Synthesis and Phase Composition of Nanosized Particles in Iron-containing Silicate Glasses

R. Harizanova\textsuperscript{1}, I. Gugov\textsuperscript{1}, C. Rüssel\textsuperscript{2}, D. Tatchev\textsuperscript{3}, V. S. Raghuwanshi\textsuperscript{4}, A. Hoell\textsuperscript{4}

\textsuperscript{1} University of Chemical Technology and Metallurgy, Sofia, Bulgaria
\textsuperscript{2} Friedrich-Schiller-Universität, Jena, Germany
\textsuperscript{3} Institute of Physical Chemistry, Sofia, Bulgaria
\textsuperscript{4} Institute of Applied Materials, Helmholtz Zentrum Berlin, Germany
$MFe_2O_4$ nanosized particles, where $M = Fe, Mn$

- Biomedical applications
  - Drug delivery systems
  - Hyperthermia
  - Contrast agents for magnetic resonance imaging

Shielding of electronic components

$MFe_2O_4$ nanosized particles, where $M =$ Fe, Mn

**Technique**

- Cooling of different systems
- Part of inks
- Sealings and solder materials

$MFe_2O_4$ nanosized particles, where $M = Fe, Mn$

**Sensor technology**

- Biochemical sensors for detection of different biological and chemical species
- Biosensors for diagnosis of infectious diseases.

Scheme of reader with interface between sensor chip and computer,
Aims of the Work:

- Investigation of the glass formation in the system $\text{Na}_2\text{O}/\text{SiO}_2/\text{MnO}/\text{Fe}_2\text{O}_3$.
- Synthesis of glasses and nanosized superparamagnetic glass-ceramics in the studied system.
- Establishment of the influence of chemical composition on the phase composition and the microstructure of the obtained glass-ceramics.
- Characterization of the phase composition of the precipitated nanocrystals.
- Magnetic measurements on precipitated nanocrystals.
Investigated system and synthesis conditions

Investigated system

\[(1-x)(16\text{Na}_2\text{O}/10\text{MnO}/74\text{SiO}_2)/x\text{Fe}_2\text{O}_3\]
for \(x = 0.05 \div 0.30\)

Raw materials: \(\text{Na}_2\text{CO}_3; \text{MnCO}_3; \text{SiO}_2; \text{Fe}_2\text{O}_3\) or \(\text{FeC}_2\text{O}_4\)

Synthesis conditions: \(\text{SiO}_2\) crucible, \(\text{MoSi}_2\) furnace, 1400–1450°C, 0.5–2.5 h, quenching between Cu blocks, annealing at 480°C for 10 min after pouring in a pre-heated C mould.

Crystallisation by applying different temperature/time regimes in order to precipitate nano-sized ferrimagnetic crystals.
Characterization methods

- Phase composition and microstructure
  - X-ray diffraction analysis;
  - SEM/TEM analysis.

- Additional phase composition investigation
  - Anomalous small angle x-ray scattering (ASAXS).

- Magnetometry
  - Vibration magnetometer
Results: phase composition and microstructure

- **X-ray diffraction**

  XRD patterns of reduced samples
  \[13.6\text{Na}_2\text{O}/8.5\text{MnO}/62.9\text{SiO}_2/15.0\text{Fe}_2\text{O}_3-y\]
  heat-treated at 600°C for different time: formation of mixed crystals \(\text{MnFe}_2\text{O}_4\) (A) and \(\text{Fe}_3\text{O}_4\) (B).

- **SEM imaging**

  SEM (SE) image of C-covered sample with 15 mol% \(\text{Fe}_2\text{O}_3-y\)
  crystallized for 10 h at 550°C.

  SEM (SE) image of C-covered sample with 15 mol% \(\text{Fe}_2\text{O}_3-y\)
  annealed for 24 h at 600°C.
Results: microstructure and average particle size

SEM (SE) image of C-covered sample with 15 mol% $\text{Fe}_2\text{O}_3$-y and 8.5 mol% MnO, annealed for 3h at 550°C.

Particle size distribution for a sample annealed at 550° for 3 h.
Results: ASAXS – elemental composition and average particle size

1) SAXS on samples annealed for 40 min for 3 h at 550°C showed formation of nanocrystals with sizes from 14 to 44 nm, respectively.

2) ASAXS effect is observed near the absorption edges of both Fe and Mn.

3) ASAXS data curves interpretation suggests formation of nearly spherical core-shell particles, containing Fe, Mn and O.

4) ASAXS predicts:
Initially formation of a Fe-rich homogenously nucleating and further growing spinel phase core.

5) ASAXS data also suggests:
rising concentration of Mn in the vicinity of the growing Fe-rich core causes heterogeneous nucleation and growth of Mn,Fe-containing spinel layer.

6) From ASAXS data: the formation of both Fe and Mn enriched nanoparticles leads to formation around them of a Fe, Mn depleted viscous shell.
Results: magnetic measurements

Magnetization vs. external magnetic field for a sample with 15 mol% Fe$_2$O$_{3-y}$, annealed at 540°C for 3 h.

Magnetization vs. external magnetic field for a sample with 15 mol% Fe$_2$O$_{3-y}$, annealed at 600°C for 24 h.
**Summary of the results**

- Nanosized spinel phase of the type (Mn, Fe)$^{II}$(Fe,Mn)$^{III}_{2}$O$_4$ is precipitated in the investigated compositions up to 600°C.

- For crystallization time over 3 h, for all temperatures, the average size of the formed nanocrystals is about 50 nm and hardly changes with time. The precipitation of the spinel nanosized phase is kinetically constrained.

- The chemical composition of the obtained nanoparticles as studied by ASAXS shows formation of Fe-Mn-O-based core-shell structures in which the core is enriched in Fe and the shell is depleted in both Fe and Mn.

- The magnetic properties of the precipitated nanocrystals vary from paramagnetic to superparamagnetic, depending on the applied time-temperature annealing programs.
Thank you for your attention!
DSC Results

![DSC Results Diagram](image)

Tg = 518°C
Magnetization versus Temperature

Sample 540C/3h

Sample 600C/24h
ASAXS curves

ASAXS effect at the Mn-absorption edge

ASAXS effect at the Fe-absorption edge