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NOVEL SINGLE PHASE QUATERNARY MAGNETIC COMPOUNDS

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U.S. Cl. 252—62.51 9 Claims

The present invention relates to novel quaternary semiconducting, magnetic compositions of matter. More particularly, it relates to novel single phase, semiconducting, magnetic materials which contain at least four elements, namely, iron, copper, chromium and sulfur, selenium or mixtures of the latter. Still more particularly, the invention is concerned with single phase, semiconducting, magnetic compounds which possess the spinel structure and are of the general composition:

$$Fe_{1-x}Cu_xCr_2D_4$$

where D is sulfur, selenium or mixtures thereof and x represents a numerical value greater than 0 but less than 1.

Semiconducting, magnetic materials possessing two or more elements are known. These materials can be both ferromagnetic and ferrimagnetic substances. It is also known that a characteristic of such ferromagnetic and ferrimagnetic materials is that can loose at a certain temperature, termed the Curie temperature, their magnetic properties and, at that moment, undergo a transition to the paramagnetic state. While there are strong attractive forces at temperatures below the Curie temperature between such magnetic substances and a permanent magnet, these forces substantially disappear above the Curie temperature. This remarkable property of either a ferromagnetic or ferrimagnetic material, namely, the loss of its attraction to either a permanent or electromagnet while passing through its Curie temperature point, can be advantageously utilized in many diverse applications, as in the design of switches, thermostats or thermometers. Many of the latter devices are useful in operations at either room temperature or at temperatures which vary widely from below to above room temperature. The necessity for employing magnetic materials possessing Curie temperatures which range from below to above room temperature is apparent. Unfortunately, known materials, such as manganese-chromium antimonides, possessing Curie temperatures between −150° C. and +200° C., are not wholly satisfactory, since they possess distinct poor properties with respect to both their low saturation magnetization and low resistivities.

Single phase spinel substances of high saturation magnetization are particularly desirable so that they can achieve a strong attraction for switching purposes by a given magnetic field. In general, the higher the saturation magnetization of the material, the lower the applied magnetic field supplied by a permanent magnet or an electromagnet. Where the latter is employed, there is realized a substantial lowering of power consumption.

Known magnetic materials possessing Curie points approximating room temperature are metals and, therefore, also possess rather low resistivities. They are, therefore, unsuitable for alternating current or high frequency applications since they exhibit undesirably high eddy current or power losses.

It is, therefore, a principal object of the invention to provide single phase, semiconducting, magnetic compounds which possess high saturation magnetization. Other objects and advantages will become apparent from a consideration of the ensuing description.

To overcome the shortcomings of the prior practice,

there are provided semiconducting, magnetic materials represented by the formula:

$$Fe_{1-x}Cu_xCr_2D_4$$

wherein x is a numerical value greater than 0 but less than 1 and D is sulfur, selenium or mixtures thereof. Unexpectedly, the elements which are admixed in accordance with the process of the present invention, produce a crystalline structure which is of a single phase and possesses a Curie temperature which varies continuously from about −80° C. to about +130° C. This is rather surprising, because there is no reason to expect that any random combination of elements will result in a single phase, semiconducting, magnetic compound and that, further, the partial substitution of iron (i.e., magnetic ion) by copper (i.e., a non-magnetic ion) in the compound:

$$FeCr_2S_4$$

would indicate a decrease in the Curie temperature of resultant compound:

$$FeCuCr_2S_4$$

to below −80° C. Unexpectedly, a Curie temperature increase and good semiconducting properties with high resistivities as well as good magnetic properties are noted.

In general, the compounds of the invention which are additionally found to possess good semiconducting and magnetic properties can be prepared in a straightforward manner. The elements are mixed in the required stoichiometric amounts, pressed into pellets, then introduced into a crucible which is evacuated and sealed and finally subjected to elevated temperatures. This is usually accomplished by placing the crucible containing the pellet comprising the mixed elements into a furnace and heating the crucible to a temperature below the melting point of the material or composition of matter to be prepared. In general, a temperature of from about 600° C. to about 900° C. will be required to accomplish this end. Depending on the temperature employed, the time required to react the elements commencing at room temperature ranges from about forty-eight to more than one hundred hours.

Resultant products are black compounds possessing a Curie transition temperature of not less than −80° C. The latter temperature may be defined as the transition point between an ordered magnetic state and a disordered magnetic state. Further, the compounds possess a high saturation magnetization of from 40 to about 90 gauss cm.^{3}/gram and high resistivities at room temperature.

The following examples are presented merely by way of illustration and are not to be deemed limitative of the present invention. The symbol σ_o stands for saturation magnetization in gauss cm.^{3}/gram and ρ stands for resistivity in ohm-cm.

EXAMPLE 1

Preparation of the compound: $Fe_{.9}Cu_{.1}Cr_2S_4$

1.0053 grams Fe, 0.1271 gram Cu, 2.0800 grams of chromium and 2.5651 grams sulfur are mixed, pressed into pellets and sealed into an evacuated quartz ampoule. This ampoule is slowly heated to 800° C. and kept at this temperature for 48 hours. It is then cooled down to room temperature and opened. Resultant pellets are ground in an agate mortar, the powder carefully pressed into pellets. These are again sealed into an evacuated quartz ampoule and annealed for 60 hours at 800° C.

Resultant material is a single phase spinel structure and posseses a Curie temperature of −43° C., a saturation magnetization of 47 gauss cm.^{3}/gram and a resistivity of 0.1 ohm-cm.

EXAMPLE 2

Preparation of the compound: $Fe_{.8}Cu_{.2}Cr_2S_4$

0.8936 gram Fe, 0.2542 gram Cu, 2.0800 grams Cr and

2.5621 grams S are admixed, pressed into pellets and sealed into an evacuated quart ampoule. The latter is then slowly heated to 800° C. and kept at this temperature for 48 hours. After cooling the ampoule to room temperature, it is opened and the pellets reground in an agate mortar. The resulting powder is mixed and pressed into pellets, which are again sealed into an evacuated quartz ampoule and annealed for 60 hours at 800° C. Resulting material is single phase possessing a Curie temperature of −8° C., σ_0 equals 52 gauss cm.^{3}/gram and ρ equals 0.15 ohm-cm.

EXAMPLE 3

Preparation of the compound: $Fe_{.5}Cu_{.5}Cr_2S_4$

0.5585 gram Fe, 0.6354 gram Cu, 2.0800 grams Cr and 2.5651 grams S are mixed, pressed into pellets and annealed in an evacuated quartz ampoule at 800° C. for 48 hours. The ampoule is cooled to room temperature, then opened, and the pellets ground. Resulting powder is mixed again, pressed into pellets and annealed in an evacuating quartz ampoule for 60 hours at 800° C. Resulting material is of a single phase possessing a Curie temperature of +87° C., σ_0 equals 55 gauss cm.^{3}/gram and ρ equals one omh-cm.

EXAMPLE 4

Preparation of the compound: $Fe_{.3}Cu_{.7}Cr_2S_4$

0.3351 gram Fe, 0.8896 gram Cu, 2.0800 grams Cr and 2.5651 grams S are pressed into pellets, sealed in an evacuated quartz ampoule and after slowly heating to 700° C. are kept at this temperature for 50 hours. After cooling to room temperature, the ampoule is opened, the material ground, mixed, pressed into pellets and annealed in an evacuated quartz ampoule at 700° C. for 70 hours. Resulting material is of a single phase and possesses a Curie temperature of +92° C., σ_0 equals 65 gauss cm.^{3}/gram and ρ equals 5×10^{-2} ohm-cm.

EXAMPLE 5

Preparation of the compound: $Fe_{.1}Cu_{.9}Cr_2S_4$

0.1136 gram Fe, 1.1630 grams Cu, 2.1151 grams Cr and 2.6083 grams S are mixed, pressed into pellets, and fired for 60 hours at 550° C. in an evacuated quartz ampoule. After cooling to room temperature and opening the ampoule, the material is again ground, mixed, pressed into pellets and annealed for 75 hours at 65° C. in an evacuated quartz ampoule. Resulting material is of a single phase and possesses a Curie temperature of +97° C., σ_0 equal 85 gauss cm.^{3}/gram and ρ equals 1×10^{-2} ohm-cm.

EXAMPLE 6

Preparation of the compound: $Fe_{.125}Cu_{.875}Cr_2Se_4$

0.0349 gram Fe, 0.2780 gram Cu, 0.5200 gram Cr and 1.5792 grams Se are mixed, pressed into pellets and fired for 60 hours at 650° C. in an evacuated quartz ampoule. A second firing is done at 600° C. Resulting material is single phase with a Curie temperature of +107° C., σ_0 equals 52 gauss cm.^{3}/gram and ρ equals 5×10^{-3} ohm-cm.

EXAMPLE 7

Preparation of the compound: $Fe_{.1}Cu_{.9}Cr_2S_{3.64}Se_{.36}$

0.1075 gram Fe, 1.1000 grams Cu, 2.0006 grams Cr and 2.2451 grams S and 0.5468 grams Se are mixed, pelletized and fired at 600° C. for four days in an evacuated quartz ampoule. A second firing is performed at 550° C. for three days. A third annealing is required at 600° C. for four days. Resulting material is single phase and has a Curie temperature of +77° C., σ_0 equals 61 gauss cm.^{3}/gram and ρ equals 10^{-2} ohm-cm.

Advantageously, the spinel structure of the present invention can be incorporated into a magnetic switch useful in automatic control and alarm devices. Such switches are found to consume substantially little electrical power. This is attributed to the high magnetization saturation value of the compounds of the invention.

We claim:

1. A semi-conducting, magnetic, single phase spinel structure having the formula:

$$Fe_{1-x}Cu_xCr_2D_4$$

wherein x is a value greater than 0 but less than 1 and D is an element selected from the group consisting of sulfur, selenium and mixtures thereof, said structure possessing a Curie temperature range between about −80° C. and +130° C. and a saturation magnetization between about 40 and about 90 gauss cm.^{3}/gram.

2. The compound according to claim 1 wherein x is 0.1 and D is sulfur.

3. The compound according to claim 1 wherein x is 0.2 and D is sulfur.

4. The compound according to claim 1 wherein x is 0.5 and D is sulfur.

5. The compound according to claim 1 wherein x is 0.7 and D is sulfur.

6. The compound according to claim 1 wherein x is 0.9 and D is sulfur.

7. The compound according to claim 1 wherein x is 0.9 and D is selenium.

8. The compound according to claim 1 wherein x is equal to 0.125 and D is selenium.

9. The compound according to claim 1 wherein x is equal to 0.1 and D is both $S_{3.64}$ and $Se_{0.36}$.

References Cited

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U.S. Cl. X.R.

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CERTIFICATE OF CORRECTION

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It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 46, "65° C." should read -- 650° C. --.

Signed and sealed this 21st day of April 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents