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FERROMAGNETIC COMPOUNDS AND METHOD OF PREPARATION

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ABSTRACT OF THE DISCLOSURE

The new rare earth compounds: Gd_2Bi, Gd_2Sb and Dy_2Sb and their solid solutions: $Gd_2(Bi_{1-x}Sb_x)$,

$$(Gd_{1-z}Dy_z)_2Sb$$

and $(Gd_{1-z}Dy_z)_2$ $(Sb_{1-x}Bi_x)$ are prepared. The constituent elements are powdered, mixed and heated in an airtight crucible to a temperature of 1300° C. and then cooled to room temperature. The new compounds and their solid solutions are ferromagnetic and exhibit varying Curie temperatures. The members of the class can be used in thermal control and safety devices.

This invention relates to new rare earth compounds and, more particularly, to those compounds having the formula: Gd_2Bi, Gd_2Sb and Dy_2Sb and solid solutions thereof. These new compounds either when pure or in solid solutions are ferromagnetic.

The rare earth metals and their compounds are important magnetic materials because they exhibit higher magnetic moments than the iron group metals (e.g., Fe, Co, and Ni) and their compounds.

The magnetic moment of the rare earth elements is either the sum or difference of the spin and orbital moments of the unpaired electrons in the *4f* shell, the difference resulting for the lighter and the sum for the heavier elements. The outer bonding orbitals effectively shield the *4f* shell so that chemical bond formation has little effect on the total magnetic moment. In contrast, the unpaired *3d* electrons of the iron group metals are directly involved in bond formation and magnetic coupling so that compounds and alloys of these elements generally have different moments.

Heretofore, most investigations of rare earth systems with Group V_a elements (e.g., N, P, As, Sb, and Bi) have been confined to the study of 1:1 compounds (Iandelli, A., "Rare Earth Research," Macmillan, New York, 1961, pages 135–151) or rare earth rich systems of the lighter rare earths (La and Ce) (Gschneidner, "Rare Earth Alloys," Van Nostrand, New York, 1961, pages 111–115).

An example of rare earth rich systems can be found in application S.N. 299,180 entitled "Ferromagnetic Compounds and Method of Preparation," by F. Holtzberg, et al.

It is an object of the invention to prepare ferromagnetic compounds.

It is another object of the invention to prepare new rare earth compounds which are ferromagnetic.

It is a further object of the invention to prepare rare earth compounds having the formula Gd_2Bi, Gd_2Sb and Dy_2Sb.

Still another object of the invention is to prepare rare earth solid solution systems which are ferromagnetic.

Another object of the invention is to prepare a ferromagnetic compound having the formula Gd_2Bi.

Still another object of the invention is to prepare a ferromagnetic compound having the formula Gd_2Sb.

Still another object of the invention is to prepare a ferromagnetic compound having the formula Dy_2Sb.

The foregoing and other objects, features and advantages of the invention will become apparent from the more particular description of a preferred embodiment of the invention.

The rare earth compounds of the invention have the formula Gd_2Bi, Gd_2Sb and Dy_2Sb and crystallize with a hexagonal structure.

Pure rare earth metal ingots (99.9 percent pure) of Gd and Dy are filed into powders in a dry oxygen free atmosphere (e.g., He, Ar, N). Rare earth metal filings are then mixed with antimony or bismuth metal (99.9 percent pure) and pressed into pellets which are then placed in a crucible which is made of a material which does not enter into the reaction (e.g., tantalum or molybdenum). The size of the pellet is such that the pellet provides a piston fit to the crucible. A tapered plug of crucible material is forced into the crucible so that it presses on the surface of the pellets in order to exclude as much dead (i.e., empty) volume as possible. The tight fit and small particle size are necessary because if there is dead (or empty) space in the crucible the Sb or Bi vapor will condense out on cooling and result in inhomogenous products. If the particles are too large, the high reaction temperature will vaporize the Sb or Bi before the reaction is completed and force the vapor out of the crucible. The excess tantalum above the plug is then peened over to form a tight closure so that Bi or Sb vapor pressure produced during the reaction can be contained within the crucible. The crucible is then placed on a pedestal in a quartz vacuum system centered in a radio frequency induction heating coil. An ambient atmosphere of helium is often used in place of the vacuum. Power is delivered to the coil at a rate such that the crucible temperature rises to 1300° C. within approximately 10–30 seconds. The temperature is maintained at 1300° C. for 15 minutes and the sample is then cooled to room temperature. When the tantalum crucible is opened, the compound appears as a dense metallic ingot.

The new rare earth compounds are brittle metallic materials which oxidize slowly when exposed to air and are pyrophoric in finely powdered form.

Although the chemistry of the rare earths is relatively uniform, there are differences in the crystallization which can arise from the differences in radii and probably from differences in electronic configurations. Certain compounds herein described result as the primary crystallization from the melt and required no further heat treatment. Others, however, crystallize as incongruent compounds and will always contain some second phase if cooled to room temperature without further heat treatment. Further heat treatment raises the temperature of the sample to the incongruent decomposition temperature in order to increase the diffusion rates to permit the compound to form under equilibrium conditions and yield a pure phase, viz., the 2:1 compound.

In certain cases, it is possible to obtain incongruently melting material with sufficient purity by the specific thermal treatment described in the examples.

Example I—Gd_2Bi

3.1454 grams of Gd is filed into a fine powder in a dry box and the filings mixed with 2.0900 grams of powdered bismuth metal. The mixture is then pressed into pellets in a nitrogen purged dry box. These pellets are then placed in an out-gassed tantalum crucible. The tapered tantalum plug is forced into the crucible so that it presses on the surface of the pellet in order to exclude as much dead volume as possible. The excess tantalum above the plug is then peened over to form a gas-tight

closure. This crucible is now placed on a pedestal in a quartz vacuum system centered in a R.F. induction coil. The temperature of the crucible is raised to a temperature of about 1300° for 15 minutes. The cooling of the crucible after completion of the reaction is controlled by radiative heat losses in the vacuum. When the crucible is at room temperature, it is cut open and the resultant product Gd_2Bi appears as a dense metallic ingot.

Example II—Gd_2Sb

The procedure of Example I is repeated except that 1.2175 grams of antimony are substituted for the bismuth. The resultant product is Gd_2Sb.

Example III—Dy_2Sb

3.2500 grams of Dy is filed into a fine powder in a dry box and the filings mixed with 1.2175 grams of powdered antimony. This mixture is then pressed into pellets in a nitrogen purged dry box. These pellets are then placed in an out-gassed tantalum crucible. The tapered tantalum plug is forced into the crucible so that it presses on the surface of the pellet in order to exclude as much dead volume as possible. The excess tantalum above the plug is then peened to form a gas-tight closure. This crucible is now placed on a pedestal in a quartz vacuum system centered in a R.F. induction coil. The temperature of the crucible is raised to 1400° C. and held there for 15 minutes. Then the crucible is rapidly cooled to room temperature. The resultant product is Dy_2Sb.

Dy_2Sb has a positive paramagnetic Curie Temperature (θ_p) of 110° K. which indicates at least a partial ferromagnetic interaction.

Solid solution systems of the rare earth compounds of the invention have the formulas:

$Gd_2(Bi_{1-x}Sb_x)$
(where $1>x>0$);
$(Gd_{1-z}Dy_z)_2Sb$
(where $1>z>0$); and
$(Gd_{1-z}Dy_z)_2(Sb_{1-x}Bi_x)$
(where $1>x>0$ and $1>z>0$)

These rare earth solid solution systems are ferromagnetic and since their Curie temperatures are a rapidly varying function of composition they can be used to prepare a series of materials with Curie temperatures arbitrarily selected from a continuous range of Curie temperatures and thus find application in thermal control and safety devices. The solid solution systems are prepared in much the same manner as the rare earth compounds.

The initial mixture is prepared by weighting and thoroughly mixing the component materials (i.e., rare earths and metalloids) in finely divided form as specified for any of the examples set forth in Table I. The mixture is then pressed into pellets and heated in a sealed tantalum crucible as in the procedure set forth for the pure compounds as prepared in Example I.

The solid solution systems prepared as shown in Examples IV–VI have the formula for each of the respective examples.

The procedure of Example I is followed except that the quantities indicated for each example in Table I are used, intimately mixed and then pressed into pellets. The resulting products is a solid solution system having the formula indicated for each example.

TABLE I

Example No.	Weight in Grams				Solid Solution System Formula
	Gd	Dy	Bi	Sb	
IV	3.1454		1.2539	0.4870	$Gd_2Bi_{0.6}Sb_{0.4}$
V	1.5727	1.6250		1.2175	$(Gd_{0.5}Dy_{0.5})_2Sb$
VI	1.1009	0.4875	1.0449	0.6088	$(Gd_{0.7}Dy_{0.3})_2Bi_{0.5}Sb_{0.5}$

The solid solutions show a linear variation of lattice constant with z which can be used to determine the ratio of Gd to Dy. The Curie temperature varies as a function of concentration of the rare earth atom. The magnetic moments of the solid solutions are an average of the individual rare earth moments weighted on the basis of their concentrations.

The solid solutions $Gd_2(Bi_{1-x}Sb_x)(Gd_{1-z}Dy_z)_2Sb$, and $(Gd_{1-z}Dy_z)_2Sb_{1-x}Bi_x$ have the average physical properties of the above solid solutions, i.e., the average moment of the rare earth part of the solid solution will vary rapidly as a function of the Sb and Bi concentration or conversely given a ratio of Sb to Bi the moment is the average of the moments of Gd and Dy according to their concentrations.

The invention herein described results in new rare earth compounds having the formulas, Gd_2Bi, Gd_2Sb, Dy_2Sb, $Gd_2(Bi_{1-x}Sb_x)$, $(Gd_{1-z}Dy_z)_2Sb$ and $(Gd_{1-z}Dy_z)_2Sb_{1-x}Bi_x$ and their preparation. As has been shown, these compounds either in their pure state or in solid solution systems are ferromagnetic.

While the invention has been particularly described with reference to preferred embodiments 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 rare earth compound selected from the group consisting of Gd_2Bi, Gd_2Sb and Dy_2Sb.

2. The rare earth compound Gd_2Bi.

3. The rare earth compound Gd_2Sb.

4. The rare earth compound Dy_2Sb.

5. The process of preparing a rare earth compound selected from the group consisting of Gd_2Bi, Gd_2Sb and Dy_2Sb which comprises:

(a) mixing together in finely divided form the rare earth constituent and the Group VA constituent of said rare earth compound in a 2:1 molar ratio;

(b) heating the thus formed mixture in a sealed crucible in a vacuum to a temperature of 1300° C. thus initiating a reaction;

(c) cooling to room temperature upon completion of said reaction.

6. A rare earth solid solution system having a formula $(Gd_{1-z}Dy_z)_2Sb$ where $1>z>0$.

7. A rare earth solid solution system having a formula $Gd_2(Sb_{1-x}Bi_x)$ where $1>x>0$.

8. A rare earth solid solution system having a formula $(Gd_{1-z}Dy_z)_2(Sb_{1-x}Bi_x)$ where $1>z>0$ and $1>x>0$.

9. The rare earth solid solution system having the formula$Gd_2Bi_{0.6}Sb_{0.4}$.

10. The rare earth solid solution system having the formula $(Gd_{0.5}Dy_{0.5})_2Sb$.

11. The rare earth solid solution system having the formula $(Gd_{0.7}Dy_{0.3})_2(Sb_{0.5}Bi_{0.5})$.

12. The process of preparing a rare earth solid solution system having the formula $(Gd_{1-z}Dy_z)_2Sb$ where $1>z>0$ which comprises:

(1) mixing together in finely divided form Gd, Dy and Sb in proportions such that the solid solution system produced by heating has the above formula;

(2) heating the thus formed mixture in a sealed tantalum crucible placed in an evacuated quartz radio frequency induction heater to a temperature of 1300° C. thus initiating a reaction;

(3) cooling to room temperature on completion of said reaction.

13. The process of preparing a rare earth solid solution system having the formula $Gd_2Sb_{1-x}Bi_x$ where $1>x>0$ which comprises:

(1) mixing together in finely divided form Gd, Sb and Bi in proportions such that the solid solution system produced by treating has the above formula;

(2) heating the thus formed mixture in a sealed tantalum crucible placed in an evacuated quartz radio frequency induction heater to a temperature of 1300° C. thus initiating a reaction;

(3) cooling to room temperature on completion of said reaction.

14. The process of preparing a rare earth solid solution system having the formula $(Gd_{1-z}Dy_z)_2(Sb_{1-x}Bi_x)$ where $1>z>0$ and $1>x>0$ which comprises:

(1) mixing together in finely divided form Gd, Dy, Sb and Bi in proportions such that the solid solution system produced by treating has the above formula;

(2) heating the thus formed mixture in a sealed tantalum crucible placed in an evacuated quartz radio frequency induction heater to a temperature of 1300° C. thus initiating a reaction;

(3) cooling to room temperature on completion of said reaction.

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