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Study of iron valence state and position in sub-site by Mössbauer spectroscopy

[1]*Young Rang Uhm**,[1]Jae Cheong Lim, [1]Kwang Jae Son, and [2]Chul Sung Kim*

[1]*Radioisotope Research Division Korea Atomic Energy Research Institute (KAERI), 989-111, Daedeok-daero, Yuseong, Daejeon 305-353, Republic of Korea*
[2]*Department of Nano-electro Physics, Kookmin University, Seoul 136-702, Republic of Korea*
**Corresponding author: uyrang@kaeri.re.kr*

1. Introduction

Mössbauer spectroscopy using ^{57}Co for a nuclear resonance with ^{57}Fe is a powerful method for the analysis of iron-containing materials [1]. This method turns out the properties of iron in target materials, which are valence state, occupied sub-site, and exchange interaction with neighbor atoms [2]. The magnetic ordering temperature and the magnitude of the magnetic fields at the iron sites of YIG can be influenced by substituting, either partially or totally, the Fe^{3+} ions at the octahedral and/or the tetrahedral sites with magnetic or diamagnetic ions, and/or by substitution the Y^{3+} ions at the dodecahedral sites with magnetic rare earth ions. It has been known for some time that Mössbauer spectroscopy is a powerful method by which iron-containing garnets can be studied. We report here on the synthesis of the compounds with garnet-related structures of composition $Y_3Fe_{4.5}Cr_{0.5}O_{12}$ and its examination by ^{57}Fe Mössbauer spectroscopy. The chromium in compounds of the $Y_3Fe_{4.5}Cr_{0.5}O_{12}$ is distributed at an octahedral site. The Mössbauer spectra can be analyzed using 3 or 4 sets of six Lorentzians with increasing amount of Cr^{3+} compounds in this system. It results from the distribution ($_4C_n$) of Fe^{3+} and Cr^{3+} at an octahedral site. A comparative study of ferrous tablets of Dynabi was carried out using Mössbauer spectroscopy. The obtained results revealed the presence of ferrous (Fe^{2+}) gluconate and ferrous fumarate in a sample. This observation is important to better control the iron state in such medicaments because their pharmaceutical effect in the body is related to the form and valence of iron [3].

2. Experimental Technique

Compounds of composition $Y_3Fe_{4.5}Cr_{0.5}O_{12}$ were prepared by a sol-gel method. Weighed amounts of $Y(NO_3)_3{\cdot}5H_2O$, $Cr(NO_3)_3{\cdot}5H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were first dissolved in ethylene glycol. The solution was refluxed at 80 ℃ for 12 h to allow gel formation and then dried at 250 ℃ for 24h. The dried powder was ground and annealed at 900 ℃ for 6h in air. These compositions of samples fired were identified from an X-ray diffractometer with CuK_α radiation. Mössbauer spectra were recorded at temperatures ranging from 14 K to room temperature using a helium closed-cycle cryogenerator and a constant acceleration Mössbauer spectrometer with a ^{57}Co in Rh matrix. All the spectra were computer-fitted to Lorentzian lines using the usual constrains of equal width for the two lines of each doublet and of equal width at a ratio of 3:2:1:1:2:3 for the six lines of sextet. A ferrous tablet of Dynabi was produced by Dong-A pharmacy. The presence of ferrous (Fe^{2+}) gluconate and ferrous fumarate was measured at 295 K through Mössbauer spectroscopy.

3. Results and discussion

It was shown that the grown powders have only a single phase of the garnet structure regardless of the amount of Cr substitution according to the X-ray diffraction patterns. All peaks of XRD patterns can be attributed to cubic structure. The lattice parameters have slowly varying values. In a previous study, the compared values of Ms and Hc at room temperature decreases as Cr compounds increases in $Y_3Fe_{4.5}Cr_{0.5}O_{12}$. Fig. 1 displays the random distribution fitting for Mössbauer spectra measured at 293 K for $Y_3Fe_{4.5}Cr_{0.5}O_{12}$. We have fitted the spectra to a model based on a random distribution of Fe or Cr ions. The Cr ion prefers to occupy in octahedral (a-site). Each octahedral Fe^{3+} is linked through oxygen to six tetrahedral coordinated Fe^{3+} ions such that all the octahedral sites have identical environments. However, the tetrahedral coordinated Fe^{3+} ions are linked to four octahedral sites containing a statistical distribution of Fe^{3+} and Cr^{3+} ions. In this way, five nonequivalent tetrahedral sites are expected, corresponding to the following configurations of neighbouring octahedral ($4Fe^{3+}$, $3Fe^{3+} + 1Cr^{3+}$, $2Fe^{3+} + 2Cr^{3+}$, $1Fe^{3+} + 4Fe^{3+}$, and $4Cr^{3+}$). We have fitted the spectra of all samples annealed at and above 900 ℃ to a model based on a random distribution for Fe and Cr ions on the a-sites. The probability that a Fe^{3+} ion has n nearest-neighbour sites occupied by Fe ions was calculated using the binomial formula Eq.1

$$\mathbf{P(n, y) = N_{(n)}\, y^n (1\text{-}y)^{4-n}},\ \mathbf{N_{(n)} = {}_4C_n} = \frac{4!}{n!(4-n)!} \quad \mathbf{(1)}$$

where y is the iron concentration. The spectra were fitted to a minimum of two sets and a maximum five sets of six Lorentzian-line patterns in which the relative intensities exceed 7.4 %. This is listed in Table 1. The Mössbauer spectra were initially fitted to two recorded quadrupoles splits with parameters characteristic of high spin Fe^{3+} ions in octahedral and tetrahedral oxygen coordination at Néel temperature, and the partial substitution of Fe^{3+} by Cr^{3+} at both the octahedral and tetrahedral sites results in a significant dilution of

magnetic moments in both sublattices and a weakening of the a-d, d-d, and a-a antiferromagnetic interactions.The Néel temperature in $Y_3Fe_{4.5}Cr_{0.5}O_{12}$ was decreased to 525 K as Cr substittuted in garnet .

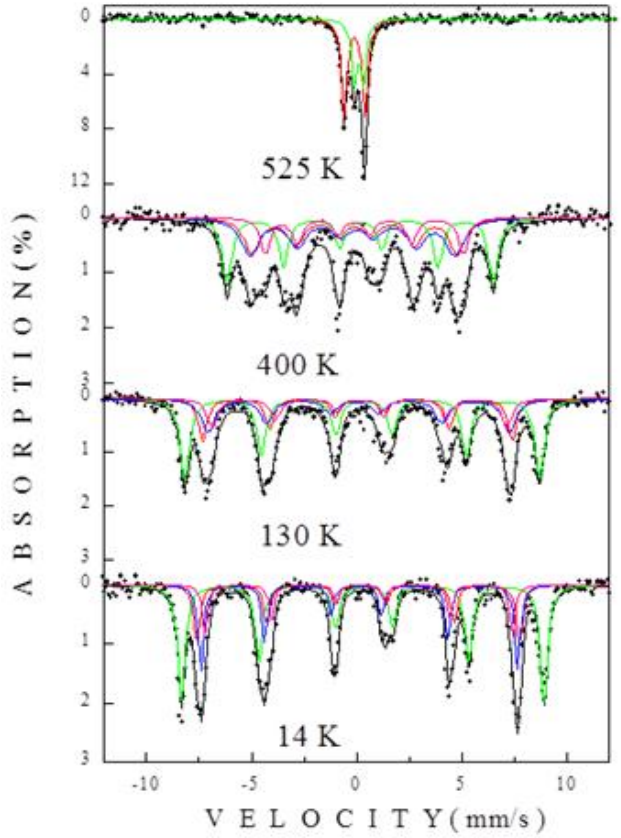

Fig. 1 Mössbauer spectra for $Y_3Fe_{45}Cr_{0.5}O_{12.}$

Table 1 The cation distribution of the iron ion at the chromium substituted garnet $Y_3Fe_{4.5}Cr_{0.5}O_{12}$. (n : nearest magnetic neighbor in octahedral site, P(n) :binomial distribution

n	N(n)	P(n)
0	1	0.316
1	4	0.421
2	6	0.211
3	4	0.047
4	0	0.004

Evaluation of ferrous and ferric Components in DynabiTab using Mossbauer spectroscopy was carried out at room temperature. The ferrous (Fe^{2+}) gluconate and ferrous fumarate were observed. The ferric (Fe^{3+}) phase was not detected.

4. Conclusions

The Cr-containing yttrium iron garnet (YIG), and the exchange interactions and site distributions were studied using ^{57}Fe Mössbauer spectroscopy. The lowering of magnetic ordering temperature results from replacing Fe^{3+} by Cr^{3+} ions in the octahedral sites. Mössbauer spectra can be analyzed using 3 or 4 sets of six Lorentzians with an increasing amount of Cr^{3+}. This results from the distribution ($_4C_n$) of Fe^{3+} and Cr^{3+} at the octahedral sites. A comparative study of ferrous tablets of Dynabi was carried out using Mössbauer spectroscopy. The obtained results revealed the presence of ferrous (Fe^{2+}) gluconate and ferrous fumarate in the sample. This observation is important better control the iron state in such medicaments because their pharmaceutical effect in the body is related to the form and valence of iron.

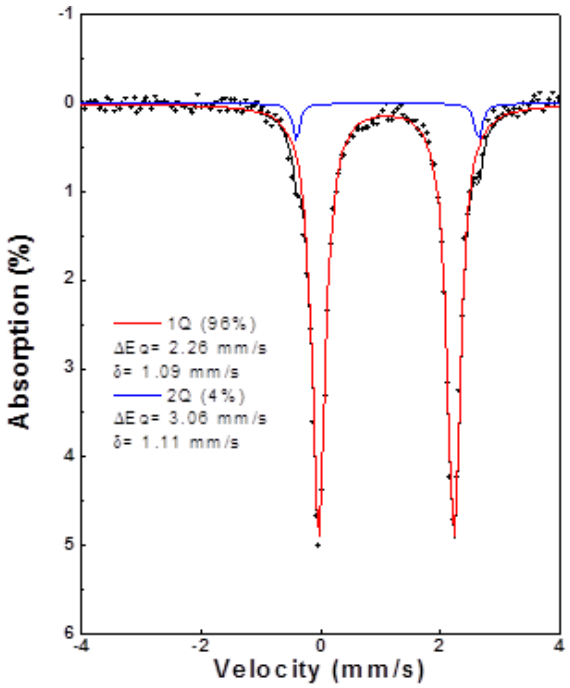

Fig. 2 Mössbauer spectrum of Dynabi tablet.

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