New precursor route to nanocrystalline powders of magnetic manganese nitride $\eta$-Mn$_3$N$_2$

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Electronics: the charge of electrons is utilized in most of contemporary electronic devices.

Spintronics: the spin of electrons is controlled in addition to or, sometimes, in place of the charge of electrons.

*Spintronics in semiconductors* - spin based electronics takes on adding the spin (magnetism) to already exploited charge of the electron (electronics) to carry information (transport) which means that the utilization of both semiconducting and magnetic properties residing in one otherwise „homogeneous“ material is anticipated.
Computed values of the Curie temperature $T_c$ for various p-type semiconductors containing 5% of Mn and $3.5 \times 10^{20}$ holes per cm$^3$.


Since 2000, numerous attempts for thin films prepared by various deposition techniques and for mono- and microcrystals have failed to demonstrate RT ferromagnetism in the GaN/Mn system.

Nanomaterials with up to 2 wt% incorporated Mn were prepared in our group with the convenient aerosol-assisted method utilizing commercially available metal precursors as well as *via* our anaerobic route utilizing the known gallium amide precursor Ga[N(CH$_3$)$_2$]$_3$.


**How about Mn$^{3+}$:**
- in nanocrystalline powders of GaN?
- on surfaces of GaN nanoparticles?
- under sintering conditions of GaN/Mn nanopowders?
Our spintronics project as of 2014

Current goal

Utilize anaerobic synthesis method and oxyden-free gallium and manganese precursors to provide best synthetic conditions for the preparation of the target nanopowders, i.e., both nanocrystalline (Ga,Mn)N substitutional DMS and (Ga,Mn)N / Mn multiphase materials.

These nanopowder are further planned to be processed via high-pressure high-temperature powder sintering as well as surface functionalization towards advantageous magnetic phases.


\[
\text{Ga}[\text{N(CH}_3\text{)}_2\text{]}_3 + \frac{3}{2} \text{NH}_3 \xrightarrow{-33 \degree \text{C}} \text{Ga(NH)}_{3/2} + \uparrow 3 \text{HN(CH}_3\text{)}_2 \xrightarrow{\Delta} \text{GaN} + \uparrow 1/2 \text{NH}_3
\]

What we aim at:

\[
\text{Ga}[\text{N(CH}_3\text{)}_2\text{]}_3 + x \text{Mn}\{\text{N[Si(CH}_3\text{)}_3\text{]}_2\} + y \text{NH}_3 \xrightarrow{? \Delta} (\text{Ga,Mn}_x\text{)}\text{N} + \uparrow \ldots
\]

http://www.sciencedaily.com/releases/2013/06/130606112036.htm
Chemistry of materials precursors – bottom-up way to nanocrystalline materials

1:1 stoichiometry of M (Group III) to E (Group V); X, Y – ligands; XY – small, volatile molecule

\[ MX_3 + EY_3 \rightarrow X_3M \cdot EY_3; \] Lewis adduct

\[ X_3M \cdot EY + EY_3 \xrightarrow{\Delta} \frac{1}{n}[X_2M - EY_2]_n + XY \]
\[ \frac{1}{n}[X_2M - EY_2]_n \xrightarrow{\Delta} \frac{1}{n}[XM - EY]_n + XY \]
\[ \frac{1}{n}[XM - EY]_n \xrightarrow{\Delta} ME + XY \]

\[ \Delta \] - temperature-driven reactions

For nanonitrides: excess of E = N; R = organic ligand

\[ M(NR_2)_3 + 3NH_3 \rightarrow M(NH_2)_3 + 3HNR_2 \]
\[ M(NH_2)_3 \xrightarrow{\Delta} \frac{1}{n}[M(NH_2)(NH)]_n + NH_3 \]
\[ \frac{1}{n}[M(NH_2)(NH)]_n \xrightarrow{\Delta} \frac{1}{n}[M(NH)_{3/2}]_n + 1/2NH_3 \]
\[ \frac{1}{n}[M(NH)_{3/2}]_n \xrightarrow{\Delta} MN + 1/2NH_3 \]

http://mathur.uni-koeln.de/902.html

transamination
deamination rxs

elimination-condensation rxs

Chemistry of materials precursors in the making...

Metathesis of Li[N(Si(CH₃)₃]₂ and MnCl₂ in diethylether solution

Manganese bis(trimethyl silylamide)
Mn{N[Si(CH₃)₃]₂}

Mixture of gallium and manganese precursors (Mn initial content 5, 10 and 20 (50) % at.)

Heating: 150 °C
18 h, NH₃ flow

Pyrolysis: 500-900 °C
4 h, NH₃ flow

GaN/Mn nanopowders (Samples XX-150)

Synthesis of highly reactive lithium dimethylamide LiN(CH₃)₂ in diethylether/hexane solutions

Lithium dimethylamide LiN(CH₃)₂

Metathesis of LiN(CH₃)₂ and GaCl₃ in diethylether solution

GaCl₃

Tris(dimethylamino) gallium Ga[N(CH₃)₃]

Heating: 200 °C
18 h, NH₃ flow

Pyrolysis: 500-900 °C
4 h, NH₃ flow

GaN/Mn nanopowders (Samples XX-NO)

Pyrolysis: 500-900 °C
4 h, NH₃ flow

GaN/Mn nanopowders (Samples XX-200)
Manganese nitrides as a reference system - plethora of compounds


Magnetic properties of manganese nitrides

Tetragonal face-centered $\theta$-MnN
– antiferromagnetic
(antiferromagnetic along [001] direction while ferromagnetic within (001) layer)

Tetragonal face-centered $\eta$-Mn$_3$N$_2$
– antiferromagnetic

Hexagonal closed-packed $\zeta$-Mn$_5$N$_2$, Mn$_2$N – antiferromagnetic

Cubic face-centered $\varepsilon$-Mn$_4$N
– ferrimagnetic
Nuclear and spin structure of η-Mn$_3$N$_2$ given for one unit cell in a face-centered tetragonal setting. The arrows represent the magnetic moments according to the antiferromagnetic structure of the first kind. The dashed lines indicate the pseudo-cubic unit cell of the rocksalt type.


Comparison of the tetragonal unit cells of η-Mn$_3$N$_2$ (left) and θ-Mn$_6$N$_5$ (right) in the F-centered setting. While in the θ-phase, the nitrogen site is not fully occupied, the order in the nitrogen substructure of η-Mn$_3$N$_2$ leads to two distinct sites for manganese: one two-fold coordinated and one surrounded by a square pyramid, and to a three times enlarged unit cell parameter $c$.  

Niewa, R. Z. Kristallogr. 2002, 217, 8
Previous work on synthesis of manganese nitrides

- Nitridation of Mn-powder with ammonia NH₃ (1945)
- Reactions of Mn-amalgams with N₂ or NH₃ (1894-1962)
- Preparation of thin films by nitridation of Mn-films with ammonia (1977)
- DC reactive sputtering in the system Mn / N₂ (1993)
- MBE-grown films in Mn / RF N-plasma (2005)
- High pressure synthesis in the system Mn / N₂, 10 GPa (2005)
- Microwave synthesis in the system Mn / N₂ (2007)

- Solvothermal metal azide decomposition to nanocrystalline Mn-nitrides (2009)


HT-HP autoclave reactions in the system MnCl₂ / NaN₃ / toluene, 290 °C

- tetragonal θ-MnN or a mixture of tetragonal η-Mn₃N₂ and cubic ε-Mn₄N
- av. crystallite sizes ca. 20 nm
This study – new precursor system
Reactions of Mn[N(TMS)$_2$]$_2$ with NH$_3$

Reaction conditions: A – 2 mmol Mn[N(TMS)$_2$]$_2$ in refluxing NH$_3$ at –33 ºC, 4 hrs; then, evaporation of NH$_3$ and an overnight evacuation of volatiles at RT

B – 1 mmol of Mn[N(TMS)$_2$]$_2$ and ammonia gas at RT, 1:4 mole ratio, 4 hrs; subsequently, 0.5 hr-evacuation of volatiles at RT

Product: light beige powders for A and B
The distinct bands at ca. 3250-3350 cm\(^{-1}\) superimposed on the broad feature at 3200-3500 cm\(^{-1}\) and the bands at ca. 1550-1600 cm\(^{-1}\) are typical for the stretching and deformation modes of N-H, respectively, in the –NH\(_2\) and =NH groups.

In the volatiles from the exps. A and B, hexamethyldisilazane HN(TMS)\(_2\) was detected by FT-IR which supports the transamination occurring in the system.

The solid products show some –TMS groups still present at RT in addition to the –NH\(_2\) and =NH groups.

The products are insoluble in hexane or diethylether pointing to their polymeric nature.

**Conclusion:** partial transamination and formation of Mn[N(TMS)\(_2\)]\(_x\)(NH\(_2\))\(_y\)(NH)\(_z\)
This study – reactions of Mn[N(TMS)$_2$]$_2$ with HN(CH$_3$)$_2$

Reaction conditions: C – 2 mmol Mn[N(TMS)$_2$]$_2$ reacted with large excess of liquid HN(CH$_3$)$_2$ at 0 ºC, 0.5 hrs; then, evacuation of volatiles at RT for 1 hr.

D – 1 mmol of Mn[N(TMS)$_2$]$_2$ and HN(CH$_3$)$_2$ gas at RT, 1:4 mole ratio, 0.5 hrs; then, collecting the volatiles in a FT-IR gas cell.

Product: grayish powder products for C and D

FT-IR spectrum of Mn[N(TMS)$_2$]$_2$

Large excess of amine

FT-IR spectrum of powder product from C

1:4 mole ratio

FT-IR spectrum of gases from exp. D
This study – reactions of Mn[N(TMS)$_2$]$_2$ with HN(CH$_3$)$_2$, cntd.

Reaction conditions: C – 2 mmol Mn[N(TMS)$_2$]$_2$ reacted with large excess of liquid HN(CH$_3$)$_2$ at 0 ºC, 0.5 hrs followed by evacuation of volatiles at RT for 1 hr.

E – powder product from C (above) reacted with large excess of refluxing NH$_3$ at –33 ºC, 4 hrs followed by evaporation of NH$_3$ and an overnight evacuation of volatiles at RT.

Product: grayish powder product for E

FT-IR spectrum of powder product from C

FT-IR spectrum of powder product from E
This study – reactions of Mn[N(TMS)$_2$]$_2$ with HN(CH$_3$)$_2$, cntd.

(i) In the volatiles from rx $D$, in addition to dimethylamine HN(CH$_3$)$_2$, hexamethyldisilazane HN(TMS)$_2$ was detected by IR which supports the transamination occurring in the system.

(ii) The solid product from rxs $C/D$, *i.e.*, Mn[N(TMS)$_2$]$_2$ + HN(CH$_3$)$_2$, shows some –TMS groups still present in addition to the dimethylamine groups supporting incomplete transamination.

\[ \text{Mn}[\text{N(TMS)}]_2 + x\text{HN(CH}_3)_2 \xrightarrow{0^\circ \text{C}} \text{Mn}[\text{N(TMS)}]_{2-x}[\text{N(CH}_3]_2]_x + x\text{HN(TMS)}_2 \]

(iii) Product from rx $E$ ($C +$ excess NH$_3$) displays by IR similar characteristics as found for rxs $A/B$ suggesting transamination/replacement of the –N(CH$_3$)$_2$ groups by, mostly, the –NH$_2$ groups; the latter is substantiated by the lack of the broad feature at ca. 3200-3500 cm$^{-1}$ typical for plausible imide-type –(H)N– linkages in a polymeric/condensing network of Mn-N that could also be formed.

\[ \text{Mn}[\text{N(TMS)}]_{2-x}[\text{N(CH}_3]_2]_x + x\text{NH}_3 \xrightarrow{0^\circ \text{C}} \text{Mn}[\text{N(TMS)}]_{2-x}[\text{NH}_2]_x + x\text{HN(CH}_3)_2 \]
Summary of our precursor systems to manganese nitride

Pyrolysis of the precursor under an ammonia flow at elevated temperatures in the range 150-900 °C

Current precursor system:

\[ \text{Mn}[\text{N(TMS)}_2]_x[\text{NH}_2]_y[\text{NH}]_z / \text{NH}_3 \]

from the rx \( \text{Mn}[\text{N(TMS)}_2]_2 + \text{excess refluxing NH}_3 \)

Other plausible precursor systems:

\[ \text{Mn}[\text{N(TMS)}_2]_{2-x}[\text{NH}_2]_x / \text{NH}_3 \]

from the rx \( \{\text{Mn}[\text{N(TMS)}_2]_2 + \text{excess N(CH}_3)_2\} + \text{excess refluxing NH}_3 \)

\[ \text{Mn}[\text{N(TMS)}_2]_2 / \text{NH}_3 \]

direct rx \( \text{Mn}[\text{N(TMS)}_2]_2 + \text{NH}_3 \) gas at high temperatures
This work – anaerobic synthesis of Mn$_3$N$_2$ nanopowders

$-\text{N(TMS)}_2 = -\text{N}[\text{Si(CH}_3)_3]_2$
bulky bis(trimethylsilyl) amide ligand

Pyrolysis: 150-900 °C, 4-18 h, NH$_3$ flow

Partially transaminated Mn-precursor
Mn[\text{N(TMS)}_2]_x[\text{NH}_2]_y[\text{NH}]_z (tentatively)

Metathesis of LiN(TMS)$_2$ and MnCl$_2$ (or MnBr$_2$)

Manganese(II) bis(trimethylsilyl)amide
Mn[\text{N(TMS)}_2]_2$

Reactions in liquid NH$_3$
(ammonolysis), –33 °C, 4 h

\[
\text{Mn[\text{N(TMS)}_2]_x[\text{NH}_2]_y[\text{NH}]_z + x\text{NH}_3} \xrightarrow{\Delta T} \text{Mn(\text{NH}_2)_{x+y}(\text{NH})_z + x\text{HN(TMS)}_2}
\]

\[
\xrightarrow{\Delta T} \frac{1}{3}\text{Mn}_3\text{N}_2 + \frac{1}{3}(2 + x + y)\text{NH}_3 \uparrow
\]

Results -

XRD diffraction patterns of powders and/or oil pastes

- 150 ºC, oil paste
- 200 ºC, oil paste
- 300 ºC, oil paste
- 300 ºC, powder, self-ignition
- 700 ºC, oil paste
- 700 ºC, powder
- 500 ºC, powder
- 900 ºC, powder

## Results –
**XRD diffraction patterns of powders and/or oil pastes, cntd.**

<table>
<thead>
<tr>
<th>Product (pyrolysis conds, sample)</th>
<th>Crystallographic phase(s)</th>
<th>Lattice constants for $\eta$-$\text{Mn}_3\text{N}_2$ [Å]</th>
<th>Av. crystallite size of $\eta$-$\text{Mn}_3\text{N}_2$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 ºC, 18 hrs - oil paste</td>
<td>$\eta$-$\text{Mn}_3\text{N}_2$ tetragonal 4/mmm</td>
<td>a=2.97 c=12.28</td>
<td>4</td>
</tr>
<tr>
<td>200 ºC, 18 hrs - oil paste</td>
<td>$\eta$-$\text{Mn}_3\text{N}_2$ tetragonal 4/mmm</td>
<td>a=2.97 c=12.35</td>
<td>5</td>
</tr>
<tr>
<td>300 ºC, 4 hrs - oil paste</td>
<td>$\eta$-$\text{Mn}_3\text{N}_2$ tetragonal 4/mmm</td>
<td>a=2.95 c=12.65</td>
<td>8.5</td>
</tr>
<tr>
<td>300 ºC, 4 hrs - powder (self-ignition)</td>
<td>$\eta$-$\text{Mn}_3\text{N}_2$, 24 % $\text{Mn}_3\text{O}_4$, 76 %</td>
<td>n/d</td>
<td>n/d</td>
</tr>
<tr>
<td>500 ºC, 4 hrs - powder</td>
<td>$\eta$-$\text{Mn}_3\text{N}_2$, 62 % $\text{MnO}$, 38 %</td>
<td>a=2.98 c=12.45</td>
<td>25</td>
</tr>
<tr>
<td>700 ºC, 4 hrs - powder</td>
<td>$\eta$-$\text{Mn}_3\text{N}_2$, 54 % $\text{MnO}$, 46 %</td>
<td>a=2.98 c=12.42</td>
<td>76</td>
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<tr>
<td>700 ºC, 4 hrs - oil paste</td>
<td>$\eta$-$\text{Mn}_3\text{N}_2$, 98 % $\text{MnO}$, 2 %</td>
<td>a=2.99 c=12.45</td>
<td>95</td>
</tr>
<tr>
<td>900 ºC, 4 hrs - powder</td>
<td>$\eta$-$\text{Mn}_3\text{N}_2$ (I), 24 % $\text{MnO}$, 70 %</td>
<td>a=2.99 c=12.34</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td>$\eta$-$\text{Mn}_3\text{N}_2$ (II), 6 % $\text{MnO}$, 70 %</td>
<td>a=2.97 c=12.13</td>
<td>170</td>
</tr>
</tbody>
</table>
Results -
FT-IR determinations (KBr pellets)

- **Powder, 150 °C, 20 hrs**
  - Determination 1
  - Determination 2

- **Powder, 700 °C, 4 hrs**
  - Determination 1
  - Determination 2

Apparently, there is no Mn-N stretch in the mid-infrared region. Observed bands at $<1000 \text{ cm}^{-1}$ are due to Mn-O modes in oxidized products.
Results – SEM/EDS examination

- Powder, 500 ºC, 4 hrs
- Higher N/O proportions for higher pyrolysis temperatures
- Powder, 900 ºC, 4 hrs

Irregular shapes of smaller particles

Particle shape is not, likely, altered by surface oxidation

"Spongy" large particles

Higher N/O proportions for higher pyrolysis temperatures

the same 5 µm scale bar
different crystallite sizes
Conclusions

- A new precursor system Mn[N(TMS)$_2$]$_2$/NH$_3$ is shown to result via transamination/deamination reactions in the rare nanocrystalline powders of manganese nitride.

- Tetragonal $\eta$-Mn$_3$N$_2$ is the only polymorph obtained in the pyrolysis range from 150 up to 900 °C, the product from the latter temperature showing some changes in polymorphism.

- The average crystallite size ranges from ca. 4 nm (pyrolysis at 150 °C) to some +100 nm (pyrolysis at 900 °C) enabling a control of the nitride’s crystallites in the nanosized region.

- Nanopowders of $\eta$-Mn$_3$N$_2$ are extremely air-sensitive.
Thank You For Your Attention