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(54) Title: PROCESS FOR PREPARING MAGNETITE OR MAGHEMITE NANOPARTICLES WITH CONTROLLED SIZE USING MILD CONDITIONS

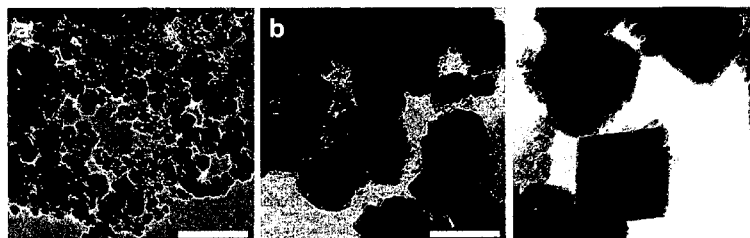


Fig. 1

(57) Abstract: The invention relates to an improved process for preparing magnetite or maghemite nanoparticles with controlled size using mild conditions. The process according to the invention comprises coprecipitation of Fe^{2+} and Fe^{3+} ions in an aqueous solution under mild alkaline conditions in a pH range from 8 to 12 and a temperature from 15 to 40°C. In a more specific embodiment of the process according to the present invention, the coprecipitation is effected by providing an aqueous reaction medium comprising deionized water set to the desired pH and continuously adding a mixed aqueous solution of Fe^{2+} and Fe^{3+} salts to the reaction medium.



**Process for preparing magnetite or maghemite
nanoparticles with controlled size
using mild conditions**

Background of the Invention

Magnetic nanoparticles are of great interest for various bio- and nanotechnological applications, such as ferrofluids, magnetic pigments, contrast agents for magnetic resonance imaging (MRI), drug delivery carriers, hyperthermia cancer treatment, sensors and others (Corchero and Villaverde, 2009; Lu et al., 2007). The iron oxide magnetite Fe_3O_4 is the preferred material for the aforementioned applications as it is easily accessible, its magnetic properties can be tuned with particle size and it is biocompatible. Typically, the smallest particles exhibit superparamagnetic behaviour meaning that their magnetization can reverse spontaneously under thermal influence. For magnetite nanoparticles the superparamagnetic size threshold varies between 25-30 nm (Muxworthy and Williams, 2006; Muxworthy and Williams, 2009). Above this size, the particles have a single magnetic domain and thus show maximum remanence and coercivity. Above the critical size of roughly 100 nm (Muxworthy and Williams, 2006; Muxworthy and Williams, 2009), particles form multiple domains to minimize their magnetostatic energy. This again leads to a decrease in remanence and coercivity.

Numerous methods have been developed for the synthesis of magnetite, including coprecipitation, thermolysis, sol-gel reactions and others (Laurent et al., 2008). The simplest

and most widely used synthesis method is the coprecipitation of ferrous and ferric iron in aqueous solution as firstly described by Massart (Massart, 1981). With this method, the nanoparticle size can be tuned between 2 and 12 nm by adjusting pH and ionic strength (Vayssieres et al., 1998). Thus, only superparamagnetic particles can be obtained this way. However, various applications specifically require particles with single domain properties for highest possible remanence and coercivity that unfortunately have remained hardly accessible by such simple synthetic routes. All the present methods producing larger particles indeed make use of high temperatures and/or pressures and/or precursors that have to be solubilized in organic solvents (WO 2006/001018 A2; Kim et al., 2009; Sugimoto and Matijevic, 1980). This is clearly unfavourable with respect to particle yield as compared to the Massart technique. Furthermore, these conditions are environmentally and economically disadvantageous.

In view of this prior art, a main object of the present invention was to provide an improved method for preparing magnetite or maghemite nanoparticles, in particular single domain nanoparticles, with controlled size in a convenient, cost-efficient and environmentally friendly manner.

Said object was achieved by providing the process of present claim 1. Specific and/or preferred embodiments of the invention are the subject of further claims.

Description of the invention

The inventive process involves the simple coprecipitation

of ferrous and ferric iron in aqueous solution in mild pH. Said process enables the control of particle size from the superparamagnetic to the single domain and possibly multidomain size ranges as shown by transmission electron microscopy (TEM), X-ray diffraction (XRD) and confirmed by magnetic measurements. The disclosed process which in particular allows producing single domain nanoparticles under soft chemical and physical conditions represents a great step forward for the development of applications based on single-domain magnetic particles.

The inventive process according to claim 1 comprises coprecipitation of Fe^{2+} and Fe^{3+} ions in an aqueous solution under mild alkaline conditions in a pH range from 8 to 12 and a temperature from 15 to 40°C.

In a more specific embodiment of the invention, the pH is in a range from 8 to 10, and preferably in a range from pH 8.5 to 9.5.

In another specific embodiment, the temperature is in a range from 20 to 30°C, more specifically from 22 to 28°C, preferably 24-26°C, in particular about 25°C.

Typically, the nanoparticles obtained in the process of the invention have diameters in a range from 10 to 100 nm, preferably from larger than 15 nm to 100 nm.

In an especially preferred embodiment, the nanoparticles are single domain nanoparticles having a diameter in a range from 20 nm to 60 nm.

In a preferred embodiment of the process according to the present invention, the coprecipitation is effected by

providing an aqueous reaction medium comprising deionized water set to the desired pH and continuously adding a mixed aqueous solution of Fe^{2+} and Fe^{3+} salts to the reaction medium.

The reaction medium may be set to the desired pH by any suitable organic or inorganic base. Preferably the base is NaOH or KOH. Typically, the desired pH will be initially set before adding any iron ion solution and subsequently monitored and re-adjusted to the desired pH by adding further base if necessary.

The Fe^{2+} and Fe^{3+} salts are preferably inorganic salts, in particular selected from the group of FeCl_2 and FeCl_3 , other halides of $\text{Fe}^{2+}/\text{Fe}^{3+}$, nitrates or sulfates of $\text{Fe}^{2+}/\text{Fe}^{3+}$.

According to a more specific embodiment of said process, in said mixed aqueous solution of Fe^{2+} and Fe^{3+} salts the Fe^{2+} and Fe^{3+} ions are present in a concentration of from 0.1 mol to 2 mol, preferably 0.1 to 1.5 mol, and in a $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of about 2:5 to 3:5, preferably about 1:2.

Preferably, the mixed aqueous solution of Fe^{2+} and Fe^{3+} salts is added with at a rate of 0.1-0.001 vol.% of the initial reaction volume per minute.

Typically, the mixed aqueous solution of Fe^{2+} and Fe^{3+} salts is added during a time period of from 1 min to 24 h, more specifically during a time period of from 1 h to 15 h, such as from 2 h to 10 h or from 3 h to 6 h. It will be evident for the skilled artisan that the time period can be optimized for any desired nanoparticle size by routine experiments based on the technical teachings

of the present application.

In a specific embodiment of the inventive process, the mixed aqueous solution of Fe^{2+} and Fe^{3+} salts is added during a time period of from 3 to 6 h, preferably from 4 to 5 h, and the prepared magnetite nanoparticles have diameters in the range from 25-30 nm.

Typically, the reaction conditions are set to provide an average growth rate of the initial magnetite particles of about 2-5, preferably 3-4, nm per hour.

Usually, the inventive process will be implemented in a non-oxidizing atmosphere, such as nitrogen or a noble gas. Preferably all media and solutions used are essentially free of oxygen, e.g. effected by purging with nitrogen or another inert gas.

Advantageously, the inventive process can be implemented at normal pressure of about 1 bar.

In one specific embodiment of the invention, the magnetite particles produced are further oxidized to maghemite particles, e.g. by exposition to an oxidating agent such as oxygen. Alternatively, if the coprecipitation is implemented in the presence of air oxygen, maghemite particles are formed initially. In the latter case, however, it is difficult to obtain larger particles than about 20 nm size.

The invention is further illustrated by the following non-limiting Examples and Figures.

FIGURES

Fig. 1. Transmission electron micrographs (TEM) of growing magnetite particles after (a) 10 min, (b) 300 min and (c) 600 min. Scale bar represents 100 nm.

Fig. 2. Synchrotron X-ray diffractogram obtained from magnetite nanoparticles after 600 min growth.

Fig. 3. Development of the mean particle size over growth time. Sampling of 3 independent reactions with a 1 M iron solution. Error bars represent standard deviation.

Fig. 4. magnetic measurements at 300 K obtained after 5, 60 and 480 min reaction time. The increasing domain size increases remanence and coercitivity of the samples.

EXAMPLE 1*synthesis of magnetite nanoparticles*

Magnetite nanoparticles with controlled size were synthesized using a modified version of the Massart route, Briefly, instead of fast addition of an iron solution to a strong base, iron was slowly added to a reactor with mild alkaline conditions.

In particular, magnetite nanoparticles were prepared by coprecipitation of FeCl_2 and FeCl_3 in a reactor maintained at 25 ± 0.1 °C by a water bath under constant pH conditions and nitrogen atmosphere. Deionized water and all solutions were initially purged with nitrogen before use.

10 mL deionized water was set to pH 9 with 1 M NaOH and

equilibrated to 25 ± 0.1 °C. A 1 M iron solution consisting of 0.33 M FeCl_2 and 0.67 M FeCl_3 was added at a rate of $1 \mu\text{l} \times \text{min}^{-1}$ using a Metrohm 776 Dosimat® pump. The pH was kept constant at $\text{pH} = 9.0 \pm 0.4$ by addition of a 1 M NaOH solution controlled by a Metrohm 719 Titrino® titration device coupled to a pH electrode (Metrohm Biotrode®). To study the evolution of nanoparticles, 60 μl samples were taken at given times after the addition of the iron solution started and were analyzed by TEM and XRD. For magnetic measurements, the final precipitate was separated by centrifugation, washed with deionized water and freeze-dried.

EXAMPLE 2

characterization of magnetite nanoparticles

TEM. Transmission electron micrographs were acquired on a Zeiss EM Omega 912X at an acceleration voltage of 120 kV. Samples were prepared by dropping the respective solution on a carbon-coated copper grid.

XRD. Wide angle X-ray powder diffraction was performed at the μ -spot beamline of the BESSY synchrotron radiation facility (Berlin, Germany), with an energy of 15 keV ($\lambda = 0.82656285$ Å), a beam size of 100 μm and a Si 311 monochromator to reduce the beam divergence. Particle sizes were estimated by using the Scherrer equation, considering a correction for the instrumental peak broadening (Paris et al., 2007).

SQUID. Measurements were performed on a MPMS at 300K.

The nanoparticles initially formed in Example 1 were made of magnetite as confirmed by XRD and lie within the

superparamagnetic size range, with mean particle dimensions of 15 nm as evidenced by TEM after 10 min reaction time (Fig. 1a). Particles of this size range are typically produced in coprecipitation syntheses when either titrating a respective iron solution to alkaline pH or addition of the iron solution to an alkaline reservoir (Berger et al., 1999; Massart, 1981). It has been reported that particle size can be tailored within 2 to roughly 12 nm by adjusting pH and ionic strength during synthesis (Vayssieres et al., 1998). However, with the present method, it is possible to obtain much larger particles that are not reported in the literature using such simple set-ups. In experiments of the inventors, the magnetite particles were able to grow with time. Figs, 1b and 1c show magnetite particles obtained according to Example 1 after reaction times of 300 and 600 min, respectively. As can be seen in the latter micrograph, single magnetite crystals can reach sizes over 100 nm after growth.

To study the mean size of crystals in the bulk, the domain size was analyzed by wide angle X-ray diffraction (Fig. 2) and Scherrer analysis based on broadening of the most prominent (311) peak. As evident from Fig. 3, continuous addition of iron to the reaction medium according to Example 1 resulted in near-linear crystal growth at an average rate of 3.5 nm per hour. Magnetite nanoparticles become magnetically remanent at room temperature at a size of around 25-30 nm. Thus, after a growth time of around 4-5 hours single domain particles can be obtained with this method.

To investigate whether the increasing crystallite size does indeed change their magnetic properties, SQUID measurements were performed on samples taken after several time points

(Table 1) .

Table 1

Synthesis time (min)	Mean particle size (nm)	Coercivity (Oe)
—	—	—
15	17	12
60	18	45
240	28	115
480	43	106

As can be seen in Fig. 4, initially formed particles show no hysteresis at room temperature in accordance with their superparamagnetic behaviour. With time, growing crystallites show increasing remanence and coercivity due to their increasing domain size. The coercivity H_c at 300 K increases over time from initially almost zero to 115 Oe after 240 min. After 480 min the coercivity reduces slightly to 106 Oe indicating the possible presence of multidomain particles. The critical size for multidomain magnetite particles is 128 nm, which is close to the size of single particles observed with TEM after 600 min (Kim et al., 2009). Consequently, the drop in coercivity might also indicate an earlier presence of such nanoparticles.

Summarizing, the present invention allows to produce nanoparticles of magnetite having a size from about 10 (superparamagnetic) to about 100 nm (limit between single to multi-domain) by simple coprecipitation of ferrous and ferric iron in mild alkaline conditions. With the presented method, particles grow from an initial superparamagnetic size of 10 to 15 nm by around 3 to 4 nm per hour on average. Thus, the magnetic domain size of

magnetite nanoparticles can be precisely controlled from superparamagnetic to single domain size and possibly even beyond. The technique is environmentally and economically favourable when compared to existing techniques leading to such sizes as the reaction proceeds under soft chemical conditions. Reactions indeed run at room temperature, ambient pressure, at mild pH and without the use of any organic solvent.

This also opens up the possibility to produce particles in the presence of sensitive additives, such as biomolecules, e.g. proteins, peptides and nucleic acids, which are necessary for the aforementioned bionanotechnological applications .

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CLAIMS

1. A process for preparing magnetite or maghemite nanoparticles with controlled size comprising coprecipitation of Fe^{2+} and Fe^{3+} ions in an aqueous solution under mild alkaline conditions in a pH range from 8 to 12 and a temperature from 15 to 40°C.
2. The process according to claim 1, wherein the nanoparticles have diameters in a range from 10 to 100 nm, preferably from larger than 15 nm to 100 nm.
3. The process according to claim 2, wherein the nanoparticles are single domain nanoparticles having a diameter in a range from 20 nm to 60 nm.
4. The process according to any one of claims 1-3, wherein the pH is in a range from 8.5 to 9.5.
5. The process according to any one of claims 1-4, wherein the temperature is in a range from 22 to 28°C, preferably 24-26°C.
6. The process according to any one of claims 1-5, wherein the coprecipitation is effected by providing an aqueous reaction medium comprising deionized water set to the desired pH and continuously adding a mixed aqueous solution of Fe^{2+} and Fe^{3+} salts to the reaction medium.
7. The process according to claim 6, wherein the Fe^{2+} and Fe^{3+} salts are inorganic salts, in particular selected from the group of FeCl_2 and FeCl_3 , other halides of $\text{Fe}^{2+}/\text{Fe}^{3+}$, nitrates or sulfates of $\text{Fe}^{2+}/\text{Fe}^{3+}$.

8. The process according to claim 6 or 7, wherein in said mixed aqueous solution of Fe^{2+} and Fe^{3+} salts the Fe^{2+} and Fe^{3+} ions are present in a concentration of from 0.1 mol to 2 mol and in a $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 2:5 to 3:5, preferably about 1:2.

9. The process according to any one of claims 6-8, wherein the mixed aqueous solution of Fe^{2+} and Fe^{3+} salts is added with at a rate of 0.1-0.001 vol.% of the initial reaction volume per minute.

10. The process according to any one of claims 6-9, wherein the mixed aqueous solution of Fe^{2+} and Fe^{3+} salts is added during a time period of from 1 min to 24 h.

11. The process according to claim 10, wherein the mixed aqueous solution of Fe^{2+} and Fe^{3+} salts is added during a time period of from 4 to 5 h and the prepared magnetite nanoparticles have diameters in the range from 25-30 nm.

12. The process according to any one of claims 1-11, wherein the reaction conditions are set to provide an average growth rate of the initial magnetite particles of about 2-5, preferably 3-4, nm per hour.

13. The process according to any one of claims 1-12, which is implemented in a non-oxidizing atmosphere.

14. The process according to any one of claims 1-13, which is implemented in the presence of biomolecules.

15. The process according to any one of claims 1-14, wherein the magnetite particles produced are further oxidized to maghemite particles.

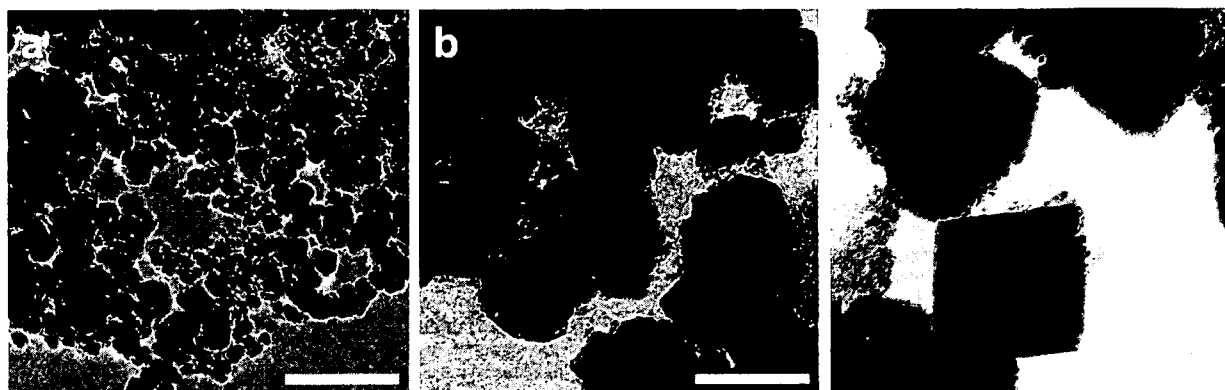


Fig. 1

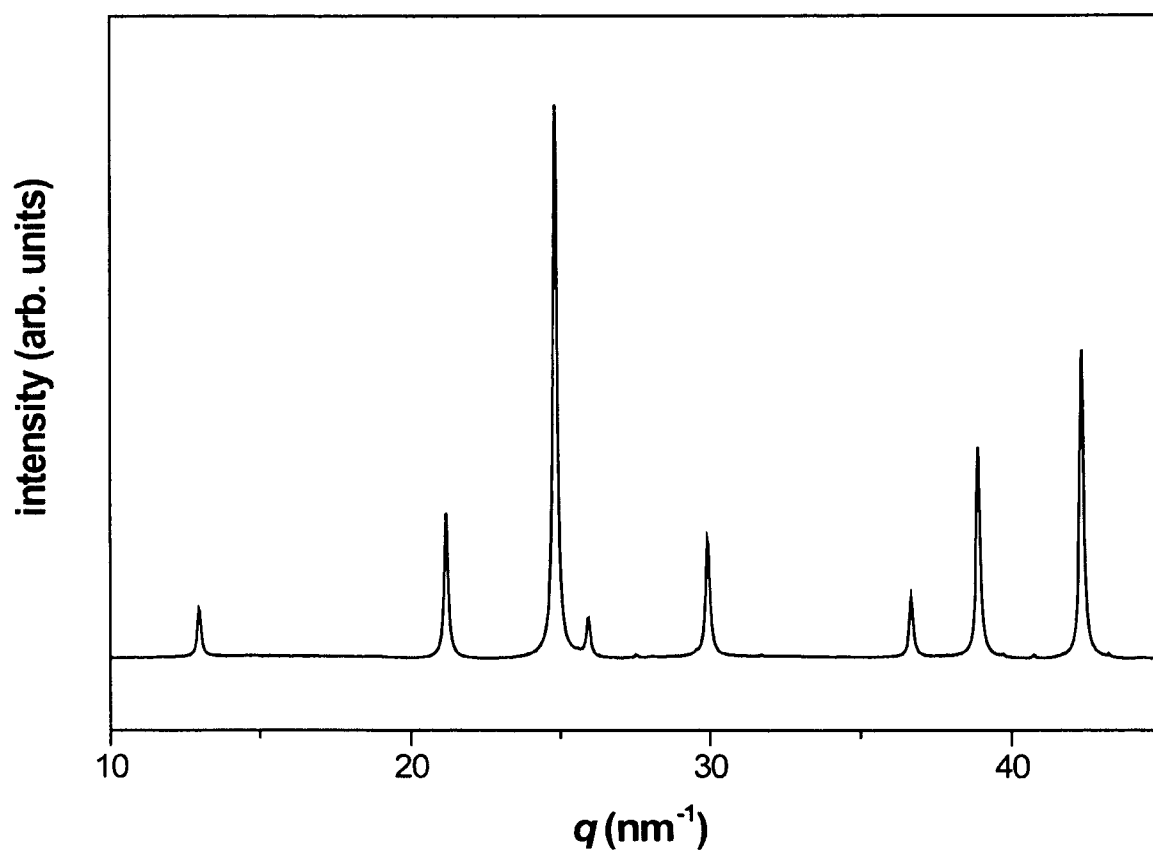
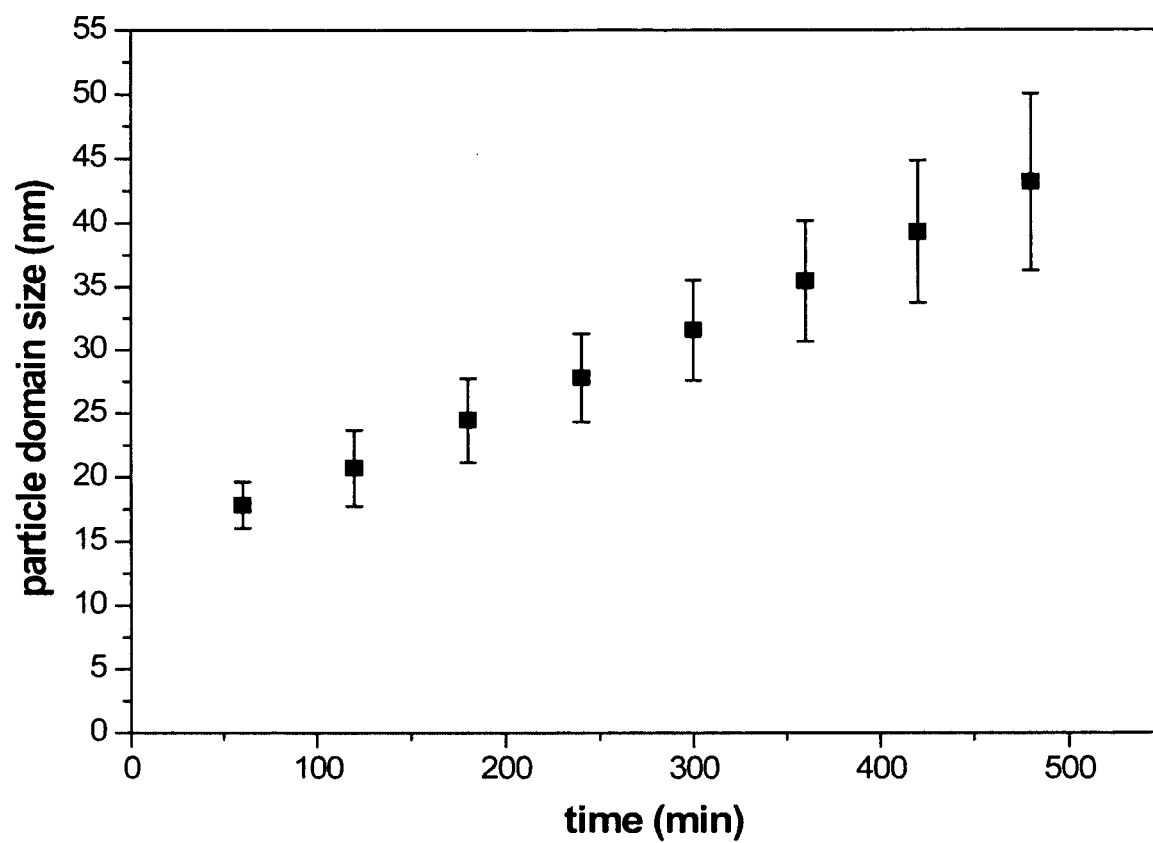


Fig. 2

**Fig. 3**

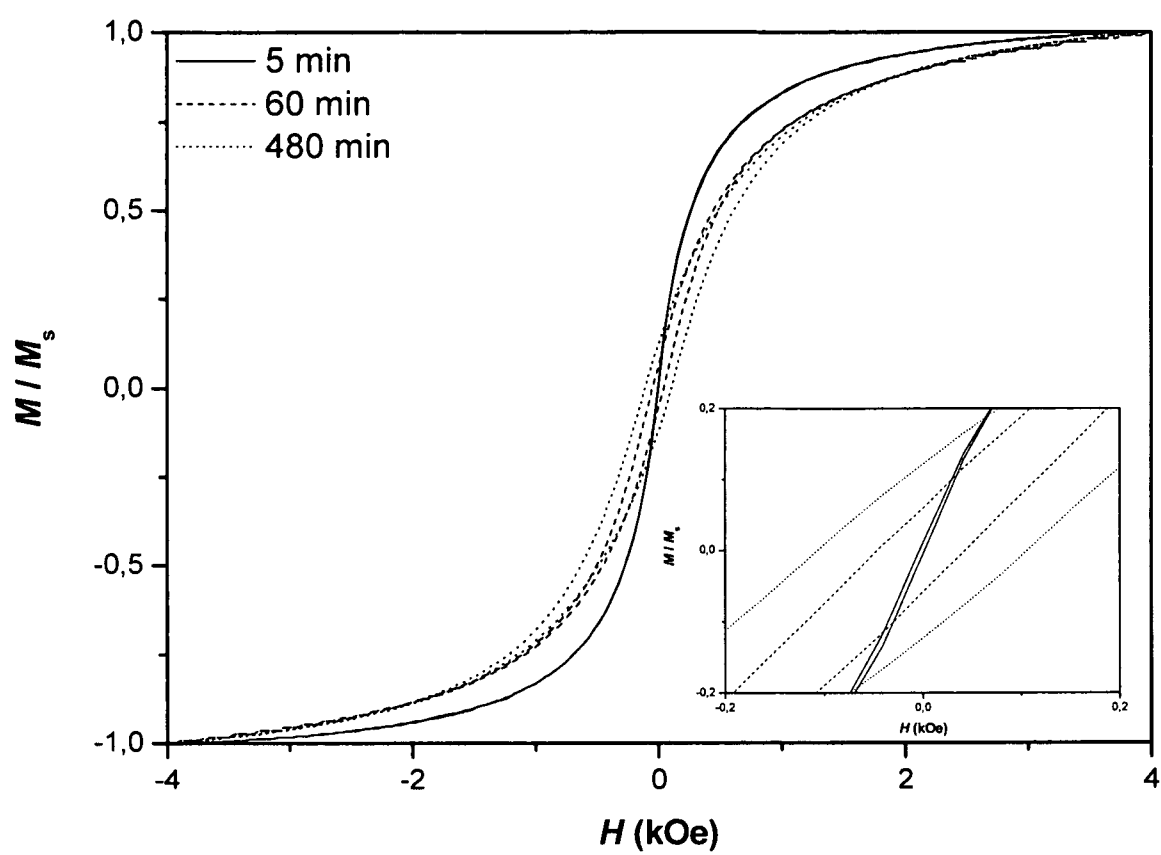


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/003983

A. CLASSIFICATION OF SUBJECT MATTER INV. C01G49/06 C01G49/08 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C01G		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	page 205, col umn 2 - page 212 figures 2-8 tabl e 1 ----- -/- .	11 , 12 , 14
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Date of the actual completion of the international search 21 January 2011		Date of mailing of the international search report 31/01/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Mari no, Emanuela

INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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Y	page 967 - page 973 figures 3-5 tables 2-9	11, 12, 14
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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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