Structure-Substitution Limit Correlation Study on Cr$^{3+}$ Substituted Polycrystalline Yttrium Iron Garnet


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Abstract. Polycrystalline samples of Cr$^{3+}$-substituted yttrium iron garnet (Y$_3$Fe$_5$O$_{12}$) system with general chemical formula, Y$_3$Fe$_x$Cr$_{3-x}$O$_{12}$, $x = 0.0, 0.2, 0.4$ and $0.6$ were synthesized by double sintering ceramic technique and characterized by X-ray powder diffraction. The Rietveld fitted X-ray diffraction patterns analysis revealed mono phase formation for $x = 0.0 – 0.4$ compositions while $x = 0.6$ composition possesses mixed phase character. The observed substitution limit has been discussed in the light of ionic size of substituent, electrostatic energy, electronic configuration and synthesis parameters. These observations strongly suggest that the electronic configuration of Cr$^{3+}$, which is favorable to the formation of d$^{sp^3}$ (octahedral) type bonds, must be important. In the case of Cr$^{3+}$, the substitution does not appear to proceed well for $x$ much greater than 0.5, this limitation probably is a consequence of the strong preference of a smaller ion Cr$^{3+}$, for a larger octahedral site which quickly leads to a condition not comparable with the requirement of the structure. The distribution of cations, mean ionic radii and theoretical lattice constant values have been determined.

INTRODUCTION

Garnet crystal belongs to the body center cubic (bcc) structure with a space group of O$_h^{10}$Ia3d and has the general chemical formula C$_3$A$_2$D$_3$O$_{12}$, where C denotes dodecahedrally, A octahedrally and D tetrahedrally coordinated crystallographic sites with point symmetries 222, 3, 4 respectively. The unit cell consists of eight formula units. Yttrium iron garnet, Y$_3$Fe$_5$O$_{12}$, is a prototype of ferrimagnetic materials which have provoked great interest since their discovery [1]. In the structure, yttrium ions occupy a dodecahedral site (24 c). Of the five iron ions present in a formula unit, three are in 24(d) sites tetrahedrally surrounded by oxygen ions and two are in 16(a) sites octahedrally surrounded by oxygen anions. The 96 oxygen ions so called h-site form a three dimensional structure in which these three kinds of interstitial sites is present [2].

It is possible to substitute a large number of cations at the c-, d- and a- sites of the garnet structure. The substitution of large rare earth cations on the Y$^{3+}$ site (c-site) as well as small transition metal ions on the Fe$^{3+}$ sites (a- or d-sites) is very common. In the latter case, with a few exceptions (e.g. In$^{3+}$ (0.80 Å), Sc$^{3+}$ (0.745 Å), Rh$^{3+}$ (0.665 Å)) the ionic radii of substituted metallic cations (e.g. Al$^{3+}$ (0.535 Å), Ga$^{3+}$ (0.62 Å), Cr$^{3+}$ (0.615 Å)) are smaller than the ionic radius of Fe$^{3+}$ (0.64 Å) ion. The upper feasible limits of In$^{3+}$ and Sc$^{3+}$ ions substitution for Fe$^{3+}$ ions in Y$_3$Fe$_5$O$_{12}$ are not precisely known but probably are, x less than about one for In$^{3+}$ and less than about two for Sc$^{3+}$ [3]. These ions apparently are too large to allow formation of yttrium-indium or yttrium-scandium garnets. On the other hand, 100% replacement of Fe$^{3+}$ by quite smaller Al$^{3+}$ and slightly smaller Ga$^{3+}$ is possible that form Y$_3$Al$_5$O$_{12}$ and Y$_3$Ga$_5$O$_{12}$ respectively [3]. In the present and previous investigations it is found that Cr$^{3+}$ ions, though smaller than Fe$^{3+}$ ions, have substitution limit $x \leq 0.6$ [3-10]. This is rather surprising and interesting too. The aim of the present work is to revisit the possible causes that restrict substitution of Cr$^{3+}$ for Fe$^{3+}$ ions in Y$_3$Fe$_5$O$_{12}$ in a systematic manner. The effect of quite large Y$^{3+}$ ion (0.89 Å) substitution for Fe$^{3+}$ ion (0.64 Å) in Y$_3$Fe$_5$O$_{12}$ garnet system on structural stability and permeability spectral evolution as well as extremely large Ca$^{2+}$ ion (0.99 Å) (whose ionic radius is near the threshold (~ 1 Å)) for
Mg$^{2+}$ in MgFe$_3$O$_4$ spinel ferrite system on structural stability, magnetic and electrical properties have been studied earlier [11,12]. It is found that the higher concentration of Y$^{3+}$ substitution ($x \geq 0.4$) leads to the formation of an unwanted secondary orthoferrite phase and non magnetic Y$^{3+}$ ions replace the magnetic Fe$^{3+}$ ions at the tetrahedral sites. In the second case it is found that maximum of 23 % of Ca$^{2+}$ ion can be substituted for Mg$^{2+}$ without disturbing single phase fcc spinel structure and Ca$^{2+}$ ion has strong preference for the tetrahedral site.

**EXPERIMENTAL DETAILS**

Conventional high temperature double sintering solid state reactions were carried out to prepare Y$_x$Fe$_{3-x}$Cr$_x$O$_{12}$, $x = 0.0, 0.2, 0.4$ and $0.6$ garnet compounds. The raw materials were weighed in stoichiometric proportions, wet ground in agate pastel and mortar for 4 h to yield the desired compositions, then compressed in the form of pellets and pre-sintered at 1200 °C for 23 hours. The pre-sintered pellets were re-grinded and the resulting powders were re-pelletized. The samples were finally sintered in air at 1500 °C for 23 hours and furnace cooled to room temperature at the rate of 2°C/min, in programmable furnace.

Room temperature (300 K) X-ray diffraction patterns for all the compositions of Y$_x$Fe$_{3-x}$Cr$_x$O$_{12}$ garnet system were recorded with a Philips, Holland, Xpert MPD automated X-ray powder diffraction system X’Pert PRO (Philips, Netherlands) using CuK$\alpha$ radiation ($\lambda = 0.15405$ nm), graphite monochromator, and Xe-filled proportional counter. Data were collected in 2θ range of 5-85° at a scan speed of 2°/min. Rietveld refinement of X-ray data was carried out using the General Scattering Analysis Software (GSAS) [13].

**RESULTS AND DISCUSSION**

Figure 1 displays Rietveld fitted XRD patterns for three typical compositions with $x = 0.2, 0.4$ and 0.6 of the system Y$_x$Fe$_{3-x}$Cr$_x$O$_{12}$. The structural refinement showed that $x = 0.0 - 0.4$ are single phase compounds, crystallizing in body center cubic (bcc) structure with a space group of O$_h^{10}$ Ia3d. It is found that the goodness-of-fit ($\chi^2$) for different samples lie in the range 1.4-1.7 (except for $x = 0.6$ composition). The $\chi^2$ values obtained in the present analysis suggest good refinement of the data. The composition, Y$_1$Fe$_{2.4}$Cr$_{0.6}$O$_{12}$ ($x = 0.6$), is not a single phase material. The atomistic simulation studies have shown that in yttrium-excess yttrium iron garnet, Y$_x$Fe$_2$O$_{12}$, formation of the perovskites YFeO$_3$ phase rather than the non-stoichiometric phase is more likely, as there is very little difference in the lattice energy of the two phases, Y$_x$Fe$_2$O$_{12}$ and YFeO$_3$ [14]. Thus, the secondary phase most probably is of yttrium orthoferrite/orthochromite, YFeO$_3$/YCrO$_3$.

This is rather surprising based on the fact that though Cr$^{3+}$ ion having ionic radius of 0.615 Å, slightly smaller than Ga$^{3+}$ ion (0.62 Å), its substitution for Fe$^{3+}$ (0.64 Å) is limited to $x \leq 0.6$ in Y$_x$Fe$_{3-x}$Cr$_x$O$_{12}$ garnet system [3-6] contrary to cent percent replacement of Fe$^{3+}$ ion by Ga$^{3+}$ in the system Y$_x$Fe$_{3-x}$Ga$_x$O$_{12}$ [3] without changing single phase formation of the garnet compounds. It is well known that site preference and substitution limit of the particular cation are mainly governed by factors such as; ionic radius of the substituent, electrostatic energy, electronic configuration (covalent bonding and hybridization) and synthesis parameters [15]. As discussed above ionic radius of Cr$^{3+}$ ion is not responsible factor for restricted substitution limit. The larger cations generally prefer to occupy the octahedral sites and smaller cations to the tetrahedral sites, because of larger volume of octahedral site than tetrahedral site (Fe$^{3+}$ - O$^{2-}$ distance of 1.88Å for the tetrahedral site and 2.0 Å for the octahedral site) [3]. Summarizing the work on ionic size of substituted cation, occupancy at the particular interstitial sites and its effect on substitution limit in yttrium iron garnet and spinel ferrites systems [11,12], very interesting and important conclusions may be drown. When non magnetic large cation, Y$^{3+}$
substituted for Fe$^{3+}$ in Y$_{3}$Fe$_{2}$O$_{12}$ system and replaces Fe$^{3+}$ ion from the tetrahedral site [11], similarly when very large cation Ca$^{2+}$ replaces Mg$^{2+}$/Co$^{2+}$ from the tetrahedral sites in Mg$_{1-x}$Ca$_{x}$Fe$_{2}$O$_{4}$/Co$_{1-x}$Ca$_{x}$Fe$_{2}$O$_{4}$ spinel ferrites systems [12], substitution limit restricted to certain concentration (x) in the systems. On the other hand, when smaller cation, Cr$^{3+}$ substituted for Fe$^{3+}$ ion in yttrium iron garnet, Y$_{2}$Fe$_{2}$O$_{12}$ and occupies the octahedral site, its substitution is restricted to 10 – 12 % only [3-6]. In short, when large cations occupy the smaller site and smaller cations enter into the larger site that lead to limited substitution. Thus, from the above discussion it is clear that when cation enters into ‘wrong’ site, its substitution is limited to certain concentration only. Furthermore, it is also found that in all the cases along with major parent phase (bcc or fcc) orthorhombic perovskites-like phase, YFeO$_{3}$, YCrO$_{3}$, CaFe$_{2}$O$_{4}$, is formed. This is due to the fact that the packing in the garnet structure is much less efficient than in the perovskite-like structure i.e. the perovskite-like phase is known to be more stable than the garnet phase [3]. This does not allow large solubility of the cation in the ‘wrong’ site and results in the formation of secondary phase as observed.

Many research reports are available on Cr$^{3+}$ ion substituted and Al$^{3+}$-Cr$^{3+}$ co-substituted Y$_{3}$Fe$_{2}$O$_{12}$ systems [3-10] prepared under different synthesis conditions including self-propagating high temperature synthesis. In general, it is found that in the case of Cr$^{3+}$ ion the substitution does not appear to proceed well for x much greater than 0.6. The present result is in agreement with the earlier reports. In short, preparative parameters may not be responsible for limited substitution of Cr$^{3+}$ for Fe$^{3+}$ in Y$_{3}$Fe$_{2}$O$_{12}$ system.

The electronic configuration of a metal ion appears to be a much more important factor than ionic size with regard to its presence in the octahedral or tetrahedral sites. Ions having filled d-shells (e.g. Ga$^{3+}$ with 3d$^{10}$ configuration) often have tendency to form sp$^{3}$ hybrid orbital and occupy the tetrahedral sites, whereas the ions with d$^{1}$ and d$^{5}$ electronic configuration have a tendency to form d$^{sp}$ hybrid orbitals and occupy the octahedral sites [15]. These appear to be structural limitations, crystallographic and electronic, on the extent to which Cr$^{3+}$ ions can be substituted for Fe$^{3+}$ ions in Y$_{3}$Fe$_{2}$O$_{12}$. Trivalent chromium assumed a pseudo-spherical electronic configuration only in an octahedral field; therefore, Cr$^{3+}$ (0.615 Å) ion, though smaller than Fe$^{3+}$ (0.64 Å) ion is limited to the octahedral site in Y$_{3}$Fe$_{2}$O$_{12}$. In other words, these observations suggest strongly that the electronic configuration of Cr$^{3+}$ (3d$^{2}$), hybridizes stable (d$^{sp}$) orbitals, two empty d-orbitals being available. These lattice orbitals are octahedral and can therefore point simultaneously towards all six oxygen near neighbors if the Cr$^{3+}$ ion is in an octahedral site [16]. Thus, this Cr$^{3+}$ substitution limitation probably is a consequence of the strong preference of smaller ion, Cr$^{3+}$, for a larger site (a-site) which quickly leads to a condition not comparable with requirements of the structure [3].

The absence of change of electrostatic energy as an important influence in the distribution of the metallic cations when all have the same valence (as in the present case all the metallic cations involved are isovalent, Y$^{3+}$, Cr$^{3+}$, Fe$^{3+}$) should be kept in mind when comparison is made with the distribution observed, for example, in iron spinels for the same substitution (e.g. it is possible to have 100% replacement of Fe$^{3+}$ by Cr$^{3+}$ ions exclusively on the octahedral site of the spinel lattice in CoFe$_{2}$O$_{4}$ [17] without disturbing monophasic fcc structure).

The lattice constant values were determined for the different compositions and are given in Table 1. It is found that lattice parameter decreases with increasing Cr - content (x) in the system Y$_{3}$Fe$_{2}$Cr$_{x}$O$_{12}$. Usually, in a solid solution of garnets within the miscibility range, a linear change in the lattice constant with the concentration of the components is observed [18]. The observed slow linear decrease in lattice constant value is due to the replacement of 6-fold high spin Fe$^{3+}$ ions with ionic radius of 0.64 Å by slightly smaller 6-fold high spin Cr$^{3+}$ ions having ionic radius of 0.615 Å in the system.

In yttrium iron garnet, Cr$^{3+}$ enters the octahedral site, probably exclusively, thus, the cation distribution for the present system can be presented as:

\[
\begin{align*}
\{Y_{3}^{3+}\}^{c} & [Fe_{2}^{3+}]^{a} [Fe_{1-x}^{3+}]^{d} O_{12}^{2-} \\
\{Y_{3}^{3+}\}^{c} & [Fe_{1.8}^{3+} Cr_{0.2}^{3+}]^{d} [Fe_{1-x}^{3+}]^{d} O_{12}^{2-} \\
\{Y_{3}^{3+}\}^{c} & [Fe_{1.6}^{3+} Cr_{0.2}^{3+}]^{d} [Fe_{1-x}^{3+}]^{d} O_{12}^{2-} \\
\{Y_{3}^{3+}\}^{c} & [Fe_{1.4}^{3+} Cr_{0.6}^{3+}]^{d} [Fe_{1-x}^{3+}]^{d} O_{12}^{2-}
\end{align*}
\]

For each composition the values of mean ionic radius per molecules of the d-, a- and c-sites have been calculated by using the relations:

\[
\begin{align*}
r_d &= (1/3) [f_c (Fe^{3+}) r (Fe^{3+})] \\
r_a &= (1/2) [f_c (Fe^{3+}) r (Fe^{3+}) + f_c (Cr^{3+}) r (Cr^{3+})] \\
r_c &= (1/3) [f_c (Y^{3+}) r (Y^{3+})]
\end{align*}
\]

where, ‘f_c’ and ‘r’ represent concentration and ionic radius of the cation on the respective site. Using these formulae, the mean values of the tetrahedral, octahedral and dodecahedral ionic radii have been calculated and are listed in Table 1.
Finally, an attempt has been made to calculate lattice constant value theoretically for the different compositions using the following relation [19] with the coefficients, $b_i = +7.068$, $b_2 = +3.25001$, $b_3 = +2.49398$, $b_4 = +3.34124$, $b_5 = (-0.90158)$, $b_6 = (-0.142777)$.

$$a_{lh} = b_1 + b_2 r_c + b_3 r_d + b_4 r_s + b_5 r_c r_d + b_6 r_c r_s$$

Here, $b_1$ to $b_6$ are exchange interactions in agreement with earlier report [20]. As the magnetic moments of c- and a-sites as well as c- and d-sites are anti parallel to each other [21], exchange constants, $b_3$ and $b_4$ are found to be negative. It is found that there is reasonable agreement between experimentally found and theoretically calculated lattice constant values.

## CONCLUSIONS

The Rietveld fitted X-ray powder diffraction patterns analysis revealed single phase formation for $x = 0.0 – 0.4$ compositions while $x = 0.6$ composition possesses mixed phase character. The substitution limit of Cr$^{3+}$ for Fe$^{3+}$ ion in Y$_3$Fe$_{5-x}$Cr$_x$O$_{12}$ garnet system is mainly govern by electronic configuration of Cr$^{3+}$ ion and electrostatic energy of the system while ionic radius of Cr$^{3+}$ ion and preparative parameters have less influence. The large or small cation when occupies the ‘wrong’ site that results in limited substitution in the system. The lattice constant values calculated theoretically are in good agreement to those determined experimentally.

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## REFERENCES


### Table 1. Lattice constant and site radius (r) for Y$_3$Fe$_{5-x}$Cr$_x$O$_{12}$ system.

<table>
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<th>Cr$^{3+}$-content (x)</th>
<th>a (Å) ± 0.002Å</th>
<th>r_d (Å)</th>
<th>r_a (Å)</th>
<th>r_c (Å)</th>
<th>a_{lh} (Å)</th>
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