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(54)Method for producing ferromagnetic garnet material, garnet material and its use

(57)The invention relates to a Method for producing iron garnet based ferromagnetic material, having the general formula (I)

$$\{{\rm Re}_{3\text{-}x\text{-}y}{\rm Fe}_{x}^{\ 3\text{+}},{\rm A}_{y}\}[{\rm Fe}_{2}^{\ 3\text{+}}]({\rm Fe}_{3\text{-}z}^{\ 3\text{+}}{\rm B}_{z}){\rm O}_{12} \qquad {\rm (I)}$$

wherein Re is one or more selected from the group of elements comprising La3+, Pr3+, Nd3+, Sm3+, Eu3+, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Y³⁺, Lu³⁺, wherein A is Bi³⁺, Sr²⁺, Ca²⁺ and

wherein B is Ga³⁺, Al³⁺, Si⁴⁺, Ge⁴⁺, V⁵⁺, Sc³⁺, In³⁺, Co²⁺,

wherein 0< x 1,5

wherein y is zero or 1

wherein 0 z 3

and if Re is two or more elements, than $\mbox{Re}_{\mbox{\scriptsize 3-x-y}}$ means that the sum of these elements constituting Re is present in the proportion 3-x-y.

comprising the steps of:

i) forming a solution-melt comprising a mixture of polycrystalline ferrogamets having the general formula (II)

$$\{Re_{3-v},A_{v}\}[Fe_{2}](Fe_{3-z}B_{z})O_{12}$$
 (II)

and orthoferrite having the general formula (III)

wherein Re, A, B, y and z are as described above;

- ii) homogenization of the mixture at sufficient temperature and period of time; and
- iii) supercooling of the mixture material to growth temperature such that orthoferrite is implanted in the ferrogarnet, furthermore the invention relates to a ferromagnetic material and the use thereof.

Description

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[0001] The present invention relates to a method for producing iron garnet based ferromagnetic material, to the material and to the use of the said ferromagnetic material to manufacture bulk single-crystals and/or epitaxial films and to other particular uses.

[0002] Ferrites are magnetic materials widely distributed and applied in contemporary physics and engineering. In radioelectronics, the most applicable ferrites are spinel ferrite, iron garnet, orthoferrite, and hexaferrite. The main properties and physical parameters of these materials have been measured for the bulk single-crystals. Among the ferrites mentioned the most remarkable by several physical properties is ytrium iron garnet (YIG) with the formula $Y_3Fe_5O_{12}$. Due to the fact that YIG structure contains trivalent ions of the same sort, which do not possess orbital angular momentum, YIG is characterized by the narrowest possible ferromagnetic linewidth $2\Delta H = 0.2 - 0.5$ Oe.

Among shortcomings of YIG are very small uniaxial anisotropy field H_A = 1 - 40 Oe and relatively small values of saturation magnetization $4\pi M$ = 1750 G. These properties are essential in magnetoelectronic devices of extremely high-frequency (EHF) band, since advance to short-wave band requires an increase in internal magnetic field and saturation magnetization, along with a small value of FMR linewidth. Both spinel ferrite and hexaferrite surpass YIG in H_A and $4\pi M$ values, but FMR linewidth of these ferrites is 10-100 times more than of YIG.

It is known that to increase H_A values, YIG thin films are compressed or stretched mechanically, grown under special conditions, or diluted with other ions. All these treatments increase $2\Delta H$ values, i.e. degrading resonance properties of the films. For example, to create materials of higher saturation magnetization values comparing to YIG, Fe ions in octahedral crystallographic sites are partially substituted with diamagnetic ions, for instance Sc^{3+} , Ge^{4+} , Si^{4+} . As a result, YIG saturation magnetization value $4\pi M$ ranges up to 2000 G approaching corresponding values of spinel ferrite and hexaferrite (2000-5000 G), but FMR linewidth increases significantly.

Other solutions apply La ions and Pb ions. As a result of for example Pb introduction, anisotropy field value H_A increases, but FMR linewidth value $2\Delta H$ increases as well. Since the lattice structure of ferrogarnet is highly immune to isomorphic substitutions, yttrium ions

of ferrogarnet structure can be substituted with combinations of rare-earth ions, the same as *Fe* ions can be substituted with various metal ions.

Magnetic properties of the substituted ferrogarnets vary over a wide range being dependent on chemical composition. However, all substitutions diminish microwave and resonance properties of ferrogarnets, i.e. increase FMR linewidth and dissipation ratios.

This review of what is known in the state of the art shows that the relevant problem of YIG for microwave applications is still to fabricate a material empowered by higher values of anisotropy field H_A and saturation magnetization $4\pi M$, also preserving narrow FMR linewidth close to $2\Delta H = 0.2$ - 0.5 Oe. All known techniques based on Fe ion substitution in sublattices of ferrogarnet result in decline of the material's frequency response.

[0003] The present invention solves this problem. According to the invention is provided a method for producing iron garnet based ferromagnetic material, having the general formula (I)

$${Re_{3-x-y}Fe_x^{3+},A_y}[Fe_2^{3+}](Fe_{3-z}^{-3+}B_z)O_{12}$$
 (I)

wherein Re is one or more selected from the group of elements comprising La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Yu³⁺, Lu³⁺,

wherein A is B i3+, Sr2+, Ca2+ and

wherein B is Ga³⁺, Al³⁺, Si⁴⁺, Ge⁴⁺, V⁵⁺, Sc³⁺, In³⁺, Co²⁺,

45 wherein $0 < x \le 1,5$

wherein y is zero or 1

wherein $0 \le z \le 3$

and if Re is two or more elements, than Re_{3-x-y} means that the sum of these elements constituting Re is present in the proportion 3-x-y.

50 comprising the steps of:

i) forming a solution-melt comprising a mixture of polycrystalline ferrogarnets having the general formula (II)

$$\{Re_{3-v},A_{v}\}[Fe_{2}](Fe_{3-z}B_{z})O_{12}$$
 (II)

and orthoferrite having the general formula (III)

ReFeO₃ (III)

wherein Re, A, B, y and z are as described above;

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- ii) homogenization of the mixture at sufficient temperature and period of time; and
- iii) supercooling of the mixture material to growth temperature such that orthoferrite is implanted in the ferrogarnet.

[0004] In a preferred embodiment the ferromagnetic material according to the invention is produced in a similar manner to that of yttrium iron garnet (YIG), that is in the form of bulk single-crystals as well as epitaxial films, resulting in better EHF properties, and higher adjustable values of anistropy field and saturation magnetization due to Fe³⁺ ions substitution only. The method according to the invention uses a solution-melt, wherein a mixture is made from polycrystalline ferrogarnets and orthoferite in acceptable proportions between them. Growing the iron garnet based ferromagnetic material from solution-melt leads to the joint crystallization of garnet and ferrous orthoferite complexes. Implantation of orthoferite complexes into garnet structure results in partial substitution of Re for Fe³⁺, and consequently emergence of additional components of uniaxial anistropy and higher magnetization.

[0005] Producing bulk crystals of the ferromagnetic material, as well as epitaxial films is preferably based upon crystallization from one and the same solution-melt using flux PbO - B_2O_3 or PbO- Bi_2O_3 and a mixture of a special content. Preferably the mixture includes iron oxide Fe_2O_3 , polycrystalline ferrogarnet, and polycrystalline orthoferrite in a certain proportion. In a preferred embodiment of the general formula is x zero or is y zero, z zero and Re yttrium. In an other preferred embodiment of the invention the mixture for solution-melt comprises 1,4-1,6 molar percents of polycrystalline ytrium iron garnet (YIG), 14,4-14,6 molar percents polycrystalline ytrium orthoferite and 83,8-84,2 molar percents iron oxide. In even another preferred embodiment a mixture for solution-melt is used comprising (Y,Eu)₃ (FeGa)₅O₁₂ and YFeO₃. The mixture preparation steps comprises an essential homogenization step, which is generally carried out at the temperature range from 900-1100 0 C, preferably from 1020-1040 0 C, and for 30 to 180 minutes, preferably 60 to 120 minutes and comprises a supercooling step which is generally carried out to growth temperature of 800-1000 0 C, preferably 920-940 0 C, more preferably 860-920 0 C.

In a preferred embodiment of the invention the solution-melt comprises preliminary fabricated polycrystalline compounds, such as polycrystalline ferrogarnets (according to formula II) and orthoferite (according to formula III). It is known that when the temperature of the solution-melt decreases quasi-crystalline clusters are being formed from particles of crystal-forming components such as oxides, salts and metals which remained fully dissociated before decreasing the temperature. These quasi-crystalline structures do not match with the structure of the crystallized compound since they are formed randomly and uncontrolled. Formation of these quasi-crystalline clusters is considered disadvantageous since they cause degradation of the solution-melt and lead to loss of crystal quality. To overcome this problem preliminary fabricated polycrystalline compounds are used to be grown in the solution-melt instead of the crystal forming components such as oxides, salts and metals. By using these preliminary fabricated polycrystalline compounds quasi-crystalline clusters are formed under incomplete (weak or partial) dissociation of the compounds, preserving the properties of the original structure of the fabricated polycrystalline compounds. Comparing to the clusters described earlier, these clusters are stable and they produce a positive effect on crystallization processes, such as a faster and steadier crystal growth and an improved reproduction of clusters's structure. These quasi-crystalline clusters also transfer heritable information from the fabricated polycrystalline compounds to growing monocrystal. This heritable information includes characteristic properties of original microcrystalline structure of the fabricated polycrystalline compounds, such as the relationships between chemical elements in lattice cell, interatomic distance and exchange interactions angles between metal ions.

An other aspect of the present invention is the ferromagnetic material itself and its use to manufacture bulk-single crystals and/or epitaxial films. Preferably ferromagnetic material is obtained and used that possesses magnetic metastable subsystems. These are anomalies in the regions of temperature curves, where values of basic magnetic properties stay invariable followed by abrupt increase, instead of a gradual increase or decrease (see Figure 1 and 3). The magnetic metastable subsystem occurs in the claimed material as a result of an implantation of an excess of iron into the ferrite structure. The magnetic metastable subsystem in the present invention differs from the metastable phase in other substances in that it coexists with a main stable magnetic phase and exhibits properties typical of liquids.

The ferromagnetic material according to the invention can for example be used in seismology, geophysics, microwave devices, computing devices, optoelectronics, data storage, magnetostatic waves devices, communications, mobile communications, magnetic storage and or recording devices, generators and detectors of gravity waves and any other radio-electronic or magneto-electronic device.

[0006] Mentioned and further features and advantages of the present invention will be appreciated on the basis of the following drawings and examples. These examples are given for illustration purposes and are not intended to limit the scope of the invention.

Example 1

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[0007] Polycrystalline YIG 1 g of weight, 2,5 g of polycrystalline yttrium orthoferrite YFeO₃, and 11,96 g of iron oxide were dissolved in 200 g of solvent PbO-B₂O₃. The solution-melt was homogenized at 1020 - 1040 C for 1-2 hours along with intensive agitation simultaneously. Then solution-melt was shifted to supercooled state. After that, with the aim to produce thin films by LPE method, on gadolinium gallium garnet substrates (GGG), oriented in the (111) plane. Epitaxially grown at temperature range 940 C - 920 C, with rotating substrate in solution-melt, were single-crystal ferrogarnet films of various thickness (4-100μm). Out of the

solution-melt at ultimate low temperature of 920 C by spontaneous crystallization were also grown bulk single crystals of ferrogarnet structure having a formula of $Y_{3-x}Fe_{5+x}O_{12}$.

X-ray diffraction analysis, as well as chemical analysis and other methods indicated that all fabricated ferrites were single-phased, had garnet structure and its iron content was higher than in YIG.

[0008] Table 1. displays chemical composition of the ferrite grown out of solution-melt at temperature range 940 C - 920 C. As a standard was used YIG film grown by conventional technology from a custom solution-melt, which chemical compound appeared to be close to theoretical one having the formula of Y^{3+} -36%; Fe^{3+} - 38%; O^{2-} - 24%.

			Table 1.						
Growth temperature		Chemical composition of the claimed ferrite							
Degrees Celsius, ± 1 C	Y ³⁺ By weight % ± 2%	Y ³⁺ Formula Units	Fe ³⁺ By weight % ± 1,5%	Fe ³⁺ Formula Units	O ²⁻ by weight %	O ²⁻ Formula Units			
940	34	2,9	39	5,1	26	12			
935	31	2,6	42	5,4	27	12			
925	26	2,0	47	6,0	27	12			
920	20	1,5	52	6,5	28	12			

[0009] X-ray analysis also indicated that a lattice parameter of the claimed ferrite as compared to YIG (a = 12,376 Å) tend towards scaling-down when increasing iron content. Thus, if x = 0.5 then a = 12.373 Å, and if x = 1.5 then a =12,371 Å.

[0010] Table 2. compares magnetic properties of standard YIG and the claimed ferrite.

Table 2

14510 2.							
Material	Magnetic properties						
	$4\pi M, G$ H_A, Oe $2\Delta H, Oe$ $\gamma 10^{-7}, s/Oe$ T°_N, C						
Y ₃ Fe ₅ O ₁₂	1750	0-60	0,2-0,5	1,76	286		
$Y_{3-x}Fe_{5+x}O_{12}$	1750-2000	60-1500	0,2-0,5	1,76	286-270		

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[0011] An increase of x value leads to increase of an uniaxial anisotropy field H_A and saturation magnetization $4\pi M$ reaching H_{Δ} =1500 Oe and $4\pi M$ = 2000 G at x = 1,5. At that, slight increase in gyromagnetic ratio is also registered. The most important factor is conservation of ferromagnetic resonance (FMR) linewidth 2∆H, whereof the Néel temperature T_N falls inconsiderably.

[0012] Results of a magneto-optic analysis with use of a polarizing microscope has shown that single-crystal layers of the claimed ferrite have a stable strip domain structure characterized by a very small coercive field H_C less then 0,1 Oe and a high contrast in a polarized light. The lattice constant of the domain structure is weakly dependent on the film thickness varying from 1,5 to 10 μm at variations of the film thickness from 4 to 20 μm. If film thickness is more than 20 µm then the domain structure type changes. The structure of custom domain walls changes into the structure of spiroid walls.

[0013] Described ferromagnetic material exibits metastable magnetic phase observed within 400 - 430K temperature range. Figure 1 compares temperature dependency of saturation magnetisation of films having the formula of $Y_{3-x}Fe_5+X$

O₁₂ and standard YIG film in different magnetic fields H which are parallel to film plane. As seen on Figure 3, stepwise anomalies of temperature dependency of saturation magnetisation are observed only in film having the formula Y_{3-x}Fe_{5-x}O₁₂. These anomalies are the action of magnetic metastable subsystem which is present in film having the formula $Y_{3-x}Fe_5+_xO_{12}$.

10 Figure 1 15 M (arbitrary units) H≈350 Oe 15 10 H≈200 Oe 20 H=90 Oe 25 H≈350 Oe 30 273 350 320 340 366 380 490 420 440 466 489 500 520 540 560 580 600 620 640 666 T,K 1. - Invention 2. - Prior art 35

Example 2

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[0014] Polycrystalline garnet 1 g of weight having the formula $Y_{2.6}Eu_{0.4}Fe_{3.9}Ga_{1.1}O_{12}$, 2,5 g of polycrystalline yttrium orthoferrite YFeO₃, and 11,96 g of iron oxide were dissolved in 200 g of solvent PbO-B₂O₃. Epitaxial films were grown on GGG (111)substrates by LPE method, as well as single crystals by spontaneous crystallization.

X-ray diffraction analysis and chemical analysis proved that obtained films and crystals have the structure of a garnet of formula $\{Y^{3+}, Eu_{3-x}^{3+}Fe_x^{3+}\}[Fe_2^{3+}](Fe_{3-z}^{3+}Ga_z^{3+})O_{12}$, where $0 < x \le 1$. **[0015]** Table 3. displays magnetic properties of obtained films comparing to properties of ordinary ferrogarnet films

having the similar composition.

Table 3

				Table 5.				
Material	Magnetic properties							
	4πM ,G	H _A , Oe	H _c , Oe	2∆H, Oe	α_{RDB}	α_{FMR}	γ 10 ⁻⁷ , OeS ⁻¹	μ, m(SOe) ⁻¹
{Y ³⁺ ,	320	800	0,1	50	0,02	0,008	1,58	160
Eu _{3-x} ³⁺ Fe _x ³⁺ } [Fe ₂ ³⁺]								
$(Fe_{3-z}^{3+}Ga_z^{3+})O_{12}$								

Table 3. (continued)

Material	Magnetic properties							
	4πM ,G	H _A , Oe	H _c , Oe	2∆H, Oe	α_{RDB}	α_{FMR}	γ 10 ⁻⁷ , OeS ⁻¹	μ, m(SOe)-1
(Y,Eu) ₃ (Fe, Ga) ₅ O ₁₂	180	1800	10	300	0,4	0,02	1,27	12

Where α_{RDB} - dissipation ratio, determined by domain walls resonance method.

 $\alpha_{\text{FMR}}\text{-}$ dissipation ratio, determined by FMR method.

H_c- coercive field of domain walls

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 $\boldsymbol{\mu}$ - mobility of domain walls

[0016] Table 3. displays that FMR linewidth $2\Delta H$ of the substituted ferrite is six times less, coercive field and dissipation ratios 100 times less, and mobility of domain walls is 10 times higher than those observed in films of ordinary ferrogarnet.

[0017] Figure 2 represents relationship between imaginary part of magnetic susceptibility " χ " and its frequency " ν " for new ferrite and ordinary one.

Figure 2



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2. Prior art

[0018] As seen on Figure 2 the resonance curve of the new ferrite is located in high frequency region having higher peak value and smaller width as compared with the ordinary ferrogarnet. Thus experimental findings prove that microwave and resonance properties of new ferrite exceed significantly those of common ferrogarnets.

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V, MGz

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Figure 3

4πMs, Gs 100 120 180 200 220 240 260 280 300

Figure 3

[0019] Temperature dependency of saturation magnetisation of crystals of new ferromagnetic material having the formula of ${Y^{3+}, Eu_{3-x}^{3+}Fe_x^{3+}}[Fe_2^{3+}](Fe_{3-z}^{3+}Ga_z^{3+})O_{12}$.

[0020] Such stepwise magnetisation anomalies within 20 - 100K temperature range are indicative of the fact that the crystals contain magnetic metastable subsystem.

Example 3

[0021] Polycrystalline garnet 1 g of weight having the formula $Eu_3Fe_5O_{12}$, 2,5 g of europium orthoferrite $EuFeO_3$, and 11,96 g of iron oxide Fe_2O_3 were dissolved in 200 g of solvent PbO-B₂O₃. Films were grown from the solution-melt on GGG and NdGG(111) substrates. Single crystals were produced by spontaneous crystallization. X-ray diffraction analysis and chemical analysis displayed that obtained films and crystals have the structure of garnet having the formula $\{Eu_{3-x}^{3+}\}Fe_{2}^{3+}\}Fe_{2}^{3+}$, where 0<x<1.

[0022] Saturation magnetization $4\pi M$ of the ferrite having the formula $(Eu_{3^-x}^{3+}Fe_x^{3+})[Fe_2^{3+}](Fe_3^{3+})O_{12}$ equals to 1350G, which is 200G more than saturation magnetization value of the ordinary ferrogarnet having the formula $Eu_3Fe_5O_{12}$. One of the unique properties of new ferrite is anisotropy of coercive field $Hc \le 0,01$ Oe. At present time none of the known ferrites possess so small Hc value.

Claims

1. Method for producing iron garnet based ferromagnetic material, having the general formula (I)

 $\{Re_{3-x-y}Fe_x^{3+}, Ay\} [Fe_2^{3+}](Fe_{3-z}^{3+}B_z)O_{12}$ (I)

wherein Re is one or more selected from the group of elements comprising La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Y³⁺, Lu³⁺,

wherein A is Bi3+, Sr2+, Ca2+ and

wherein B is Ga^3+, Al^3+, Si^4+, Ge^4+, V^5+, Sc^3+, In^3+ , Co^2+,

wherein $0 < x \le 1,5$

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wherein y is zero or 1

wherein $0 \le z \le 3$

and if Re is two or more elements, than Re_{3-x-y} means that the sum of these elements constituting Re is present in the proportion 3-x-y.

comprising the steps of:

i) forming a solution-melt comprising a mixture of polycrystalline ferrogarnets having the general formula (II)

$$\{Re_{3-v}, A_v\}[Fe_2](Fe_{3-z}B_z)O_{12}$$
 (II)

and orthoferrite having the general formula (III)

$$_{20}$$
 ReFeO $_{3}$ (III)

wherein Re, A, B, y and z are as described above;

- ii) homogenization of the mixture at sufficient temperature and period of time; and
- iii) supercooling of the mixture material to growth temperature such that orthoferrite is implanted in the ferrogarnet.
- 2. Method as claimed in claim 1, wherein the ferromagnetic material is used to manufacture bulk single-crystals and/ or epitaxial films.
- 30 **3.** Method as claimed in claims 1 or 2, wherein the solution-melt comprises PbO-B₂O₃ or PbO-Bi₂O₃.
 - 4. Method as claimed in claims 1-3, wherein y is zero.
 - **5.** Method as claimed in claims 1-4, wherein Re is Y and y and z are zero.
 - **6.** Method as claimed in claims 1-5, for producing a ferromagnetic material having the formula (IV), from a mixture of a polycrystalline ferrogarnet having the formula (V) and a polycrystalline orthoferrite having the formula (VI).

$${Y^{3+}, Eu_{3-x}^{3+} Fe_{x}^{3+}} [Fe_{2}^{3+}] (Fe_{3-z}^{3+} Ga_{z}^{3+}) O_{12}$$
 (IV)

$$(Y,Eu)3(Fe,Ga)5O12 (V)$$

 ${\rm YFeO_3} \hspace{1.5cm} {\rm (VI)}$

wherein:

0<x≤1:

- Y^{3+} , Eu_{3-x}^{3+} means that the sum of both elements Y and Eu is present in the proportion 3-x; and (Fe,Ga)₅ means that the sum of both elements Fe and Ga is present in the proportion 5.
- 7. Method as claimed in claims 1-6, wherein homogenization of solution-melt is carried out at the temperature range from 900-1100°C, preferably from 1020-1040°C and wherein homogenization of solution-melt is carried out for 30 to 180 minutes, preferably 60 to 120 minutes.
- 8. Method as claimed in claim 1-7, wherein supercooling is carried out till growth temperature of 800-1000⁰C, pref-

erably 920-940°C, more preferably 860-920°C.

- **9.** Method as claimed in claims 1-8, wherein the mixture for solution-melt comprises 1,4-1,6 molar percents of polycrystalline ytrium iron garnet (YIG), 14,4-14,6 molar percents polycrystalline ytrium orthoferite and 83,8-84,2 molar percents iron oxide.
- **10.** Method as claimed in claims 1-9, wherein the solution-melt comprises preliminary fabricated polycrystalline compounds.
- **11.** Ferromagnetic material as obtainable with the method according to claims 1-10.
 - **12.** Ferromagnetic material according to claim 11, containing a magnetic metastable subsystem exhibiting itself within 20-100K and 400 420K temperature ranges.
- **13.** Use of a ferromagnetic material according to claim 11 or 12, to manufacture bulk single-crystals and/or epitaxial films.
 - **14.** Use of a ferromagnetic material according to claim 11 or 12 in seismology, geophysics, microwave devices, computing devices, optoelectronics, data storage, magnetostatic waves devices, communications, mobile communications, magnetic storage and or recording devices, generators and detectors of gravity waves and any other radio-electronic or magneto-electronic device.



EUROPEAN SEARCH REPORT

Application Number

EP 02 07 9701

		ERED TO BE RELEVAN		
Category	Citation of document with ir of relevant pass	dication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Ci.7)
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X : part Y : part doc A : tect O : nor	ATEGORY OF CITED DOCUMENTS licularly relevant if taken alone licularly relevant if combined with anotument of the same category inological background —written disclosure rmediate document	E : earlier pate after the filir her D : document c L : document c	inciple underlying the nt document, but publ ng date itted in the application itted for other reasons the same patent famil	ished on, or

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 02 07 9701

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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