Effect of Substituted Concentration on Structure and Magnetic Properties of $Y_3Fe_{5-x}In_xO_{12}$

Vu Thi Hoai Huong, Dao Thi Thuy Nguyet, Nguyen Phuc Duong*

ITIMS, Hanoi University of Science and Technology, No. 1, Dai Co Viet, Hai Ba Trung, Hanoi, Vietnam

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Abstract: This study examines the effect of substituted concentration on the structure and magnetic properties of $Y_3Fe_{5-x}In_xO_{12}$ ($x = 0.1 \div 0.7$) powder samples prepared using the sol-gel method. The morphological properties of the samples were analysed using XRD, SEM. The single phase of garnet was obtained in $x = 0.1 \div 0.6$ samples. The lattice parameters of the samples exhibit a linear increase with the increasing $In^{3+}$ content, which can be explained by a substitution of $In^{3+}$ ions for $Fe^{3+}$ ions, considering the larger ionic radius of $In^{3+}$ compared with that of $Fe^{3+}$. Crystallite sizes were determined via the XRD data which are of 38 – 49 nm while the particle sizes were estimated from SEM images to be in range of 50 - 100 nm. Magnetization and Curie temperature of the single phase samples were studied by magnetization curves in fields up to 10 kOe and in the temperature range from 80 K to 560K. With the increase of $In^{3+}$, the magnetization gradually increases while the Curie temperature decreases due to the occupation of $In$ atoms at the $a$ sites and the reduction of intersublattice interaction, respectively.

Keywords: Yttrium iron garnet, Indium substitution, cation distribution, magnetization, Curie temperature.

1. Introduction

Yttrium ferrite garnet $Y_3Fe_{5}O_{12}$ (YIG) is known as one of the most important garnets for microwave applications. It is material that widely used in microwave devices, transformers, electric generators, bio-processing, and storage devices [1-7] because of its combine good high-frequency dielectric properties with a ferrimagnetic order. YIG has three different crystallographic sites with 16 $Fe^{3+}$ ions in the octahedral [$a$] site, 24 $Fe^{3+}$ ions in the tetrahedral site ($d$) and 24 $Y^{3+}$ ions in the dodecahedral {$c$} site. The Fe atoms on the octahedral sites couple anti-ferromagnetically to the Fe atoms on the tetrahedral...
sites \((J_{ad} < 0)\) and there is no coupling to the dodecahedral sites because yttrium is a nonmagnetic atom. The magnetization of YIG per formula unit calculated by 3 tetrahedral and 2 octahedral sites, corresponding to a net moment of \(5 \times (3 - 2)\mu_B = 5\mu_B\). The interest in the structural, microstructural and magnetic properties of YIG has been due to the fact that all these properties can be widely varied by dopant substitutions [8-10]. In previous studies, nonmagnetic ion as \(V^{5+}\) was substituted on Fe ions at \(d\) site and that is reason leading to reduce magnetization and Curie temperature of the system [11, 12]. In most applications of ferrite garnets, enhancement of the magnetization of the materials is required which can be achieved by substituting non-magnetic ions on the \(a\) sublattice. In this work, \(In^{3+}\) ions were substituted for \(Fe^{3+}\) and the effect of the presence of non-magnetic ions on the structure and magnetic properties were investigated.

2. Experimental

2.1. Sample preparation

The \(Y_3Fe_{5-x}In_xO_{12}\) nanoparticle samples \((x = 0 \div 0.7)\) were prepared by using sol-gel method. Starting materials for preparation of the samples were high purity \(Fe(NO_3)_3\), \(Y_2O_3\), \(In_2O_3\) (99.99%, Sigma Aldrich). The oxides were dissolved in \(HNO_3\) 1M to form nitrate solutions. The metal nitrate solutions were mixed the required amount of the metal ions in a stoichiometric ratio of \(Y: Fe: In = 3: (5 - x): x\). An aqueous solution of citric acid was added into the solution with the total cation/citric acid molar ratio is 1/3. The mixtures were stirred at 400 rpm and slowly evaporated at 80°C to form gels. The gels were dried at 95°C for more than 12 hours in order to form xero-gels. The nanoparticle samples were obtained after burning the xero-gels at 400°C in 2 hours and annealing at 900°C in 5 hours.

2.2. Analytical methods

The phase structure and crystallite sizes of the powder samples at room temperature were investigated using X-ray diffraction (XRD) (Cu-Kα, Siemens D-5000) operating with Cu-Kα radiation \((\lambda =1.54060 \text{ Å})\) in the range of 20°-70° by a 2θ scan mode and 0.03° scan step at room temperature. The grain size and morphology of samples were measured by using Scanning Electron Microscope (SU3500). Magnetic measurements were carried out by using a vibrating sample magnetometer (VSM) in maximum applied magnetic field of 10 kOe and at temperatures from 88 to 550 K. For the magnetic measurements, the nanoparticles were pressed in the forms of platelets.

3. Results and discussion

3.1. Structure, cation distribution and morphology of particle samples

Fig. 1 shows the XRD patterns of the \(Y_3Fe_{5-x}In_xO_{12}\) \((x = 0 \div 0.7)\) nanoparticle samples sintered at 900°C in 8 hours in which, the planes of a cubic unit cell of garnet structure were indexed as (321), (400), (420), (422), (521), (611), (444), (640), (642), (800), (752), (840). On the others XRD studies of samples sintered at 800°C and 850°C in 8 hours, the amount of YFeO\(_3\) phase is present. Therefore, the temperature of 900°C in 8 hours is the lowest temperature of the sol-gel method for preparing In substituted YIG nanoparticle samples. This temperature is also lower than the 1000°C of the mechanical alloying method [13] and conventional mix oxide route [14].
The samples with the In concentrations, \(x \leq 0.6\) are of single phase while the sample \(x = 0.7\) exhibited the second phase orthoferrite \(YFeO_3\). Similar result is also observed in other study on indium substituted YIG polycrystalline samples [15]. The lattice constant, \(a\), was computed using the interplanar spacing \(d\) and the corresponding Miller indices \((h,k,l)\). It is also observed that \(a\) increases from 12.38 Å to 12.442 Å as \(x\) increasing from 0.1 to 0.7. Fig. 2 shows monotonous increasing of lattice constants with increasing of \(\text{In}^{3+}\) contents. The observed variation in lattice constant can be explained by Vegard’s law, according to that, if the radius of displacing ion is larger than the displaced ion, the lattice is expanded and the lattice constant increases [16]. The ionic radius of \(\text{In}^{3+}\) (0.79 Å – in octahedral site) is larger than that of \(\text{Fe}^{3+}\) (0.645 Å – in octahedral site; 0.49 Å – in tetrahedral site), resulting in the gradual increase of the lattice constant with increasing \(\text{In}^{3+}\) content. The diffraction peaks (420) of the substituted samples are found to shift to lower Bragg angles in comparison with the pure sample \((x = 0)\) as shown in the small Fig. 1. The value of \(a\) obtained at \(x = 0.1\)–0.4 samples in this study are similar to the polycrystalline samples with the same concentration prepared by conventional mixed oxide [14] and mechanical alloying [13].

Table 1. Lattice parameter \(a\) (Å) and average crystallize size \(D_{\text{XRD}}\) (nm) of \(Y_3\text{Fe}_5\text{In}_x\text{O}_{12}\) \((x = 0 \div 0.7)\)

<table>
<thead>
<tr>
<th>(x)</th>
<th>(a) (Å)</th>
<th>(D_{\text{XRD}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.371</td>
<td>38</td>
</tr>
<tr>
<td>0.1</td>
<td>12.38</td>
<td>49</td>
</tr>
<tr>
<td>0.2</td>
<td>12.387</td>
<td>47</td>
</tr>
<tr>
<td>0.3</td>
<td>12.398</td>
<td>46</td>
</tr>
<tr>
<td>0.4</td>
<td>12.407</td>
<td>43</td>
</tr>
<tr>
<td>0.5</td>
<td>12.423</td>
<td>41</td>
</tr>
<tr>
<td>0.6</td>
<td>12.433</td>
<td>43</td>
</tr>
<tr>
<td>0.7</td>
<td>12.442</td>
<td>42</td>
</tr>
</tbody>
</table>

The average crystal size \(D_{\text{XRD}}\) determined based on the width of the (420) peak using the Debye – Scherrer varies from 41 to 49 nm as shown in Table 1. On the other hand, the morphological shape particle of samples were characterized by SEM images shown that average sizes are in the range of 50 – 100 nm. SEM image of \(Y_3\text{Fe}_{2.4}\text{In}_{0.6}\text{O}_{12}\) \((x = 0.2; 0.3; 0.4; 0.6)\) samples were indicated in Fig. 3, in which, due to the influence of temperature during annealing process, the grains are melted and clustered...
together, forming a porous structure. The difference in average crystal size and particle size is explained by the fact that each particle observed on the SEM image contains several crystallites which have dimensions in the orders of \( D_{\text{XRD}} \) values. The structural heterogeneity region between these grains is also known as crystal dislocation region where the crystal growth temporarily halted [17].

![Figure 2. Lattice constant of \( \text{Y}_3\text{Fe}_{5-x}\text{In}_x\text{O}_{12} \) (x = 0 ÷ 0.7) samples.](image)

![Figure 3. SEM micrographs of \( \text{Y}_3\text{Fe}_{5-x}\text{In}_x\text{O}_{12} \) (x = 0.2; 0.3; 0.4; 0.6).](image)

### 3.2. Magnetic properties

Magnetic properties of samples were studied by means of origin magnetization curves measured in magnetic fields up to 10 kOe at temperature from 88 K to 570 K. Fig. 4 demonstrates the \( M(H) \) curves of \( \text{Y}_3\text{Fe}_{5-x}\text{In}_x\text{O}_{12} \) (x = 0.1 ÷ 0.6) samples at 88 K. At all of the survey temperatures, the \( M(H) \) curves reach saturation state in a magnetic field greater than 2 kOe. The value of the saturation magnetization \( M_s \) were determined based on the flat part of the curves in the higher field region. \( M_s(T) \) curves in Fig. 5 show the dependence of \( M_s \) value of samples on the temperature. The saturation magnetization \( M_s(0) \) at 0 K were determined by extrapolation of the graphical plot of \( M_s \) against \( T \) to \( T = 0 \) according to a modified Bloch law [18]:

\[
M_s(T) = M_s(0) (1 - BT^\alpha)
\]

where \( B \) is the Bloch’s constant and \( \alpha \) is the Bloch exponent. The experimental curves were the best reproduced with \( \alpha \approx 1.6 \) as shown in Fig. 5. The extrapolated magnetic moments in ground state express in Bohr magneton per formula unit (\( \mu_B/\text{f.u} \)) were calculated according to the formula:

\[
m(0) = M_s(0) \times W/5585
\]

where \( W \) is the molar mass.

In order to evaluate the effect of substituted concentrations on the magnetic moment of samples, the experimental magnetization values are identified at 0 K and compared with theory values. Applying the Néel model for the assumption that In ions substituted in a sublattice, the theoretical values of \( m(0) \text{theo} \) of substituted samples are identified based on formula (4):

\[
m(0) \text{theo} = n_{\text{tetra}} - n_{\text{octa}} = 3 \times 5 \mu_B - (2 - x) \times 5
\]
where \( m^{(\text{tetra})} \) and \( m^{(\text{octa})} \) are magnetization of tetrahedral and octahedral sites at 0 K. The theory and experimental values \( m(0)_{\text{exp}} \) of magnetizations are listed in Table 2.

The increase of magnetic moment with increasing indium contents indicates that In atoms prefer to enter the \( a \) site. The experiment values are smaller than the theoretical values for all the samples which can be explained due to both dislocations and canting of the magnetic moments in the main phase. The canting effect was reported previously for Sc substituted YIG samples in which non-magnetic Sc atoms occupy the \( a \) site [18].

The Curie temperature \( T_C \) values of \( \text{Y}_3\text{Fe}_{5-x}\text{In}_x\text{O}_{12}\) samples are listed in Table 2. The \( T_C \) of YIG sample is similar to that of the bulk counterpart [19] while the \( T_C \) of substituted samples decreases gradually with \( x \). The reduction of \( T_C \) is due to the magnetic dilution effects. Comparison is made among the \( T_C \) values of magnetically diluted YIG systems which is shown in Table 2. It is seen that with the same substitution level, \( T_C \) decreases faster in the systems with substitution takes place at the \( d \) sites compared to that at the \( a \) sites. This phenomenon can be explained by the fact that the number of pair interactions between Fe ions in the \( a \) and \( d \) sublattice for the case \( (3-x) \times 2 \) is larger than that for the case \( 3x(2-x) \) where \( x \) represents the mole fraction of non-magnetic ions.

Table 2. Saturation magnetization \( M_s \) and Curie temperature \( T_C \) of \( \text{Y}_3\text{Fe}_{5-x}\text{In}_x\text{O}_{12}\) (\( x = 0 \div 0.7 \)) samples

<table>
<thead>
<tr>
<th>( x )</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_{\text{exp}} ) (0 K) (emu/g)</td>
<td>35.5</td>
<td>41.05</td>
<td>43.58</td>
<td>44.5</td>
<td>46.56</td>
<td>47.58</td>
<td>49</td>
<td>50</td>
</tr>
<tr>
<td>( m(\mu_B/f.u.)_{\text{exp}} ) (0 K)</td>
<td>4.72</td>
<td>5.47</td>
<td>5.84</td>
<td>6.04</td>
<td>6.34</td>
<td>6.54</td>
<td>6.78</td>
<td>6.98</td>
</tr>
<tr>
<td>( m(\mu_B/f.u.)_{\text{theo}} ) (0 K)</td>
<td>5.0</td>
<td>5.5</td>
<td>6.0</td>
<td>6.5</td>
<td>7.0</td>
<td>7.5</td>
<td>8.0</td>
<td>8.5</td>
</tr>
<tr>
<td>( T_C ) (K)</td>
<td>560</td>
<td>546</td>
<td>530</td>
<td>512</td>
<td>493</td>
<td>478</td>
<td>460</td>
<td>405</td>
</tr>
<tr>
<td>( T_C ) (Y_3Fe_2(Fe_3Al_x)O_12) [20]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>480</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( T_C ) (K)</td>
<td>-</td>
<td>530</td>
<td>-</td>
<td>502</td>
<td>-</td>
<td>463</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( {\text{Y}_3\text{Ca}<em>x}<a href="%5Ctext%7BFe%7D_3">\text{Fe}_{2.5}\text{Sn}_x</a>\text{O}</em>{12} ) [21]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4. Conclusion

In summary, the present study has shown that $Y_3Fe_5-In_xO_{12}$ ($x = 0 \div 0.7$) powders with size between 50 – 100 nm were fabricated using the sol-gel method. The single phase structural was observed for $x$ as large as 0.6. At $x = 0.7$, a small amount of orthoferrite $YFeO_3$ appears (~ 2%). The value of lattice constant increases with increasing $x$. Our results show that $In^{3+}$ ions can replace for Fe with the concentration up to $x = 0.7$. Saturation magnetization of substituting samples increases with increasing of $In^{3+}$ concentration $x$ while the Curie temperature gradually decreases. The magnetic properties can be understood with assumption that In atoms mainly occupy the octahedral sites.

Acknowledgments

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