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$Ba_6Si_6N_{10}O_2(CN_2)$ – A Nitridosilicate with a NPO-Zeolite Structure Type Containing Carbodiimide Ions

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A new precursor approach leading to NPO-zeolite analogous nitridosilicates with cavities containing carbodiimide ions is presented. The reaction of amorphous "$Si(CN_2)_2$" and barium in liquid sodium afforded $Ba_6Si_6N_{10}O_2(CN_2)$ as yellow crystals. The structure is a rare example of the NPO-zeolite framework type and the first nitridosilicate incorporating carbodiimide ions. The partially ordered integration of carbodiimide moieties in the channels leads to the formation of a superstructure ($P\bar{6}$, no. 174, a = 16.255(2), c = 5.4690(11) Å, Z = 3, R_1 = 0.0299, 2139 data, 100 parameters) and merohedral twinning. A comprehensive structure solution is presented, taking all possible ordering variants and twin laws into account.

Introduction

Silicates are a very important class of minerals due to their wide distribution and abundance in the Earth's crust. Whereas almost all naturally occurring silicates are oxosilicates, an increasing number of nitridosilicates has been synthesised in the last decade.[1–4] Owing to their remarkable materials properties (e.g. high mechanical, thermal and chemical stability), a variety of industrial applications has been developed. Highly condensed networks built up from $[SiN_4]$ tetrahedra are used as high-temperature materials,[5,6] whereas alkaline-earth nitridosilicates and oxonitridosilicates have attracted much attention as host lattices for rare-earth doped luminescent materials in phosphor-converted LEDs (pcLEDs).[7–11] With regard to the materials properties and the high stability of nitridosilicates it seemed to be intriguing to synthesise zeolite-like, microporous network structures made up of $[SiN_4]$ tetrahedra. Only a few such compounds and related materials (e.g. oxonitridosilicates or SiAlONs) are known.[3,12] This is probably due to the high-temperature reactions (> 700 °C) necessary for the formation of (Al,Si)–N bonds. Under such conditions highly condensed structures are favoured and standard templates known from conventional zeolite chemistry are ineligible. Furthermore, kinetic control typical for template synthesis does usually not occur at such high temperatures. Oxidic zeolites typically exhibit a molar ratio of tetrahedral centres to bridging atoms T/X of 1:2 (T = Al, Si; X = O) and a framework density (tetrahedral centres in a volume of 1000 Å^3) ranging from 12.5 to 20.2.[13] The discovery of zeolite-like nitridic frameworks was more or less serendipitous since, up to now, no systematic routes have been available which promote the formation of open channels or large cavities. In this context, $Ba_2Nd_7Si_{11}N_{23}$ was probably the first example of a nitridosilicate with a framework density in the range of zeolites (18.5).[3] The oxonitridophosphate $Li_xH_{12-x-y+z}[P_{12}O_yN_{24-y}]Cl$ represents the first nitridic zeolite with an unusual framework type (NPO) that has initially been claimed as a possible SiO_2 structure type. However, it has not been observed as yet (cf. Figure 1).[14,15]

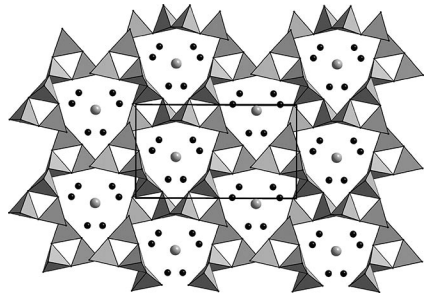

Figure 1. Crystal structure of $Li_xH_{12-x-y+z}[P_{12}O_yN_{24-y}]Cl_z$. Chains of 3 rings are connected to a 3D oxonitridophosphate framework in the b,c-plane. Thus, 12 ring channels are formed. $[P(O,N)_4]$: gray polyedra; Cl^-: dark gray; Li^+: black; view along [100].[14] The orthorhombic unit cell is depicted in black.

Recently, Francesconi et al. reported $Ba_3Si_3N_5OCl$, an oxonitridosilicate exhibiting the NPO structure type.[12] In this case, the 12-ring channels of this framework are built up from $[Si(N,O)_4]$ tetrahedra and are filled with Ba^{2+} ions around a strand of disordered chloride ions. $Ba_3Si_3N_5OCl$ is one of the rare examples of a zeolite-like oxonitridosilic-

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ate obtained by means of a standard solid-state synthetic route. The development of a systematic approach for the formation of porous materials based on nitridosilicates is a major goal of our current investigations. In this context, low-temperature routes as well as temperature-resistant structure directing agents favouring the formation of cavities are required. We have recently reported on the employment of amorphous "$Si(CN_2)_2$"[16] as a promising precursor for the low-temperature synthesis of nitridosilicates.[17] In combination with this precursor, carbodiimide ions might serve as temperature-resistant spacers. The resultant carbodiimide-containing frameworks might be the first step towards porous structures obtained by replacement of the carbodiimide moieties. In this paper, we report the synthesis of the first carbodiimide-containing oxonitridosilicate and its structure determination.

Results and Discussion

Synthetic Approach

Commonly, nitridosilicates (e.g. $M_2Si_5N_8$ with M = Ca, Sr, Eu or Ba)[18,19] are synthesised using high-temperature reactions in the range of 1550–1650 °C starting from metals or oxides and silicon nitride or silicon diimide [$Si(NH)_2$]. At temperatures of 900–1000 °C, decomposition of $Si(NH)_2$ with subsequent formation of amorphous silicon nitride is observed. In turn, using $Si(NH)_2$ as a reactive precursor for Si_3N_4, the reaction temperatures can be lowered significantly.[20] In the past, DiSalvo et al. have synthesised the nitridosilicate $Ba_5Si_2N_6$ from silicon and sodium melts at surprisingly low temperatures (760 °C).[4] This synthetic route, employing the decomposition of sodium azide as a nitrogen source, has also been used for synthesis of $MSiN_2$ (M = Ca, Sr, Ba).[2] In addition to the low temperatures, the solubility of alkaline earth metals as well as traces of silicon and nitridic species in liquid sodium favours the formation of single crystals. The excess of sodium used as a flux can be removed under dynamic vacuum by distillation at about 320 °C. These reaction conditions in combination with "$Si(CN_2)_2$" as a precursor for carbodiimide-containing nitridosilicates seem to be promising as a number of carbodiimide-containing nitrides have been obtained by the sodium flux method {e.g. $Sr_4GaN_3(CN_2)$[21] and $(Sr_6N)[CoN_2](CN_2)_2$}.[22] Systematic investigations of the system "$Si(CN_2)_2$"/Ba/NaN_3/Na afforded the formation of yellow crystals of $Ba_6Si_6N_{10}O_2(CN_2)$. $BaSiN_2$[2] which has a higher density, seems to be the thermodynamically controlled product of this reaction and usually occurs as a by-product. This could be corroborated by applying several temperature programs to the synthesis of $Ba_6Si_6N_{10}O_2(CN_2)$. These experiments revealed that $BaSiN_2$ is predominantly formed upon elevating the temperature (> 900 °C) or extending the annealing time. However, good yields of $Ba_6Si_6N_{10}O_2(CN_2)$ could be obtained by quick heating to 900 °C and subsequent cooling to 500 °C. In addition, it was shown that increasing the carbodiimide concentration by adding Na_2CN_2 promotes the formation of $Ba_6Si_6N_{10}O_2(CN_2)$. As indicated by X-ray powder diffraction, the addition of Na_2CN_2 increases the molar ratio of $Ba_6Si_6N_{10}O_2(CN_2)$ to $BaSiN_2$ significantly. However, under these conditions the product becomes microcrystalline which impedes the mechanical separation of the desired product.

Sample Characterisation

For sample characterisation, agglomerated yellow crystals of $Ba_6Si_6N_{10}O_2(CN_2)$ were selected from the reaction mixture. When exposed to air, the crystals decompose forming a white product. The approximate molar ratio of elements (Ba, Si, N and O) was determined by energy dispersive X-ray microanalysis. FTIR spectra of $Ba_6Si_6N_{10}O_2(CN_2)$ show the typical absorption bands for carbodiimides ν_{as} and ν_s at 1974 and 674, 665 cm^{-1}, respectively. The observed vibrations are comparable with those of $BaCN_2$ (ν_{as} and ν_s at 1947 and 673, 662 cm^{-1}).[23] The diffraction pattern of $Ba_6Si_6N_{10}O_2(CN_2)$ powdered agglomerates separated manually from the reaction products match well with simulations based on the results of our single-crystal structure analysis (cf. Supporting Information). Only a few weak reflections originating from the by-product $BaSiN_2$ can be detected.

Crystal Structure Determination

The strong reflections in the diffraction patterns of $Ba_6Si_6N_{10}O_2(CN_2)$ can be indexed on the basis of a primitive hexagonal unit cell with a_{basic} = 9.421 Å and c_{basic} = 5.477 Å. This corresponds to the basic lattice translations of the NPO framework type.[14] Although the framework topology exhibits high symmetry (space group $P6_3/mmc$), reasonable structural data could only be refined in subgroups with lower symmetry. Using only the strong reflections, the structure could be solved by direct methods and refined straightforwardly assuming the space group $P\bar{6}2c$. In this setting (cf. Figure 2, top), there is one 12-ring channel per unit cell. Although the structure model can be refined to R_1 = 0.021, there remain significant shortcomings. The channels are filled with Ba atoms (similar positions to the Li in Figure 1) and are centred by an equidistant chain of atoms (interatomic distance 1.37 Å). If these atoms are interpreted as C and N, one site is fully occupied and the other about half-occupied. Assigning the less occupied position to N atoms, the chain can be interpreted in terms of disordered carbodiimide ions. C atoms are always present and, in 50% of the cases, interconnected by N atoms to form infinite chains of collinear carbodiimide ions. Absence of N means a gap between consecutive ions. Any ordered arrangement must involve at least two symmetrically independent channels or much lower symmetry. The displacement parameters of the C and N positions are quite large and the refined bond length is not reasonable. The average C–N distance of carbodiimides (N=C=N) and related cyanamides (N–C≡N) has been reported to be between 121 and 128 pm.[24] The model obtained from considering only the

strong reflections thus corresponds to the average superposition structure of either a disordered compound, one with lower symmetry or a superstructure which is corroborated by extremely elongated displacement ellipsoids of the Ba atoms which probably follow the (real or apparent) disorder of the carbodiimide ions.

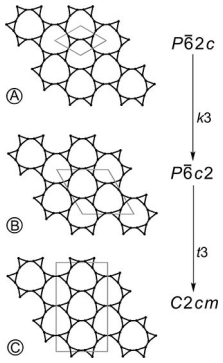

Figure 2. Framework scheme viewed along [001] (black: interconnected Si atoms) and corresponding unit cells (gray).

Close inspection of the diffraction pattern after prolonged exposure times revealed weak superstructure reflections and only a marginal amount of hardly detectable diffuse scattering. Upon consideration of the superstructure reflections, a hexagonal unit cell with a = 16.225 Å and c = 5.469 Å can be derived. A reciprocal $hk0$ layer (reconstructed from imaging-plate data) with basic and superstructure unit cells can be found in the Supporting Information. The Laue symmetry has been unequivocally determined as 6/*mmm*. The supercell is related to the basic unit cell by $\boldsymbol{a} = -\boldsymbol{a}_{basic} + \boldsymbol{b}_{basic}$, $\boldsymbol{b} = 2\boldsymbol{a}_{basic} + \boldsymbol{b}_{basic}$ and $\boldsymbol{c} = \boldsymbol{c}_{basic}$. Thus it contains three channels per unit cell as shown in Figure 2. This does not correspond to the structure of $Li_xH_{12-x-y+z}[P_{12}O_yN_{24-y}]Cl_z$ which is orthorhombic and exhibits two channels per unit cell. Also, the relationship between the structures of the silicate and the phosphate cannot be interpreted in terms of twinning by reticular pseudomerohedry, as no superstructure reflections of $Ba_6Si_6N_{10}O_2(CN_2)$ correspond to reciprocal lattice nodes of the orthorhombic NPO oxonitridophosphate structure. As there are no unusual systematic absences in the diffraction pattern of the superstructure and its cell volume is three times that of the basic structure, it is impossible to assume a superposition of diffraction patterns corresponding to smaller unit cells. Thus, twinning by reticular pseudomerohedry can be ruled out. Although this means that the basis vectors of the superstructure are the true ones, (pseudo-)merohedral twinning may be present and is not unlikely. The superstructure was solved and refined taking into account group-subgroup relationships as shown in Figure 3. The enlargement of the unit cell in the superstructure when compared with the basic structure corresponds to a *klassengleiche* subgroup (index 3), leading to a structure model in $P\bar{6}c2$. However, as neighbouring channels are related by glide planes in this space group, an ordered arrangement of carbodiimide ions is intrinsically impeded by this symmetry. Trial refinements did not yield satisfactory results, especially concerning displacement parameters of the Ba atoms. All refinements employing lower symmetry must include twin laws as the Laue symmetry of all subgroups is lower than the observed 6/*mmm*. We have performed refinements in all space groups depicted in Figure 3 except *P*312 and *P*3*c*1, since the latter are supergroups of *P*3 which has been tested in detail without success (and could describe the trigonal variants with additional symmetry elements 2 or *c* as well). The corresponding unit cell settings are shown in Figure 2. All *translationengleiche* subgroups involve twinning − if two steps are needed, complex twins must be assumed. It turned out that the best refinement was achieved in $P\bar{6}$, taking into account twinning by a twofold axis ∥[210]. Only for this symmetry all displacement parameters were positively defined, convergence was stable and a maximum degree of carbodiimide ordering in the channels resulted. Also, the R values were the best obtained. Both twin domains exhibit the same polarity. Additional inversion twinning was checked for, but not confirmed, and the Flack parameter also proves that only one polarity is present. Although the displacement parameters of the carbodiimide moieties are still indicative of a very small degree of disorder, further symmetry reduction did not yield any improvement. Marginal disorder is corroborated by minute amounts of diffuse scattering which, due to its very low intensity, shall not be further discussed.

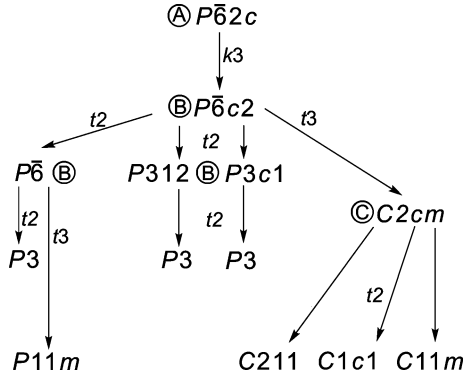

Figure 3. Group-subgroup relationships and type/index of subgroups, letters indicating the cell settings correspond to Figure 2.

Refinements based on low-temperature data were slightly better and are reported here. At ambient temperature, the structure model obtained is essentially the same. For the final refinement, the C–N distances were assumed to be equal in three crystallographically independent carbodiimide ions. The average value of 1.27(1) Å corresponds better to that observed in other carbodiimides.[24] Table 1 sums up crystal data and refinement results.

Structure Description

The framework is built up from exclusively vertex-sharing $[Si(N,O)_4]$ tetrahedra with all Si−(N,O) distances [1.64(3)–1.79(3) Å] being in the range known from bridging $N^{[2]}$ atoms in nitridosilicates and $O^{[2]}$ atoms in oxonitridosilicates. In comparison the distances in $Ba_3Si_3N_5OCl$ range

from 1.71(3) to 1.749(4) Å.[12] From one side, each Ba atom is coordinated by O/N atoms of the tetrahedral framework [Ba–(N,O) distances 2.71(1)–3.16(2) Å], whereas the other side is coordinated by two N atoms originating from the carbodiimide moieties [distances Ba–N 3.118(7)–3.126(8) Å]. The Ba–(N,O) bond lengths are in the typical range for oxonitridosilicates (e.g. $BaSi_6N_8O$)[25] but relatively long distances between Ba and carbodiimide ions are observed [e.g. $BaCN_2$: Ba–N 2.77(1)–2.84(1) Å].[23] The Ba–Ba distances between atoms on opposite sides of the 12-rings [6.386(1) Å] are shorter than in $Ba_3Si_3N_5OCl$ [Ba–Ba: 6.692(2) Å[12]]. This narrowing of the channels is due to the smaller ionic radius of nitride ions (and thus carbodiimide ions) compared with Cl^-, the difference being approximately 35 pm.[26] Additionally, the calculated framework density of 14.4 for $Ba_6Si_6N_{10}O_2(CN_2)$ is worthy of further investigation (cf. zeolite beta: 15.1, faujasite: 12.7).[13] The pore size is approximately 5.1 Å if the free diameter of the channels is calculated from the atomic coordinates of the Si(N,O)-framework (N5–N9) considering the ionic radius of N^{3-} (1.46 Å).[26] Figure 4 shows the unit cell of the final structure model viewed along [001]. In Figure 5, the arrangement of the carbodiimide groups is illustrated.

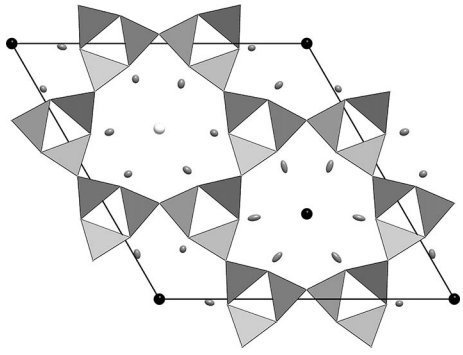

Figure 4. Extended unit cell of $Ba_6Si_6N_{10}O_2(CN_2)$, viewing direction along [001]. $[Si(N,O)_4]$ units are depicted as closed gray polyhedrons, Ba^{2+} ions gray and anions black or white (Ba ellipsoids with a probability of 50%). Carbodiimide ions in different channels occupy positions in different heights are distinguished by black and white spheres, respectively.

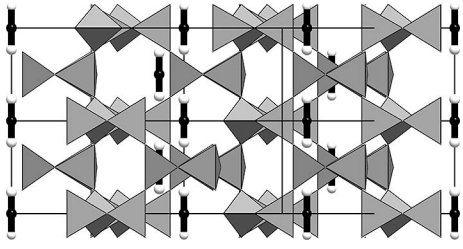

Figure 5. Section of the structure of $Ba_6Si_6N_{10}O_2(CN_2)$, viewing direction approximately along [120]. Ba atoms are omitted to illustrate the CN_2^{2-} arrangement.

The model in $P\bar{6}$ exhibits three symmetrically independent channels but only two possible positions with different relative heights for the strands of carbodiimide groups. Accordingly, carbodiimide strands with the same relative heights form a honeycomb pattern. In Figure 4, this is illustrated by different colours corresponding to the relative heights. These findings can nicely explain why for all crystals investigated, twinning by a twofold axis occurs but no inversion twinning. The 2:1 ratio of different heights is inverted in different twin domains related by the twofold axis that is lost when the independent channels are allowed after the superstructure is formed (*translationengleiche* group-subgroup relationship, cf. Figure 3). The $[Si(N,O)_2]$ network itself is polar. Since no inversion twinning occurs, a framework with $\bar{6}2m$ point symmetry is probably formed at elevated temperatures. The respective high temperature phase would probably exhibit disordered carbodiimide moieties. Upon cooling, ordering of the carbodiimide groups might occur, enforcing symmetry reduction associated with twinning. Although the thermal energy available is not sufficient to achieve a rearrangement of the $[Si(N,O)_2]^{2-}$ network, the overall polarity is conserved.

Conclusions

The synthesis of a carbodiimide containing nitridosilicate is encouraging in terms of a systematic approach towards porous nitridosilicates. Using the precursor "$Si(CN_2)_2$" in liquid sodium, we obtained a zeolite-like nitridosilicate besides the thermodynamically controlled reaction product $BaSiN_2$. To the best of our knowledge, $Ba_6Si_6N_{10}O_2(CN_2)$ is the second example of a nitridosilicate incorporating complex anions (cf. $Ba_4Pr_7[Si_{12}N_{23}O][BN_3]$).[27] The extensive crystal structure determination illustrates the structural changes in the NPO zeolite-type by formal replacement of Cl^- by carbodiimide ions and their temperature-dependent ordering. Our future aims are directed towards the synthesis of new zeolite-like nitridosilicates by the "$Si(CN_2)_2$" precursor route and to gain a deeper insight into the stability of the $[Si(N,O)_2]^{2-}$ framework by exchange or replacement of the carbodiimide moieties.

Experimental Section

Synthesis: All manipulations were performed with rigorous exclusion of oxygen and moisture using Schlenk techniques or an argon-filled glove box (Unilab, MBraun, Garching, $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). Argon (Messer-Griessheim, 5.0) was purified by passage over columns of silica gel (Merck), molecular sieves (4 Å; Fluka), KOH (≥ 85%; Merck), P_4O_{10} (≥ 99%, granulate; Roth) and titanium sponge (99.5%, grain size ≤ 0.8 cm; Johnson Matthey) at 700 °C. "$Si(CN_2)_2$" was synthesised as described in the literature and calcined at 350 °C under vacuum (10^{-3} mbar) for 18 h.[16] NaN_3 was purchased from Acros (99%), Na from Merck (99%) and Ba from Sigma–Aldrich (99.99%). $Si(NH)_2$[6] and Na_2CN_2[28] were synthesised according to the literature.

For all reactions, tantalum crucibles (wall thickness 0.5 mm, internal diameter 10 mm, length 300 mm) were cleaned in a mixture of HNO_3 (concd.) and HF (40%). They were arc-welded under a pressure of 1 bar of purified argon. The crucible holder was water cooled in order to avoid decomposition reactions during welding.

Single crystals of $Ba_6Si_6N_{10}O_2(CN_2)$ were synthesised from Na (150 mg, 6.5 mmol), "$Si(CN_2)_2$" (42 mg, 0.39 mmol), NaN_3 (30 mg, 0.46 mmol) and Ba (36 mg, 0.26 mmol) in closed tantalum crucibles placed in silica tubes. The silica tube (under argon) was placed in the middle of a tube furnace. The temperature was raised to 900 °C (rate 180 °C h^{-1}), maintained for 48 h, subsequently cooled to 650 °C (rate 5 °C h^{-1}) and finally quenched to room temperature by switching off the furnace. A higher yield of the product $Ba_6Si_6N_{10}O_2(CN_2)$ could be achieved by the addition of Na_2CN_2 (34 mg, 0.39 mmol) and a modified temperature program (heating to 900 °C with a rate of 600 °C h^{-1}, maintaining this temperature for 0.25 h, cooling to 500 °C with a rate of 5 °C h^{-1} and finally quenching to room temperature). The tantalum tube was opened in a glove box and transferred into a silica glass tube positioned in a tube furnace using Schlenk techniques. Excess sodium was removed under dynamic vacuum by distilling at 320 °C for 3 h.

X-ray Diffraction: Under a microscope integrated into the glove box, yellow single crystals of the title compound were isolated and sealed in glass capillaries. Single-crystal X-ray data were collected on a STOE IPDS diffractometer (Mo-K_α radiation). Several crystals were investigated and the superstructure was confirmed for all of them (Table 1). The program package SHELX-97 was used for structure solution and refinement.[29] Ba and Si were refined anisotropically without any constraints, light atoms were refined isotropically with common displacement parameters for chemically equivalent atoms.

Table 1. Crystallographic data of $Ba_6Si_6N_{10}O_2(CN_2)$.

Formula	$Ba_6Si_6N_{10}O_2(CN_2)$
Formula mass [g mol^{-1}]	1204.59
Crystal system	hexagonal
Space group	$P\bar{6}$ (no. 174)
Cell parameters [Å]	a = 16.225(2), c = 5.4690(11)
Cell volume [10^6 pm^3]	V = 1251.4(3)
Formula units/cell	3
Crystal size [mm]	0.24 × 0.08 × 0.05
$\rho_{calcd.}$ [g cm^{-3}]	4.796
μ [mm^{-1}]	14.40
F(000)	1578
Temperature [K]	100(2)
Radiation, monochromator	Mo-K_α, (λ = 71.073 pm), graphite
Absorption correction	numerical
Min. / max. transmission	0.047 / 0.251
θ range [°]	2.3–30.45
Measured reflections	13335
Independent reflections	2648
Observed reflections	2139
Refined parameters	100
GoF	1.001
R indices [$F_o^2 \geq 2\sigma(F_o^2)$]	$R1$ = 0.0299, $wR2$ = 0.0775
R indices (all data)	$R1$ = 0.0387, $wR2$ = 0.0799[a]
Max. / min. residual electron density [e Å^{-3}]	1.334 / –1.259

[a] $w = [\sigma^2(F_o^2) + (0.0389\ P)^2 + 0.00\ P]^{-1}$ where $P = (F_o^2 + 2\ F_c^2)/3$.

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-420257 [for $Ba_6Si_6N_{10}O_2(CN_2)$], the names of the authors and citation of the publication. Powder diffraction data were collected in Debye–Scherrer geometry on a STOE Stadi P powder diffractometer with Ge(111)-monochromated Mo-$K_{\alpha1}$ radiation (λ = 0.7104 Å).

Microanalysis: EDX spectra of selected crystals were obtained using a JSM 6500F scanning electron microscope (JEOL) equipped with an EDX detector 7418 (Oxford Instruments). The approximate molar ratio of the elements Ba/Si/N/O was found to be 16(2):17(2):54(2):11(4) (average from 4 independent measurements).

Vibrational Spectroscopy: FTIR measurements were carried out on a Bruker IFS 66v/S spectrometer. The preparation procedures were performed in a glove box under a dry argon atmosphere. Spectra were recorded at ambient conditions in the range between 400 and 4000 cm^{-1} by dispersing the samples in anhydrous KBr pellets.

Supporting Information (see also the footnote on the first page of this article): PXRD pattern of $Ba_6Si_6N_{10}O_2(CN_2)$ in comparison to the simulation from single-crystal structure analysis. Reciprocal $hk0$ layer (reconstructed from imaging-plate data) with basic and superstructure unit cells.

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