Rietveld Refinement of the Crystal Structure of α-Be$_3$N$_2$ and the Experimental Determination of Optical Band Gaps for Mg$_3$N$_2$, Ca$_3$N$_2$ and CaMg$_2$N$_2$

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α-Be$_3$N$_2$ powder was obtained by reacting Be metal with dry, flowing N$_2$ at 1600 K. The product contained 5.9(7) wt.% of BeO. The anti-bixbyite structure suggested earlier was verified through Rietveld refinement on the basis of X-ray powder data ($Ia\bar{3}$ (#206); $a = 814.518(6)$ pm). The optical band gaps of α-Be$_3$N$_2$, Mg$_3$N$_2$ and Ca$_3$N$_2$ are compared with newly measured values for Mg$_3$N$_2$, Ca$_3$N$_2$ and CaMg$_2$N$_2$.

Introduction

Much progress has been made again recently in the field of binary nitrides of the first and second main group metals. A prominent example is the long sought after Na$_3$N [1] which was finally synthesized and characterized. Also the diazenide N$_2^{2-}$ anion was found in the compounds SrN ($\equiv$ Sr$_4$(N)$_2$(N$_2$)) [2], Sr$_4$N$_3$ ($\equiv$ Sr$_8$(N)$_4$(N$_2$)) [3], SrN$_2$ [2] and BaN$_2$ [4]. Transparent red "Ca$_{11}$N$_8$" was found to be Ca$_{11}$N$_6$(CN$_2$)$_2$ [5], and the yellow transparent high-temperature form of Ca$_3$N$_2$ ($\equiv$ γ-Ca$_3$N$_2$) was shown to be Ca$_4$N$_2$(CN$_2$) [5, 6]. Subnitrides such as Ca$_2$N [7,8], Sr$_2$N [8, 9] Ba$_2$N [8, 10] (of which the latter is still not completely characterized and understood) and Ba$_3$N [11] were found to exist, but so far the reported ionic nitrides Sr$_3$N$_2$ or Ba$_3$N$_2$ are not proven to exist as binary phases since hydrogen or oxygen might be incorporated in significant amounts [9, 10].

So it must come as a surprise, that, while the structures of Mg$_3$N$_2$ [12,13], Ca$_3$N$_2$ [13,14], and the high temperature form of Be$_3$N$_2$ ($\equiv$ β-Be$_3$N$_2$) [15,16] are known, the structure of α-Be$_3$N$_2$ was never refined. The lattice constants and the space group were reported [13,17,18], but only an estimate of the structure on the basis of a Guinier powder diffractogram [17] is to be found in literature. These data were relied on thereafter [13, 18].

We report here the first full Rietveld refinement of α-Be$_3$N$_2$ on the basis of X-ray powder data as well as measurements of the optical band gaps by diffuse IR reflectance spectroscopy on powders of Mg$_3$N$_2$, Ca$_3$N$_2$ and CaMg$_2$N$_2$.

Experimental Section

Due to the air sensitivity of these materials, all manipulations were carried out under a continuously purified and monitored argon atmosphere in glove boxes.

White microcrystalline material was obtained by reacting X-ray tube windows (Be, 99.999%, Phillips) which were placed in an alumina crucible in a alumina tube with dry, flowing N$_2$ at 1600 K. The resulting product was ground and reheated under these same conditions. After repeating this treatment three times, the final product contained some 5.9(7) wt.% of BeO (identified and the amount estimated by the refinement of the X-ray powder pattern). This impurity in the product is probably due to partial oxidation of the beryllium X-ray tube window which was not obvious with the naked eye. This oxidation of the otherwise fairly unreactive Be under the influence of the X-rays is quite common.

Mg$_3$N$_2$, Ca$_3$N$_2$ and CaMg$_2$N$_2$ have been synthesized following literature methods [13]. The optical band gaps have been determined by diffuse IR reflectivity measurements on powdered materials enclosed in quartz glass cuvettes (100-QX, Fa. Hellma, Germany) to protect the air-sensitive materials during the measurements. The absorption data can be calculated from the Kubelka-Munk function [19] (α/S) =
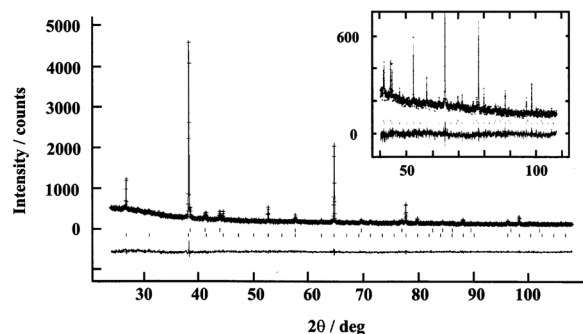
Fig. 1. Rietveld refinement of the powder diffractogram of α-Be$_3$N$_2$ with 5.9(7) wt.% BeO (0.2 mm capillary, Stoe STADI P II Powder Diffractometer). Tick marks indicate calculated Bragg peak positions for α-Be$_3$N$_2$ and BeO, the difference plot illustrates the difference between the observed (crosses) and calculated powder diffractogram (close line).

$(1-R)^2/2R$, where R is the reflectance at a given wavelength, and α and S are the absorption and scattering coefficients. S was assumed to be wavelength independent for particle sizes used here (larger than 5 μ) [19]. The optical band gap E$_g$ was obtained by extrapolating the intercept from the step absorption edge in the plot $(\alpha/S)^2$ vs. hν following literature [19].

X-ray investigations

The ground product was loaded in 0.2 mm, thin-walled glass capillaries. A powder diffractogram of the title compounds was recorded on a Stoe STADI P II powder diffractometer. All observed reflections could be indexed either to α-Be$_3$N$_2$ or BeO [20]. The program used for all the subsequent refinements was GSAS [21]. A plot of the final fit is displayed in Figure 1.

Information regarding the Rietveld refinement and the structural parameters are displayed in Tables 1 – 2.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +(49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412667.

Discussion

α-Be$_3$N$_2$ crystallizes like Mg$_3$N$_2$ and Ca$_3$N$_2$ in the anti-bixbyite structure which is often referred to as C-sesquioxide type (defect-type of the flourite structure, distorted cubic closest packing of the nitrogen atoms, the metal atoms occupy 75% of the tetrahedral holes in an ordered manner). The coordination pattern can be expressed as $\frac{3}{\infty}\left[\text{Be}_3^{[4]}\text{N}_2^{[16]}\right]$, where the polyhe-
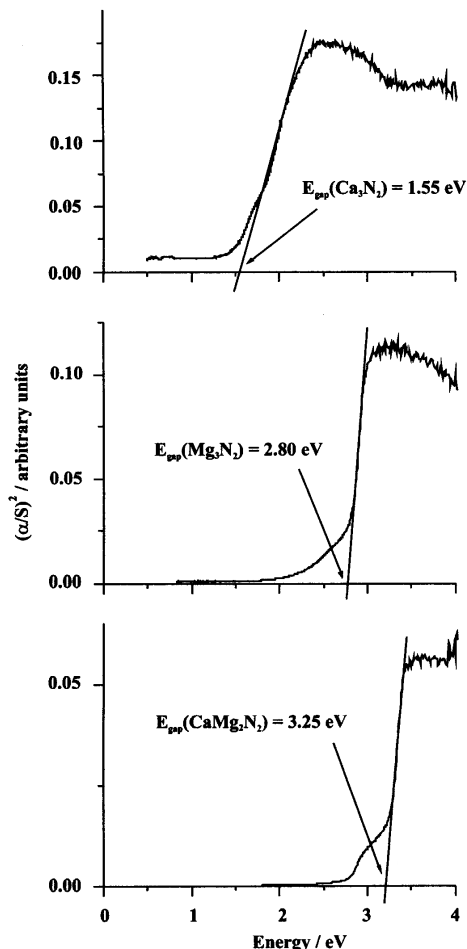

Fig. 2. Diffuse reflexion spectra of (from top to bottom) Ca$_3$N$_2$, Mg$_3$N$_2$ and CaMg$_2$N$_2$.

dra around Be and around the nitrogen positions N1 and N2 are both distorted. The crystal structure of α-Be$_3$N$_2$ in itself is not completely unexpected, but the details remained elusive until now probably due to the reported toxicity of beryllium and most of its compounds. Despite the considerable amount of BeO in the product, a comparison with the lattice constants for α-Be$_3$N$_2$ and BeO obtained from literature indicates that no nitride oxide phases form under the conditions the product was produced (Table 1).

Be$_3$N$_2$ in both modifications is colorless, Mg$_3$N$_2$ is known as a yellow crystal and powder, and Ca$_3$N$_2$ is dark red-brown. The measured optical band gaps for Mg$_3$N$_2$, CaMg$_2$N$_2$ and Ca$_3$N$_2$ and also experimentally determined optical band gaps for α-Be$_3$N$_2$, Mg$_3$N$_2$ and Ca$_3$N$_2$ are listed in Table 3.

Compound	α-Be₃N₂	BeO
Space group, Z	$Ia\bar{3}$, 16	$P6_3mc$; 2
Lattice constants a, c [pm]	814.518(6)	269.67(1), 437.78(1)
Literature data [pm]	814.82 [18]	269.79(2) / 437.72(2) [20]
Density [gcm⁻³]	2.707	3.013
Phase fractions [%]	94.1(7)	5.9(7)
Diffractometer; temperature	Stoe STADI P II (equipped with a Mini-PSD Detector); 293(2) K	
Monochromator; radiation	Germanium, Cu-K$_{\alpha 1}$	
Refinement range [°]	$24 \leq 2\theta \leq 108$	
Datapoints	4199	
Peak shape	Pseudo-Voigt function	
Background	Power series with 7 variables	
Observed reflections	136	
Fitted parameters	15	
$R_P, R_{wp}, R(F^2)$ / %; χ^2	6.00, 7.54, 10.11; 1.246	

Table 1. Results of the Rietveld refinement of the X-ray powder diffraction data for α-Be₃N₂ and BeO.

Atoms	Wyckoff-Site	x/a	y/a	z/a	U_{iso} [pm²]
Be	48e	0.3865(11)	0.1465(10)	0.3758(15)	156(10)
N1	24d	0.9784(4)	0	1/4	114(11)*
N2	8b	1/4	1/4	1/4	114(11)*

Atoms	d [pm]	Atoms	d [pm]	Atoms	d [pm]
Be-N1	174.2(7)	Be-N1	172.4(9)	Be-Be	216.1(20)
Be-N1	181.6(7)	Be-N2	173.1(15)		

* U_{iso} of N1 and N2 were constrained to each other.

Table 2. Atomic positions and isotropic displacement factors of α-Be₃N₂.

Compound	Appearance	Measured, optical band gap [eV]		Calculated band gap [eV]
		Literature	This work	(WIEN97; VASP)
α-Be₃N₂	white	3.8 [24]	—	3.35; 5.2 [23]
CaMg₂N₂	white with yellow tint	—	3.25	2.27; 2.05 [23]
Mg₃N₂	yellow	2.8 [25]	2.80	1.63; 1.85 [23]
α-Ca₃N₂	dark red	1.9 [23]	1.55	1.26; 1.17 [23]

Table 3. Experimentally determined and theoretically calculated band gaps of alkaline earth metal nitrides.

The decrease of the gap value upon increasing atomic weight is a well known fact, *e.g.* from the group 4 elements and the isoelectronic Grimm-Sommerfeld phases. However, the remarkable color changes within the group 2 metal nitrides as well as the change from colorless Rb₂O to orange-red Cs₂O still seems to be puzzling with respect to the more electropositive character of higher homologues and, hence, the larger ionicity of their M-X bonds. It was Phillips [22] who pointed out the complex nature of the optical band gap. The two components, the homopolar and the heteropolar contribution to the gap size in our case work against each other as the heteropolar contribution is increasing with atomic number, but this increase is overcompensated by the decrease of the ho-

mopolar contribution. This tendency is quantified by a recent theoretical study [23] on alkaline earth metal nitrides, in terms of the decrease of covalency from Be—N *via* Mg—N to Ca—N. In this work the calculated values for the band gaps refer to the difference between top of the valence band and bottom of the conduction band, *i.e.* the electrical band gap. They are significantly smaller than the experimental values for the optical band gap, however, there is good agreement in the general tendency.

Acknowledgements

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