Magnetic Properties and Phase Transformation Of ε -Fe$_2$O$_3$

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Abstract

The synthesis of ε-phase Fe_2O_3 has long been a hot topic in physical chemistry. The Pt-substituted Fe_2O_3 and Ru-substituted Fe_2O_3 were designed and synthesized using the combination of Reverse-micelle and sol-gel techniques. Followed by the X-ray differentiation, the crystal structure of Pt-substituted Fe_2O_3 and Ru-substituted Fe_2O_3 were analyzed. Then a superconducting quantum interference device (SQUID) was employed to measure the magnetic properties (Quantum Design, MPMS 7). The magnetic properties of the synthesized nanowire form of the product were analyzed by Magnetic Hysteresis Test (MH 300). The ε-phase of the products was analyzed by comparing to the products that synthesized in a range of temperatures.

Keyword: ε-phase Fe_2O_3, Magnetic Hysteresis, Pt and Ru substitution

Introduction

Fe_2O_3 can be obtained in various crystal structures, such as α and γ phases of iron adopt octahedral coordination geometry (i.e. each Fe center is bound to six oxygen ligands). ε-phase Fe_2O_3 has a orthorhombic structure which can be prepared by thermal transformation of γ-phase Fe_2O_3. ε-phase Fe_2O_3 shows properties intermediate between alpha and gamma. The structure of ε-phase Fe_2O_3 is shown in Fig.1.

The object of this experiment is to provide good conditions for forming ε-phase Fe_2O_3 in several tens of nanometers size range. The synthetic procedure also involves doping of other ions in the final product. In the end of the experiment, a microemulsion system was formed by trimethyl ammonium bromide (CTAB) and 1-butanol in n-octane.
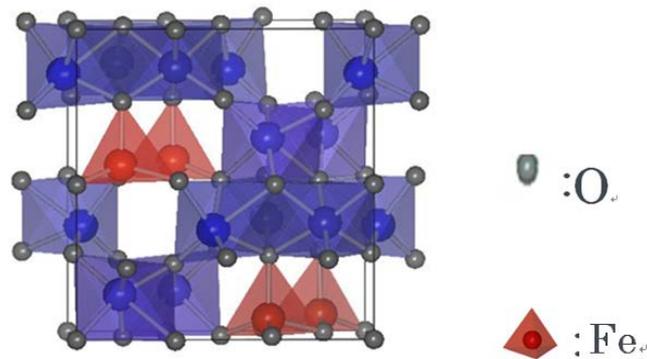

Fig. 1: ε-Fe₂O₃

In order to obtain a good observation condition for magnetic properties of metal oxide, the well-dispersed iron oxide nanocrystals were prepared. The theory behind the experiment is the intermediate phase of iron oxide that leads to observable magnetic properties.

Synthesis

There are two methods involved in the synthesis of ε-FePt, namely reverse micelle and sol-gel methods. Firstly, microemulsion systems were formed by $Fe(NO_3)_3 \cdot 9H_2O$ (0.72,0.684,0.648,0.612 mmol). Micelle solution 1 was prepared by stirring 0.72 mmol $Fe(NO_3)_3 \cdot 9H_2O, H_2PtCl_6$ with H_2O in 4 clean 100 ml flasks. H_2PtCl_6 was then added into the flasks (0, 0.036, 0.072, 0.108 mmol, where x=0, 0.1, 0.2, 0.3 respectively). The solution of 1-butanol, octane, CTAB and TEOS will be added into the flasks. Then solution 2 was prepared by mixing same amount of NH3, H_2O, CTAB,1 -butanol, and octane in 4 flaks.

Synthesis: Combination method of reverse-micelle and sol-gel procedures

Reverse-micelle process

Reverse-micelle I + Reverse-micelle II → mix → Reaction → 30min → Precursor particles ($d \approx 5$ nm)

Oil phase: n-octane
Surfactant: $C_{16}H_{33}N(CH_3)_3Br$ CTAB
Water phase: NH_3 aq
Water phase: $Fe(NO_3)_3$ $Ba(NO_3)_2$ (or $Ca(NO_3)_2$)

$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$

$Fe(OH)_3$

Sol-gel process

+ $(C_2H_5O)_4Si$ TEOS → 24h →

Condensation
$(C_2H_5O)_4Si + 2H_2O \rightarrow 4C_2H_5OH + SiO_2$

Sintering process

Separation by centrifugation → Powder → Sintering (900~1200°C) in air, 4 hr →

Etching process

SiO_2 is removed → NaOH aq. → Sample

CTAB = centyl trimethyl ammonium bromide   TEOS = Tetraethyl orthosilicate
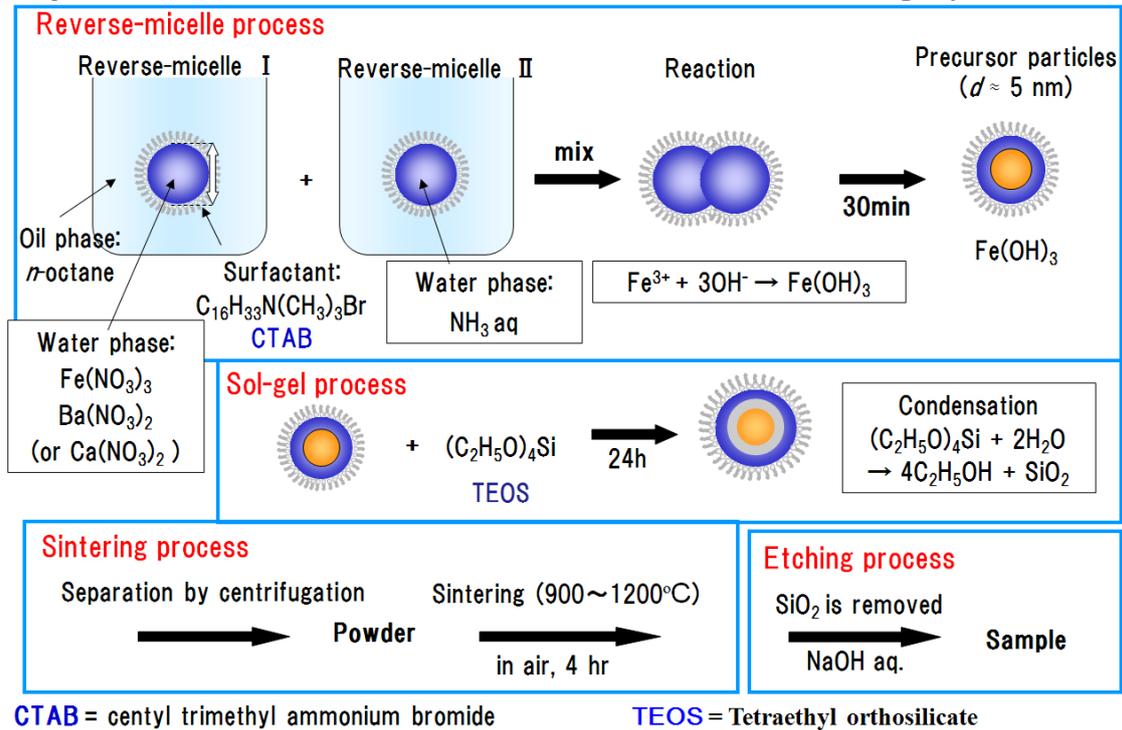
Fig.2 Flowchart of the synthesis

After stirring and mixing, the solution 1 will be titrated against solution 2 in the speed of 1 drop per second. This solution will be stirred with NaOH solution at 60 degrees for 24 hours. The color of the mixing solution will change from light yellow to brown. To obtain the solution, centrifugation was employed four times for each mixed solution. Then, the solution was dried in air for two days to yield Pt-substituted Fe_2O_3(FePt 5, 6, 7 and 8) powder. 100mg of each FePt 5-8 powder was sintered for 4 hours in air for 980, 1050 and 1100 degrees respectively. The FePt series powder was collected and then analyzed later.

Changing conditions

Sample	FePt 5	FePt 6	FePt 7	FePt 8
$Fe(NO_3)_3 \cdot 9H_2O$/ mol L^{-1}	0.720	0.684	0.684	0.612
$RuCl_3 \cdot xH_2O$	0	0.036	0.072	0.108
Sintering Temperature /°C	980 1050 1100	980 1050 1100	980 1050 1100	980 1050 1100
H_2PtCl_6/mol	0	0.036	0.072	0.108

Table 1 The changing conditions in the Pt-substituted Fe_2O_3 synthesis process

Sample	FeRu1	FeRu2	FeRu3	FeRu4
$Fe(NO_3)_3 \cdot 9H_2O/$ mol L^{-1}	0.72	0.69	0.65	0.61
$RuCl_3 \cdot xH_2O$	0	0.036	0.072	0.108
Sintering Temperature/$°C$	980 1050 1100	980 1050 1100	980 1050 1100	980 1050 1100
H_2PtCl_6/mol	0	0.036	0.072	0.108

Table 2 The changing conditions in the Ru-substituted Fe_2O_3 synthesis process

The different Fe:Pt and Fe:Ru ratio(table 1 and Table 2) can change the particle size, hence resulting in different degree of aggregation occuring. Also by decreasing the sintering temperature, the glass coating is less soft and this again prevents aggregation, both giving a decrease in particle size. Then a matrix was made to change the sintering temperature.

Results and Discussion

X-ray diffraction (XRD) results

X-ray diffraction (XRD) is a commonly used way to identify the structures of lattice constants. By observing the X-ray absorption spectrum, we can obtain the information of the photon energy of a material; therefore, the X-ray absorption spectrum reflects the specific and bonding structure of the elements in the compound.

In the experiment, FePt 5-8 (with increasing amount of Pt doped respectively) were made into annealed thin FePt nanoparticles and tested by XRD. Since the different structures of nanoparticles result in different thickness of FePt particle, we can identify the thicker assembly as the compound with relatively more metallic Fe.
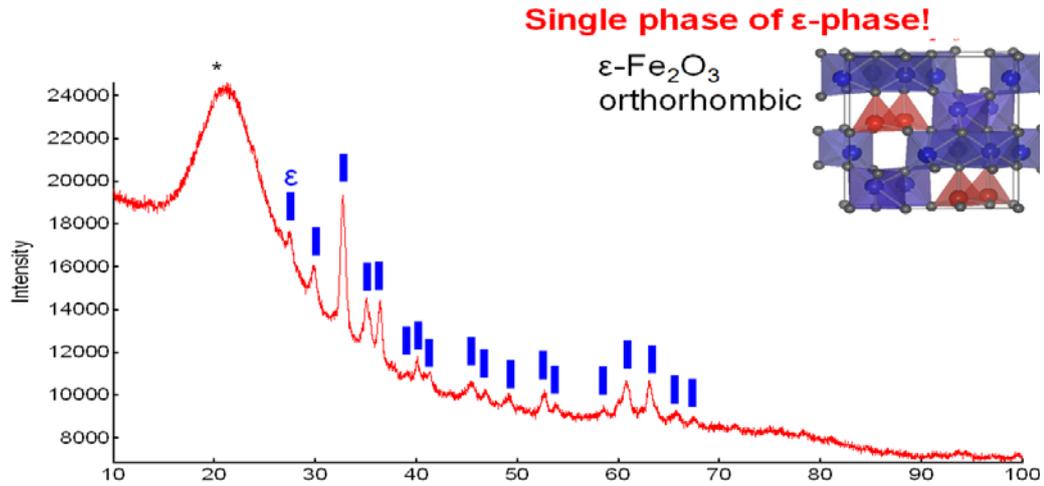
1050ºC sintered sample

Single phase of ε-phase!

ε-Fe_2O_3
orthorhombic

Fig 3. XRD results indicate ε-phase Fe_2O_3

Moreover, by comparing the XRD results of the same component sintered at different temperatures, we can identify a positive correlation of the rising temperatures and thickness of assemblies. For example, the diagram of FePt 5 and 8 sintered at 1100 degrees, FePt 8 XRD results show more observable sharp peaks than FePt 5.The peaks on the XRD results indicate the part with increased metallic Fe composition(Fig 3. XRD results indicate ε-phase Fe_2O_3).
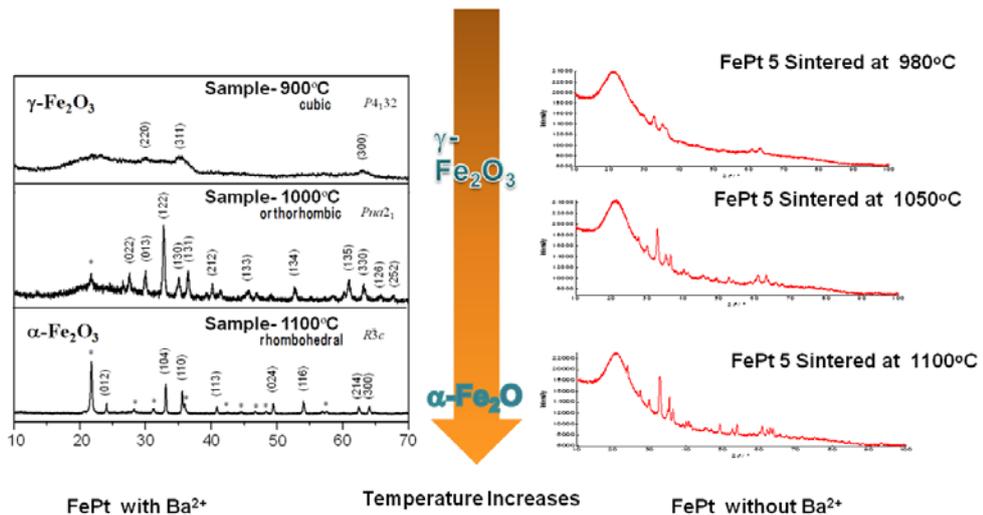
Fig 4. The XRD results with Ba^{2+} and without Ba^{2+}

By comparing the XRD results, there are differences in patterns of characteristic peaks and its corresponding sintering temperature. The samples with Ba^{2+} that are sintered at lower temperatures show the similar characteristic peaks and without Ba^{2+}. This is because the Ba^{2+} lowers the glass melting temperature of SiO_2 matrix. Ba^{2+} cation is known to adsorb on the surface of the particles and effect the morphology. Rod-shaped particles are obtained. In the present case without barium cation, the morphology is expected to be spherical.

Conclusion

Using the combination of reverse micelle and sol-gel methods, we successfully synthesized ε- Fe_2O_3
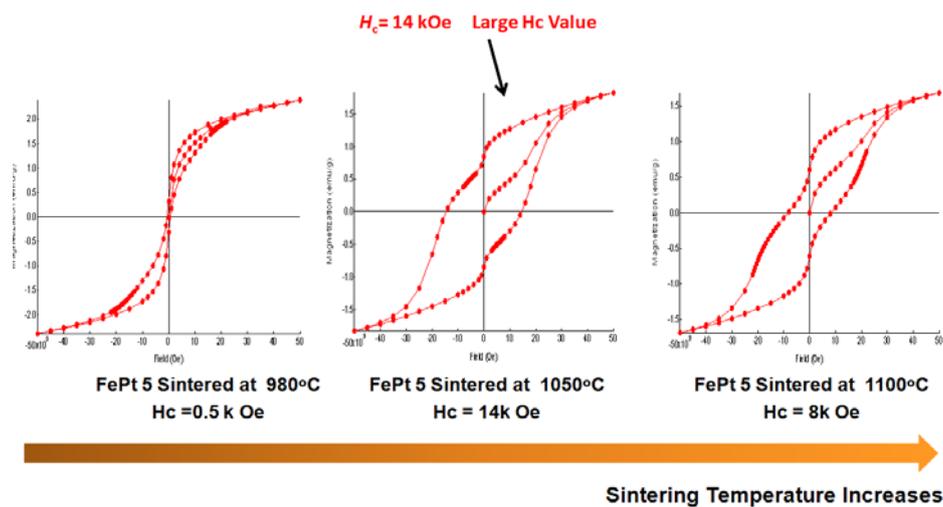

Fig.5 Magnetic Hysteresis Results for FePt 5

By comparing the results of XRD(X-ray diffraction) of FeRu1-4 obtained in different sintering temperatures (i.e. 980, 1050 and 1100), we can observe that the position and number of peaks on the diagrams are very similar. It suggests that the structures of FeRu1-4 are very similar in X-ray, even though the amount of Ru used for synthesizing FeRu1-4 are very different. Thus, FeRu 1-4 may have similar crystal structures. And Ru has been doped into the structure, so that X-ray cannot detect observable differences in the crystal structures.

While temperature increases, particle size of $\varepsilon\text{-}Fe_2O_3$ becomes larger (shown by XRD results), HC value increases, implying larger coercive forces increasee(Fig. 5 Magnetic Hysteresis Results).

Acknowledgements

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