Structural properties and ELNES of nanoporous high-purity Mg_3N_2

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Magnesium nitride (Mg_3N_2) has recently been pushed into the spotlight for its potential in optoelectronics, gas separation, as well as in catalysis. However, these applications require high material purity and crystallinity, which has seldom been demonstrated in the past due to the high reactivity with H_2O. One way to evaluate the degree of crystalline near-range order and atomic environment is electron energy loss spectroscopy (EELS) of the N-K edge. However, there is no high-quality spectroscopic data of Mg_3N_2 or of related nitrides, which makes identification of electron energy-loss near-edge structure (ELNES) features of the N-K edge difficult. Therefore, there is a need to analyze the N-K edge of Mg_3N_2 in detail. This will also support N-K edge analysis of similar group-II nitrides, since they all have an antibixbyite cubic crystal structure and an "ionic" bonding character [1]. For Mg_3N_2, there are four independent Mg-N distances R_1-R_4 of 2.145 Å, 2.084 Å, 2.160 Å and 2.179 Å, respectively [2].

Nanoporous crystalline high-purity Mg_3N_2 was synthesized using a novel liquid-NH_3 technique and analyzed with a FEI Titan 80-300[3] (300 keV) equipped with a Gatan Tridiem 865 HR imaging filter and an energy resolution 0.5 eV. Cumulative spectra were obtained from ΔE 246-656 eV and calibrated with respect to the C K-edge to compensate for zero-loss shift. X-ray diffraction, HRTEM and EDXS analysis were performed to characterize structure and chemical composition.

The synthesized material consists of nanocrystallites with an average size of 3 nm and pore channels with dimensions between 1-10 nm (Fig.1). The Fourier transform (FT) of the HRTEM image (Fig. 1c) is consistent with the Ia-3 structure expected for Mg_3N_2. The Mg K-edge is without characteristic features due to poor signal/noise ratio (Fig. 2b). Fig. 2a shows the N-K edge of a Mg_3N_2 aggregate after background subtraction. The N-K edge starts at 399±0.5 eV with a sharp peak followed by a second sharp peak at 406 eV which can be assigned to π*-transitions. At higher energies there is a small peak at 412 eV followed by a broad σ* area with a triplet of peaks at 422, 426 and 431 eV and a last peak at 448 eV. These last four peaks within the σ* area could be indications of the four different Mg-N distances R_1-R_4. This relationship between varying distances giving rise to peaks in this region of the N-K edge, has previously been reported for BeP_2N_2 [3], which is in accordance with predictions [4].

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[3] T.K. Dennenwaldt, Dissertation, LMU München, 2013.

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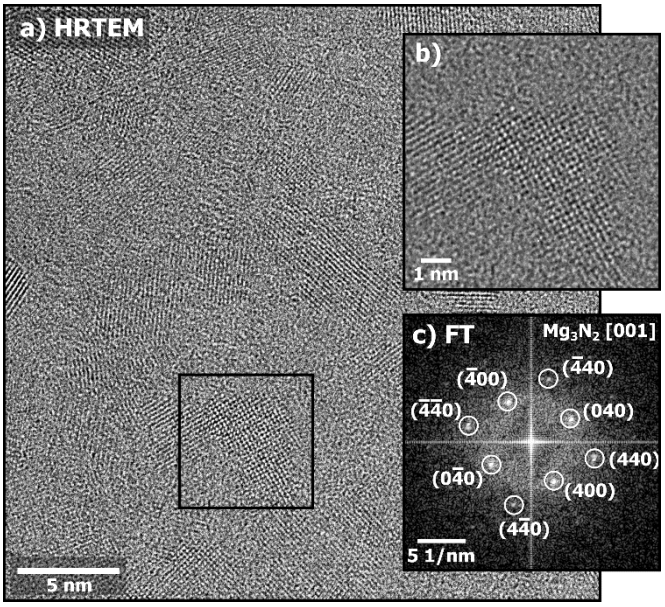

Figure 1: HTEM image of Mg_3N_2 with square marking the magnified region shown in b). c) FT of crystallite in b) with Miller-indices for [001] zone-axis orientation.

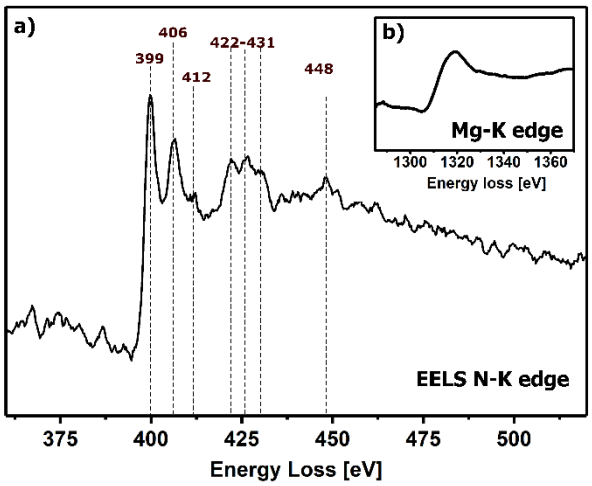

Figure 2: a) EELS N-K edge of Mg_3N_2 with ELNES features (dashed lines) with inset b) of smoothed Mg-K edge.