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Magnetic Properties of $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ Garnets

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ABSTRACT

A comprehensive study of the magnetic properties of $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ ($0 \le x \le 1$) has been performed. The garnet ferrites samples were prepared by the ceramic technique, and X-ray diffraction analysis indicates the formation of single cubic phase. Vibrating sample magnetometry (VSM) and a superconducting quantum-interference device (SQUID) were used to measure the magnetic properties, especially the magnetization and thermo-magnetic behavior. The magnetization curves exhibit the typical characteristics of ferrimagnetic materials at both 4.2 K and at room temperature. The samples have a low coercivities (between 20 and 40 Oe) and saturation magnetizations as high as 36 emu/g at 4.2 K. The saturation magnetization decreases with V and Ca contents, reaching about 8 emu/g at 4.2 K ($x = 1$). For all samples, the saturation magnetization decreases with increasing temperature, whereas the Curie temperature increases for small values of x, from 557 K for $x = 0$ to a maximum of 590 K for $x = 0.2$. For larger values of x, it decreases and reaches 525 K for $x = 1.0$. The basic experimental trends reflect the occupancy of the tetrahedral 24d sites by vanadium in combination with the predominant intersublattice exchange constant J_{ad}, although the nonzero magnetization at $x = 1.0$ indicates that about 10% of the substituted V atoms goes onto the octahedral 16a sites.

Keywords: Yttrium Iron Garnets; Curie Temperature; Saturation Magnetization; Magnetic Moment

1. Introduction

Many ferrites are valued as soft-magnetic materials, because they combine good high-frequency dielectric properties with ferrimagnetic order. They are widely used in applications such as microwave devices, transformers, electric generators, bio-processing, and storage devices [1-8]. The properties of the ferrites can be tailored in different ways, especially by chemical substitutions and by controlling the preparation method [9-17]. This is important for element-strategic reasons, such as the need to replace rare-earth elements.

Ferrites crystallize in a variety of crystal structures, such as spinel, garnet, and magnetoplumbite. The yttrium iron garnets (YIG) has a cubic structure composed from 160 atoms with the general formula $Y_3A_2B_3O_{12}$, where Y ions occupy the 24c sites in the Wyckoff notation, Fe the octahedral 16a and tetrahedral 24d sites, and oxygen the 96h sites. YIG is a ferrimagnets where the Fe atoms on the octahedral sites couple antiferromagnetically to the Fe atoms on the tetrahedral sites ($J_{ad} < 0$). The intrasublattice interactions J_{aa} and J_{dd} are less important [18], and there is no coupling to the 24c sublattice, because yttrium is a nonmagnetic rare earth. There are three tetraheral and two octahedral sizes per formula unit, corre-sponding to a net moment of $[5\ (3 - 2)\ \mu_B] = 5\ \mu_B$. The garnets are chemically very stable, have high Curie temperatures (about 500 to 550 K), high electrical resistivities, and low dielectric losses over a wide range of frequencies.

Various YIG substitutions have been investigated in the past. Kim *et al.* [19] studied the effects of substitution of Fe by Al on the crystallographic and magnetic properties of YIG garnet and found that Al prefers the 24d-tetrahedral sites, and the lattice constant decreases linearly with increasing the Al concentration. They also found that the saturation magnetization for the parent compound is about 33 emu/g at room temperature and it decreases with increasing the Al concentration, at room temperature and at 77 K. Different studies for the substitution of Y by other elements such as Tb [9], Sm [10], Gd [16], Bi [17], and Ce [13], indicate that the saturation magnetization tends to decrease with decreasing Y content. Furthermore, these papers show that the saturation magnetization depends on the preparation method. Furthermore, nanoparticles having sizes between 30 nm to 70 nm exhibit a magnetization that decreases with decreasing particle size due to the surface-spin effects.

The objectives of the present work are to prepare a se-

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ries of $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnet ferrites (x = 0.2, 0.4, 0.6, 0.8, 1.0) between 0.0 and 1.0) and to study the magnetic properties of these garnet ferrites at different temperatures. In these ferrites each V^{5+} ion requires two Ca^{2+} ions for electrostatic compensation [20], and the amount of Y^{3+} ions required is considerably reduced compared with the tetravalent or trivalent ion substitution.

2. Experimental Methods

A series of $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnet ferrites (x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) samples were prepared by ceramic technique. First, the appropriate masses of Y_2O_3, CaO, Fe_2O_3, and V_2O_5 were grounded using an agate mortar, followed by wet-mixing in acetone for 1 hr. Second, the mixtures were dried and annealed at 1500˚C for 15 hrs, followed by mechanical milling for 1 hr. Finally, they were sintered at 900˚C for 8 hrs. The samples were characterized by powder x-ray diffraction using a Philips diffractometer with Cu-K_α radiation. The magnetic properties were measured by vibrating sample magnetometry (VSM) in magnetic fields of up to 13.5 kOe and in the temperature range 77 - 1000 K. A superconducting quantum-interference device (SQUID) was used in magnetic fields up to 70.0 kOe and in the temperature range 4.2 - 300 K. The correct cubic crystal structure has been confirmed by x-ray diffraction (XRD) analysis.

3. Results and Discussion

Figure 1 Shows a typical x-ray diffraction pattern for a representative sample of the $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnet ferrites, with x = 0.2. All samples studied in this paper show similar XRD patterns with a shift in the peaks' positions due to the increase in the lattice constant. All the pecks are indexed with the cubic crystal structure indicating a single cubic phase for all the concentrations.

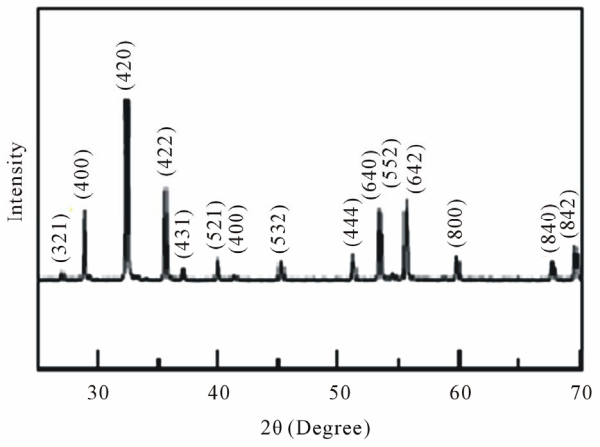

Figure 1. Typical x-ray diffraction pattern for a representative sample of the $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnet ferrites, with x = 0.2.

Figure 2 shows the linear dependence of the lattice constant (a) on the concentration x, where a = (12.375 + 0.057x). The lattice constant for the parent compound (x = 0) is (12.375 ± 0.002) Å and it increases linearly with increasing concentration x, reaching (12.432 ± 0.002) Å for x = 1.0. This value for x = 0.0 is in good agreement with previous reported value of 12.381 Å by Kim *et al.* [21] for $Y_3Fe_5O_{12}$ garnet ferrite.

Figure 3 shows the temperature dependence of the magnetization for the different $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ samples in an applied magnetic field of 13.5 kOe. All samples order ferrimagnetically below the Curie temperature T_c. Using the method of intersecting tangents for the M vs. T curves we obtained the Curie temperatures for the different $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnet ferrites. For small values of x, T_c increases from 557 K at x = 0, reaches a

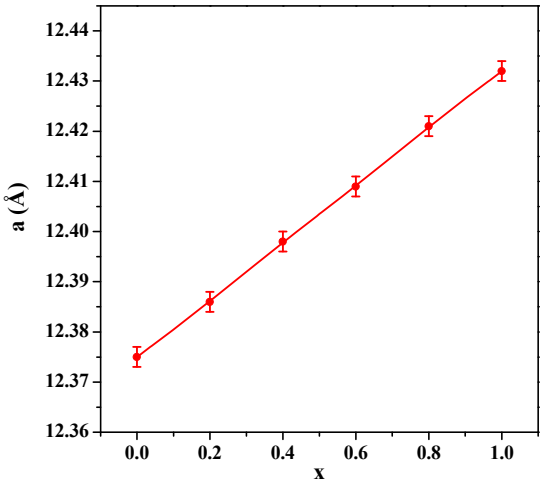

Figure 2. Dependence of the lattice constant (a) on the concentration (x) for $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnet ferrites.

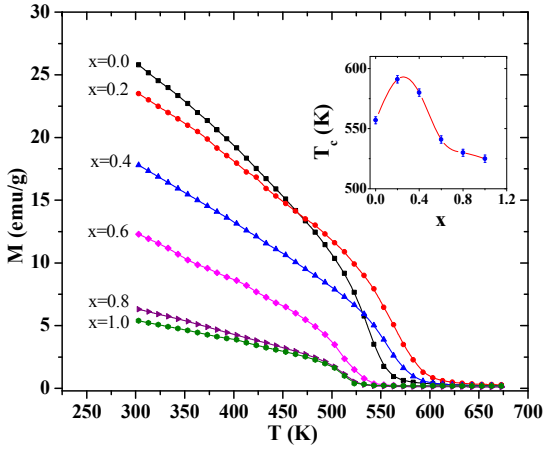

Figure 3. Temperature dependence of the magnetization for $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) in an applied magnetic field of 13.5 kOe. The inset shows the Curie temperature T_c as a function of the concentration x.

maximum of 590 K at $x = 0.2$, then decreases to 525 K at $x = 1.0$, as shown in the inset of **Figure 3**. Our T_c value of (557 ± 3) K at $x = 0$ is in agreement with previously obtained values of 550 K by Sanchez *et al.* [11] and Nimbore *et al.* [22], and of 560 K by Köbler and Hoser [23].

Figures 4 and **5** show the magnetization curves for the $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnets at different temperatures, at 4.2 K and at 300 K. We see that the saturation magnetization decreases with increasing Ca and V concentrations. Furthermore, the saturation magnetization increases with decreasing temperature, as it is expected for a system with ferrimagnetic coupling below T_c. The samples show very low coercivities (between 20 Oe and 40 Oe), which is in agreement with previous results for similar ferrites $Y_3Fe_{5-x}Al_xO_{12}$ by Kim *et al.* [19]. **Figure 6** summarizes the increase in the saturation magnetization with decreasing temperature and the decrease in M_s with increasing concentration x.

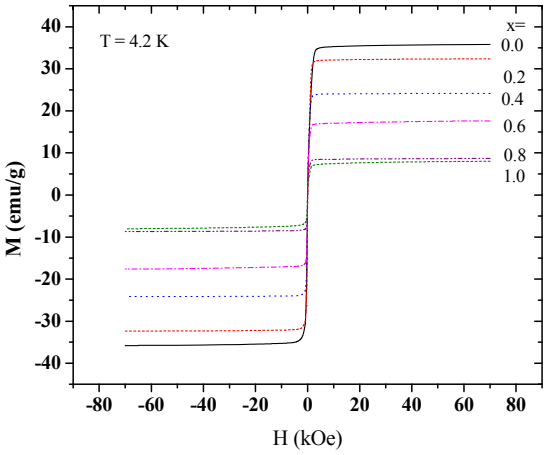

Figure 4. Low-temperature magnetization curves for $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnet ferrites at a temperature of 4.2 K.

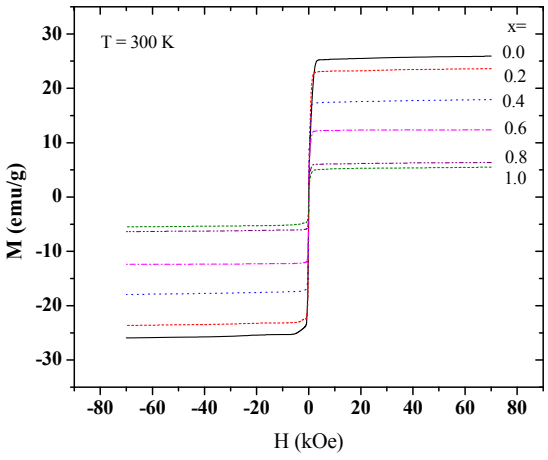

Figure 5. Room temperature magnetization curves for the $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnet ferrites.

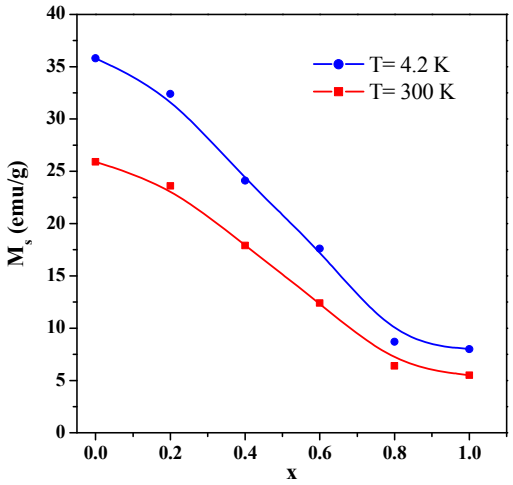

Figure 6. The saturation magnetization M_s of $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ as a function of the concentration x at two temperatures (4.2 K and 300 K).

Garnets contain only trivalent ions; therefore no electron hopping occurs through the materials, leading to an extremely high resistivity and a low magnetic loss, even at high frequencies. Among the best ultrahigh frequencies (UHF) magnetic materials, single crystalline YIG has the narrowest resonance linewidth $\Delta H \approx 0.1$ G at 10 GHz [24]. Its saturation magnetization, temperature sensitivity and magnetocrystalline anisotropy can also be tuned by changing the compositions. In these garnet ferrites Y^{3+} ion (with a $4f^0$ electronic configuration) does not have a magnetic moment and Ca^{2+} (with a $4S^0$ electronic configuration) can be a substitution for Y^{3+} on dodecahedral sites and for the charge compensation. The substitution of Fe^{3+} ion by diamagnetic V^{5+} ion (with a $3d^0$ electronic configuration) improves the magnetic properties such as the Currie temperature and the optical properties such as Faraday rotation. The low magnetic loss in these ferrites is primarily attributed to the V^{5+} substitution for Fe^{3+} in the tetrahedral sites. A previous study for the substitution of Fe by (V and In) in the gadolinium garnet system $Gd_zY_{3-2x-z}Ca_{2x}Fe_{2-y}In_yFe_{3-x}V_xO_{12}$ by Shinohara *et al.* [25] showed that V decreases the anisotropy constant (K_1) which minimizes the ferromagnetic resonance linewidth and make the garnets as a suitable material for the microwave devices

The reduced magnetization ($x > 0$) and the reduced Curie temperature ($x > 0.2$) reflect the occupancy of the tetrahedral 24d sites by vanadium, in combination with the predominant intersublattice exchange constant J_{ad}. Mean-field theory predicts the Curie temperature to decrease as $T_c(x) = T_c(0)\,(1 - x/3)^{1/2}$, because the Fe atoms on the octahedral sites have a reduced number of magnetic neighbors [26]. The initial increase in Curie temperature probably reflects structural distortions of the crystal lattice due to the substitution of the large Ca^{2+}

Table 1. Dependence of the experimental low-temperature saturation magnetization, extrapolated to $T = 0$, on the Ca and V concentration x in $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnet ferrites.

x	0.0	0.2	0.4	0.6	0.8	1.0
M_s ($T = 0$) (emu/g)	35.4	32.2	24.1	16.8	8.4	7.4

ions for Y^{3+} [27]. However, if all the V atoms went onto 24d sites, the magnetization would approach zero at x = 1.0. In the present case, there reamins a residual magnetization of 7.4 emu/g, as compared to 35.4 emu/g at x = 0, **Table 1**. This indicates that a certain fraction (about 10%) of the V goes onto the octahedral sites.

The flat shape of the $M(T)$ curves is a consequence of the ferrimagnetic two-sublattice structure [28]. By solving the corresponding secular equations [26,29], one can show that the ratio of the two sublattice magnetizations is $3/2$ at low temperatures but $\sqrt{3/2}$ below T_c. This corresponds to a relative magnetization reduction of $2\left(\sqrt{3/2}-1\right) = 0.449$. For a one-sublattice ferromagnet, this ratio would be 1 and independent of temperature.

4. Conclusion

In this study, we were able to prepare $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnets with less Y and Fe ions, with the same cubic structure and with higher Currie temperatures. The magnetic data in this paper indicate that the $Y_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ garnet ferrites is ferrimagnetically ordered for all the samples below T_c with the cubic structure being present up to the maximum Ca and V concentration x = 1.0. The samples exhibited very low coercivity (between 20 Oe and 40 Oe) with saturation magnetization (M_s), as high as ~36 emu/g (at 4.2 K). We also found that the saturation magnetization decreases with V and Ca contents reaching ~8 emu/g at 4.2 K. The obtained dependence of the Curie temperature and the saturation magnetization on the Ca and V concentration are due to the exchange interaction when Fe substituted by V, which increases the exchange interaction, and hence increases the Curie temperature for low x concentrations. All the results of the present work indicate homogenous solid solution when Y is substituted by Ca and Fe is substituted by V.

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