Synthesis, structural, electronic and magnetic properties of α”-$(Fe_{1-x}M_x)_{16}N_2$ (M = Ti, Zr)

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Abstract: In this work the structural, electronic and magnetic properties of α"-$Fe_{16-x}M_xN_2$ (M = Ti, Zr) compounds were investigated. Electronic structure calculations show that while the Fe moment increases, the volume magnetization decreases when doping the α“ phase with Ti or Zr. It was shown that doping is detrimental for magnetization, but it could be beneficial for phase stability. Powder samples were prepared by milling a mixture of commercial Fe and NH_4NO_3 up to 50h. X-ray diffraction measurements show that the α”-$Fe_{16}N_2$ is formed along with the Fe_2O_3 phase after 30h of mechanical milling (MM). It was found that annealing promotes the formation of the α”-$Fe_{16}N_2$ phase. Coercivity values increase while the saturation magnetization decreases with milling time. M_s values suffer only a small decrease from 4 to 300 K, pointing to the ordering of the α”-$Fe_{16}N_2$ well above room temperature. An exchange bias was evidenced at low temperatures due to the presence of the ferrimagnetic Fe_2O_3 phase in the milled samples.

Experimental Details:

- The starting powders, commercial NC 100.24 Fe powder (Hoganas product) and commercial ammonium nitrate (Azomureş S. A.) were **mixed in a ratio of 2:1 Fe:NH_4NO_3**.
- The mixtures were **dry-milled** under Ar using Ø = 10 mm diameter balls for **up to 50 h** in a high-energy planetary mill. The ratio between the rotation speed of the disk and the relative rotation speed of the vials was **Ω/ω=400/800 rpm** with a **ball-to-powder weight ratio of 10:1**. The samples of milled powder were wrapped in tantalum foil, sealed in quartz tubes and **annealed under vacuum at 200 °C for 20 h**.
- The **crystal structure** was investigated using a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation.
- For **magnetic measurements**, the powder samples were blocked in epoxy resin. Magnetic measurements were performed using a VSM in applied fields up to 10 T at temperatures between 4 and 300 K.

Computational Details:

- The electronic structure of $(Fe_{1-x}M_x)_{16}N_2$ (M = Ti, Zr; x = 0, 0.03 and 0.05) was calculated using the SPR-KKR method in the atomic sphere approximation (ASA) [1]. The local spin density approximation (LSDA) was used for the exchange-correlation energy using the parameterization of Vosko et al. [2]. The strong on-site Coulomb interactions from the localized 3*d* electrons of the *M* atoms have been accounted for by the LSDA + U method in combination with the Coherent Potential Approximation (CPA) [3,4,5].
- The Hubbard U parameters are 3.12, 3.52 and 3.99 eV for Fe/M 4*e*, 8*h* and 4*d*, respectively, while the J parameters values are 0.59, 0.61 and 0.64 eV for the same sequence of sites.

Electronic Structure Calculation Results:

- ***N*** – strong ***affinity*** for Ti, Zr [6].
- Fe 8*h* – proximity to N.

↓

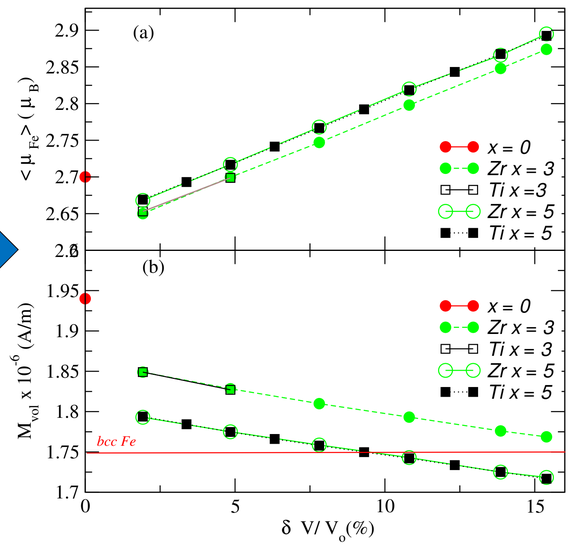
Preferential occupancy of ***Ti*** and ***Zr*** for ***Fe 8h*** positions [6,7].

↓

Volume expansion.

↑

Atomic radii of ***Ti*** (1.76 Å) and ***Zr*** (2.06 Å) ***larger than*** that of ***Fe***.



Magnetovolume effect.

↓

Fe moments increase.

Volume magnetization decreases.

↑

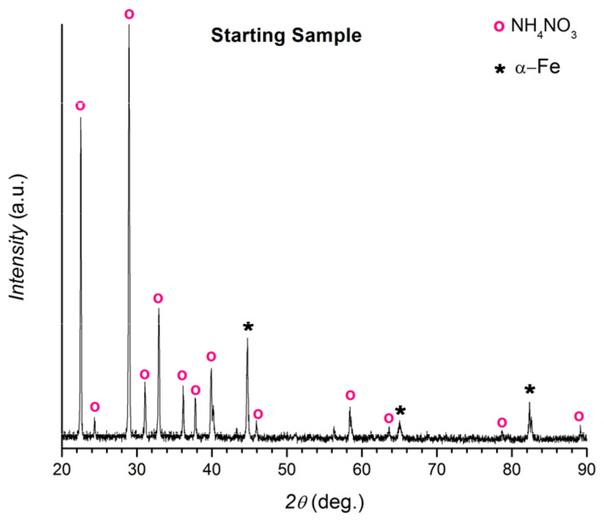
Volume ***expansion larger*** than the magnetic moment ***enhancement***.

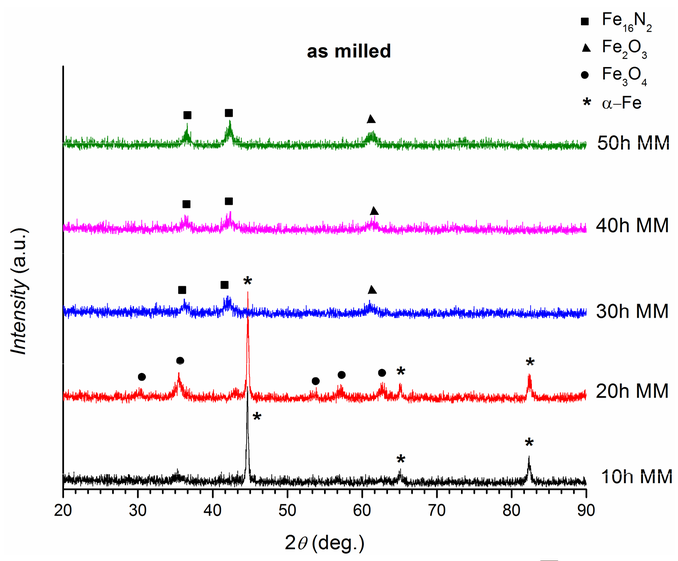
Magnetic moments calculated for $(Fe_{1-x}M_x)_{16}N_2$ with a volume expansion of 1.9% (in agreement with the experiment [8])

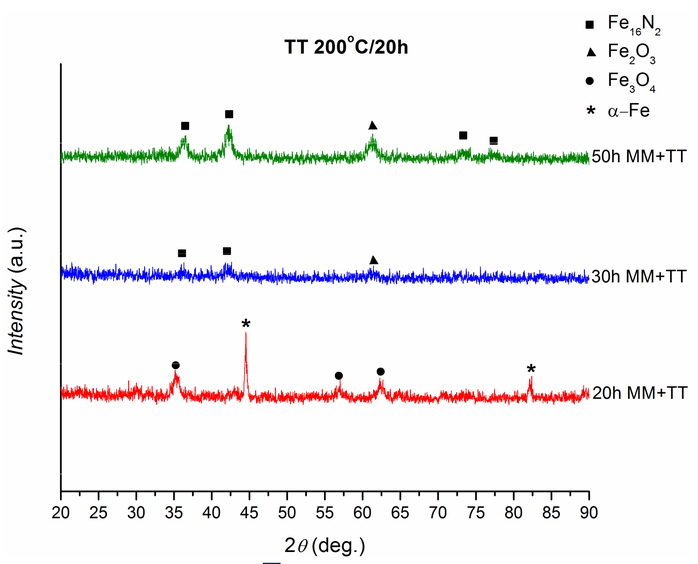
dopant/ concentration		N	Fe 4*e*	Fe 8*h*	*M* 8*h*	Fe 4*d*
-	m_s	-0.19	2.48	2.53	-	2.98
	m_l	0.00	0.11	0.09	-	0.11
experiment [9]	m_s	-	2.33	2.45	-	3.05
Zr 3%	m_s	-0.18	2.44	2.58	-0.48	2.91
	m_l	0.00	0.11	0.09	0.02	0.12
Zr 5%	m_s	-0.16	2.39	2.59	-0.48	2.85
	m_l	0.00	0.11	0.09	0.02	0.12
Ti 3%	m_s	-0.18	2.47	2.57	-0.77	2.94
	m_l	0.00	0.12	0.09	0.03	0.12
Ti 5%	m_s	-0.16	2.44	2.57	-0.75	2.90
	m_l	0.00	0.11	0.09	0.03	0.12

- Ti/Zr doping is ***detrimental for magnetization***.
- Ti/Zr doping could be ***beneficial for phase stability*** [6,7].

Experimental Results:





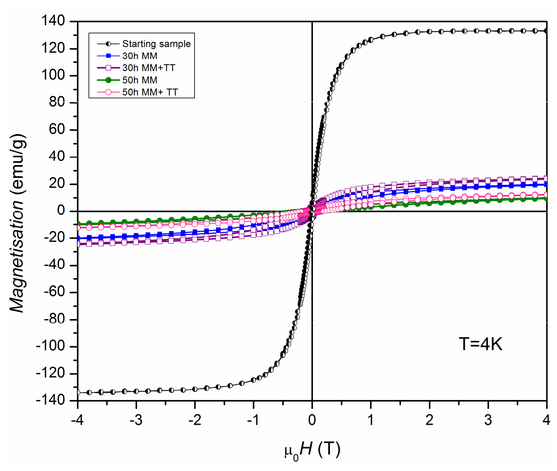


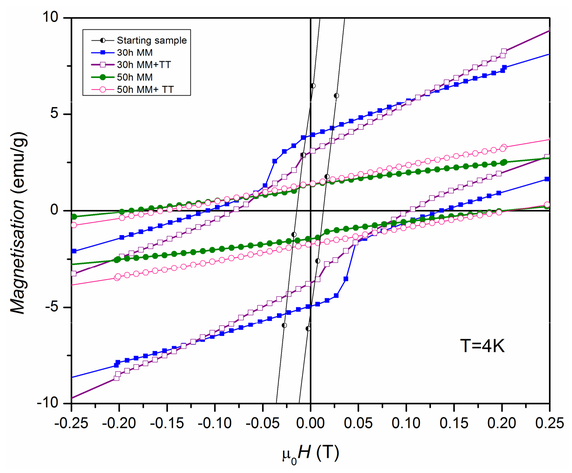
- up to 20h MM: α-Fe + Fe_3O_4
- **30-50h MM**: **α”-$Fe_{16}N_2$** + Fe_2O_3

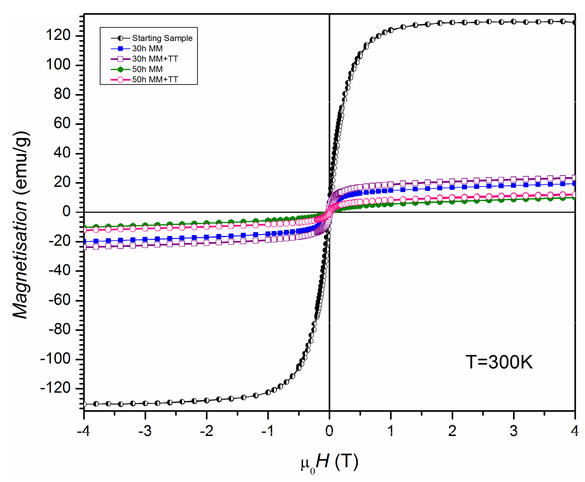
← NH_4NO_3 decomposes during milling.

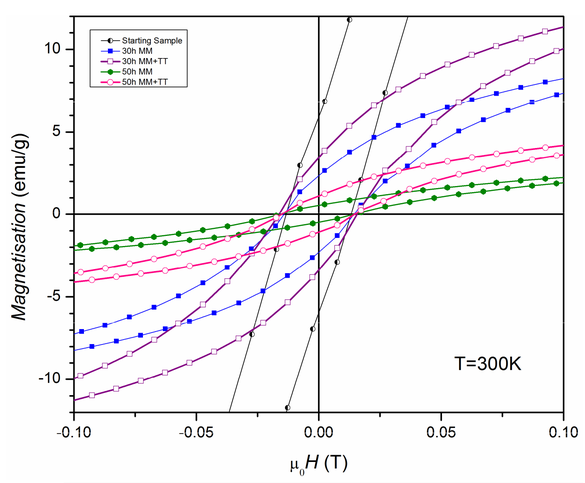
Broad diffraction peaks suggest that the particles might be nanometric.

50h MM α”-$Fe_{16}N_2$ XRD peak intensity increases after annealing. → Annealing promotes α”-$Fe_{16}N_2$ formation









Lower M_s and M_r values in milled samples compared to the starting sample.

↑

In addition to the α”-$Fe_{16}N_2$ synthesis, milling-induced strain and formation of Fe_2O_3.

Coercivity increases with milling time.

↑

Increased defect density and increased α”-$Fe_{16}N_2$ content with milling time.

M_s values suffer only a ***small decrease*** from ***4*** to ***300 K.***

↓

Ordered α”-$Fe_{16}N_2$ magnetic phase well ***above room temperature***.

Coercivity decreases from 4 to 300 K and remains roughly unchanged with milling time/annealing.

↑

Decrease of the anisotropy field with temperature.

Sample	M_s (4K) (emu/g)	M_s (300K) (emu/g)	M_r (4K) (emu/g)	M_r (300K) (emu/g)	$\mu_0 H_c$ (4K) (mT)	$\mu_0 H_{bias}$ (4K) (mT)	$\mu_0 H_c$ (300K) (mT)	$\mu_0 H_{bias}$ (300K) (mT)
Start	129.5	135.7	5.6	5,9	13.9	0.6	13.3	0.1
30h MM	17.4	16.3	3.9	2.3	122.3	14.9	14.8	0.6
50h MM	5.2	5.2	1.0	0.4	194.1	8.5	15.2	0.4
30h MM+TT	21.1	20.5	3.0	3.4	92.1	12.2	15.9	0.3
50h MM+TT	10.1	8.4	1.4	1.1	181.3	27.2	15.8	0.6

→ ***M_s values increase after annealing.***
→ Coercivity decreases after annealing.

← ***Formation of α”-$Fe_{16}N_2$***
← Strain relaxation.

→ Shifted hysteresis loops along the field axis at low temperature.

→ ***Exchange bias*** due to the presence of the ***ferrimagnetic Fe_2O_3 phase***.

Conclusions:

- Electronic structure calculations show an increase of the Fe moment and a decrease of the volume magnetization with Ti/Zr doping. ***Doping is detrimental for magnetization but could promote phase stability***.
- The ***α”-$Fe_{16}N_2$*** phase was ***obtained after 30h MM***. It was found that ***annealing promotes the formation of the α”-$Fe_{16}N_2$ phase***.
- ***Coercivity values increase with milling time*** due to an increased defect density. ***M_s*** values suffer only a ***small decrease*** from ***4*** to ***300 K***, showing that α”-$Fe_{16}N_2$ is ordered well ***above room temperature***.
- An ***exchange bias*** was evidenced at low temperature due to the presence of the ***ferrimagnetic Fe_2O_3 phase*** in the milled samples.

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