Structural and luminescence studies of the new nitridomagnesoaluminate CaMg$_2$AlN$_3$

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CaMg$_2$AlN$_3$ was synthesized in a closed system by solid state reaction from binary nitrides. Structure refinements based on powder X-ray diffraction data suggested ambiguity about the occupancy of magnesium and aluminum tetrahedral sites. Solid-state $^{27}$Al and $^{25}$Mg NMR studies were used to adjudicate amongst possible space groups. With reference to projector augmented wave calculations of the quadrupolar coupling constants, the measured values of $C_Q$ and the numbers of crystallographically inequivalent Al and Mg sites indicate that CaMg$_2$AlN$_3$ crystallizes in the space group P6$_3$/mmc with partial occupancy of the distorted tetrahedral Al site and possibly also mixing of Mg$^{2+}$ and Al$^{3+}$ ions on opposite sites. The compound obtained by synthesis with a flux shows orange defect-related luminescence at room temperature.

Introduction

Many new ternary and quaternary nitrides have been obtained in recent years, however their synthesis is very challenging because of required synthesis conditions and reaction partners. The reactants and products are often easily hydrolyzed or oxidized in air.1 Preparations of nitrides with a highly condensed network structure are mainly performed by high-temperature solid state syntheses.2 However, it is also possible to synthesize such nitrides at low temperature via solid state metathesis reactions.3 A steady increase in the importance of nitride-based materials is devoted to the employment of these materials as host structures of phosphors. The temperature and pressure conditions for the production of the nitride-based phosphors are crucial because the starting materials behave chemically inert in reactions.4 A flux agent can be used to enhance the yield of nitrides synthesis, e.g. molten sodium,5 or liquid lithium.6 In many cases pure nitrides without oxygen impurities are difficult to make and special attention should be paid to the choice of substrates.7

Ternary nitrides can be divided into two groups, intermetallic with dominant metal–metal interactions and ionic/covalent where metal–nitrogen bonding is dominant. Intermetallic nitrides with ionic or covalent bonds may have many different metal–anion coordination environments with structures related to oxides or sulfides.8 Nitridosilicates, nitridosiluminosilicates, oxonitridosilicates, and oxonitridosiluminosilicates are usually constructed of [M(N,O)$_4$] tetrahedra (M = Al, Si) which are connected with each other to form isolated polyhedra, or one-, two- and three-dimensional structures.2,9 For example edge-bridged dimers of tetrahedra were reported as [AlN$_4$] in the structure of Ca$_4$Al$_2$N$_8$.10 One-dimensional chains of edge sharing [AlN$_4$] units contain M$_2$Al$_2$N$_4$ structures with M = Sr and Ba.10 Two-dimensional sheets built from corner- and edge-sharing tetrahedra are found in MMg$_2$N$_2$ with Ca and Sr.11 Layered structures also appear for β-Ca$_3$Al$_2$N$_4$ and LiCaAlN$_2$ containing edge- and vertex-sharing [AlN$_4$]-tetrahedra.11b,12 An important nitride is CaAlSiN$_3$ with a three-dimensional network structure built from vertex-sharing [(Si,Al)N$_4$]-tetrahedra forming [(Si,Al)$_3$N$_4$] rings.5 CaAlSiN$_3$ doped with Eu$^{3+}$ ions is one of the most successfully commercialized nitride which can be used in LEDs.13 In view of the technological significance of this material, we have targeted the closely related compound, CaMg$_2$AlN$_3$, by complete substitution of silicon by magnesium, resulting in a unique luminescent nitride which does not require doping by activator elements.

Solid-state NMR is becoming increasingly common as a complementary tool in the determination of crystal structures, particularly for materials possessing some degree of disorder or lacking sufficiently large crystals for single-crystal X-ray crystallography.14 Along with high-level computations of magnetic shielding and electric field gradients, precisely measured NMR parameters can provide key constraints in atomic positions, local symmetry elements and the number of crystallo-
graphically inequivalent sites. Improvements in hardware and methodology continue to expand the range of nuclei for which structurally informative NMR spectra may be obtained.

**Experimental section**

**Synthesis**

Preparation of the reaction mixture for the synthesis of CaMg2AlN3 was performed under argon atmosphere inside a glove box. The reaction carried out in a fused niobium reaction container, sealed into a silica ampoule. 128 mg Mg3N2 (Alfa Aesar, 99.6%) with 94 mg Ca3N2 (Aldrich, 99%), and 78 mg AlN (ABCRI, grade C) were mixed in an agate mortar. For luminescent applications the material was synthesized additionally with 10 wt% of a flux. The flux was a mixture of LiCl (Sigma, 99.0%) with KCN (Merck, 96%) in molar ratio one to one.

The mixtures were heated in a furnace to 1100 °C with a heating rate of 2 °C min⁻¹, held at this temperature for 48 h, and cooled to room temperature with rate 2 °C min⁻¹. The containers were opened under argon atmosphere, and the products were quickly flushed with dry ethanol in order to remove any possible impurities. The reaction product was analyzed by powder X-ray diffraction measurements.

**X-Ray diffraction**

Powder X-ray diffraction measurements were carried out with a powder diffractometer (Stoe, STADI-P, Ge-monochromator) using CuKα1 (λ = 154.06 pm) radiation.

**N/O analysis**

All nitrogen and oxygen contents were determined using a TC-400C from Leco Corporation, equipped with TCWin Analysis software, version 4.03, and Helium 4.6 (Westfalen) as purge gas. For every analysis between 10–20 mg of the material were weighed, transferred into tin capsules and sealed. For a more homogeneous combustion three scraps of highly pure nickel wire were added. The subsequent analysis was conducted at 1000 A in high purity carbon crucibles and repeated three times.

**Nuclear magnetic resonance spectroscopy**

27Al MAS NMR was performed on a Varian Inova 600 (B0 = 14.1 T) spectrometer (ν0 = 156.3 MHz) with a 1.6 mm TR Varian-Chemagnetics MAS probe at a 30 kHz rotational frequency. 200k transients were co-added using the Bloch-decay sequence with an optimized recycle delay of 1 s and excitation pulse of 0.5 μs (ca. 40° tip angle). The frequency axis is referenced to 1 M Al(NO3)3 (aq.) at 0 ppm.

25Mg NMR was done on a Bruker Avance II 900 MHz (B0 = 21.1 T) spectrometer. The rotor-synchronized spin-echo MAS NMR spectrum was collected with a 4 mm low-γ probe at a rotor spinning frequency of 18 kHz, a recycle delay of 1 second and 60k scans. 25Mg quadrupole-echo NMR spectra of a non-spinning sample were collected with a 5 mm low-γ probe using an optimized recycle delay of 1 second and 54k scans. Chemical shifts are referenced to 1 M MgCl2 (aq.) at 0 ppm.

Spectral fits were achieved using WSOLIDS and dmfit.15 All samples were handled in a glove box under a dry nitrogen atmosphere.

**Quantum chemical calculations**

Density functional theory (DFT) calculations were performed using CASTEP,16 which incorporates GIPAW optimized for the calculation of electronic properties in periodic solids.17 Calculations implemented Perdew–Burke–Ernzerhof (PBE) functionals. Fine accuracy plane-wave basis sets with a 400 eV cutoff were used. The CASTEP code was run in the Materials Studio 4.4 environment on an HP sx4400 workstation with a single Intel Dual-Core 2.67 GHz processor and 8 GB DDR RAM.

The input data for the GIPAW calculations used the experimental lattice parameters and atomic coordinates. Geometry optimizations allowed atomic positions to change within fixed lattice parameters and space-group symmetry. The construction of supercells maintained the atomic positions found by X-ray refinement but removed some atoms to mimic partial occupancy.

**Luminescence spectroscopy**

Excitation and emission spectra were recorded with an Edinburgh Instruments FSL920 spectrometer equipped with a 450 W Xe arc lamp, mirror optics for powder samples and a cooled (−20 °C) single-photon counting photomultiplier from Hamamatsu (R2658P). The correction file for the emission spectra was obtained from a tungsten incandescent lamp certified by the NPL (National Physics Laboratory, UK).

**Results and discussion**

In the past, relatively little attention has been paid to magnesium nitride compounds and many of them may not be structurally characterized. As expected magnesium nitrides should form a similar structural diversity as the Ca, Sr or Ba compounds and only recently new materials such as SrMg3GeN4, SrMg2Ga2N4, MGM2Al2N4 (M = Ca, Sr, Ba, Eu), BaMg3Ga3N6, Mg2MgN1, Li2Ta22+2N9, Mg2.6–xTa1.3x+2N9, BaMg3.33M0.67N4 (M = Nb, Ta), Li0.51Mg2.49N1.83 or Li1.12Mg0.88N0.96 were obtained and described.1,9,18

The new nitridomagnesioaluminate compound CaMg2AlN3 was prepared at 1100 °C in a straightforward manner from Mg3N2, Ca3N2, and AlN (1).

2Mg3N2 + Ca3N2 + 3AlN → 3CaMg2AlN3

The obtained product exhibited sensitivity to moist air and had to be kept under inert air conditions. An N/O-analysis did not indicate a significant substitution of nitride versus oxide in the structure of CaMg2AlN3. The overall oxygen content according to the measurement was about 0.6%.

The crystal structure of CaMg2AlN3 is closely related to the structures of ScAl2C3 (a = 3.355(1) Å, c = 16.776(3) Å) and...
UAl₃C₃ (a = 3.389(1) Å, c = 17.394(3) Å). The crystal structure determination of these compounds was not straightforward. Reminiscent of previous work on carbides, the refinements of the ScAl₃C₃ and UAl₃C₃ were performed in the high-symmetry space group P6₃/mmc with a large displacement parameter for one aluminum position or, alternatively, with a split aluminum position. Afterwards, the crystal structures were redetermined with full occupancy of the aluminum sites in the space group P6₃mc. The main difference between the structural results is a trigonal bipyramidal, or split tetrahedral environment of aluminum in the space group P6₃/mmc, and a tetrahedral environment when the structures are refined in the space group P6₃mc. A similar picture is evident in the case of aluminum ions in the structure of CaMg₂AlN₃. An analysis of the extinction conditions in the X-ray diffraction data set clearly leads to the space groups P6₃/mmc and P6₃mc, including related subgroups and supergroups. Structure refinements for CaMg₂AlN₃ were carried out in both space groups by the Rietveld method using the FullProf-WinPLOTR software, with the results displayed in Table 1 and Fig. 1.

The structure refinement in P6₃/mmc resulted in a 50% split position of the Al³⁺ ions on a 4f site, introducing alternating occupations of two closely adjacent Al³⁺ positions (0.44(2) Å apart from each other) as a result of presence of a mirror plane perpendicular to the crystallographic c-axis at z = 1/4, 3/4. Mg²⁺ ions occupy another 4f site in a regular manner (Fig. 1, at left). The coordination environment of the aluminum ion in the structure of CaMg₂AlN₃ is trigonal pyramidal with one long distance to the N₁ atom parallel to the c-axis direction. The combination of both closely adjacent (split) Al³⁺ sites into one would introduce a trigonal bipyramidal environment. A trigonal coordination environment of Al ions in nitrides appears unknown to us, but has been reported for [GaN₃] units in nitrides, e.g. Sr₃GaN₃ or Sr₆GaN₅. A similar trigonal bipyramidal coordination was found for magnesium ions in Mg₅BN₃ (P6₃/mmc) whose structure appears somehow related to that of CaMg₂AlN₃. According to the structure refinement of CaMg₂AlN₃ with the non-centrosymmetric space group P6₃mc, two Mg²⁺ ions occupy two 2b sites, and one Al³⁺ ion occupies another 2b site.

### Table 1 Crystal parameters, atomic positions, and Rietveld quality parameters of the structure refinement of CaMg₂AlN₃

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*Split position: 1/3, 2/3, z; 1/3, 2/3, −z + 1/2, with 50% occupancy.*
Therefore, we focus our structural view on the assignment of the space group $P6_3/mmc$. This choice is based on the similarity of both structural models, these values are quite close to each other and may indicate the possibility of a coexistence of both arrangements. Moreover, these MAPLE values represent the sum of the constituting binary nitrides with a deviation of less than 2%.

The bond lengths are summarized in Table 2. The distances in CaMg$_2$N$_3$ (2.596 Å) are known to have tetrahedral coordination environments with Mg$^{2+}$ and Ga$^{3+}$ ions occupying the same crystallographic sites. A similar situation appears to exist in CaMg$_2$AlN$_3$, where the Al$^{3+}$–N distance in AlN (1.902 Å) and in AlN. Observed powder XRD pattern (grey circles), calculated pattern (black line), Bragg positions (grey ticks), and difference curve (black bottom line) after Rietveld refinement.

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The NMR analysis described in the following part of this article indicates that the correct space group is $P6_3/mmc$. Therefore, we focus our structural view on the assignment of the space group $P6_3/mmc$ (no. 194) with lattice parameters $a = 3.4087(1)$ Å and $c = 17.3760(5)$ Å for two formula units CaMg$_2$AlN$_3$. The recorded diffraction pattern was fitted with two phases: CaMg$_2$AlN$_3$ and AlN as shown in Fig. 2. The relative weight proportions of CaMg$_2$AlN$_3$ and AlN in the sample determined by Rietveld refinement were 97 and 3%, respectively. The parameters of the refinement, obtained crystal data, and atomic coordinates are presented in Table 2. A pseudo-Voigt profile function was used to fit the reflection peaks.

The crystal structure of CaMg$_2$AlN$_3$ is based on a hexagonal closest packing of nitride ions (N1 and N2). One third of octahedral sites are occupied by Ca$^{2+}$ and one half of tetrahedral sites are occupied by Mg$^{2+}$ and Al$^{3+}$ ions. The distributions of these cations result in a layered arrangement with two alternating layers, [CaN]$^+$ and [Mg$_2$AlN$_2$]$^+$, the first of which corresponds to the NaCl type, and the second corresponds to an Al$_4$C$_3$-type structure. These layers are stacked in an alternating fashion along the crystallographic c-axis direction. Projections of related CaMg$_2$AlN$_3$, ScAl$_2$C$_3$, Al$_4$C$_3$ and Mg$_3$BN$_3$ structures are shown in Fig. 3.

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absence of inversion symmetry in the structure. A SHG signal of the powder sample was not observed, in comparison to other noncentrosymmetric powders which clearly did show such an effect. This “observation” is consistent with the other evidence suggesting a centrosymmetric space group (P63/mmc). However, it must be noted that only the opposite case, i.e., the appearance of a SHG signal (beyond surface SHG), can provide definitive proof of a noncentrosymmetric structure.

27Al and 25Mg nuclear magnetic resonance

In order to resolve the ambiguity between space groups, solid-state NMR and theoretical calculations were used to probe the coordination environments and measure the number of crystallographically inequivalent Al3+ and Mg2+ sites in CaMg2AlN3. Whereas these two elements have similar X-ray scattering cross-sections, their NMR spectroscopic responses are completely different and can be probed independently. 27Al NMR is well established and readily available on most solid-state NMR spectrometers, but 25Mg NMR is less common and remains experimentally challenging even on state-of-the-art ultrahigh-field NMR spectrometers.26 Besides its 10% natural abundance and quadrupolar nature, the low magnetogyric ratio of 25Mg makes it inherently insensitive relative to many other typical NMR nuclei. To mitigate this limitation, all 25Mg NMR spectra were obtained using a 21.1 T magnet at the Canadian Ultrahigh-Field NMR Facility for Solids.

Fig. 3 Crystal structure of (a) CaMg2AlN3 P63/mmc, (b) ScAl2C3 P63mc, (c) Al2C3 R3m25 and (d) Mg3BN3 P63/mmc30 projected on the (110) plane. Atoms connected by solid lines represent NaCl-type layers, atom connected by dashed lines can be related to Al4C3-type layers. Unit cells are outlined with solid grey lines.

From an NMR perspective (i.e., short-range order), the structural differences between the proposed space groups are straightforward. P63/mmc (no. 194) is characterized by a single [AlN4] site with highly distorted tetrahedral geometry and a single, slightly distorted [MgN4] tetrahedron. P63mc (no. 186) possesses a single [AlN4] site in a trigonal pyramidal environment and two distinct Mg sites, one in standard tetrahedral environment (Mg2) and the other in trigonal pyramidal environment (Mg1). NMR is capable of quantifying the number of crystallographically inequivalent sites for each nucleus and measuring the quadrupole coupling constants (CQ) at 27Al and 25Mg as a good indication of the degree of deviation from ideal tetrahedral symmetry. Pure cubic point symmetry produces a constant electric field at the cubic site, whereas geometric distortions generate progressively larger electric field gradients which couple with the nuclear electric quadrupole moment and thus produce the quadrupolar interaction. To assist in predicting the CQs associated with a given geometric arrangement, theoretical calculations of the proposed structures were employed.

Fig. 4 27Al MAS NMR spectrum of CaMg2AlN3 acquired at 14.1 T. The top trace is calculated using a Czjzek distribution with δiso = 120 ± 2 ppm and CQ = 5.6 ± 0.2 MHz.

Likewise, the 25Mg MAS NMR spectrum consists of a single peak with a line shape indicative of disorder (Fig. 5). The chemical shift indicates the presence of structural disorder, appearing more like a typical glassy 27Al NMR signal than a crystalline line shape. This spectrum was fit using a Czjzek model to account for the presence of local geometric distributions,15,28 yielding an average quadrupole coupling constant in the range of 5.4 to 5.8 MHz. Long acquisitions times and a wide spectral window provided no evidence of a second aluminum site with a larger quadrupolar interaction.

Fig. 5 25Mg MAS NMR spectrum of CaMg2AlN3 acquired at 21.1 T. The top trace is calculated using a Czjzek model with δiso = 44 ppm and CQ = 6.5 ± 0.5 MHz.
spinning rate, a quadrupole-echo experiment on a non-spinning sample was acquired to seek additional intensity signifying a high-$C_Q$ site (Fig. 6). The spectrum obtained can be successfully modelled using the same parameters as the $^{25}$Mg MAS NMR spectrum and provides no evidence of additional sites. While the presence of structural disorder – and hence, a distribution of NMR parameters – implies that this fit may not be unique, it places an upper limit on the average value of $C_Q$.

Even without calculations, these NMR results point toward P6$_3$/mmc (194) as the correct space group, since there is no experimental evidence of the second Mg$^{2+}$ site required by P6$_3$/mc (186). Gauge-including projector augmented wave (GIPAW) calculations provide a firmer basis for this conclusion by estimating the quadrupolar interactions expected for each of the putative space groups. GIPAW calculations of P6$_3$/mc CaMg$_2$AlN$_3$ predicts a $C_Q(27$Al$)$ of 6.4 MHz and $C_Q(25$Mg$)$ values of 2.9 and 17 MHz for the four- and three-coordinate Mg, respectively. Unusually large residual forces in the

c-dimension resulting from direct usage of the X-ray coordinates suggested that geometry optimization may provide a more physically realistic structure. After energy minimization, the quadrupolar coupling constants changed to $C_Q(27$Al$) = 9.2$ MHz and $C_Q(25$Mg$) = 8$ and 19 MHz. While these values are substantially different than the unoptimized $C_Q$s, the main conclusion remains the same: two very different Mg sites are expected to be observed for this space group.

Due to the partial Al occupancy, GIPAW calculations of P6$_3$/mmc (194) necessitated the use of a $2 \times 2 \times 1$ supercell. Various vacancy configurations gave a range of $C_Q(25$Mg$)$ values between 1.3 and 6.2 MHz, while $C_Q(27$Al$)$ of the highly distorted [AlN$_4$] tetrahedron ranged from 9.5 to 10.3 MHz. While none of these calculations is expected to yield precise $C_Q$ values – especially those for the disordered model – they serve as useful guidelines for the relative magnitudes associated with particular local geometries. As such, they provide a perspective on the experimental results, indicating that for this space group a single disordered Mg$^{2+}$ and a single disordered Al$^{3+}$ site is predicted, each with moderate quadrupolar coupling constants. The unusual geometry adopted by Al in the crystallographic refinement leads to calculated $C_Q$ values which are likely overestimated since local distortions are expected to maximize tetrahedral regularity, consequently leading to reduced $C_Q$s. It is worth noting that the $^{27}$Al chemical shift is in excellent agreement with that of pure wurtzite AlN, suggesting that the local Al symmetry is approaching tetrahedral. A full energy minimization of the supercell would be required to test this hypothesis, but is beyond our current computational capacity. The experimental data confirm that a single type of each cation is observed with moderate $C_Q$s, consistent with the P6$_3$/mmc space group. Perhaps most importantly, the spectral observation of a distribution of local Mg and Al geometric environments is compatible only with the space group implicating partial Al site occupancy, as subtle geometric distortions would undoubtedly accompany such vacancies and produce the observed line shapes. An alternate or additional explanation for this observation is that some degree of Mg/Al antisite disorder is present in the structure, which is only expected in the P6$_3$/mmc space group.

**Luminescence spectroscopy**

The excitation, emission and reflection spectra measured at room temperature of CaMg$_2$AlN$_3$ are presented in Fig. 7.

The reflection spectrum is composed of an absorption edge around 350 nm (3.54 eV), with an onset at 370 nm. The main feature of the excitation spectrum is a broad band with a maximum at 330 nm. Since excitation above 350 nm is not efficiently possible, the material is for the moment not of interest for solid state lighting, since (In,Ga)N chips emit between 370 nm and 500 nm. The Gaussian-type emission band is likely caused by defects introduced by the flux during the solid state reaction. The possible origins of the luminescence are structural and point defects as well as impurities incorporated during the synthesis process which affect the electrical and optical properties of the nitride host.
The full-width-half-maximum (FWHM) obtained for CaMg$_2$AlN$_3$ is about 152 nm, much larger than for typical emission bands of Eu$^{2+}$ ions in nitrides, for example 75 to 90 nm from CaAlSiN$_3$:Eu$^{2+}$ prepared by different methods. It is possible to draw a comparison between CaMg$_2$AlN$_3$ and the related compounds MMg$_2$Al$_2$N$_4$:Eu$^{2+}$ (M = Ca, Sr, Ba). BaMg$_2$Al$_2$N$_4$:Eu$^{2+}$ has similar luminescent properties even at room temperature with the large spectral width of emission (FWHM $\sim$ 115 nm) and large Stokes shift. These properties were ascribed to the emission from the trapped exciton states, for the calcium and strontium compound at higher temperatures a normal emission from Eu$^{2+}$ ions was dominant.

Decay of the defect transition was investigated (Fig. 8), and the kinetics were determined by a multi-exponential decay curve fitted with three time constants $\tau_1 = 52 \pm 3$ (7%), $\tau_2 = 308 \pm 21$ (34%) and $\tau_3 = 817 \pm 35$ μs (59%). The values are significantly higher than for the [Xe]4f$^6$5d$^1$-[Xe]4f$^7$ transitions of Eu$^{2+}$, usually about 1 μs. Defects in the crystal lattice lead usually to many pathways for the excitation energy and for this reason the luminescence lifetime of emission is long for such structure. A detailed explanation of the character of the luminescent centers with the measured lifetimes needs more study on structurally related and/or doped compounds.

Conclusions

CaMg$_2$AlN$_3$ was successfully synthesized in a closed system by solid state reaction, leading to a layered crystal structure. X-ray powder diffraction indicates two possible space groups: $P\bar{6}_3$mc and $P\bar{6}_3/mmc$. The NMR results clearly indicate that the compound crystallizes in the space group $P\bar{6}_3/mmc$ (194) with a distorted tetrahedral environment around the aluminum atoms, including the possibility of a disordering of Mg$^{2+}$ and Al$^{3+}$ ions over opposite lattice sites in the structure. CaMg$_2$AlN$_3$ can undergo hydrolysis and oxidation, the same as most of the nitrides having low condensed network structures. The material prepared with a flux shows orange luminescence at room temperature. Its luminescence properties of this new material without a luminescent activator may open up a range of possible applications of undoped materials with advantages including broad, eye-friendly emission and cost efficiency. However, this requires a primary radiation source which emits below 350 nm.

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Notes and references