Classroom Photocopying Permission

Laboratory Safety

DISCLAIMER

Safety information is included in each chapter of the Companion as a precaution to the readers. Although the materials, safety information, and procedures contained in this book are believed to be reliable, they should serve only as a starting point for laboratory practices. They do not purport to specify minimal legal standards or to represent the policy of the American Chemical Society. No warranty, guarantee, or representation is made by the American Chemical Society, the authors, or the editors as to the accuracy or specificity of the information contained herein, and the American Chemical Society, the authors, and the editors assume no responsibility in connection therewith. The added safety information is intended to provide basic guidelines for safe practices. Therefore, it cannot be assumed that necessary warnings or additional information and measures may not be required. Users of this book and the procedures contained herein should consult the primary literature and other sources of safe laboratory practices for more exhaustive information. See page xxv in the Text 0 Preface file in the Companion Text folder for more information.

Experiment 14

Magnetic Garnets, $Y_xGd_{3-x}Fe_5O_{12}$

Margret J. Geselbracht, Ann M. Cappellari, Arthur B. Ellis, Maria A. Rzeznik, and Brian J. Johnson

Notes for Instructors

Purpose

To determine the magnetic properties of the $Y_xGd_{3-x}Fe_5O_{12}$ ($0 \leq x \leq 3$) family of solid solutions.

Method

Each student prepares $Y_xGd_{3-x}Fe_5O_{12}$ for a particular value of $0 \leq x \leq 3$ (*see* Chapter 3). The sample is prepared from a mixed metal hydroxide precursor by firing in a furnace at 900 °C for 18–24 hours. A visible color change from reddish-brown to olive green indicates that a reaction has taken place. The strength of the attraction of the garnet product to a strong magnet is observed at room temperature, dry-ice temperature, and liquid-nitrogen temperature. Above a characteristic compensation temperature (*see* literature values in Table 1), a sample pellet will be attracted to a strong magnet.

2725-X/93/0455$06.00/1

Table 1. Compensation Temperature, T_{comp}, for $Y_xGd_{3-x}Fe_5O_{12}$

Composition	T_{comp} (K)
$Y_3Fe_5O_{12}$	—[a]
$Y_{2.7}Gd_{0.3}Fe_5O_{12}$	—[b]
$Y_{2.1}Gd_{0.9}Fe_5O_{12}$	—[b]
$Y_{2.0}Gd_{1.0}Fe_5O_{12}$	70
$Y_{1.8}Gd_{1.2}Fe_5O_{12}$	93
$Y_{1.2}Gd_{1.8}Fe_5O_{12}$	158
$Y_{1.0}Gd_{2.0}Fe_5O_{12}$	175
$Y_{0.6}Gd_{2.4}Fe_5O_{12}$	218
$Gd_3Fe_5O_{12}$	289

[a]No compensation temperature was observed down to 5 K.
[b]No compensation temperature was observed down to 73 K.
SOURCE: Data were taken from Harrison, G. R.; Hodges, L. R., Jr. *J. Appl. Phys.* **1962**, *33*, 1375–1376 and Geselbracht, M. J.; Cappellari, A. M.; Ellis, A. B.; Rzeznik, M. A.; Johnson, B. J. *J. Chem. Educ.*, in press.

Materials

1 M aqueous solution of $Y(NO_3)_3{\cdot}5H_2O$ (an average of about 3 mL per student, *see* Table 2)

1 M aqueous solution of $Gd(NO_3)_3{\cdot}6H_2O$ (3 mL per student)

1 M aqueous solution of $FeCl_3{\cdot}6H_2O$ (10 mL per student)

6 M NaOH (10 mL per student)

pH paper

Funnels and filter paper

Drying oven (120 °C)

Firing oven (900 °C)

Strong magnet (cow magnet or rare earth magnet; *see* Supplier Information)

Table 2. Volumes of Reagents to Synthesize $Y_xGd_{3-x}Fe_5O_{12}$

x	mL of Gd^{3+} Solution	mL of Y^{3+} Solution
0	6.0	0
0.6	4.8	1.2
1.0	4.0	2.0
1.2	3.6	2.4
1.5	3.0	3.0
1.75	2.5	3.5
2.0	2.0	4.0
2.25	1.5	4.5
3	0	6.0

X-ray Powder Diffraction

The powder diffraction pattern of the sample with the nominal composition $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ is shown in Figure 1. The major product of the reaction is the garnet phase, $R_3Fe_5O_{12}$ (R is a rare earth element). The peaks indicated with an asterisk in Figure 1 are due to $RFeO_3$, which is a common impurity in samples of $R_3Fe_5O_{12}$. Grinding the olive green solid, repelletizing, and firing a second time at 900 °C (or higher temperatures) for 24 hours led to a noticeable decrease in the intensities of the peaks of the impurity phase in the diffraction pattern. The presence of a small amount of the $RFeO_3$ phase in the samples does not adversely affect the investigation of the magnetic properties in this experiment.

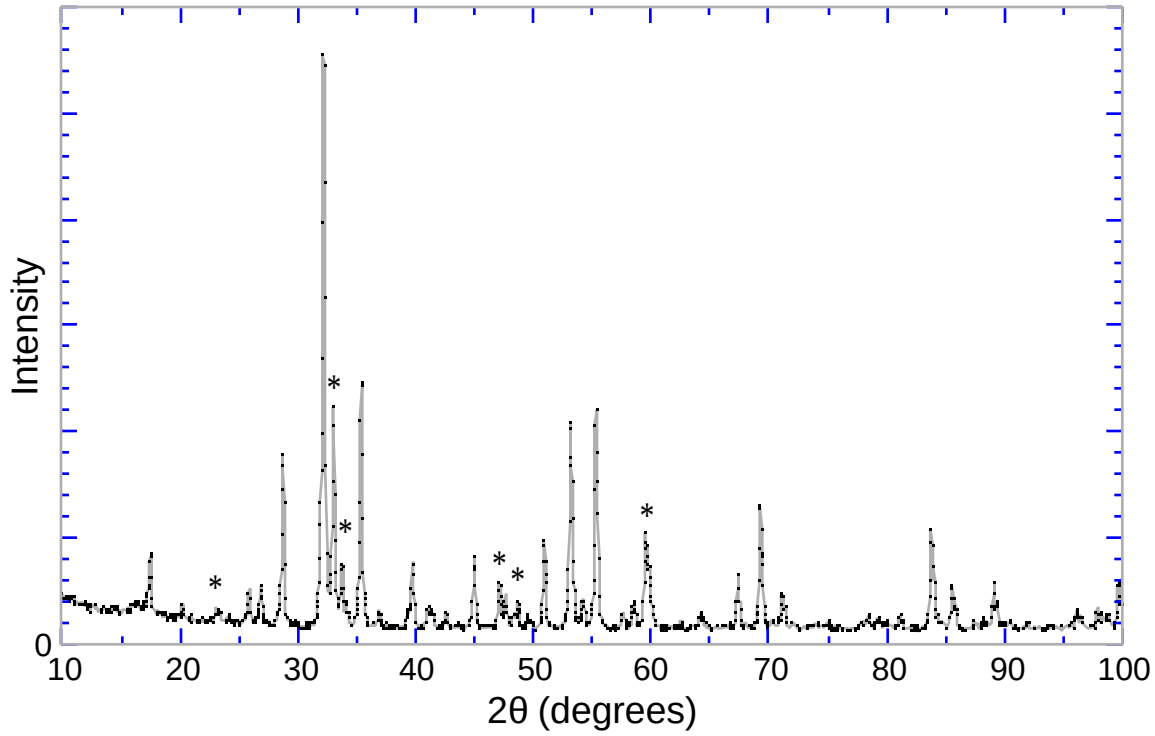

Figure 1. X-ray powder diffraction pattern of a sample of $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ prepared via a mixed metal hydroxide precursor. Diffraction peaks that are marked with an asterisk correspond to the impurity $RFeO_3$ (R is Y or Gd).

Acknowledgement

We thank Professor Francis DiSalvo of Cornell University for the original suggestion of this laboratory experiment.

Magnetic Garnets, $Y_xGd_{3-x}Fe_5O_{12}$

Purpose

To determine the magnetic properties of the $Y_xGd_{3-x}Fe_5O_{12}$ ($0 \le x \le 3$) family of solid solutions.

Introduction

In the majority of molecules and solids that we encounter, all of the electrons are paired, and the molecule or solid is said to be diamagnetic. Some solids exhibit interesting magnetic behavior due to the cooperative effect of many electrons in the solid acting in concert. Ferromagnetism is such a property and is exploited in the use of permanent magnets, magnetic recording media, and transformers.

Garnets are a family of solids exhibiting cooperative magnetic behavior. Their magnetic properties depend on composition (the presence of magnetic ions), on the underlying crystal structure (the geometrical arrangement of the ions in three dimensions), and on temperature. The garnets can form solid solutions that permit changing the composition of the solid without disrupting the crystal structure. This condition allows the magnetic properties of the family to be tuned while preserving the crystal structure. Rare earth iron garnets, $R_3Fe_5O_{12}$, can be prepared with all of the rare earth ions, R, except La, Ce, Pr, or Nd.

Structure

Gadolinium iron garnet (GIG) and yttrium iron garnet (YIG) are members of the garnet structural family of complex oxides. The general formula for a garnet is $C_3A_2D_3O_{12}$ where the C cations occupy dodecahedral sites, the A cations occupy octahedral sites, and the D cations occupy tetrahedral sites in the crystal structure. The unit cell of the garnet structure has cubic symmetry and contains eight formula units for a total of 160 atoms. A portion of the unit cell of $Gd_3Fe_5O_{12}$ is drawn in Figure 1 with only the cations and selected oxygen atoms shown for clarity.

In the case of $Gd_3Fe_5O_{12}$, Gd^{3+} occupies dodecahedral sites and Fe^{3+} occupies both octahedral and tetrahedral sites in the structure. However, a wide variety of cations in different valence states can reside in the cation

NOTE: This experiment was written by Margret J. Geselbracht, Ann M. Cappellari, and Arthur B. Ellis, Department of Chemistry, University of Wisconsin—Madison, Madison, WI 53706; Maria A. Rzeznik, Department of Chemistry, University of California Berkeley, Berkeley, CA 94720; and Brian J. Johnson, Department of Chemistry, St. John's University and the College of St. Benedict, St. Joseph, MN 56374.

sites, as the primary consideration for site occupancy is ionic size. This capacity leads to many compositions that form the garnet structure.

Because of the similarity in ionic radii of the rare earth ions, many rare earth iron garnets will form solid solution phases. In the case of yttrium (ionic radius = 0.900 Å) and gadolinium (ionic radius = 0.938 Å), the complete family of solid solutions can be prepared: $Y_xGd_{3-x}Fe_5O_{12}$ ($0 \leq x \leq 3$). Substitution of yttrium for gadolinium occurs on the dodecahedral site. Gd^{3+} is slightly larger than Y^{3+}; hence, the lattice parameter, *a* (the length of the side of the cubic unit cell), would be expected to increase with increasing gadolinium content. This trend is clearly seen in the data presented in Table 1.

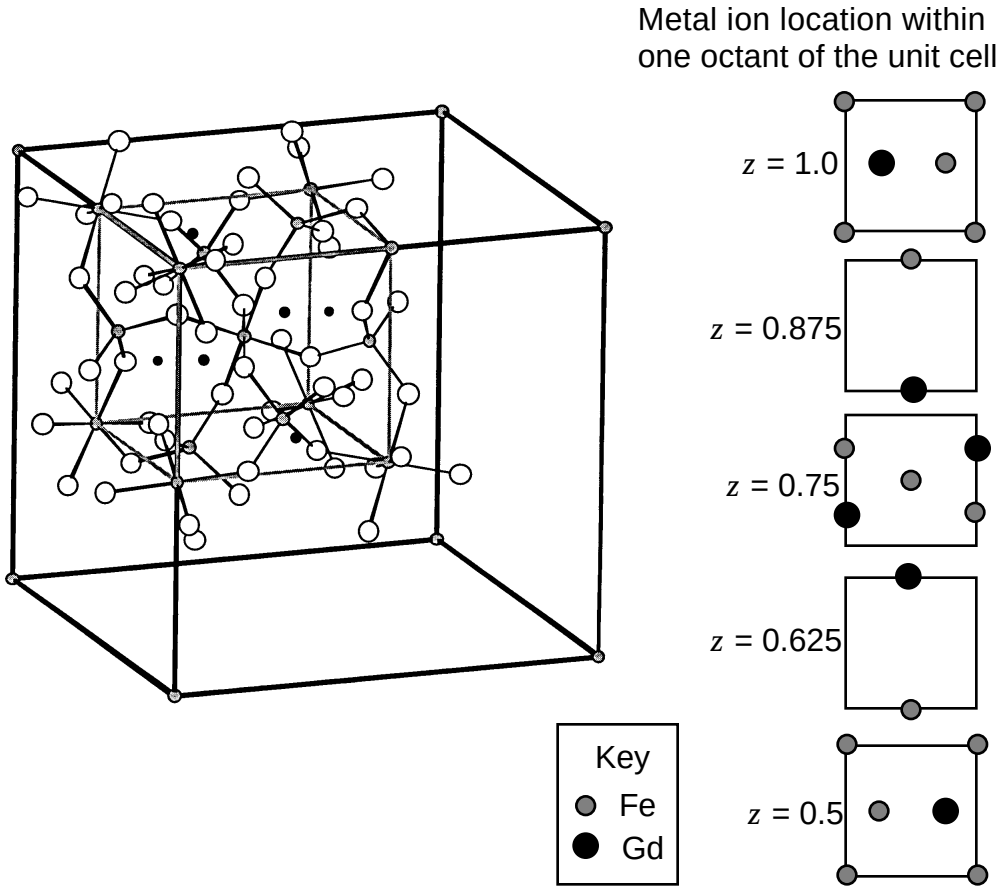

Figure 1. Portion of the unit cell of the garnet structure of $Gd_3Fe_5O_{12}$ is shown at left. All of the metal ions in one-eighth of the unit cell are drawn along with the oxygen ions that complete the octahedral or tetrahedral coordination around the iron atoms. The rest of the atoms have been deleted for clarity. At the right, horizontal sections perpendicular to the *z* direction are shown to indicate the positions of the iron and gadolinium ions within this octant of the unit cell.

Table 1. Variation in Cubic Unit-Cell Parameter, *a*, with *x* for $Y_xGd_{3-x}Fe_5O_{12}$

Composition	Lattice Parameter (Å)
$Y_3Fe_5O_{12}$	12.370
$Y_{2.5}Gd_{0.5}Fe_5O_{12}$	12.382
$Y_2Gd_1Fe_5O_{12}$	12.402
$Y_{1.5}Gd_{1.5}Fe_5O_{12}$	12.423
$Y_1Gd_2Fe_5O_{12}$	12.437
$Y_{0.5}Gd_{2.5}Fe_5O_{12}$	12.450
$Gd_3Fe_5O_{12}$	12.468

Magnetic Properties

For the material $Y_3Fe_5O_{12}$, the Fe^{3+} ions (with five unpaired electrons) in the octahedral holes have their electron spins aligned in the opposite direction from those of the Fe^{3+} ions (also with five unpaired electrons) in the tetrahedral holes. However, because three tetrahedral sites and two octahedral sites are present in the garnet formula, a net magnetic moment of five unpaired electrons per formula unit results. No magnetic contribution comes from the closed-shell yttrium ion. Thus, $Y_3Fe_5O_{12}$ is strongly magnetic at all temperatures.

At the other extreme in the solid solution, $Gd_3Fe_5O_{12}$ has the same net five unpaired electrons from the two kinds of iron sites. But, in addition, each Gd^{3+} ion (there are three in the garnet formula) has seven unpaired electrons. The electrons in the gadolinium sites have their electron spins aligned opposite to those of the net five unpaired electrons of the iron atoms in tetrahedral sites. This feature suggests that the magnetic moment of $Gd_3Fe_5O_{12}$ should be 16 (=3 × 7 – 5) unpaired electrons. This result is true if the magnetic moment is measured at very low temperatures. However, the unpaired electrons associated with Gd^{3+} ions and with Fe^{3+} ions thermally randomize their spins to different extents as a function of temperature. The net result is a compensation temperature, T_{comp}, where the net magnetization is zero. In $Gd_3Fe_5O_{12}$, the compensation temperature is just below room temperature.

The effect of combining both yttrium and gadolinium in the garnet structure in the solid solution compounds is that the compensation temperature becomes a strong function of composition, that is, it can be tuned.

Procedure

Wear eye protection.

CAUTION: The yttrium and gadolinium compounds used in this experiment are oxidizing agents and irritants. Avoid creating or breathing dust. Avoid eye and skin contact. Wash your hands thoroughly after handling.

Synthesis

You will prepare one member of the $Y_xGd_{3-x}Fe_5O_{12}$ family, that is, you will be assigned a particular value of x. A description of the synthesis of $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ via a mixed metal hydroxide precursor follows. Other compositions in the series can be prepared by varying the volumes of $Gd(NO_3)_3$ and $Y(NO_3)_3$ used, such that the amount of $Gd(NO_3)_3$ plus the amount of $Y(NO_3)_3$ totals 6 mL.

Put 10 mL of 1 M $FeCl_3$ in a beaker. Add 3 mL of 1 M $Gd(NO_3)_3$ solution and 3 mL of 1 M $Y(NO_3)_3$ solution. Add 5–10 mL of 6 M NaOH dropwise to the metal ion solution in order to precipitate a reddish-brown solid. Decant the solution, and wash the remaining solid repeatedly with water until the wash is no longer basic (test with pH paper). Filter and dry the solid in a drying oven (120 °C) overnight.

Press the powder into 1/2-inch-diameter pellets using a standard pellet press, and fire in a furnace at 900 °C for 18–24 hours. A visible color change from reddish-brown to olive green after firing indicates that a reaction has taken place.

Magnetic Properties

Determine the strength of the attraction of your pellet of garnet to a strong magnet at room temperature, dry-ice temperature, and liquid-nitrogen temperature. Discuss your procedure with other students in the class and agree on a method that will allow comparison of the magnetic effects as a function of the garnet composition.