Institut za nuklearne nauke Vinča

# Observation of $Fe_3O_4 \rightarrow \alpha\text{-}Fe_2O_3$ phase transformation at low temperature

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Abstract

The magnetic behavior of nanoparticles of magnetite coated with oleic acid ($Fe_3O_4$ /OA), synthesized by the hydrothermal method, was investigated in detail by SQUID measurements, performed by Nikolić et al [1]. In order to get a better insight into the behavior of the prepared sample subjected to thermal treatment, a more detailed thermo-gravimetric analysis was performed (thermal analyzer TA-SDT 2090). TG and DTA curves were measured by a standard protocol. Additional measurements of the sample dried under the lowered pressure were also performed. The results revealed that the processes, observed as a consequence of thermal treatment, have a strong exothermic nature; the most intense DTA maximum is observed around T = 289 °C. Having in mind the results of XRD and TEM analysis [1], as well that the transformation of the magnetite phase into hematite represents an exothermic process: $Fe_3O_4 + ¼\ O_2 = 3/2\ \alpha\text{–}Fe_2O_3 + \Delta H$, $\Delta H = 115$ kJ/mol [2,3], the observed exothermic process is attributed to $Fe_3O_4 \rightarrow \alpha\text{–}Fe_2O_3$ phase transformation at low temperatures (< 300 °C). The observed behavior could be ascribed to the presence of cation deficiency in the magnetite crystal lattice.
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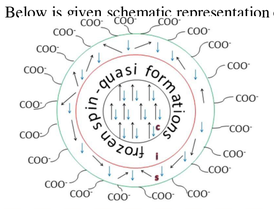
## Background

- Characterization of the $Fe_3O_4$/OA nanoparticles
- Confirmation of the possibility to use M(T) magnetic measurements to track changes of the magnetite electronic structure
- Below is given schematic representation of the internal structure of the investigated $Fe_3O_4$/OA nanoparticle [1]




## Introduction and Methodology

- The aim of the study was to gain a deeper insight into the influence of thermal treatment on the behavior of the examined magnetite nanoparticles
- The sample (consisted of $Fe_3O_4$/OA nanoparticles) is dried under the lowered pressure, with the aim to measure DTA curves
- DTA curves were measured in the air, and in the inert atmosphere

## Results

- DTA curves were measured using the same amount of powder, dried under reduced pressure. The DTA curves presented in Figure 1a) and b) are measured in the temperature ranges (0-1100 oC) and (0-350 oC), respectively

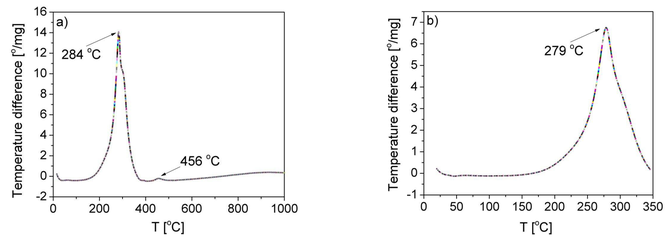



Figure 1. DTA curves of the sample $Fe_3O_4$/OA, measured in the air

- DTA curve measured in the inert atmosphere, Figure 2

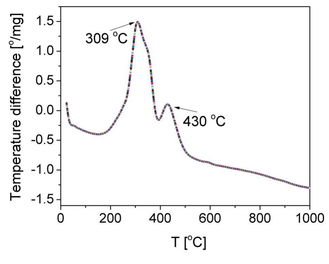



Figure 2. DTA curves of the sample $Fe_3O_4$/OA, measured in the inert atmosphere

## Discussion

- The observed processes have strong exothermic nature
- The appearance of exothermic maxima (at 284 °C and 456 °C, Fig. 1, as well at 309 °C and 430 °C, Fig. 2) is ascribed to the $Fe_3O_4 \rightarrow \alpha\text{–}Fe_2O_3$ phase transformation [4]
- Although it is common for magnetite to undergo a phase transformation into hematite at about 500 °C [5], hydrothermal synthesis allows this phase transformation to occur at a significantly reduced temperature [6]
- Nasrazadani et al. assumed that nucleation of the hematite nanoparticles could occur at temperatures lower than 300 °C, which is process dependent on the cation deficiency in magnetite [7]

## Conclusion

- The performed study considered the magnetite nanoparticles coated with oleic acid, prepared by hydrothermal synthesis
- DTA measurements confirmed the lowered transition temperature of the $Fe_3O_4 \rightarrow \alpha\text{–}Fe_2O_3$ phase transformation
- Strong exothermic nature of the observed maxima is interesting, since literature review revealed that endothermic maxima at the same positions could be ascribed to the decomposition of weakly bonded oleic acid and covalently bonded oleic acid molecules, respectively [8]
- Accordingly, the endothermic processes are hidden by the strong exothermic nature of the represented maxima
- The observed feature could be ascribed to the increased cation deficiency of magnetite, which impacts the temperature of the $Fe_3O_4 \rightarrow \alpha\text{–}Fe_2O_3$ phase transformation
- In other words, fine adjustment of the synthesis conditions enables preparation of the magnetite nanoparticles characterized by a various degree of a cation deficiency, which is reflecting on the temperature of the magnetite phase transformation

## Literature

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