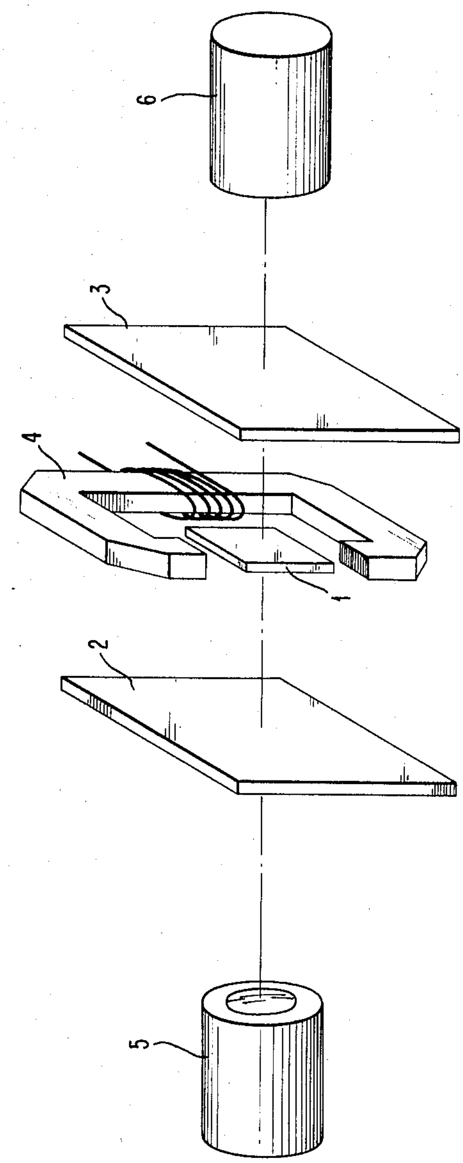
Feb. 27, 1968 M. W. SHAFER 3,370,916

MAGNETIC MATERIALS AND PROCESS OF PREPARATION

Filed June 27, 1963



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United States Patent Office

3,370,916
Patented Feb. 27, 1968

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3,370,916

MAGNETIC MATERIALS AND PROCESS OF PREPARATION

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Filed June 27, 1963, Ser. No. 291,043
6 Claims. (Cl. 23—21)

ABSTRACT OF THE DISCLOSURE

A method for forming a group of europium silicate magnetic materials the members of which have unpaired electrons and are transparent in relatively thick layers at wavelengths greater than about 4500 A. in which intimate mixtures of EuO or $EuCO_3$ or $Eu(OH)_2$ and SiO_2 are reacted at elevated temperatures in a non-oxidizing or insert gas environment. Other europium compounds such as $Eu_2(C_2O_4)_3$, $Eu(OH)_3$ or Eu_2O_3 may be mixed with SiO_2 and reacted at elevated temperatures in a reducing atmosphere to provide the same europium silicate group. The compositions resulting from the process are europium silicates having the formula

$$Eu_xSiO_{x+2}$$

where $x=1$–3.

Magnetic materials generally fall into two classes, those which exhibit cooperative magnetism, and those which do not. Those with the cooperative magnetic effect are the ferromagnetic, ferrimagnetic and anti-ferromagnetic materials. The great majority of the ferromagnetic materials are metals and good electrical conductors, hence, opaque materials. The ferrimagnetic materials can have a range of restivities, but their conduction bands are partially filled and also are opaque for all practical purposes. Although the antiferromagnetic materials can have unfilled conduction bands, their net magnetic moments are small and consequently have little practical use.

The existence of insulating ferromagnetic or ferrimagnetic materials is rare since they would require that the conduction band be unfilled and still exhibit a positive interaction involving unpaired electrons. Examples of these materials would be $CrBr_3$ and $Na_5Fe_3F_{14}$. On the other hand, the yttrium iron garnets, e.g., $Y_3Fe_5O_{12}$ and rare earth iron garnets only partially fill these requirements since they are only transparent in very thin sections.

It is well known that when a light is passed through a magnetic material in which there are unpaired electrons, there will be an interaction and the light will be rotated in a manner which is dependent on the alignment and the number of unpaired electron spins of the material (i.e., the Faraday effect). This Faraday effect is usually defined in terms of the Verdet's constant which is the observed rotation in minutes per gauss per centimeter thickness. This is also true in the case of paramagnetic materials as well as in the case of ferromagnetic and ferrimagnetic materials. Thus, the greater the number of unpaired electrons and their ability to align in a magnetic field, the greater will be the specific rotation of the light that the material can transmit (i.e., the specific rotation is directly proportional to the magnetic susceptibility of the material).

A group of europium silicate magnetic materials has been prepared, the members of which have unpaired electrons and are transparent in relatively thick layers in the visible and near visible spectrum (i.e., wavelengths greater than about 4500 A.). These materials have the formula Eu_xSiO_{x+2} where $x=1$–3. Those europium silicates where $x=2$ or 3 exhibit a high saturation magnetization. The europium silicate where $x=1$ is paramagnetic. All the europium silicates are chemically stable under ordinary conditions and optically transparent in single crystal form.

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It is an object of the invention to prepare europium silicate magnetic materials.

It is a further object of the invention to prepare europium silicate magnetic materials having the formula Eu_xSiO_{x+2} where $x=1$–3 and which are transparent.

Another object of the invention is to prepare a paramagnetic material having the formula $EuSiO_3$.

Still another object of the invention is to prepare a ferromagnetic material having the formula Eu_2SiO_4.

A still further object of the invention is to prepare a ferromagnetic material having the formula Eu_3SiO_5.

Further, another object of the invention is a magneto-optical device utilizing a crystal of Eu_xSiO_{x+2} where $x=1$–3.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of a preferred embodiment of the invention, as illustrated in the accompanying drawing.

The drawing is a diagrammatic showing of a magneto-optical device utilizing a europium silicate crystal of the present invention.

In the magneto-optical device shown diagrammatically in the drawing, a single crystal (or crystal section) **1** of a ferro- or paramagnetic europium silicate of the present invention is mounted between spaced crossed polarizing filters (i.e., polarizer **2** and analyzer **3**). The crystal is placed in a magnetic field (e.g., that produced by an electromagnet **4** or by Helmholtz coils). A light source **5** and a photosensitive cell **6** are so disposed that the light to which the photosensitive cell is exposed is that which originates at the light source and passes successively through polarizer **2**, crystal **1** and analyzer **3**. Since the degree of rotation of the plane of polarized light passing through the paramagnetic crystal is dependent upon the magnetic field, the amount and orientation of light originating in the light source and passing through the polarizer and analyzer and crystal to the photosensitive cell can be varied by varying the strength of the magnetic field of the magnet. In the ferromagnetic region, above magnetic saturation, the rotation is independent of the applied magnetic field and the maximum rotation can be obtained.

All these europium silicate materials have high Verdet's constants even at room temperature because of their high magnetic susceptibility and high degree of transparency. This Verdet's constant is higher by a factor of about 10 than that of any previously-known material. As a result of this high Verdet's constant, all these europium silicate materials can be used in magneto-optical devices such as laser beam modulators, light switches, etc. The compounds Eu_2SiO_4 and Eu_3SiO_5 exhibit a very large Faraday rotation at helium temperature. In addition, the new ferromagnetic materials, which are insulators, have properties which find application in memory elements, transformer cores, or in any device where high magnetic susceptibility material is desired at low temperatures.

Table I gives the magnetization data showing magnetic susceptibility versus temperature in degree Kelvin for the three europium silicates. The saturation magnetization and Curie temperature data are shown in the right column. All measurements were made using standard techniques.

TABLE I

Temp. (° K.)	Magnetic Susceptibility (X) (10^{-6} c.g.s.)	Magnetic Saturation Properties
		$EuSiO_3$
262	126	Paramagnetic to 1.8° K. consequently no saturation magnetization or Curie temperature measurements could be made.
194.5	176	
167.3	207	
107.7	311	
82.5	402	
72	452	
51.5	665	
38.5	925	
4.2	5,800	
		Eu_2SiO_4
258.5	136	Ferromagnetic saturation magnetization 6.54 Bohr Magnetrons or 185 e.m.u./gm. Curie temperature 10° K.
236.7	152	
209.3	172	
179.5	201	
77	485	
75.5	501	
72	532	
67.5	571	
62.5	630	
53.5	738	
48	866	
		Eu_3SiO_5
270	140	Ferromagnetic saturation magnetization 6.16 Bohr Magnetrons or 175 e.m.u./gm. Curie temperature 4° K.
241	157	
194.5	195	
180.3	209	
161.7	235	
132.5	285	
112.5	340	
101.5	374	
70.3	504	
47.3	879	
16.5	3,320	

All the europium silicates of the invention exhibit magneto-optical and optical properties. In Table II below, these properties are set forth for Eu_2SiO_4.

TABLE II [1]

Photon Energy, $\times 10^3$ Cm.$^{-1}$	Wave Length, A.	Absorption Coefficient $\times 10^2$ Cm.$^{-1}$	Percent Transmission
10	----------------	0.8	90
15	7,000	0.85	80
17.5	6,000	1.0	30
20	5,000	2.0	5
21	----------------	3.0	1.0
25	4,000	3.0	1.0
30	----------------	3.0	1.0
35	3,000	3.0	1.0

[1] All measurements were made at room temperature using standard techniques.
Verdet constant at 25° C.=2.5 min./oe./cm.±15%.

The Eu_xSiO_{x+2} (where $x=1-3$) magnetic materials are prepared by reacting intimate mixtures of EuO or $EuCO_3$ or $Eu(OH)_2$ and SiO_2 at elevated temperatures between 800°–1600° C. under nonoxidizing conditions such as an oxygen free vacuum or any condition in which there is an absence of oxygen, such as argon, nitrogen, etc., or under reducing atmosphere containing large percentages of hydrogen, e.g., nitrogen with hydrogen added (1–100 percent hydrogen), CO_2 with approximately 20–80 percent hydrogen, argon containing 1–100 percent hydrogen and pure hydrogen. Alternately, these materials can be prepared by reacting either $Eu_x(C_2O_4)_3$, $Eu(OH)_3$ or Eu_2O_3 with SiO_2 in a pure hydrogen atmosphere at temperatures between 1500–2000° S. The crucible used in preparing these materials is composed of iridium, platinum, or carbon.

The following specific examples represent embodiments of the invention and, more particularly, disclose the preparation of the europium silicate magnetic materials.

Example I

(Eu_2SiO_4)

33.6 grams of EuO are intimately mixed with 6.0 grams of SiO_2. This mixture is then placed in an iridium crucible. The crucible was raised to a temperature greater than 800° C. in a pure hydrogen atmosphere and held at that temperature for 24 hours. The crucible was then cooled to room temperature at a rate of 50° C. per minute. The resultant product Eu_2SiO_4 is a lemon-yellow polycrystalline powder with a Curie temperature of 10° K.

Example II

($EuSiO_3$)

16.8 grams of EuO are intimately mixed with 6.0 grams of SiO_2. This mixture is then placed in a platinum crucible. The crucible is placed in an oven and the temperature is raised to 1200° C. in a pure argon atmosphere and held at that temperature for 15 hours. The crucible was then cooled to room temperature at a rate of 50° C. per minute. The resultant product $EuSiO_3$ is a lemon-yellow powder which is paramagnetic down to 1.8° K.

Example III

(Eu_3SiO_5)

50.4 grams of EuO and 6.0 grams of SiO_2 are intimately mixed with 6.0 grams of SiO_2. This mixture is placed in a carbon crucible and the crucible is placed in an oven. The temperature was raised to 1600° C. in a pure nitrogen atmosphere and held at that temperature for 12 hours. The resultant product Eu_3SiO_5 is a powder with a lemon-yellow color and a Curie temperature of 4° K.

Example IV

(Eu_2SiO_4)

35.2 grams of Eu_2O_3 are intimately mixed with 6.0 grams of SIO_2 and placed in a carbon crucible. The crucible is placed in an oven and the temperature raised to 1600° C. in a pure hydrogen atmosphere and held at that temperature for 36 hours. The crucible is then cooled to room temperature at a rate of 10° C. per minute. The resultant product are amber-colored crystallites, some of which are large enough that optical and magneto-optical measurements may be made thereon.

The devices of the present invention have been described as made up essentially of a crystal containing Eu_xSiO_{x+2} which is placed in a magnetic field and associated optical instrumentation in order to utilize the Faraday effect. These devices may be manufactured according to the technique known in the art for the manufacture of analogous devices embodying other crystal bodies. The best results are obtained when the specific rotation of the light passing through the crystal varies linearly with the applied magnetic field.

However, the maximum rotation obtainable for this material can be obtained when operated in the ferromagnetic state, i.e., below their Curie temperature 10° K. for Eu_2SiO_4 and 4° K. for Eu_3SiO_5.

The new europium silicates of the invention have the formula Eu_xSiO_{x+2} where $x=1-3$. These silicates are transparent and thus are used in magneto-optical devices.

While the invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A compound having the formula Eu_xSiO_{x+2} where $x=1-3$.
2. The compound $EuSiO_3$.
3. The compound Eu_2SiO_4.
4. The compound Eu_3SiO_5.

5. A process of preparing an europium silicate material having the formula Eu_xSiO_{x+2} where $x=1\text{–}3$ which comprises the steps of:

(a) intimately mixing SiO_2 with an europium compound selected from the group consisting of EuO, $EuCO_3$, and $Eu(OH)_2$;

(b) heating this mixture in a nonoxidizing atmosphere at elevated temperatures between 800°–1600° C. to form thereby the europium silicate and then cooling.

6. A process of preparing an europium silicate material having the formula Eu_xSiO_{x+2} where $x=1\text{–}3$ which comprises the steps of:

(a) intimately mixing SiO_2 with an europium compound selected from the group consisting of Eu_2O_3, $Eu(OH)_3$ and $Eu_2(C_2O_4)_3$;

(b) heating this mixture in a hydrogen atmosphere at temperatures between 1500°–2000° C. to form thereby the europium silicate and then cooling.

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