

Site occupancy and magnetic study of Al^{3+} and Cr^{3+} co-substituted $\text{Y}_3\text{Fe}_5\text{O}_{12}$

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ABSTRACT

Single-phased polycrystalline $\text{Y}_3\text{Fe}_{5-2x}\text{Al}_x\text{Cr}_x\text{O}_{12}$ garnet samples ($x = 0, 0.2, 0.4$ and 0.6) have been prepared by the conventional ceramic technique. Rietveld refinement of X-ray diffraction patterns of the samples shows them to crystallize in the $Ia\bar{3}d$ space group and the corresponding lattice constant to decrease with increasing Al^{3+} and Cr^{3+} contents (x). Mössbauer results indicate that Cr^{3+} substitutes for Fe^{3+} at the octahedral sites whilst Al^{3+} essentially replaces Fe^{3+} at the tetrahedral sites. This result indicates that co-doping of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ does not affect the preferential site occupancy for separate individual substitution of either Cr^{3+} or Al^{3+} . The magnetization measurements reveal that the Curie temperature (T_c) monotonically decreases with increasing x while the magnetic moment per unit formula decreases up to $x = 0.4$ and then slightly increases for $x = 0.6$. This reflects a progressive weakening of the ferrimagnetic exchange interaction between the Fe^{3+} ions at octahedral and tetrahedral sites due to co-substitution. The magnetic moment was calculated using the cations distribution inferred from the Mössbauer data and the collinear ferrimagnetic model, and was found to agree reasonably with the experimentally measured value. The phenomenological amplitude crossover, characterized by the temperature T^* , has also been observed in the doped YIG and briefly discussed.

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1. Introduction

Since its discovery in 1956, yttrium iron garnet (YIG) and substituted-YIG have attracted a lot of attention because of their application in microwaves domain [1] and magneto-optical devices [2]. YIG has the chemical composition $\{\text{Y}_3\}\{\text{Fe}_2^a\}_d\{\text{Fe}_3^b\}_t\text{O}_{12}$, where Y ions occupy the dodecahedral site with 12 O^{2-} ligands, a represents the octahedral site with six O^{2-} ligands, and d the tetrahedral site with four O^{2-} ligands. Its crystal structure is described in the cubic space group $Ia\bar{3}d$ by Bonnet et al. [3] and in the trigonal space group $R\bar{3}$ by Rodic et al. [4], to account for the lowering of symmetry due to spontaneous magnetostriction. YIG is ferrimagnetic with two magnetic a and d sublattices of Fe^{3+} that are coupled antiparallely. It is well established that composition modification alters the magnetic properties of garnets by magnetic dilution associated with the replacement of Fe^{3+} ions by diamagnetic ions of approximately the same size and by magnetoelastically active ion substitutions usually in small concentration [5]. Also, monitoring the selective site doping can shed light on the magnetism of each sublattice from fundamental point of view as well as enable control of physical properties for applications purposes. Various levels and

types of doping of Fe^{3+} sites have been performed. Among others, substitution of magnetic Fe^{3+} by nonmagnetic Al^{3+} has shown interesting features [6]. It was shown that Al^{3+} goes to the tetrahedral 24d sites in Al-doped YIG [7,8] whereas Cr^{3+} preferentially occupies the unexpected octahedral site, which is attributed to the electronic configuration of Cr^{3+} [7,9]. On co-substituting nonmagnetic Al^{3+} and magnetic Cr^{3+} for Fe^{3+} ions [10], it was reported that Cr^{3+} and 60% of Al^{3+} ions go to the tetrahedral sites whereas the remaining 40% of Al go to octahedral sites. However, a recent study [11] showed both Cr^{3+} and Al^{3+} substitute for Fe^{3+} in the octahedral sites only. Therefore, the site occupancy of both Cr^{3+} and Al^{3+} in YIG is controversial. It is to be mentioned that the cation distribution in the latter two studies was based on measurements at room temperature of either magnetization [10] or Mössbauer spectroscopy [11].

The canting effect induced by substitution of magnetic ions by non-magnetic or less magnetic ones leads to a decrease on one site of the effective exchange [12]. In fact, this phenomenon is very sensitive to local disorder and inhomogeneities in the substitutions. It can lead to various local canted structures with different hyperfine fields, but the thermal disorder can only make the difference when the balance of the exchange interactions is close to the canting condition. However, the magnetic ordering of ferrites like YIG changes significantly from its arrangement at room temperature, as shown for $x = 0.4$ and $x = 0.6$ in this study. In particular, the thermal disorder would reduce the net

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magnetization, making the Neel's collinear ferrimagnetic model not valid. For example, the cations distribution reported by Lahlooh et al. [11] for $Y_3Fe_{5-2x}Al_xCr_xO_{12}$ garnets would lead to magnetic moment inconsistent with that obtained from magnetization measurements reported in this study. In this work, three techniques, namely, X-ray diffraction, low temperature magnetization and Mössbauer spectroscopy, were employed to clarify the site preference of Cr^{3+} and Al^{3+} ions in $Y_3Fe_{5-2x}Al_xCr_xO_{12}$ garnets. It is shown that the preferential sites occupancy for Al and Cr in co-doped YIG remains nearly identical to that corresponding to separate doping of either Cr^{3+} or Al^{3+} in YIG.

2. Experimental

Samples with nominal composition $Y_3Fe_{5-2x}Al_xCr_xO_{12}$ ($x = 0, 0.2, 0.4$ and 0.6) have been prepared by the conventional ceramic technique. The starting materials Y_2O_3 , Fe_2O_3 , Al_2O_3 and Cr_2O_3 were weighted in appropriate proportions and wet-mixed for 1 h in acetone to obtain homogeneous mixtures. The mixtures were dried and then calcined at $1200^\circ C$ for 10 h followed by mechanical milling for 1 h to get homogeneous sub-micronic powders. The powders were pressed in blocks under 2 tons/cm^2 using polyvinyl alcohol (PVA) as binder and then sintered in oxygen atmosphere at $1400^\circ C$ for 10 h. The sintered blocks were crushed into powder and then annealed at $700^\circ C$ for 2 h.

The crystalline nature of the resulting compounds was analyzed using a Philips PW 1700 X-ray diffractometer with a $CuK\alpha$ source. The magnetization was measured with a DMS 1660 vibrating sample magnetometer (VSM) in a magnetic field up to 13 kOe, and in the temperature range 77–573 K. The VSM was initially calibrated using pure nickel ($M_s = 54.9 \text{ emu/g}$). The Mössbauer spectra were recorded at 78 K using $^{57}Co/Rh$ source with the spectrometer in the transmission mode. The spectra were fitted with a distribution of hyperfine fields using NORMOS program.

3. Results and discussion

The X-ray powder diffraction patterns recorded from the $Y_3Fe_{5-2x}Al_xCr_xO_{12}$ samples are shown in Fig. 1. All patterns refine

to a cubic structure (space group $Ia\bar{3}d$), reflecting that the compounds are single-phased. The lattice constant decreases with increasing concentration x of the doped ions as shown in Fig. 2. Such a decrease in the lattice parameters is generally attributed to the smaller ionic radii of Al^{3+} and Cr^{3+} relative to that of high-spin Fe^{3+} ions at both tetrahedral and octahedral sites. It is interesting to note that the lattice constant does not decrease linearly, in line with the Vegard's law, as expected when both Al^{3+} and Cr^{3+} substitute Fe^{3+} ions at either site. While Cr^{3+} ions are known to have a strong octahedral site preference [7,9], the decrease, though limited, in the lattice parameters with increasing x value suggests that Al^{3+} ions do partly replace tetrahedral Fe^{3+} ones. The smaller tetrahedral ionic radius of Al^{3+} (0.53 \AA) relative to that of tetrahedral Fe^{3+} (0.69 \AA) supports this view [13]. It should be noted that the Rietveld analysis of the spectrum of sample $x = 0.4$ has also revealed the presence of a very minor phase (6–7%) that was not identified but possibly magnetic (such as traces of $YCrO_3$ or $\alpha-Fe_2O_3$ impurity phases [9]), which can be at the origin of the relatively larger broadening of the Mössbauer spectrum as shown below.

The magnetization curves recorded at room temperature of the four samples are shown in Fig. 3. It can be noticed that the

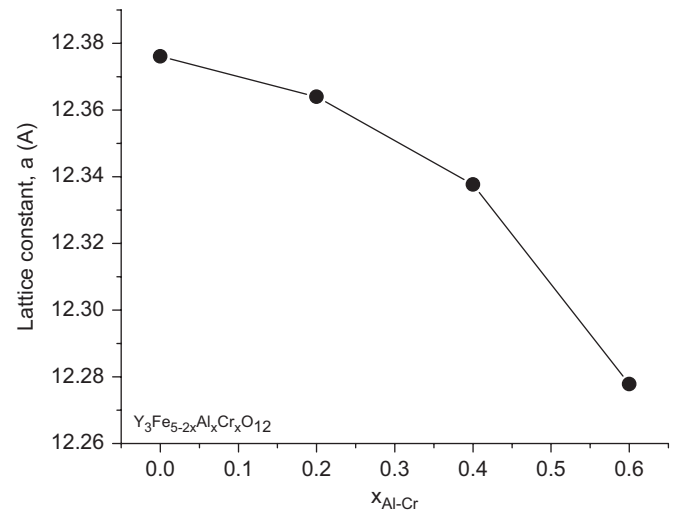


Fig. 2. The variation of the lattice parameters of $Y_3Fe_{5-2x}Al_xCr_xO_{12}$ with the concentration x .

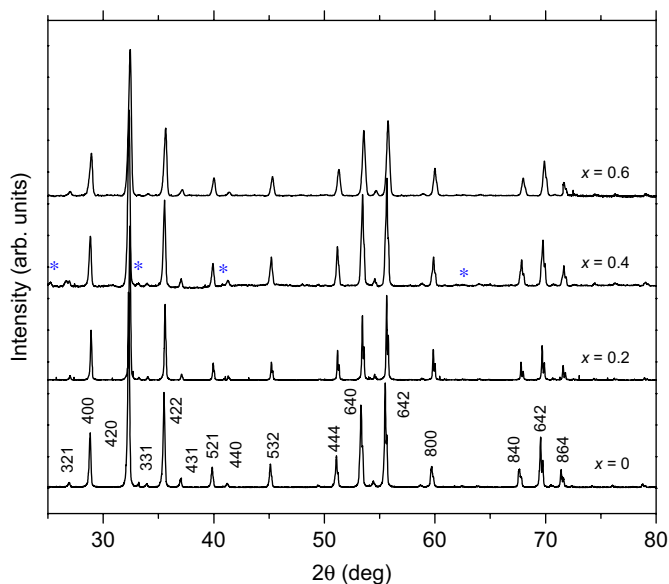


Fig. 1. Powder X-ray diffraction patterns of $Y_3Fe_{5-2x}Al_xCr_xO_{12}$ garnet samples. The symbol (*) indicates the presence of a non-identified impurity phase for $x = 0.4$.

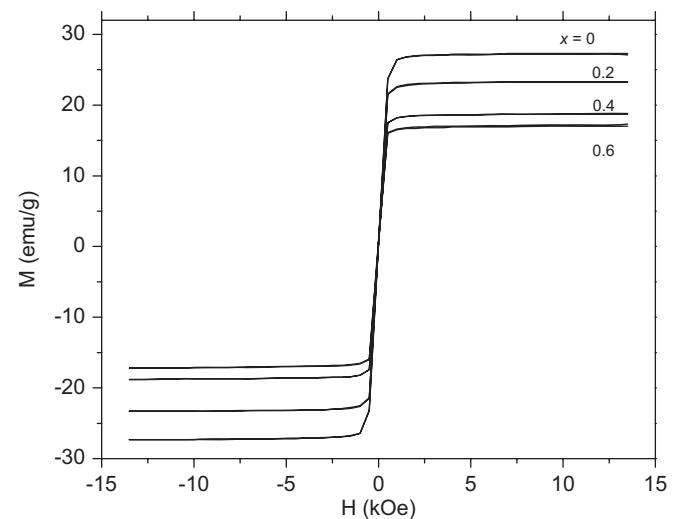


Fig. 3. Room temperature hysteresis loops of $Y_3Fe_{5-2x}Al_xCr_xO_{12}$ garnet samples.

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