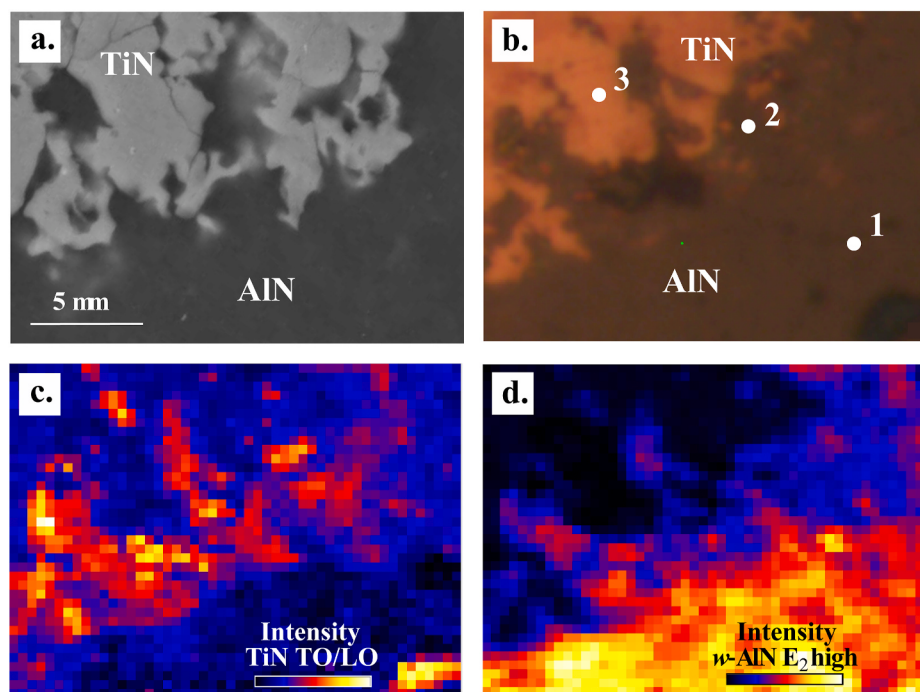


Fig. 3. a. BSE image of sample 1 in the region with a phase boundary of TiN and AlN, b. optical image at reflected light, c. the intensity of Raman band at 550 cm^{-1} corresponding to TiN TO/LO (Fig. 5), d. the intensity of Raman band at 610 cm^{-1} corresponding to w-AlN E_2 high (Fig. 5).

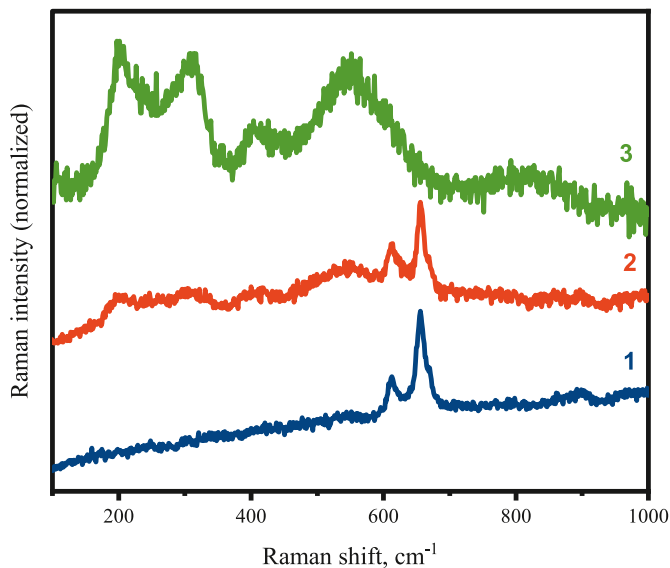


Fig. 4. Raman spectra registered in points 1, 2 and 3 (Fig. 3).

whereas in ceramic sample 2, the opposite behaviour is observed. In their turn, the intensities of both bands are comparable in the spectrum of sample 1. Besides, narrow maxima are present in all the measured spectra that are marked by black cursors. According to the independent data [40], these “background” peaks can be related to luminescence of

molecular and ionised nitrogen in air under the electron beam excitation.

Intrinsic and impurity defects in aluminium nitride form different optically active centres which promote luminescence in a wide spectral range. The obtained PCL energy spectra were quantitatively described by three Gaussian-shaped components (Fig. 7). The calculated parameters are listed in Table 2. The similar type of spectral components have been observed earlier in a number of independent works focussed on the study of optical properties of AlN ceramics, nano-whiskers, sub-micro-crystals, and bulk single crystals by photo-, electro-, cathodo- and thermoluminescence techniques [3–8,38,39]. The responsible radiative transitions were identified using the independent data from Ref. [41]. Considering the obtained PCL spectra, we can conclude that the valence band (VB) states, donor-acceptor pairs based on oxygen-vacancy complexes ($V_{Al}-O_N$), as well as nitrogen vacancies V_N and shallow donors (SD), play a significant role in the emission mechanisms of all examined samples (Table 2).

Aluminum nitride with a wurtzite crystal lattice is a direct bandgap semiconductor with a forbidden gap that varies in the range 6.13–6.28 [53]. However, technological impurities (O, C, Si etc.) lead to a significant distortion of the shape of absorption spectra in the intrinsic edge region and suppression of short-wavelength band-edge luminescence in w-AlN [41], what is observed in the samples under study. In its turn the minimal value of the forbidden gap 3.8–4.8 eV for rs-AlN corresponds to indirect electron transition in points Γ -X of the Brillouin zone [54–56]. No new peaks were observed in the measured PCL spectra of samples after HPHT treatment as compared with the spectrum of the initial mixture. It can be concluded that a low content of the formed cubic

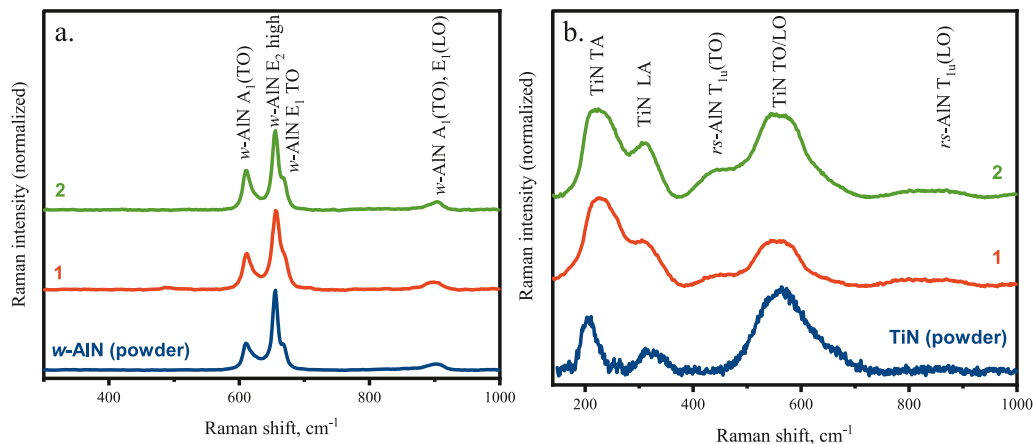


Fig. 5. Raman spectra of a. aluminium nitride in initial powder, samples 1 and 2 and b. titanium nitride in initial powder, samples 1 and 2.

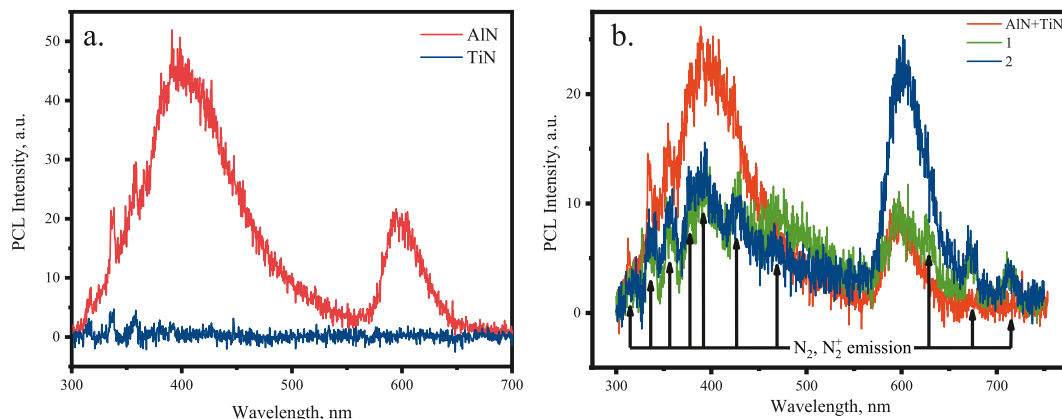


Fig. 6. Experimental PCL spectra of a. AlN and TiN powders and b. initial powder mix, samples 1 and 2.

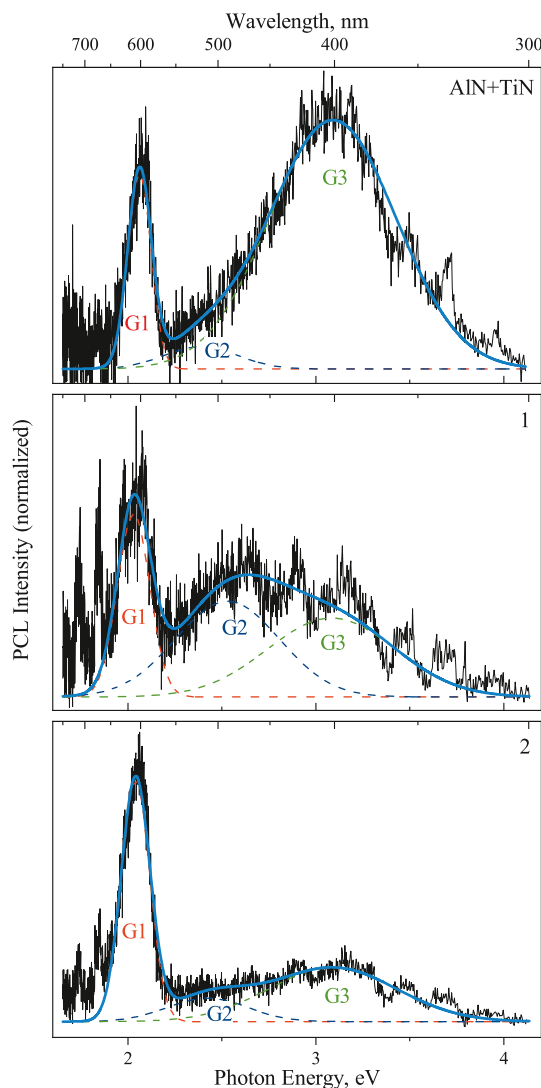


Fig. 7. Approximation of PCL energy spectra in initial powder, samples 1 and 2. Black line – experimental data; blue line – resultant curve; dotted lines – Gaussian components. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Parameters of emission components in measured PCL spectra.

Spectral parameters	AlN + TiN	Sample 1	Sample 2	Optical transitions
G1				
$E_m, \pm 0.05$ eV	2.06	2.03	2.04	$(V_{Al}-O_N) \rightarrow VB$
FWHM, ± 0.05 eV	0.15	0.20	0.18	[42–45]
G2				
$E_m, \pm 0.05$ eV	2.39	2.53	2.42	$(V_{Al}-3O_N) \rightarrow VB$ [46]
FWHM, ± 0.05 eV	0.47	0.65	0.50	$SD \rightarrow (V_{Al}-2O_N)$ [47–50]
G3				
$E_m, \pm 0.05$ eV	3.09	3.08	3.09	$V_N \rightarrow (V_{Al}-3O_N)$ [51]
FWHM, ± 0.05 eV	0.79	0.80	0.80	$SD \rightarrow (V_{Al}-O_N)$ [47–49,52]

phase does not manifest itself in the cathodoluminescence of the studied samples.

The redistribution of relative intensities of the G1, G2 and G3 components in the analysed PCL spectra can be associated with the changing of the concentration of aluminium vacancies in the hexagonal AlN phase, under the high temperatures and high pressures, due to the incorporation of aluminium atoms into the TiN lattice with the

formation of solid solutions at the interfaces. The higher the temperature is, the stronger these effects are, which corresponds to a higher degree of aluminium introduction into the TiN lattice and, consequently, to a larger specific volume per solid solution.

4. Conclusion

The microstructure of composite ceramic materials, that have been synthesized by HPHT treatment of AlN–TiN (3 mol % TiN) mechanical mixture, was analysed by means of combination of diffraction and optical spectroscopy methods to investigate synthesis-structure-properties correlation. It was found that while the pointwise selected Raman spectra characterize the local microstructure and do not reflect the variation in the macroscopic properties of the sample, the cathodoluminescence method with a spectrum selection from the whole surface of the samples allows the study of the macroscopic properties. The increase in microhardness and darkening of AlN–TiN ceramics after HPHT treatment was shown to be related both to areas of mixed chemical composition at the phase interfaces which can be assigned to the formation of solid solutions of $Al_{1-x}Ti_xN$ and the changing of concentration of aluminium vacancies in w-AlN. Aluminium atoms are embedded in the TiN lattice with the formation of solid solutions at the phase interfaces, which manifests itself in the redistribution of the relative intensities of the Gaussian components – 2.0, 2.4 and 3.1 eV – in the PCL spectra of the examined samples. When the temperature of the HPHT treatment grows, these effects become stronger, which corresponds to a higher degree of aluminium incorporation into the TiN lattice and, consequently, to a larger specific volume per solid solution.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ceramint.2021.02.263>.

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Supplementary information

1. Method of samples preparation

The TiN powder used in this study was supplied by Aldrich, Inc. and had a grain size of $< 3 \mu\text{m}$ with a purity of 99 %. The AlN powder was supplied by Plasmotherm Inc. (Russia) and had a grain size of $< 4 - 5 \mu\text{m}$ with a purity of 98 %. The powders (3 mol. % TiN – 97 mol. % AlN) were firstly mixed in agate mortar in ethanol medium during 60 minutes.

The tablets with height of 5 mm and diameter of 3 mm were formed from the powder mixture and placed in high pressure lithographic stone cell (fig. S1). The high-temperature high-pressure (HTHP) treatment was held in uniaxial compression “double toroid” type chamber [1] under 12.0 GPa pressure and 1200-1500 °C temperature. The chemical composition of the samples and experiment conditions are listed in Table 1.

Table 1 – The chemical composition of the samples and experiment conditions

Sample	Concentration of TiN additive, mol. %	Temperature, °C	Pressure, GPa	Time of treatment, min
1	3	1200	12	3
2	3	1500	12	3

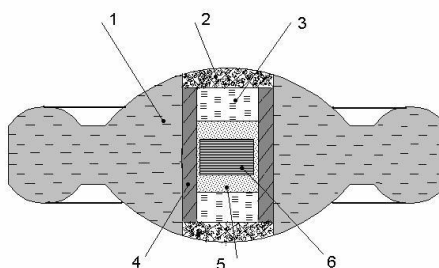


Figure S1 – High-pressure cell filling schematic diagram:
1 – lithographic stone cell; 2, 3 – graphite with BN disks; 4 – graphite heater;
5 – medium powder mix, 6 – sample.

The chamber consists of two coaxial carbide anvils with a special shape, fastened with the steel rings. The lithographic stone cell was placed between carbide anvils. The pressure calibration was performed in the preliminary experiments by observation phase transition in bismuth and barium under room temperature.

The HTHP treatment was performed in the following procedures: the cell compression at room temperature with a force of 7 MN during 30 min, next heating of the reaction zone to the desired temperature at a rate of 15 °C/s, thermal retardation at this temperature for 3 min, cell quenching under pressure at a rate of 500 °C/s, gradual load dropping, cell extraction from the chamber and sample extraction from the cell.

The part of a sintered specimen was crushed by multiple squeezing between the hard-faced profile anvils for XRD analysis. The differences in the phase composition of the initial powder mixture and HPHT treated materials are illustrated on the XRD patterns, which were measured by Huber Imaging Plate Guinier camera G670 (Cu $K_{\alpha 1}$ radiation). Peaks identification and Rietveld full-profile analysis were performed by Xpert High Score Plus (Panalytical) software and PDF-2 database.

2. Structural analysis

XRD patterns of the initial powder mixture and samples after HPHT treatment are presented in Fig. S2.

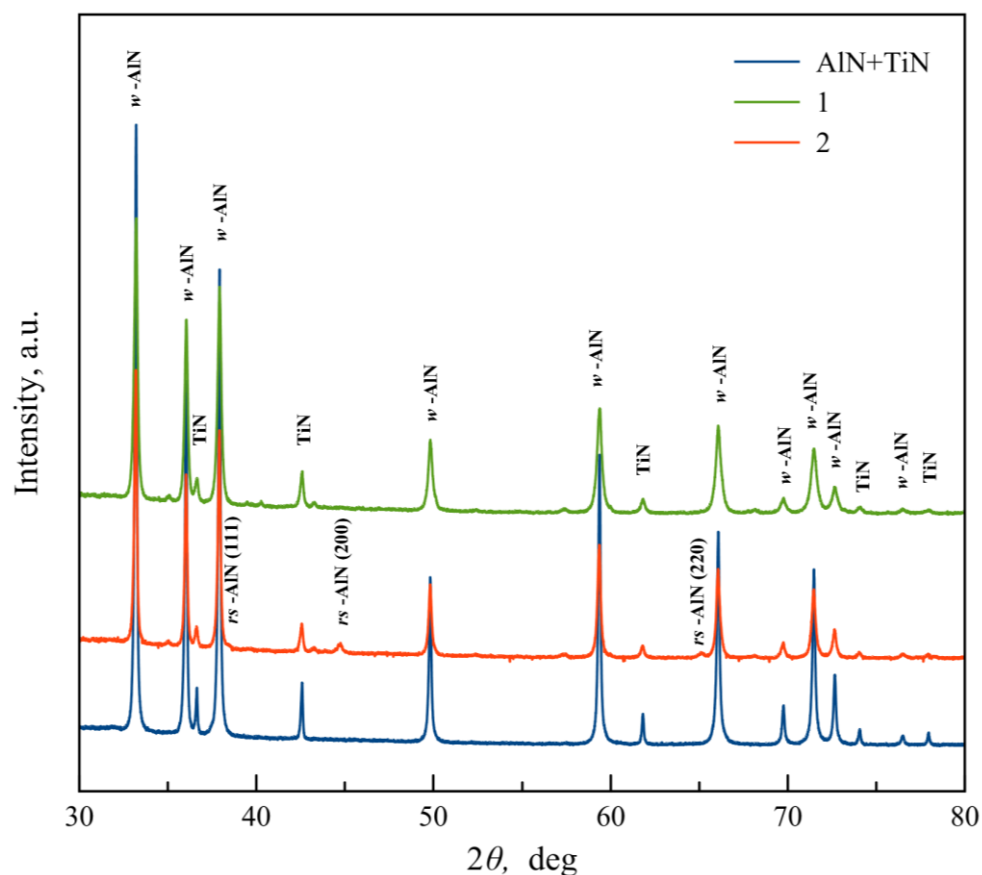


Figure S2 – XRD patterns of the initial powder mixture and HPHT treated samples

The XRD patterns of the initial powder mixture and sample 498 contain reflexes only from the w-AlN (JCPDS № 01-070-2543) and TiN (JCPDS № 01-071-9845). The additional peaks on the XRD pattern of the 563 sample were detected, by 2θ value and intensity correlation corresponding to the reflexes from *rs*-AlN (200), (220) and (111) crystal faces [2]. The concentration of the *rs*-AlN in the 563 sample is about 3.1 %, w-AlN – 93.8%, TiN – 3.1%.

It demonstrates, that *rs*-AlN was observed due to phase transition from w-AlN rather than $\text{Al}_{1-x}\text{Ti}_x\text{N}$ solid solution formation as concentration of the TiN phase wasn't changed significantly after HPHT treatment. The lattice constant $a = 4.05(2) \text{ \AA}$ was determined for *rs*-AlN and it is in good agreement with the powder diffraction file JCPDS № 00-046-1200 ($a = 4.0450 \text{ \AA}$).

Nevertheless, the obtained lattice constant is higher than it was measured early in [2] what can be attributed to the lattice parameter increase due to Ti incorporation.

In fig.S3 profile of the second order XRD reflex from w-AlN (102) plane at the initial mixture and HPHT treated sample is presented. It demonstrates increase in intrinsic stress due to micro strains [3, 4], accompanied by an increase in XRD peak broadening. The micro strains was estimated by increasing of the FWHM peaks of the HPHT treated samples in respect to initial powder mixture and its values are no less than 0.18 % for sample 1 and 0.16 % for sample 2.

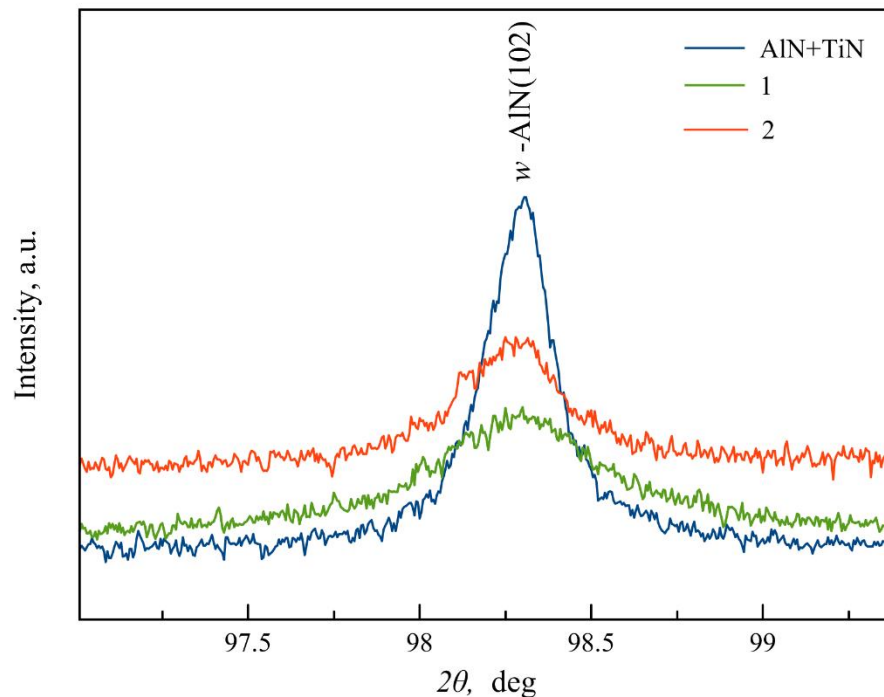


Figure S3 – Profile of the second order XRD reflex from w-AlN (102) plane at the initial mixture and HPHT treated sample

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