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Magnetic Properties and Mössbauer spectroscopy of NdFe$_{1-x}$Mn$_x$O$_3$

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Abstract The effect of particle reduction to nanoscale size and substitution of Mn$^{3+}$ ions for Fe$^{3+}$ ions on the crystal structure, lattice dynamics, Mössbauer spectra and magnetic properties in NdFe$_{1-x}$Mn$_x$O$_3$ compounds have been studied. X-ray powder diffraction and Raman spectroscopy revealed that the Jahn-Teller distortion of lattice dominates for samples with $x > 0.4$. The average particle size of NdFeO$_3$ nanoparticles (NAP) increases with annealing at 600$^\circ$C from about 15 nm to 25 nm. The presence of superparamagnetic particles was indicated by Mössbauer measurements in NdFeO$_3$ NAP system. Sextets in NdFe$_{1-x}$Mn$_x$O$_3$ Mössbauer spectra can be modelled with several local environments of Fe$^{3+}$ induced by substitution. The reduction of dimensionality and the substitution induce a decrease of the Néel temperature $T_{N1}$ from 691 K to 544 K for NAP or to 356 K for $x = 0.4$, however the temperature of spin reorientation $T_{SR}$ increases with substitution. The saturated magnetization obtained at 1.9 K increases and ferromagnetic component is removed below $T_{SR}$ with the substitution.

1. Introduction
The physical and structural properties of NdFeO$_3$ are widely studied and they attract large attention due to interesting magnetic properties such as spin-reorientation phase transition [1]. Magnetic properties of NdFeO$_3$ are mostly determined by Fe-Fe, Fe-Nd and Nd-Nd exchange interactions. Magnetic ordering of Fe$^{3+}$ ions creates a canted antiferromagnetic ordering of G-type below the Néel temperature at about $T_{N1} = 690$ K and the magnetic moments of Fe$^{3+}$ exhibit spin reorientation from $G_x$ type to combination of $G_x$ and $G_z$ type in the region from 100 K to 200 K. The moments of Nd were found to undergo a collective C-type antiferromagnetic ordering at $T_{N2} = 1.5$ K [2]. In our paper we study the effect of nano-metric size and substitution of the Mn$^{2+}$ ion for the Fe$^{3+}$ ion on the crystal structure, lattice dynamics, magnetic environment of iron and magnetization in NdFe$_{1-x}$Mn$_x$O$_3$ system.

2. Sample preparation and experimental details
NdFeO$_3$ nanoparticles (NAP) were prepared by the self-propagating high-temperature synthesis (SHS) which is based on a brief, exothermic burning reaction between oxidizing agent (potassium nitrate),
organic fuel (glucose) and relevant metal nitrates [3]. The as prepared samples were annealed at 600°C for 2 hours in air using a muffle furnace. Ingots of NdFe_{x-1}Mn_{x}O_{3} compounds have been grown by the optical floating technique (OFT) in a mirror furnace equipped with four mirrors. Stoichiometric ratio of starting materials Nd_{2}O_{3}, Fe_{2}O_{3} and MnO_{2} was mixed in the agate mortar in order to obtain homogenous powder. The powders were pressed into rods by isostatic cold pressing and sintered at 1100°C in air for 20 hours. The crystals were grown in air atmosphere with grown rate of 7 mm/hr and 15 rpm rotation of both shafts.

All samples have been characterized by scanning electron microscope (SEM) methods including the energy - dispersive X-ray (EDX) microanalysis on Mira III FE SEM produced by Tescan. Crystal structure of all samples was investigated by X-ray powder diffraction (XRD) technique on different diffractometers always in the Bragg-Brentano geometry. XRD on NdFeO_{3} nanoparticles was studied by a D8 (Bruker) diffractometer using Cu Kα1,α2 doublet radiation. Crystal structure of NdFe_{x-1}Mn_{x}O_{3} for x ≤ 0.4 was determined by the X’Pert (PanAnalytical) diffractometer powered by Co Kα1,α2 doublet radiation with a help of qualitative analysis provided by HighScore® software and the JCPDS PDF-4 database. For a quantitative analysis HighScore plus® with Rietveld structural models based on the ICSD database was applied. Crystallographic data of samples with higher Mn content were taken from [4].

Raman experiment was performed on the Jobin-Yvon LabRAM spectrometer (Horiba Inc.). The spectrometer was equipped with He-Ne laser (λ = 632.8 nm) which was used for excitation, charge coupled device (CCD) detector and notch filter which filtered out the Raman shifts smaller than 85 cm\(^{-1}\). The Raman spectra were collected with 1 cm\(^{-1}\) resolution and at room temperature. Mössbauer spectra of powder samples were collected in a standard transmission geometry using a radioactive source of \(^{57}\)Co in Rh matrix (50 mCi) at room temperature. A calibration was done using a 25 μm thick natural foil; isomer shifts values are referred to α-iron. Magnetization measurements were performed by SQUID magnetometer (MPMS XL-5) in the temperature range from 2 to 750 K and in applied magnetic fields up to 5 T. Magnetic measurements were performed on NdFeO_{3} nanoparticles and powdered NdFe_{x-1}Mn_{x}O_{3} samples.

3. Results and discussion

The material particle size reduction down to nano- dimensions may result not only in remarkable changes of physical properties, like magnetic phase temperature, size dependence of saturation magnetization and coercive field but also in the emergence of the qualitatively new one, like superparamagnetism. Very similar situation can be observed in the case of proper substitution, for instance if the Fe\(^{3+}\) ion, which is inactive Jahn-Teller (JT) ion, is substituted by the Mn\(^{3+}\) JT active ion. In such a case the electronic properties and electron phonon-coupling can change significantly.
The analysis of SEM images taken from NdFeO$_3$ NAPs (Figure 1.) revealed that aggregations of very well crystalized cuboid micro-sized particles with large distribution of size are randomly spread on the surface of agglomerates which are built from NAP with relatively uniform size. The amount of NAP agglomerates in the sample is higher than 90%. The average particle size, which was determined from SEM photos, increases from about 15 nm for as prepared NAP to about 25 nm for annealed NAP. In agreement with [5] both samples adopt orthorhombic crystal structure (space group Pnma). The relatively broad peaks in XRD pattern indicate presence of NAP in the sample (Figure 2).

No parasitic inclusions, secondary phases or concentration gradients were observed either by SEM methods including EDX analysis on NdFe$_{1-x}$Mn$_x$O$_3$ ingots or from XRD on powders. The substitution of the Mn$^{3+}$ for the Fe$^{3+}$ ion introduces both the JT distortions of the unit cell and distortion resulting from structural mismatch. The symmetry of the orthorhombic crystal structure (space group Pnma) remains unchanged in the whole concentration range. The lattice parameters and the unit cell volume change non-monotonically with substitution showing two distinguished regions below and above $x = 0.5$ (Figure 3). In the high Fe - concentration region with $x \leq 0.4$ the unit cell volume is almost intact by substitution and lattice distortion is given mainly by tilting of Mn/FeO$_6$ octahedrons. The unit cell volume increases on further substitution and the lattice distortion can be attributed to both the JT distortion and the tilting of octahedrons.

Unpolarised Raman spectra of NdFe$_{1-x}$Mn$_x$O$_3$ which were recorded at room temperature are shown in Figure 4. The Raman spectra of the parent compounds NdFeO$_3$ and NdMnO$_3$ are in good agreement with published data, corroborating the orthorhombic symmetry space group Pnma of both compounds [6, 7]. Factor group analysis considering the site symmetry for the $\Gamma$-point phonons of orthorhombic NdFeO$_3$ indicates that the following 24 modes are Raman active among 60 zone-center phonon modes in the Pnma structure: $\Gamma_{\text{Raman}} = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$. As the Mn-content increases, the Raman bands become broader and the peak between 620 and 635 cm$^{-1}$ dominates in the spectra up to $x = 0.45$. This peak can correspond to the peak at 643 cm$^{-1}$ which was observed in room-temperature second-order Raman spectra of the orthorhombic NdFeO$_3$ single crystal [6] and was attributed to a two-phonon scattering caused either by two $B_{1g}$ phonons or by two $B_{2g}$ phonons. The observed mode was assigned as Fe-O breathing mode [6]. Features typical for the Raman spectrum of NdMnO$_3$ [7] become dominant for Mn concentration higher than $x = 0.70$. The Raman mode $B_{2g}$ at 606 cm$^{-1}$ is assigned to in-plane O$_2$ stretching leading to JT distortions. The change of the Raman profile along with the unit cell volume at $x = 0.4$ point toward the probable switch between JT non-distorted dominated regime to JT distorted dominated regime.

### Figure 3.
Evolution of lattice parameters and the unit cell volume with substitution.

### Figure 4.
Unpolarised Raman spectra, recorded at room temperature for several compositions.
3.2. Mössbauer spectroscopy
The six fold coordinated Fe$^{3+}$ ion of NdFeO$_3$ crystal is sitting in the centre of an octahedron and is in high spin state. The corresponding room temperature Mössbauer spectrum consists of a single sextet component [8]. Our results shows that the fit of the room temperature Mössbauer spectra for both as prepared and annealed NdFeO$_3$ nanoparticle samples is based on the superposition of three sextet and quadrupole doublet components (Figure 5 and Figure 6). The invariant values of hyperfine parameters $\delta$ and $\varepsilon$ in all sextets confirm that the components describe the same iron crystal site (Table 1). Different values of hyperfine field $B_{hf}$ in three sextet components indicate several slightly different local surroundings of the Fe$^{3+}$ ions. The relative area of doublet components is reduced with the annealing of nanoparticle sample, i.e. with the increase of mean particle size (Table 1). Such an effect indicates that the observed doublet components can be attributed to the fraction of Fe$^{3+}$, which is in the superparamagnetic state at room temperature.

Table 1. $^{57}$Fe Mössbauer parameters calculated from recorded spectra; af-area fraction of total, $B_{hf}$-hyperfine induction, $\delta$-isomer shift, $\varepsilon$-quadrupole shift.

| Sample       | NdFeO$_3$ SHS as prepared | NdFeO$_3$ SHS 600°C/2h |
|--------------|--------------------------|------------------------|
| Sextet/Doubt | af $B_{hf}$ $\delta$ $\varepsilon$ | af $B_{hf}$ $\delta$ $\varepsilon$ |
| S1           | 0.275 50.5 0.37 -0.05 0.475 50.6 0.37 -0.03 |
| S2           | 0.075 48.5 0.36 -0.06 0.207 48.6 0.37 -0.06 |
| S3           | 0.171 46.0 0.37 -0.08 0.130 45.3 0.34 -0.08 |
| S             | 0.521 48.7             0.812 49.3           |
| D1           | 0.292 0.36 0.79 0.130 0.37 0.78 |
| D2           | 0.092 0.14 0.71 0.040 0.04 0.69 |
| D3           | 0.095 0.28 1.40 0.017 0.23 1.63 |
| D             | 0.479              0.188 |

The room temperature Mössbauer spectra of NdFe$_{1-x}$Mn$_x$O$_3$ contain only sextets. The analysis of these spectra is summarized in Table 2. The width of peaks increases with increasing content of Mn. In the analysis of spectra we consider various environments around octahedral Fe$^{3+}$ ions due to random distribution of Mn$^{3+}$ ions. The probability of octahedral site having $n$ nearest neighbor of Mn is:

$$P(n, x) = \frac{6!}{n!(6-n)!}x^n(1-x)^{6-n}$$

where $x$ is concentration of Mn and $n$ is the number of Mn ions among the nearest - neighbor Fe$^{3+}$ ions.
Effect of sample preparation on the reorientation and the magnetic phase transition. 

Table 2. $^{57}$Fe Mössbauer parameters calculated on the basis of recorded spectra; $af$-area fraction of total, $prob$-probability of surrounding, $B_{hf}$-hyperfine induction, $\delta$-isomer shift, $\epsilon$-quadrupole shift/splitting.

| Sample | NdFeO$_3$ | NdFe$_{1-x}$Mn$_x$O$_3$ |
|--------|------------|------------------------|
| Sextet | $af$ | $B_{hf}$ | $\delta$ | $\epsilon$ | $af$ | $prob$ | $B_{hf}$ | $\delta$ | $\epsilon$ |
| S1     | 1.0 | 51.39 | 0.369 | -0.006 | 0.17 | 0.26 | 50.99 | 0.366 | -0.147 |
| S2     | 0.28 | 0.39 | 49.17 | 0.374 | -0.006 |
| S3     | 0.30 | 0.25 | 46.88 | 0.373 | -0.012 |
| S4     | 0.15 | 0.08 | 44.29 | 0.381 | -0.016 |
| S5     | 0.07 | 0.02 | 41.15 | 0.369 | 0.058 |
| S6     | 0.03 | <0.01 | 37.23 | 0.340 | 0.298 |
| S      | 51.39 | | | | 47.16 | |

3.3. Magnetic properties

The magnetic transition at $T_{N1}$ and the spin-reorientation temperature $T_{SR}$ were determined from magnetization measurements $\mu(T)$ (Figure 7). Spin reorientation is a more general phenomenon observed in many rare-earth orthoferrites. In the case of NdFeO$_3$ a spin reorientation transition is observed between 100 and 200K with gradual changes of the directions of the Fe$^{3+}$-ordered magnetic moments [1]. In our paper we defined $T_{SR}$ as the temperature at which the process of reorientation is finished and we assign it to the local minimum on $\mu(T)$ curve (Figure 7). The reduction of dimensionality to nano-scale decreases $T_{SR}$ from 85 K to 20 K. Synthesis of NAP introduces distortion of lattice which can be considered as an effective barrier for spin reorientation and as result the reorientation process is finished at lower temperature. The substitution has an opposite effect and $T_{SR}$ is rising with increasing content of Mn from 85 K to 123 K, 177 K, 223 K, 267 K and 283 K for $x = 0.00, 0.10, 0.15, 0.20, 0.3$ and $0.4$, respectively. The magnetic moment of Mn$^{3+}$ is smaller and energy required for spin reorientation is smaller too and therefore the $T_{SR}$ increases with Mn concentration.

The Néel temperature $T_{N1}$ was determined from a minimum on the $d\mu/dT(T)$ curve. System of NPA contains superparamagnetic particles and the magnetic interaction can be reduced due to surface effect that is why the magnetic transition occurs at lower temperature $T_{N1} = 544$ K. The magnetic transition of NdFe$_{1-x}$Mn$_x$O$_3$ becomes broader and $T_{N1}$ decreases from 691 K to 356 K for $x = 0.4$ with Mn doping (Figure 8). Broadening of the transition can be attributed to enhanced probability of different surroundings of Fe with substitution as it was already considered in the analysis of Mössbauer spectra. The transition from paramagnetic to canted antiferromagnetic state is accompanied in several cases with sharp peak on $\mu(T)$ curves (Figure 8), which can be attributed to Hopkinson effect. Such a peak
this region for Fig. 9(a) and (b)). Loops appear at low magnetic field while linear dependence of \( \mu(B) \) is observed in high fields above 50 K. The slope of linear part of \( \mu(B) \) curves, corresponding to the high field susceptibility, increases with decreasing temperature down to 50 K which is consistent with antiferromagnetic magnetic ordering having a ferromagnetic component. The magnetic loop has S-shape at 1.9 K indicating the change of magnetic ordering in the vicinity of \( T_N^2 \). Magnetizations taken at 1.9 K for 5 T show nearly no change for small concentrations of Mn and an increase at higher concentrations (\( \mu_{N1} = 1.098 \mu_B, 1.073 \mu_B, 1.096 \mu_B, 1.131 \mu_B, 1.304 \mu_B, 1.412 \mu_B \) for \( x = 0.00, 0.10, 0.15, 0.20, 0.30 \) and 0.40, respectively). Remnant magnetization and coercive force increase with substitution (Figure 9(b)). Ferromagnetic component can be suppressed by Mn substitution in the range between 0.00 and 0.15 (Figure 9(a)). The reduction of particle size to nano scale does not change \( \mu(B) \) curves drastically (Figure 10). Main features of bulk material like presence of hysteresis loop (Figure 10(a)) are still present only the magnetization at 1.9 K is slightly reduced to 0.88 \( \mu_B \) and tiny changes in the shape of the loop (Figure 10(b)) indicates that \( T_N^2 \) can be reduced, too.

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