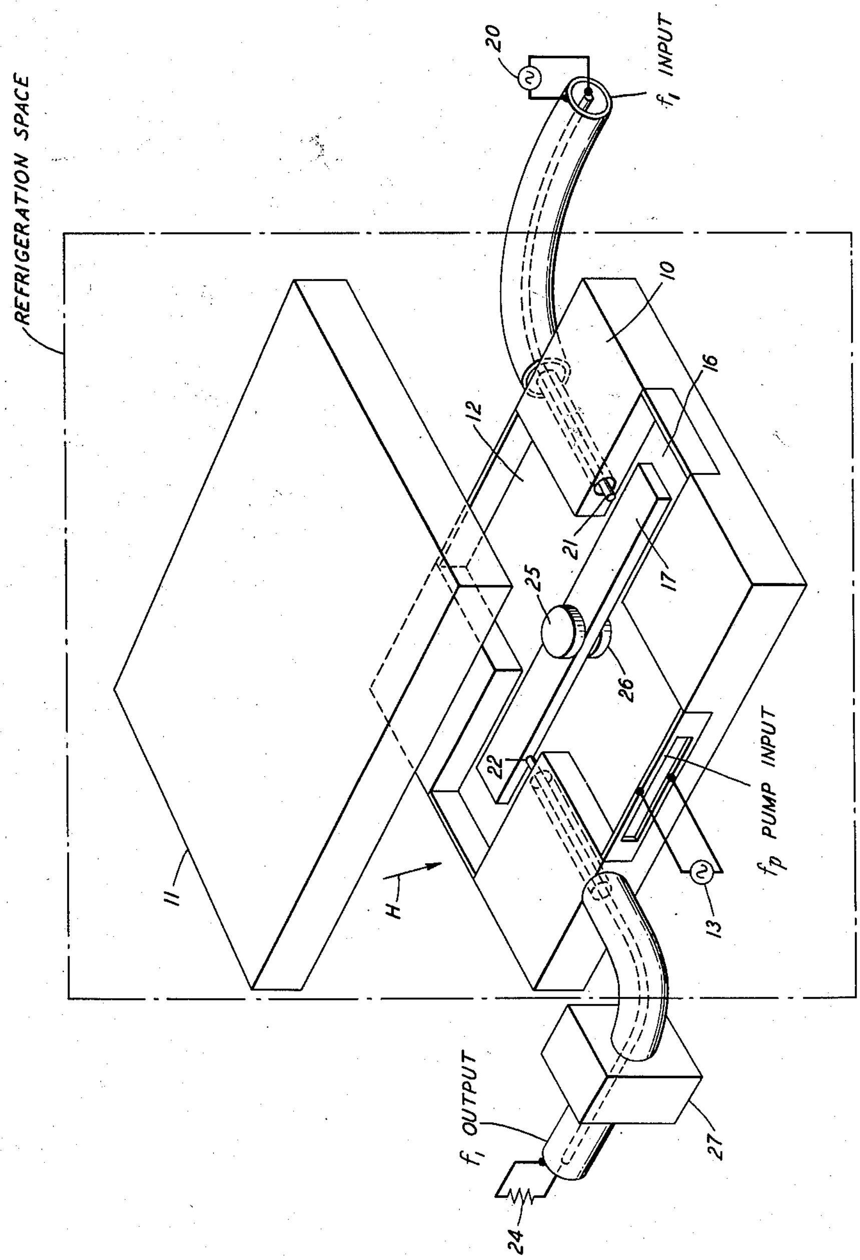
July 19, 1960 K. KNOX 2,945,744

MAGNETIC MATERIALS

Filed Feb. 14, 1958



INVENTOR
K. KNOX
BY Lucian C. Canepa
ATTORNEY

2,945,744

MAGNETIC MATERIALS

Kerro Knox, Summit, N.J., assignor to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York

Filed Feb. 14, 1958, Ser. No. 715,415

4 Claims. (Cl. 23—50)

This invention relates to magnetic materials, and more particularly to ferrimagnetic fluoride compounds.

Ferromagnetic materials, which include the elements iron, nickel and cobalt, are made up of domains. The atoms within each domain behave like magnetic dipoles, and are aligned parallel to one another even in the absence of an applied magnetic field. This alignment is known as spontaneous magnetization, and is the basic characteristic feature of ferromagnetic materials.

Ferrimagnetic materials (of which ferrites are the prototypes) also have a domain structure and exhibit spontaneous magnetization. These materials have their magnetic dipoles arranged in two or more sub-lattices of crystallographically different sizes. The exchange forces between the magnetic dipoles in the sub-lattices are negative, i.e., the magnetic moments of the sub-lattices tend to align in an antiparallel manner. When the vector sum of the magnetic moments of the sub-lattices is not zero, either because the magnetic moments of the sub-lattices are different in magnitude and/or because the magnetic moments are not strictly antiparallel, spontaneous magnetization results and the material is ferrimagnetic.

Ferrimagnetic materials are utilized in a variety of microwave communications devices, for example, circulators, isolators, attenuators and amplifiers. More specifically, these materials may be employed as the active elements of low noise parametric amplifiers of the type described by H. Suhl in the Physical Review, volume 106, page 384, Apr. 15, 1957, and by him in The Journal of Applied Physics, volume 28, page 1225, November 1957. An illustrative amplifier device of the Suhl type is shown in the accompanying drawing. The device includes suitable means (not shown) for supplying a steady external magnetic field (represented in the drawing by a vector H) to a block member **10** having a cover plate **11**, which block **10** and plate **11** define a reaction zone.

The block **10** includes two intersecting resonators, the first of which is of the wave guide type and comprises a rectangular channel **12** whose input end is connected to a source **13** of pumping power at a frequency f_p.

The second resonator of the illustrative device shown in the drawing is of the strip-line type and comprises a channel **16** extending at right angles to the channel **12**. Suitably supported within the channel **16** is a thin conductive member **17**, the elements **16** and **17** comprising a strip-line wave supporting structure **16—17**.

A wave at f_1, the frequency to be amplified, is launched upon the strip-line assembly **16—17** from a source **20** by means including a probe **21**.

The amplified output signal may be taken from the line assembly **16—17** by a probe **22** which is connected by suitable means including a filter **27** to a load **24**.

Nonlinear coupling between the energy supported in the resonators **12** and **16—17** is provided by two bodies **25** and **26** which may advantageously be formed from a material made in accordance with aspects of the principles of this invention.

The dashed lines in the drawing schematically represent a refrigeration space within which portions of the amplifier device are enclosed, thereby maintaining the bodies **25** and **26** below the Curie temperature.

A microwave device similar to the one described above is fully disclosed in an application of M. T. Weiss, Serial No. 660,280, filed on May 20, 1957.

An object of the present invention is to improve devices of the type above-described by providing improved constituent materials therefor.

Another object of this invention is an improved class of ferrimagnetic materials.

A more specific object of the present invention is a class of ferrimagnetic fluoride compounds.

These and other objects of the present invention are realized in compounds having the formula $Na_5X_3F_{14}$, wherein X represents a trivalent metallic ion chosen from a group consisting of the following: chromium, cobalt, copper, iron, manganese, molybdenum, nickel, palladium, rhodium, tantalum, titanium and vandium.

Each member of the group above is a transition element whose trivalent ion exhibits a magnetic moment and, further, whose trivalent oxidation state is known to exist in fluoride compounds.

One specific illustrative embodiment of the present invention is a compound having the formula $Na_5Fe_3F_{14}$. In a specific process for making this embodiment, there were mixed together the compounds NaF and FEF_3 in the mole ratio of 5NaF to $3FEF_3$, which corresponds to the stoichiometric proportions. This mixture, in an amount of 1.3 grams, was placed in a platinum vessel and heated to 700 degrees centigrade for two hours in an anhydrous hydrogen fluoride atmosphere. Such heating resulted in the formation of the compound $Na_5Fe_3F_{14}$, which is a red-brown material.

When stoichiometric proportions of the ingredients NaF and FEF_3 were mixed together, there was obtained the compound $Na_5Fe_3F_{14}$ substantially free of other residue. However, when proportions other than stoichiometric (in the composition range 70 mole percent NaF with 30 mole percent FeF_3 to 50 mole percent NaF with 50 mole percent FeF_3) were used, the product was a polyphase material made up of a transparent red-brown phase, $Na_5Fe_3F_{14}$, and other phases.

In a reaction which produces the red-brown and other phases, the desired red-brown phase may be separated out by a mechanical separation process which includes grinding the material obtained from the reaction into relatively small pieces (more specifically, pieces having largest dimensions across falling in the range 1 to 50 thousandths of an inch), and then picking out therefrom the transparent red-brown elements. Alternatively, the desired red-brown elements may be separated from the unwanted pieces by cooling the ground material to a temperature below the Curie point of the red-brown phase, and then attracting the desired elements with a magnet.

It is noted that any other non-reacting vessel, for example, a graphite one, and any other inert atmosphere, for example, one of nitrogen or argon, may be employed in the above-recited method.

Additionally, it is noted that the specified temperature of 700 degrees centigrade is not critical. It is feasible, for example, to employ lower temperatures, in which cases the times required for a given reaction would be increased over that recited above.

Similarly, higher temperatures than that specified may be employed. It has not, however, been found particularly advantageous to utilize much higher temperatures.

Low temperature magnetization measurements down to 1.7 degrees Kelvin have demonstrated that the compound $Na_5Fe_3F_{14}$ is ferrimagnetic, having a Curie temperature of about 80 degrees Kelvin. (Microwave amplifiers of the Suhl type may advantageously be operated at temperatures below this relatively low Curie point, thereby enhancing the low noise characteristics thereof.)

Further investigations of the properties of the compound $Na_5Fe_3F_{14}$ indicated that the resistivity of a pellet thereof is greater than 10^8 ohm-centimeters, which relatively high electrical resistivity is particularly advantageous for adapting the materials for use in the microwave devices above-mentioned.

The method described above is suited for making nine other specific illustrative embodiments of the present invention, namely, $Na_5Co_3F_{14}$ (formed from NaF and CoF_3), $Na_5Cr_3F_{14}$ (formed from NaF and CrF_3), $Na_5Mn_3F_{14}$ (formed from NaF and MnF_3), $Na_5Mo_3F_{14}$ (formed from NaF and MoF_3), $Na_5Pd_3F_{14}$ (formed from NaF and PdF_3), $Na_5Rh_3F_{14}$ (formed from NaF and RhF_3), $Na_5Ta_3F_{14}$ (formed from NaF and TaF_3), $Na_5Ti_2F_{14}$ (formed from NaF and TiF_3), and $Na_5V_3F_{14}$ (formed from NaF and VF_3).

NaF and the trifluorides of cobalt and manganese are commercially available compounds. The other trifluoride compounds, namely, CrF_3, FeF_3, MoF_3, PdF_3, RhF_3, TaF_3, TiF_3, and VF_3, may advantageously be prepared in accordance with the procedures given in Fluorine and Its Compounds, by R. N. Haszeldine and A. G. Sharpe, Methuen, London, 1951, at the following pages respectively: 51, 52, 53, 56, 56, 59, 50 and 50.

The compounds $Na_5Cu_3F_{14}$ and $Na_5Ni_3F_{14}$ require for their synthesis methods different from that recited above. The method for preparing the compound $Na_5Cu_3F_{14}$ comprises the following steps: (1) combining the commercially-available compounds NaCl and CuCl so that sodium and copper exist in the mixture in the proportion 5:3 by mole ratio; (2) containing the mixture in an inert vessel, such as a nickel boat, and then passing elementary fluorine over these compounds in a reaction zone heated to 700 degrees centigrade, thereby converting the chloride compounds to fluoride compounds, oxidizing the copper ions from their +1 to their +3 states, and reacting NaF with the trivalent copper ions and available fluoride ions to form $Na_5Cu_3F_{14}$.

Similarly, the method for preparing the compound $Na_5Ni_3F_{14}$ comprises the following steps: (1) combining NaCl and $NiCl_2$ (the latter is formed by heating in a well-known manner the commercially-available compound $NiCl_2 \cdot 6H_2O$) so that sodium and nickel exist in the mixture in the proportion 5:3 by mole ratio; (2) containing the mixture in an inert vessel, such as a nickel boat, and then passing elementary fluorine over these compounds in a reaction zone heated to 700 degrees centigrade, thereby converting the chloride compounds to fluoride compounds, oxidizing the nickel ions from their +2 to their +3 states, and reacting NaF with the trivalent nickel ions and available fluoride ions to form $Na_5Ni_3F_{14}$.

It is to be understood that the above-described arrangements are illustrative and not restrictive of the principles of the present invention. Other arrangements may be devised by those skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. A class of ferrimagnetic materials having the formula $Na_5X_3F_{14}$, wherein X is a trivalent metallic ion chosen from a group consisting of chromium, cobalt, and iron ions.
2. A ferrimagnetic material having the formula $Na_5Fe_3F_{14}$.
3. A ferrimagnetic material having the formula $Na_5Co_3F_{14}$.
4. A ferrimagnetic material having the formula $Na_5Cr_3F_{14}$.

References Cited in the file of this patent

UNITED STATES PATENTS

2,723,182	Sibert	Nov. 8, 1955
2,793,097	McKenna	May 21, 1957
2,825,765	Marie	Mar. 4, 1958

OTHER REFERENCES

Chemical Abstracts, vol. 18, page 2478; vol. 40, cols. 1637, 7038.

A Comprehensive Treatise on Inorganic and Theoretical Chemistry, by Mellor, vol. 9, pp. 797, 916–918 (1929); vol. 11, pp. 363, 364, 610 (1931); vol. 14, p. 9 (1935); vol. 15, p. 658 (1936), pub. by Longmans, Green, London.