Rietveld Refinement of the Crystal Structure of $\alpha$-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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We report here the first full Rietveld refinement of $\alpha$-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$_2$.

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$_2^-$ 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$_6$” was found to be Ca$_{11}$N$_6$(CN$_2$)$_2$ $^5$, and the yellow transparent high-temperature form of Ca$_3$N$_2$ ($\equiv$ $\gamma$-Ca$_3$N$_2$) was shown to be Ca$_4$N$_2$(CN$_2$)$_2$ $^5$. Subnitrides such as Ca$_2$N $^7$, Sr$_2$N $^8$, 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$_2$N$_2$ or Ba$_2$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$_2$ ($\equiv$ $\beta$-Be$_3$N$_2$) $^{15,16}$ are known, the structure of $\alpha$-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 diffraction graph $^{17}$ is to be found in literature. These data were relied on thereafter $^{13,18}$.

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 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 $\alpha$-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$_2$.

Key words: Beryllium Nitride, Optical Band Gap, Rietveld Refinement, Structure Elucidation
Fig. 1. Rietveld refinement of the powder diffractogram of \( \alpha \text{-Be}_3\text{N}_2 \) with 5.9(7) wt.% BeO (0.2 mm capillary, Stoe STADI P II Powder Diffractometer). Tick marks indicate calculated Bragg peak positions for \( \alpha \text{-Be}_3\text{N}_2 \) and BeO, the difference plot illustrates the difference between the observed (crosses) and calculated powder diffractogram (close line).

\[
(1 - R)^2/2R, \quad \text{where } R \text{ is the reflectance at a given wavelength,}
\]
\( \alpha \) and \( S \) are the absorption and scattering coefficients. \( S \) was assumed to be wavelength independent for particle sizes used here (larger than 5 \( \mu \)m) [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. \( h\nu \) following literature [19].

\section*{Discussion}

\( \alpha \text{-Be}_3\text{N}_2 \) crystallizes like \( \text{Mg}_3\text{N}_2 \) and \( \text{Ca}_3\text{N}_2 \) in the anti-bixbyite structure which is often referred to as C-sesquioxide type (defect-type of the fluorite 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 \( 2\left[\text{Be}^{[16]}_4\text{N}_2^{[4]}\right] \), where the polyhe-
<table>
<thead>
<tr>
<th>Compound</th>
<th>Appearance</th>
<th>Measured, optical band gap [eV]</th>
<th>Calculated band gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Be₃N₂</td>
<td>white</td>
<td>3.8 [24]</td>
<td>3.35; 5.2 [23]</td>
</tr>
<tr>
<td>CaMg₂N₂</td>
<td>white with yellow tint</td>
<td>—</td>
<td>2.27; 2.05 [23]</td>
</tr>
<tr>
<td>Mg₃N₂</td>
<td>yellow</td>
<td>2.8 [25]</td>
<td>1.63; 1.35 [23]</td>
</tr>
<tr>
<td>α-Ca₃N₂</td>
<td>dark red</td>
<td>1.9 [23]</td>
<td>1.26; 1.17 [23]</td>
</tr>
</tbody>
</table>

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

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

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 homopolar 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.

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