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Crystal Structures of Two Polymorphs of $Ca_3[Al_2N_4]$

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Green transparent single crystals of α-$Ca_3[Al_2N_4]$ (monoclinic, $P2_1/c$, No. 14, $a = 957.2(3)$ pm, $b = 580.2(3)$ pm, $c = 956.3(5)$ pm, $\beta = 111.62(3)°$; $Z = 4$) were obtained from reactions of mixtures of the representative metals with nitrogen above temperatures of 1000 °C. β-$Ca_3[Al_2N_4]$ (monoclinic, $C2/c$, No. 15, $a = 1060.6(2)$ pm, $b = 826.0(2)$ pm, $c = 551.7(1)$ pm, $\beta = 92.1(1)°$; $Z = 4$) was formed as a byproduct of a reaction of calcium with alumina under nitrogen at $T = 930$ °C in form of colorless crystals. The crystal structures of the two polymorphs contain edge- and corner-sharing AlN_4 tetrahedra, leading to different layered anionic partial structures: $^{2}_{\infty}[(AlN_{2/2}N_{2/3})_2(AlNN_{2/2}N_{1/3})^{12-}_{6/3}]$ in the α-phase and $^{2}_{\infty}[Al_2N_2N^{6-}_{4/2}]$ in the β-polymorph.

Introduction

From a large number of nitridometalates[1−3] only few examples of nitridoaluminates of lithium and alkaline earth metals are known and characterized in terms of their chemical compositions and crystal structures. The crystal structure of $Li_3[AlN_2]$[4] was reported by Juza et al. as early as 1948 and can be understood as a CaF_2-type superstructure. Nitride species are arranged to form the motif of a distorted cubic close packing. Lithium and aluminum occupy the tetrahedral holes in an ordered way, resulting in a framework of vertex-sharing AlN_4 tetrahedra $^{3}_{\infty}[AlN^{3-}_{4/2}]$. The crystal structure of $Ca_6[Al_2N_6]$[5] contains isolated units $[Al_2N_6]^{12-}$ built of two edge-sharing AlN_4 tetrahedra. In the crystal structures of the isotypes $Sr_3[Al_2N_4]$[6] and $Ba_3[Al_2N_4]$[5] AlN_4 tetrahedra are condensed to infinite chains of trans edge-sharing tetrahedra $^{1}_{\infty}[AlN^{3-}_{4/2}]$.

Here we report on the preparation and crystal structures of two polymorphs of $Ca_3[Al_2N_4]$ with anionic partial structures of corner- and edge-sharing tetrahedra resulting in two different two-dimensional anionic networks.[7−9]

Experimental Section

Syntheses and Characterization. α-$Ca_3[Al_2N_4]$ was obtained from mixtures of calcium (99.9%, Degussa) and aluminum (99.9%, Merck) in molar ratios in the range from 1:1 to 3:1 (typical sample sizes were 1−2 g). The mixtures of the metallic elements were first fused under argon (99.995%, Messer-Griesheim) at 1200 °C. In a second step these mixtures were heated under static nitrogen at ambient pressure to temperatures between 1000 and 1200 °C. At maximum temperatures below 1200 °C the multiphase products contained green crystals of α-$Ca_3[Al_2N_4]$ and colorless crystals which might be due to a third polymorph of $Ca_3[Al_2N_4]$.[7] Samples heated to 1200 °C contained crystals of α-$Ca_3[Al_2N_4]$ together with large amounts of binary metal nitrides which were identified by powder X-ray diffraction. α-$Ca_3[Al_2N_4]$ is obtained in the form of green transparent platelets.

β-$Ca_3[Al_2N_4]$ was found as a byproduct of reactions of calcium with silver under static nitrogen at ambient pressure in alumina crucibles at 930 °C.[8] The colorless needles grow at the wall of the crucibles. Microprobe investigations on these crystals revealed the presence of no other metals than calcium and aluminum. Charge balance is only attained with nitrogen on the crystallographic sites of the anions.

Both phases are moisture sensitive, forming ammonia. Single-phase products of any of the two polymorphic forms could not be obtained during our investigations. α-$Ca_3[Al_2N_4]$ was shown also to form from mixtures of Ca_3N_2 and AlN by heating to temperatures between 1000 and 1100 °C in welded niobium tubes sealed within quartz tubes.[10,11] According to powder X-ray diffraction the reaction product contained only a small amount of impurity phases.

Crystal Structure Determinations. Unit cell dimensions for crystals of both phases were first estimated from precession photos (lattice explorer, Stoe, Darmstadt, Germany). X-ray diffraction intensity data were taken on a Philips PW 1100 with graphite-monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique. Unit cell parameters were determined from automatic centering of 25 reflections ($10° < \theta < 15°$) and refined by least-squares methods. For the α-modification 5536 reflections were measured in the range $2.3° < \theta < 30.0°$; 1351 reflections were unique ($R_{int} = 0.0235$), and 1329 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. For the β-form 1459 reflections were measured in the range $3.1° < \theta < 30.0°$; 688 reflections were unique ($R_{int} = 0.0404$), and 573 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 100 reflections as intensity and orientation control; no significant decay was observed. Lorentz and polarization corrections were applied. An absorption correction[12] was only applied for the crystal of the α-phase. Crystallographic data are summarized in Table 1. The

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Table 1. Crystallographic and Refinement Data

	α-$Ca_3[Al_2N_4]$	*β*-$Ca_3[Al_2N_4]$
unit cell parameters		
a, pm	957.2(3)	1060.6(2)
b, pm	580.2(3)	826.0(2)
c, pm	956.3(5)	551.7(1)
β, deg	111.62(3)	92.1(1)
V, 10^6 pm^3	493.7(3)	483.0(2)
Z	4	4
fw, g/cm^3	230.24	230.24
space group	$P2_1/c$, No. 14	$C2/c$, No. 15
T, K	293	293
radiation λ, pm	71.073	71.073
density ρ_{calc}, g cm^{-3}	3.097	3.166
μ(Mo Kα), mm^{-1}	3.57	3.65
$R(F_o)^a$	0.0226	0.0677
$R_w(F_o^2)$ (all data)^b	0.0622	0.1594

[a] $R = \sum|F_o| - |F_c||/\sum F_o|$with $(F_o^2 \geq 2\sigma(F_o^2))$. [b] $R_w = [\sum(|F_o^2| - |F_c^2|)^2/\sum|F_o^2|^2]^{1/2}$.

crystal structures were solved using direct methods[13] and refined with the SHELX software package.[14] All atoms were refined with anisotropic displacement parameters. An extinction correction was refined for the crystal of the α-phase. The α-polymorph is characterized by two axes nearly identical in length, *a* and *c*. After application of the respective twin matrix for a pseudo-merohedric twin, the R/R_w values dropped from 0.0835/0.2050 to 0.0226/0.0622, resulting in a twin ratio of $x = 0.1402(9)$. A total of 84 parameters (α) and 42 parameters (γ) were refined. The minimum and maximum peaks in the final e^- difference map (in 10^{-9} pm^{-3}) were −0.40, 0.42 (α) and −1.38, 1.07 (β). Refinements of the occupancies of the metal sites, especially for β-$Ca_3[Al_2N_4]$, that may indicate a partial exchange of nitrogen by oxygen did not result in any significant deviations from fully occupied sites.

Results and Discussion

The crystal structures of the title compounds contain aluminum in distorted tetrahedral coordination by nitrogen. A further common feature of the polymorphs is the presence of dimers, Al_2N_6, formed from two edge-sharing tetrahedra. The crystal structures differ in the way these edge-sharing pairs of tetrahedra are connected with other Al_2N_6 or AlN_4 units via common vertexes. The dimeric units in the crystal structure of the α-phase are connected with six neighboring AlN_4 tetrahedra by sharing common vertexes. The latter AlN_4 tetrahedra do not share common edges with other tetrahedra; they are exclusively connected with dimers. These tetrahedra are characterized by one terminal, two bridging, and one three-connecting nitrogen atom ($AlNN_{2/2}N_{1/3}$). Hence, the formal motif of connection within the anionic framework of α-$Ca_3[Al_2N_4]$ can be described as ${}^2_\infty[(AlN_{2/2}N_{2/3})_2(AlNN_{2/2}N_{1/3})^{12-}_{6/3}] \hat{=} {}^2_\infty[AlN_2^{3-}]$. A section of the complex crystal structure of the α-modification is shown in Figure 1. The α-phase contains open anionic framework layers with channels formed from 4-, 5- and 6-membered rings of tetrahedra. Calcium is located between the layers and in the channels within the layers. The resulting coordination spheres by nitrogen atoms can be described as distorted octahedral and trigonal bipyramidal.

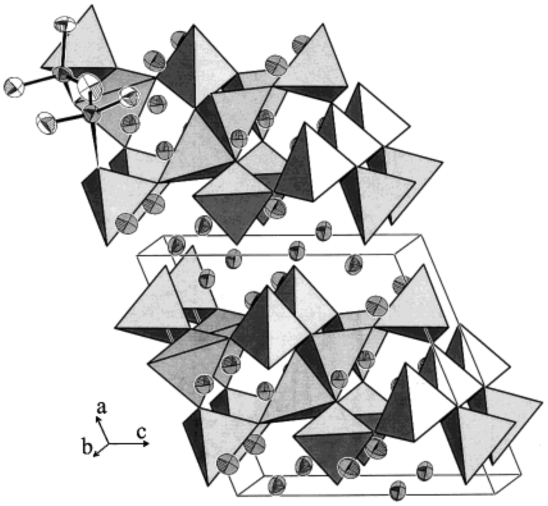

Figure 1. Crystal structure of α-$Ca_3[Al_2N_4]$. Open framework layers ${}^2_\infty[AlN_2^{3-}]$ of edge- and corner-sharing AlN_4 tetrahedra. Calcium (gray circles) are located within and between the layers. Displacement ellipsoids are plotted at the 99% probability level. The unit cell is indicated.

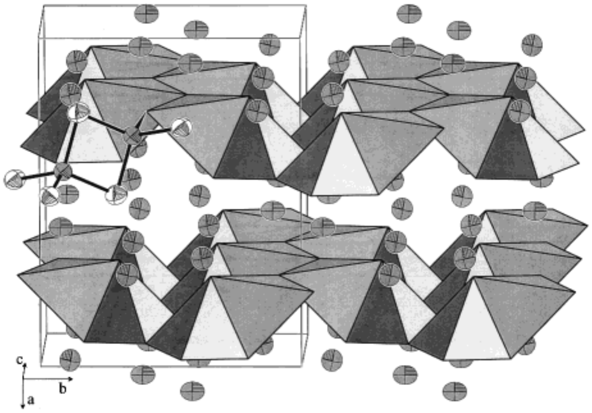

Figure 2. Crystal structure of β-$Ca_3[Al_2N_4]$. Layers ${}^2_\infty[AlN_2^{3-}]$ of edge- and corner-connected AlN_4 tetrahedra. Calcium ions (gray circles) are located mainly between the layers. Displacement ellipsoids are plotted at the 99% probability level. The unit cell is indicated.

The structure of the β-phase exclusively contains dimers Al_2N_6, which share common nitrogen vertexes resulting in a layer ${}^2_\infty[Al_2N_2N_{4/2}^{6-}]$. All nitrido ligands solely bridge two aluminum centers of adjacent tetrahedra. Figure 2 shows a part of the crystal structure of the β-polymorph, which contains puckered, but comparable flat layers ${}^2_\infty[Al_2N_2N_{4/2}^{6-}]$ of corner-sharing dimers Al_2N_6. Calcium ions between the nitridoaluminate layers occupy distorted octahedral holes. β-$Ca_3[Al_2N_4]$ is an isotype of, e.g., $Ca_3[Al_2As_4]$,[15] $Sr_3[Al_2P_4]$,[16] $Ba_3[In_2P_4]$,[17] and (α-)$Ca_3[Ga_2N_4]$.[18] Interestingly, the latter nitridogallate was reported to form a polymorphous modification which consists of exclusively corner-sharing GaN_4 tetrahedra.[19] In the crystal structure of (β-)$Ca_3[Ga_2N_4]$ two independent interpenetrating networks ${}^3_\infty[(Ga_4N_6)N_{4/2}^{6-}]$ are formed from P_4O_{10}-analogous units, interconnected at all terminal nonmetal functions. No aluminum analogue to this phase has been reported so far. From the strontium and barium nitridoaluminates with the respective composition, $Sr_3[Al_2N_4]$[6] and $Ba_3[Al_2N_4]$,[5] only one modification is known which contains infinite chains of trans edge-sharing tetrahedra ${}^1_\infty[AlN_{4/2}^{3-}]$. That may be due to the larger

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Table 2. α-$Ca_3[Al_2N_4]$: Selected Interatomic Distances (pm) and Angles (deg) (Standard Deviations in Parentheses)

Al(1)−N(2)	187.6(2)	N(1)−Al(1)−N(2)	110.39(9)
Al(1)−N(1)	188.3(2)	N(1)−Al(1)−N(3)	108.27(9)
Al(1)−N(4)	190.7(2)	N(1)−Al(1)−N(4)	115.15(9)
Al(1)−N(3)	194.1(2)	N(2)−Al(1)−N(3)	103.49(8)
		N(2)−Al(1)−N(4)	104.42(9)
Al(2)−N(2)	182.2(2)	N(3)−Al(1)−N(4)	114.40(9)
Al(2)−N(4)	187.6(2)		
Al(2)−N(3)	192.2(2)	N(2)−Al(2)−N(3)	106.03(9)
Al(2)−N(3)	198.1(2)	N(2)−Al(2)−N(3)	115.18(9)
		N(2)−Al(2)−N(4)	110.00(9)
Al(2)−Al(2)	277.6(1)	N(3)−Al(2)−N(3)	89.34(9)
		N(3)−Al(2)−N(4)	116.20(9)
Al(1)−N(2)−Al(2)	169.0(1)	N(3)−Al(2)−N(4)	118.18(9)
Al(1)−N(3)−Al(2)	118.67(9)		
Al(1)−N(3)−Al(2)	128.8(1)		
Al(2)−N(3)−Al(2)	90.66(9)		
Al(1)−N(4)−Al(2)	148.0(1)		
Ca(1)−N(2)	239.8(2)	Ca(2)−N(4)	263.3(2)
Ca(1)−N(1)	243.0(2)	(Ca(2)−N(4)	302.7(2))
Ca(1)−N(1)	250.9(2)		
Ca(1)−N(1)	260.6(2)	Ca(3)−N(4)	243.9(2)
		Ca(3)−N(2)	251.3(2)
Ca(2)−N(1)	234.2(2)	Ca(3)−N(3)	251.7(2)
Ca(2)−N(2)	256.6(2)	Ca(3)−N(2)	254.6(2)
Ca(2)−N(1)	259.3(2)	Ca(3)−N(4)	279.8(2)
Ca(2)−N(3)	261.3(2)	Ca(3)−N(3)	281.6(2)

Table 3. β-$Ca_3[Al_2N_4]$: Selected Interatomic Distances (pm) and Angles (deg) (Standard Deviations in Parentheses)

Al(1)−N(1)	189.7(4)	N(1)−Al(1)−N(1)	104.8(1)
Al(1)−N(1)	189.9(4)	N(1)−Al(1)−N(2)	111.3(2)
Al(1)−N(2)	192.6(4)	N(1)−Al(1)−N(2)	111.9(2)
Al(1)−N(2)	197.8(5)	N(1)−Al(1)−N(2)	114.9(2)
		N(1)−Al(1)−N(2)	115.7(2)
Ca(1)−N(1) 2×	245.2(4)	N(2)−Al(1)−N(2)	98.5(2)
Ca(1)−N(1) 2×	248.2(4)		
Ca(1)−N(2) 2×	257.8(5)		
Ca(2)−N(1)	245.4(5)	Al(1)−N(1)−Al(1)	126.3(2)
Ca(2)−N(1)	253.3(4)	Al(1)−N(2)−Al(1)	81.5(2)
Ca(2)−N(2)	256.3(4)		
Ca(2)−N(2)	262.8(5)		
Ca(2)−N(2)	265.8(4)		
Ca(2)−N(2)	290.6(4)	Al−Al	254.8(3)

ionic radii of strontium and barium, not fitting into the hole areas of the two- and three-dimensional networks.

In agreement with the other alkaline earth nitridoaluminates[5,6] the tetrahedra in all three polymorphs are strongly distorted due to the different connectivities of the various nitrogen sites and to the repulsion between the aluminum species of edge-sharing tetrahedra across the short distances of $d(\mathrm{Al{-}Al}) = 254.8-277.6$ pm (compare Tables 2 and 3).

The occurrence of edge-sharing tetrahedra in all alkaline earth nitridoaluminates known up to now is remarkable. The only nitridoaluminate of an alkali metal, $Li_3[AlN_2]$,[4] forms an anionic framework $^{3}_{\infty}[AlN^{3-}_{4/2}]$ of solely vertex-sharing tetrahedra. The situation for nitridogallates(III) with tetrahedral coordinated gallium is similar: $Li_3[GaN_2]$[4] is an isotype of $Li_3[AlN_2]$ with exclusively vertex-sharing tetrahedra, while the crystal structures of (α-)$Ca_3[Ga_2N_4]$[18] and $Sr_3[Ga_3N_5]$[19] contain edge- and vertex-sharing tetrahedra. $AE_3[Ga_2N_4]$ (AE = Sr, Ba)[19,20] finally are built from solely edge-sharing tetrahedra. In the crystal structures of nitridosilicates edge-sharing of tetrahedra is only observed for the barium compounds $Ba_5[Si_2N_6]$[21] and $Ba[Si_7N_{10}]$,[22] while the crystal structures of the other nitridosilicates reported so far do not exhibit edge-sharing of tetrahedra.[23]

Phase relations between the crystalline modifications of $Ca_3[Al_2N_4]$ are not investigated in detail up to now. The proposed assignment given in the present paper is based on experimental conditions during preparation and includes the general principle declaring the polymorph with the highest thermal stability to be the α-modification. Syntheses of calcium nitridoaluminates were carried out at maximum temperatures of 1200 °C. At that temperature α-$Ca_3[Al_2N_4]$ is obtained as the only ternary phase. Below 1200 °C (down to 1000 °C) always mixtures of crystals of the green α-phase and further colorless crystals are found. The colorless crystals may be due to a further polymorph of $Ca_3[Al_2N_4]$,[7] but the results of our single-crystal investigations could not be interpreted unambiguously so far. These observations may be consistent with the α-phase being the high-temperature modification, supported by the lower ρ_x-value (3.079 g/cm^3, compare Table 1). β-$Ca_3[Al_2N_4]$ was accidentally obtained as a byproduct in the course of reactions of Ca (and Ag) with Al_2O_3 (crucible) and molecular nitrogen at 930 °C. These reaction conditions might indicate a metastable nature of the β-modification, an assumption which is consistent with the comparable high ρ_x-value of 3.166 g/cm^3. Finally it should be pointed out clearly again that the proposed phase relations between the modifications of crystalline $Ca_3[Al_2N_4]$ should just be regarded as a first approach which has to be confirmed by detailed experimental facts.

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Supporting Information Available: X-ray crystallographic files in CIF format, providing more details regarding data collection and structure refinement. This material is available free of charge via the Internet at http://pubs.acs.org.

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