March 30, 1971 A. DESCHAMPS 3,573,207

MICROWAVE MAGNETIC MATERIALS WITH A HEXAGONAL STRUCTURE

Filed Feb. 20, 1969 5 Sheets-Sheet 1

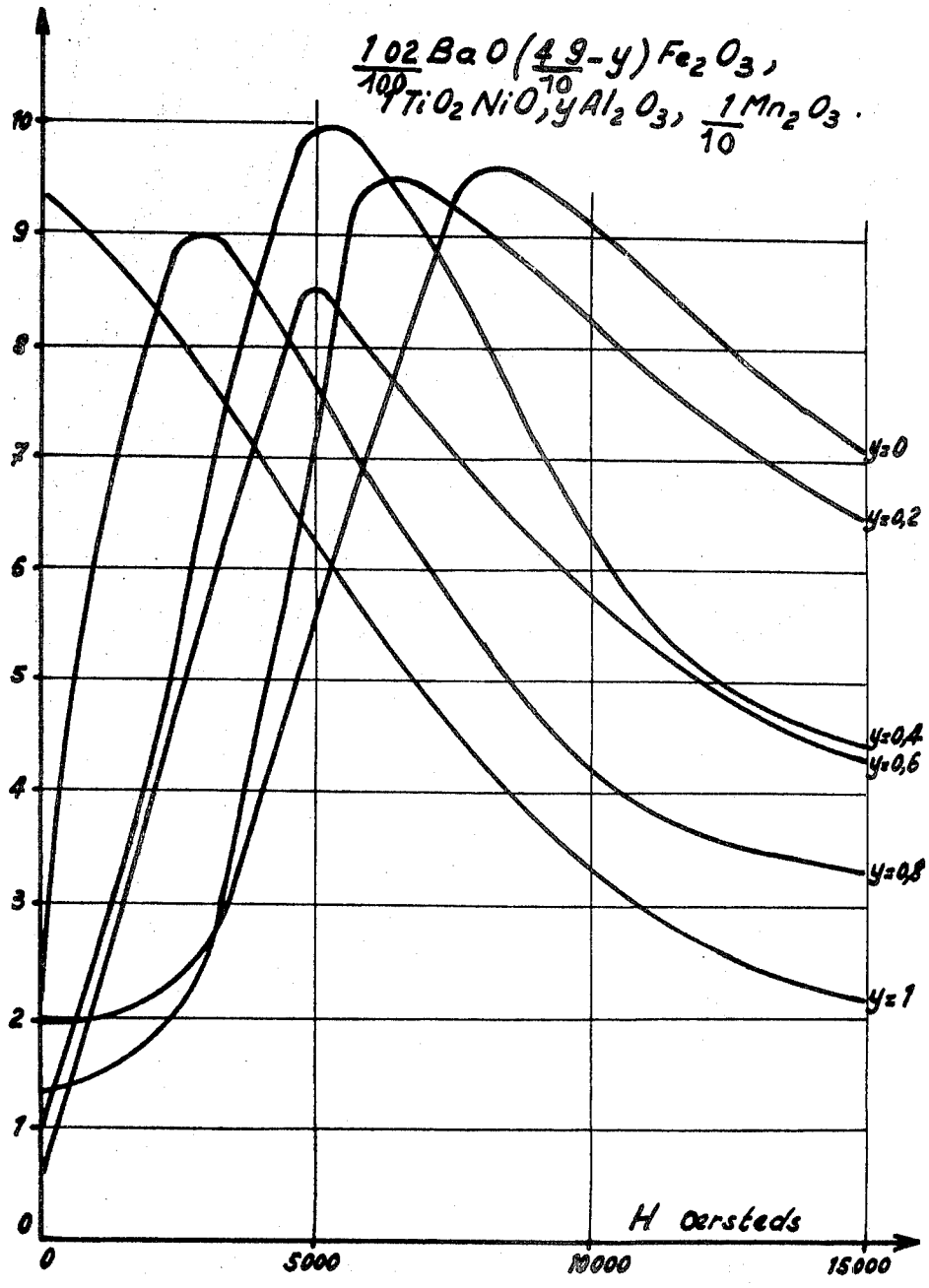


Fig. 1

MICROWAVE MAGNETIC MATERIALS WITH A HEXAGONAL STRUCTURE

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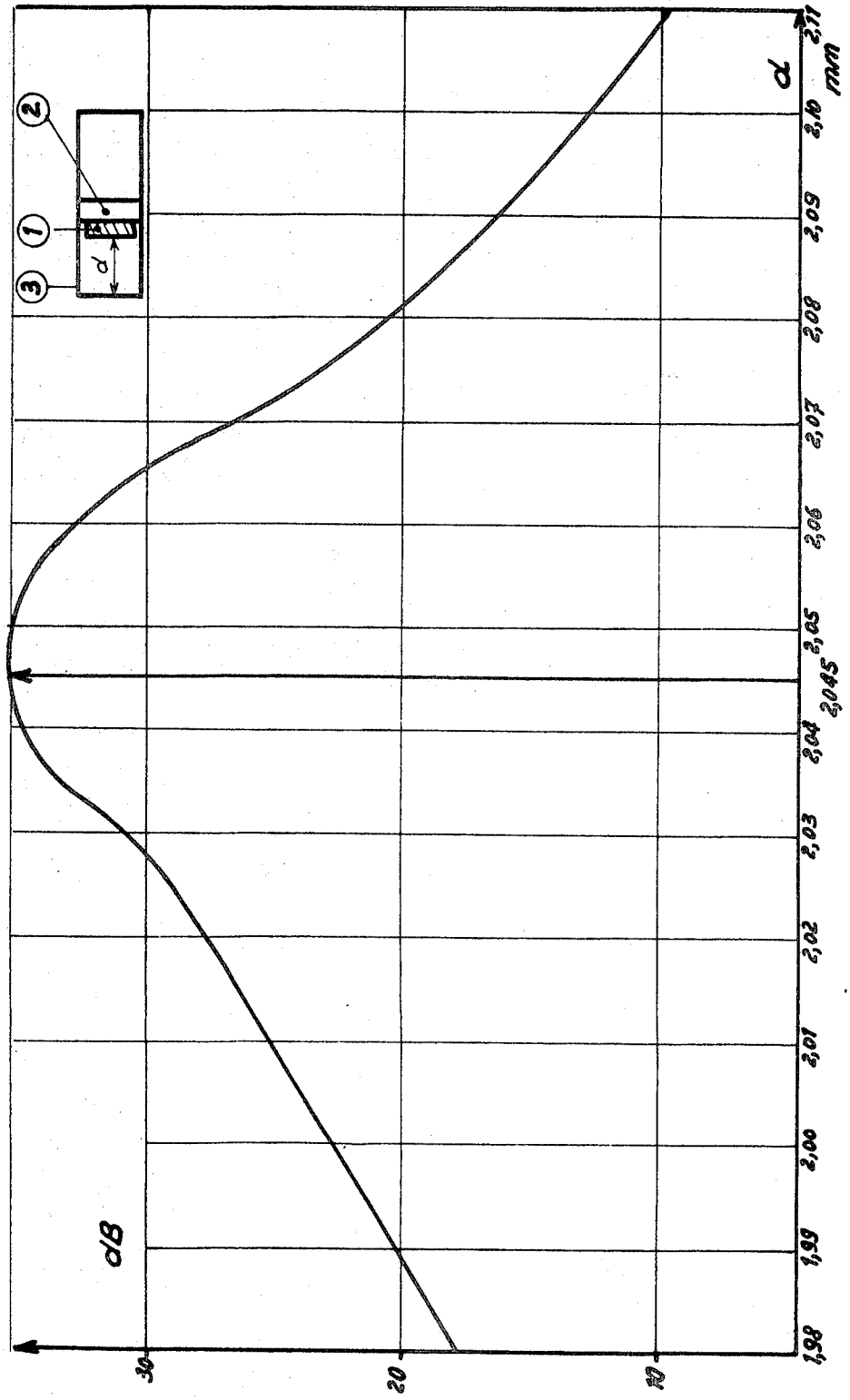


Fig. 2

MICROWAVE MAGNETIC MATERIALS WITH A HEXAGONAL STRUCTURE

Filed Feb. 20, 1969 5 Sheets-Sheet 3

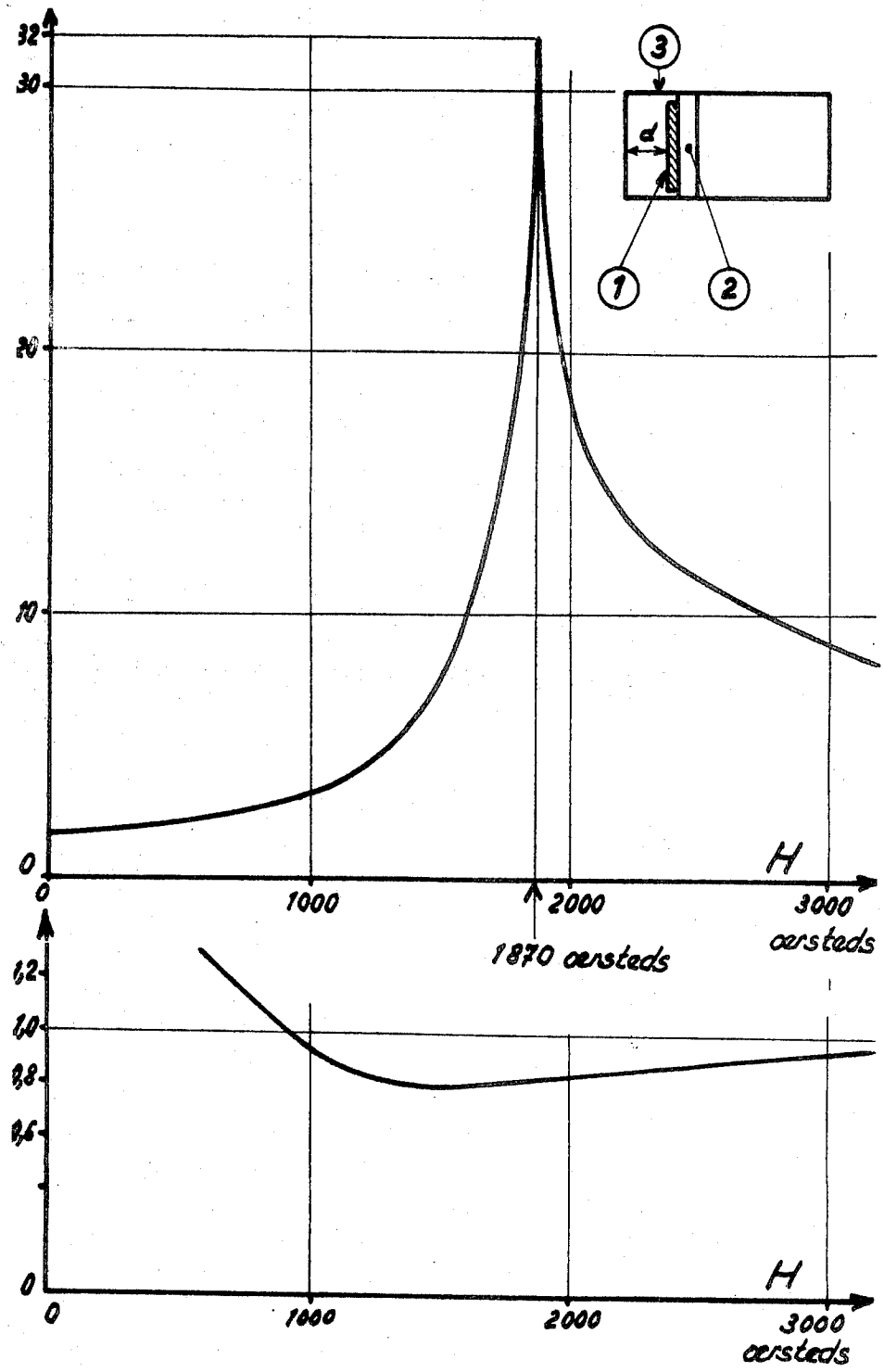


Fig. 3

MICROWAVE MAGNETIC MATERIALS WITH A HEXAGONAL STRUCTURE

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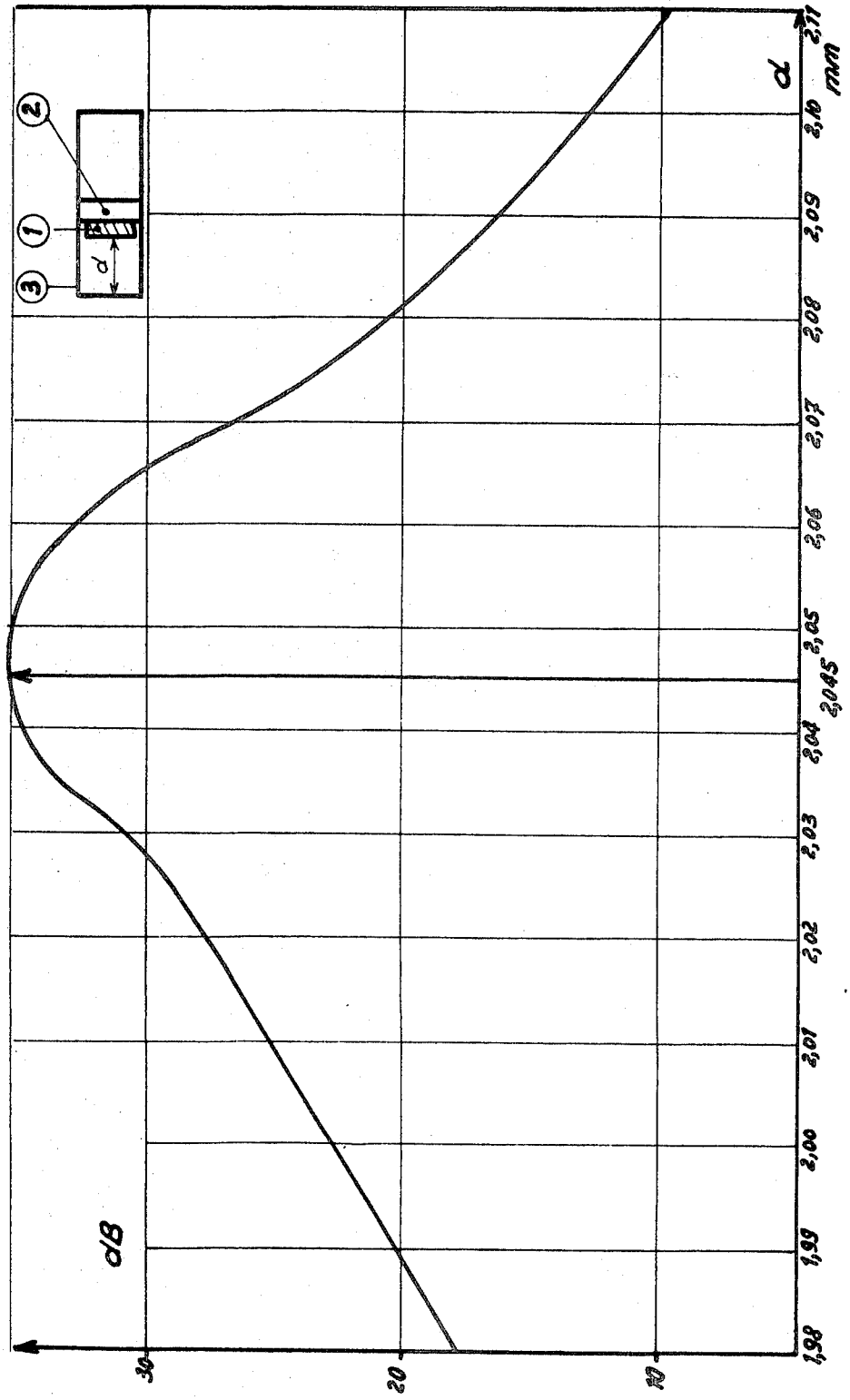


Fig. 2

MICROWAVE MAGNETIC MATERIALS WITH A HEXAGONAL STRUCTURE

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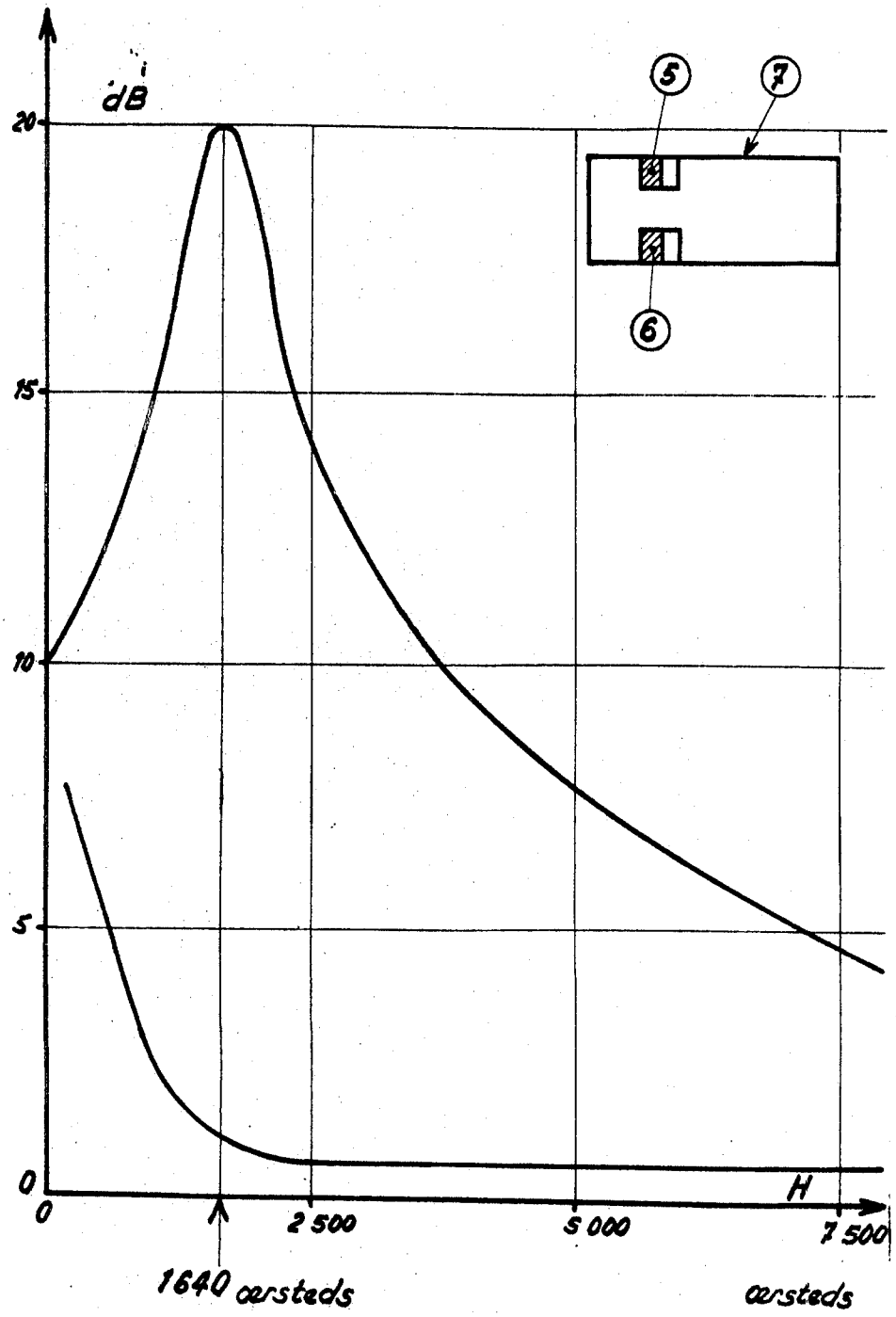


Fig. 5

United States Patent Office 3,573,207 Patented Mar. 30, 1971

3,573,207

MICROWAVE MAGNETIC MATERIALS WITH A HEXAGONAL STRUCTURE

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Int. Cl. H01b 1/10
U.S. Cl. 252—62.58 2 Claims

ABSTRACT OF THE DISCLOSURE

An hexagonal ferrite composition for microwave devices is obtained by double substitution of a part of the ferric ions in a conventional alkaline-earth ferrite ($MO, 6Fe_2O_3$) by couples of ½ (Ti^{4+}, Ni^{2+}) and Mn^{3+} or by triple substitution adding Al^{3+} to the two groups above. The manufacturing process includes sintering of single-crystal flakes of the ferrite material the dimensions of which are not larger than .5 mm.

BACKGROUND OF THE INVENTION

The present invention relates to magnetic materials of ferrite type with high anisotropy, to be used in the microwave range (more particularly at millimetre wavelengths), whereby it is possible to design resonance devices operated with a weak applied magnetic field.

According to their composition, these materials of hexagonal structure have a spontaneous magnetisation, and therefore an anisotropy field H_A, directed along the crystallographic axis C (preferred axis), or situated in a plane perpendicular to the said axis (preferred plane).

Located in a microwave circularly polarised field, the plane of which is perpendicular to the external magnetic field H_0, these ferrites show a resonance at a frequency f which, in a spherical specimen, is given by:

$$\frac{f}{v}=(H_0+H_A)$$

for a material having a preferred axis of anisotropy and H_0 is applied along the said axis, and by:

$$\left(\frac{f}{v}\right)^2=H_0\cdot(H_0+H_A)$$

for a material having a preferred plane, and H_0 is situated in the said plane.

These formulae show that, by utilising ferrite materials with a high internal anisotropy field, it is possible either to reduce the value of the external field at a given operating frequency, or to increase the frequency of operation of a resonance device at a given value of the external field. This feature is all the more interesting since in the millimetre and inframillimetre ranges the microwave circuits (wave-guides, three-plate lines or integrated circuits) are of small dimensions. It is well known that the production of intense magnetic fields in such structures raises considerable technological difficulties, involving the provision of equipment, the bulk of which is incompatible with the user's requirements.

PRIOR ART

Structures of hexagonal ferrites are known per se. They are formed by a stacking of spinel blocks and

$$(MFe_{16}O_{11})^{2-}$$

and ($M_2Fe_8O_{14}$) blocks (M representing a large divalent ion, such as Ba, Sr, Pb), differently ordered, which leads to different structures. There are numerous compounds

in O_{60}, in O_{82}, in O_{104}, in O_{126}, in O_{148} and in O_{170}, of O_{22} period. For microwave use, however, the structures in O_{19}, in O_{22}, in O_{27} and in O_{41} are usually employed.

The formulae of these hexagonal ferrites may be classified in the following manner according to their magnetic characteristics:

Hexagonal ferrites	Magnetic characteristics
MN_2O_4	Non-magnetic.
$MN_{12}O_{19}$	Preferred C axis.
$MMe_2N_{16}O_{27}$	Preferred C axis leading to a preferred plane perpendicular to the C axis if partial or total substitution of the Me ions by Co ions is effected.
$M_3Me_2N_{24}O_{41}$	Do.
$M_3Me_2N_{12}O_{22}$	Preferred plane perpendicular to the C axis.

where:

M is a large divalent ion, such as Ba, Sr, Pb (and Ca in certain limits),
Me is a divalent ion such as Ni, Cu, Zn, Co,
N is one or more trivalent ions, such as Mn^{3+}, Fe^{3+}, Al^{3+}, Ga^{3+}.

The compounds in O_{27} or O_{41}, which admit a preferred axis, have a positive anisotropy constant. In this group of materials, if substitution by the Co ion is carried out, it is found that for given Co contents, the preferred axis is converted into a preferred plane. The anisotropy, at first positive, gradually acquires a negative value while passing through zero. The behaviour of these materials in a microwave field has been studied. The following publications refer to this problem, among others:

"Hexagonal ferrites for resonance isolator in millimetre wave range" by D. R. Taft, G. R. Harrison and L. R. Hodges in the periodical Electro-Technology of January 1964,

"Studies of ferrite material in the millimetre wave range" by I. Wolfe in the periodical "Frequenz" of May 21, 1967.

The design of resonance devices using these ferrites has been studied many times. Variation of anisotropy is obtained by mixing two or three divalent ions with the Co ions, for matching the anisotropy field to the frequency used. The operating ranges are, with nickel H_A: from zero to 14.2 koe., with zinc: from zero to 7.3 koe. and with copper: from zero to 6.9 koe.

No publication is known which mentions the use of compounds with O_{19} or with O_{22} in resonance devices.

The compounds with O_{19} have a preferred axis. Their very high anisotropy fields, varying from 6,000 to 53,000 oe., according to the substitutions, enable them to be used in a very wide frequency band. However, in the selection of ferrite materials to operate in the microwave range, and particularly in the selection of materials for resonance devices, the value of the losses and more particularly the dielectric losses, is a decisive parameter. Materials corresponding to the general formula M, N_{12}, O_{19} have a dielectric loss which usually makes them useless in the millimetre wave range. It has been found that a ferrite of formula $BaO, 6Fe_2O_3$ has an anisotropy field of 17.5 koe., but the dielectric loss tan $\delta=4.10^{-3}$ measured at 8 mm. Similarly, a ferrite of formula $SrO, 6Fe_2O_3$ has an anisotropy field of 17.5 koe. and a dielectric loss identical with the preceding value. See more particularly: "Anisotropy Felds in Hexagonal Ferromagnetic Oxides by Ferrimagnetic Resonance" by D. J. De Bitetto, Philips Laboratories, Irvington on Hudson, New York, published in the Journal of Applied Physics, vol. 35, December 1964.

BRIEF DISCLOSURE OF THE INVENTION

The object of the present invention is to improve the characteristics of hexagonal ferrites of general formula M, N_{12}, O_{19} where M is a large divalent ion and N is a trivalent ion, in order to reduce their dielectric loss. It

is characterised by the following features taken in combination, totally or partly:

(a) double substitution or a first fraction of the N^{3+} ions by ½ (Ni^{2+}, Ti^{4+}) ion groups, and a second fraction by Mn^{3+} ions;

(b) substitutions according to (a) and substitution of a third fraction of the N^{3+} ions by Al^{3+} ions;

(c) combination of the three substitutions according to (a) and (b) to obtain a ferrite of general formula:
MO, $(6-x-y-z)\ Fe_2O_3$, $x(TiO_2NiO)$, yAl_2O_3, zMn_2O_3
where

$$M=Ba,\ Pb\ or\ Sr$$

and where

$$\cdot 1<x<2,\ 0<y<3,\ \cdot 1<z<\cdot 7$$

(d) the ferrites according to (c) are used as parts prepared by sintering of agglomerates of single-crystal flakes of dimensions less than .5 mm. obtained by sifting a mixture of precalcined oxides and elimination from the mixture corresponding to the grains of larger dimensions.

The substitution according to the invention of ½ ($Ti^{4+}Ni^{2+}$) groups for part of the Fe^{3+} of the hexagonal ferrite, principally results in a reduction in dielectric loss. At the same time, however, there is a reduction in the internal anisotropy field. This reduction may be partly compensated by a substitution, of some of the Fe^{3+} ions by Al^{3+} ions, as known from the men of art and mentioned in the first article cited in reference. It is, of course, understood that this second substitution was applied to a ferrite without ½ ($Ti^{4+}Ni^{2+}$) groups, and did not permit the desired reduction in dielectric loss. In the ferrites according to the invention, it is used to adjust the resonance frequency to correspond to a given external field, as set by the user.

The third substitution of Mn^{3+} ions for Fe^{3+} ions, which appears in the general formula, has already been proposed for ferrites but for ferrites without ½ ($Ti^{4+}Ni^{2+}$) substitution.

The combination of these different substitutions characterises the ferrites according to the present invention. Table I below compares the values of tan δ, measured at 8 mm. wavelength, obtained with a barium ferrite without substitution, a barium ferrite comprising only one substitution of Mn^{3+} ions for Fe^{3+} ions and a barium ferrite comprising a double substitution of Fe^{3+} ions by Mn^{3+} ions, and by the ½ ($Ti^{4+}Ni^{2+}$) groups, according to the present invention.

The same substitutions made in a strontium ferrite give similar results.

TABLE I

Composition of the ferrites:	Value of tan δ measured at 37.5 gHz.
$BaO,\ 6Fe_2O_3$	4.10^{-3}
$BaO,\ 5.9\ Fe_2O_3,\ .1Mn_2O_3$	3.10^{-3}
$BaO,\ 4.9\ Fe_2O_3,\ (TiO_2NiO),\ .1Mn_2O_3$	10^{-3}

DETAILED DISCLOSURE OF THE INVENTION

The present invention will be well understood by referring to the following description and the accompanying figures, in which:

FIG. 1 gives the result of measurements made for determining the optimum value of the coefficient assigned to the substitution of Fe^{3+} ions by Al^{3+} ions:

FIG. 2 gives the constitution of a 36 gHz resonance isolator and the adjustment curve for this isolator;

FIG. 3 gives the performances of a resonance isolator operating at 36 gHz.;

FIG. 4 gives the constitution of a high-level isolator operating at 72 gHz., together with its performances;

FIG. 5 gives the constitution of a high level isolator operating at 72 gHz., together with its performances.

The preparation of the ferrites according to the invention:
MO, $(6-x-y-z)\ Fe_2O_3$, $x(TiO_2NiO)$, yAl_2O_3, zMn_2O_3
in which M=Ba, Pb, Sr and where:

$$\cdot 1<x<2$$
$$0<y<3$$
$$\cdot 1<z<\cdot 7$$

according to the invention follows the process to be described now.

The TiO_2NiO material duly prepared is sintered at about 1000° C. in air for one hour, then crushed and intimately mixed in a ball mill with the oxides BaO (or PbO and/or SrO), Fe_2O_3, Mn_2O_3 and possibly Al_2O_3 in quantities corresponding to the desired composition.

To take into account iron pick-up in the mill, the MO oxides are always weighed with excess according to the formula

$$KMO,\ (6-x-y-z)\ Fe_2O_3,\ xTiO_2\ NiO,\ yAl_2O_3,\ zMn_2O_3$$

where K is a number between 1 and 1.2 according to the grinding mill used. The best results are obtained by determining K such that the formula will be stoichiometric at the end of the production.

The mixture thus obtained is presintered in air, without pressure, at 1,100° C. After heating for one to two hours, it is sifted, without regrinding, for retaining the fraction of the powder having a particle size below .5 mm.

This powder is moulded and compressed in air under a pressure of 5 ton/cm.², in a continuous magnetic field of the order of 7,000 oe., produced by means of a magnetic die and a coil mounted around the body of the compression mould.

The last operation is a reheating at high temperature (about 1,300° C.) in an oxygen atmosphere for 24 hours.

The materials thus prepared have a density in the vicinity of 5 g./cm.³. They appear in the form of an agglomerate of single-crystal plates oriented under the combined action of the magnetic field and compression. Sifting without regrinding to the dimension .5 mm. has the effect of eliminating the excessively large grains, which would not be orientable, and of preserving intact the grains of optimum dimensions, corresponding to an adequate viscosity.

As the following examples will specify, ferrites of this type have been used in microwave devices operating in the millimetre wave range.

The influence of the various substitutions on the internal anisotropy field and on the dielectric loss will be explained in connection with the characteristics of these devices.

Device No. 1: Resonance isolator at 36 gHz.

It is known that barium ferrite of general composition $BaO,\ 6Fe_2O_3$ has an internal anisotropy field of 17,500 oe., and excessively high dielectric loss at the operating frequency of 36 gHz. The diminution of the internal anisotropy field and dielectric loss is obtained by substituting for Fe^{3+} ion pairs of ($Ti^{4+}Ni^{2+}$) ions (which diminish the field and the loss) and a slight percentage of Mn^{3+} ion pairs (which diminish the loss).

The influence of these substitutions on the dielectric loss and on the internal anisotropy field of this barium ferrite is summarized in the following Table II, in which different values are allotted to the coefficients x and z, assigned respectively to the substitutions by the (TiO_2, NiO) group and by Mn_2O_3.

TABLE II

$BaO,\ (6-x-z)\ Fe_2O_3,\ x(TiO_2,\ NiO)\ z\ Mn_2O_3$	Values of x and z ($y=0$)			
	$x=z=0$	$x=0,\ z=.1$	$x=.5,\ z=.1$	$x=1,\ z=.1$
Dielectric loss Value of tan δ at 37.5 gHz.	4.10^{-3}	3.10^{-3}	2.10^{-3}	1.10^{-3}
Value of anisotropy field (in oersted)	17,500	17,500	12,000	5,000

A compromise giving an anisotropy field compatible with the external field values acceptable by the user, and low dielectric loss for which tan δ does not exceed 10^{-3}, is found for $x=1$ and $z=.1$.

Matching of the resonance frequency to the operating frequency is obtained by modification of the anisotropy

field by substitution of Al^{3+} ions for Fe^{3+} ions. Measurements made in a 36 gHz. rectangular resonant cavity on various spherical specimens of ferrite have made it possible to determine the optimum value of the coefficient y. The results of these measurements are given in FIG. 1 showing, for each value of y studied, the absorption of the cavity as a function of the applied magnetic field. Resonance, shown by the maximum of the curves, is obtained for applied magnetic fields which become increasingly weaker with increase in y. A good value of the coefficient of substitution by Al_2O_3 is found to be at $y=.6$.

The composition of the ferrite intended to operate at 36 gHz. is the following:

$$BaO,\ 4.3\ Fe_2O_3,\ TiO_2NiO,\ .6Al_2O_3,\ .1Mn_2O_3$$

At this frequency, the characteristics are:

Anisotropy field: of the order of 9,000 oe.
Value of tan $\delta=1.10^{-3}$.

The isolator is shown in FIG. 2. It comprises plates 1, 50 to 10μ thick and 3.4 mm. wide for 15 mm. length, adhesively secured to pure alumina supports **2**. These plates are placed in a rectangular waveguide **3**, parallel to the small walls of the waveguide, and at a distance "*d*" from the side walls. As shown by the curve of FIG. 2, adjustment of this distance is to be made with great precision, and the use of a micrometer is necessary, since optimum positioning requires a precision of 10μ. The characteristics of such an isolator are shown in FIG. 3. With an applied continuous magnetic field not exceeding 1,870 gauss, the direct attenuation is .8 db for an inverse attenuation of 32 db.

Device No. 2: low-level 72 gHz. isolator

It is known that strontium ferrites of general composition SrO, $6Fe_2O_3$ have an anisotropy field greater than that of barium ferrites. This field attains 19,000 oersteds, and the dielectric loss is too high for it to be useful. The mechanism of the substitutions effected on the simple ferrite is analogous to that effected in the preceding example. A compromise has been found by setting in the general formula according to the invention:

$$x=.5,\ y=.4,\ z=.1$$

which gives the formula for the composition as follows:

$$SrO,\ 4Fe_2O_3,\ .5(TiO_2NiO),\ 1.4Al_2O_3,\ .1Mn_2O_3$$

The low level isolator, FIG. 4, operating at 72 gHz., comprises a plate 4, 50μ thick, 1.3 mm. wide and 15 mm.

long, positioned according to the technique set forth for device **1**.

The performances of this device are shown in FIG. 4. A direct attenuation of .85 db is obtained for an applied field of 2,000 gauss.

Device No. 3

With the material used for device No. 2 a 72 gHz. high level isolator has been constructed, FIG. 5, consisting of two plates **5** and **6**, adhesively secured to the long sides of the guide **7**. These plates have the following dimensions: thickness .05 mm., width .4 mm., length 1.5 mm.

The performance of this device is shown in FIG. 5. Maximum direct attenuation is found to be .8 db for an applied field of 1,640 gauss.

What I claim:

1. A ferrite of the formula

$$MO,\ (6-x-y-z)\ Fe_2O_3,\ x(TiO_2\ NiO),\ yAl_2O_3,\ zMn_2O_3$$

in which M is a metal selected from the group consisting of barium, strontium and lead and wherein the coefficients x, y, and z have values within the following ranges:

$$.1<x<2,\ 0<y<3,\ .1<z<.7$$

2. A ferrite body of the formula

$$MO,\ (6-x-y-z)\ Fe_2O_3,\ x(TiO_2\ NiO),\ yAl_2O_3,\ zMn_2O_3$$

where M is a metal selected from the group consisting of barium, strontium and lead and wherein the coefficients x, y and z have values within the following ranges:

$$.1<x<2,\ 0<y<3,\ .1<z<.7$$

said ferrite being a sintered body of single crystal flakes the dimensions of which are smaller than .5 mm.

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