Structural and Magnetic Properties of (CoFe₂O₄)_{0.5}(Y₃Fe₅O₁₂)_{0.5} Powder

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Cobalt ferrite and garnet powders were grown using a conventional ceramic method in two different ways for understanding the magnetic interaction between structurally different materials. Structures of these powders were investigated by using an X-ray diffractometer (XRD) and the magnetic interaction between iron ions and the magnetic properties of the powders were measured by a Mössbauer spectroscopy and a vibrating sample magnetometer (VSM), respectively. The result of the XRD measurement showed that the annealing temperature higher than 1200°C was necessary to grow a (CoFe₂O₄)_{0.5}(Y₃Fe₅O₁₂)_{0.5} powder. Mössbauer spectra for the powders grown separately and mixed mechanically consisted of sub-spectra of cobalt ferrite and garnet, however, powders annealed together had an extra sub-spectrum, which was related with the magnetic interaction between the grain surface of cobalt ferrite and the one of the garnet. In case of annealing the powders at the temperature large enough to crystallize them, raw chemicals became fine cobalt ferrite and garnet particles at first and then these fine particles were aggregated and formed large grains of ferrite powders. The result of the VSM measurement showed that the powders prepared at 1200°C had the similar saturation magnetization and the coercivity regardless of the preparation method.

Key words: Mössbauer spectra, Inter-diffusion, Composite ferrite, Cobalt ferrite and garnet

1. Introduction

Recently, much attention has focused on the fabrication of structurally different materials and hetero-structural films, such as perovskite manganite/cobalt ferrite [1] and garnet/hematite [2]. Most of studies are considered only about their electrical and magnetic properties. However, there has been no much study on the inter-diffusion between different materials. During the growth of structurally different materials, high annealing temperatures, which are caused to change their structures, are necessary to obtain the good structural quality [2, 3]. Studies on ferrite powders have been focused on obtaining their magnetic and electric properties suitable for their applications [4-6], however, the effect of growing two structurally different materials has not been studied very much. It is a reason that the electro-magnetic properties of these materials are not reproducible and that sometimes they become a completely different material. These changes can be caused by the inter-diffusion between structurally different materials and their electro-magnetic properties strongly depend on the history of varying rate of temperature, annealing temperature and period.

In this report, cobalt ferrite and garnet powders will be used to study their magnetic effects when structurally different materials are annealed together and the structural and magnetic properties of mixed materials. When different ferrite powders were mechanically mixed, the interaction between them will be negligible. However, when their raw materials are annealed together, structurally different ferrite are located closely each other and some of elements may be replaced on unintended sites. A Mössbauer spectroscopy is an useful tool to study the magnetic interaction between iron ions and other ions [7, 8]. XRD and Mössbuaer spectroscopy will be good tools to invest the change of lattice distances and the location of iron sites due to the misplacement. VSM measurement will give us the macroscopic change of the magnetic properties.

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2. Experiment

(CoFe₂O₄)_{0.5}(Y₃Fe₅O₁₂)_{0.5} powders were prepared in two different ways by using a conventional ceramic method [9]. One of them was made following as a proper amount of CoO, Fe₂O₃, and Y₂O₃ were mixed together and annealed at 1000°C, 1200°C and 1400°C for 12 hours, respectively. The other powder was prepared as cobalt ferrite and garnet powders were annealed at 1200°C for 12 hours separately and then two ferrite powders were mixed mechanically at room temperature called as a mixed powder. The starting materials had a 99.99% purity and dehydrated for 5 hours at 100°C before weighted. The composite ferrite powders consisted of 27% of weighted cobalt ferrite and 73% of weighted garnet powders. Structures, composition and shapes of the ferrite particles were analyzed and observed by using Xray diffractometer (XRD) and scanning electron microscopy (SEM). Magnetic properties and magnetic interaction between iron ions in cobalt ferrite powders and other ions in garnet were measured and identified by using a vibrating sample magnetometer (VSM) and a Mössbauer spectroscopy.

3. Results

XRD patterns of $(CoFe_2O_4)_{0.5}(Y_3Fe_5O_{12})_{0.5}$ powders annealed at 1000°C and 1200°C and the mixed powder are shown in Fig. 1. When the annealing temperature was higher than 1200°C, clean diffraction peaks of cobalt ferrite and garnet were observed without any additional line corresponding to any other phase. This pattern is identical with the one shown in Fig. 1(c), which was measured with the cobalt ferrite and the garnet grown separately at 1200°C and mixed mechanically. Figure 1 shows that the peak intensity of garnet powders was higher than the one of cobalt ferrite. It is reasoned that the composite ferrite powders had more amount of garnet powders, as explained before. The XRD measurement indicated that even though two different ferrites were mixed and annealed together, two structurally different ferrite powders grew with their own structures: all of raw chemicals became cobalt ferrite and garnet powders. The inter-diffusion between the cobalt ferrite and the garnet was not observed, i.e., Y ions were not replaced with Fe and Co ions in Co ferrite and cobalt ions in cobalt ferrite were not located on garnet powders. If any, the peak positions and the unexpected peaks might be observed in Fig. 1(b). The XRD pattern of the powder fired at 1000°C, as shown in Fig. 1(a), indicated that some of the powder was crystallized but some of them remained as

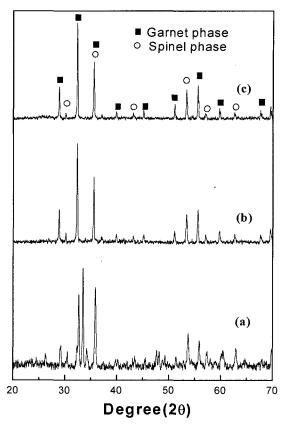
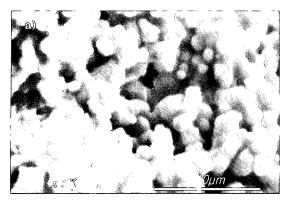


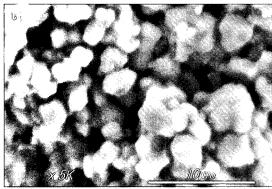
Fig. 1. X-ray diffraction diagrams of $(CoFe_2O_4)_{0.5}(Y_3Fe_5O_{12})_{0.5}$ powders annealed at (a) 1000°C and (b) 1200°C and (c) the mixed powder.

 Fe_2O_3 and Y_2O_3 . It is because that the cobalt ferrite was crystallized with the annealing temperature higher than $700^{\circ}C$, however, the garnet was formed at above $1100^{\circ}C$ [8].

SEM micrographs of a) CoFe₂O₄, b) (CoFe₂O₄)_{0.5}-(Y₃Fe₅O₁₂)_{0.5} and c) Y₃Fe₅O₁₂ powders annealed at 1200°C are shown in Figs. 2(a)-(c). The composite powder had the morphology different from the ones of garnet or cobalt ferrite powders: most parts of the powders exhibited similar like a garnet powder, however, its surface was not smooth and round as much as the one of the garnet as shown in Fig. 2(c). The SEM micrograph of Fig. 2(b) indicated that the cobalt ferrite and the garnet powders were aggregated and completely formed together. It was very hard to identify which part of the powders was the garnet or the cobalt ferrite.

Figure 3 shows Mössbauer spectra of ferrite powders measured at room temperature. Figure 3(a) is the Mössbauer spectrum of the mixed powder, which was grown separately and mixed mechanically. The spectrum consisted of the absorption sub-spectra of the cobalt ferrite and the garnet powder. It was not to find any other





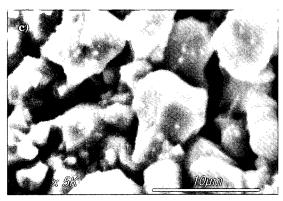


Fig. 2. Scanning electron micrograph of a) $CoFe_2O_{4,}$ b) $(CoFe_2O_4)_{0.5}(Y_3Fe_5O_{12})_{0.5}$ and c) $Y_3Fe_5O_{12}$ powders annealed at 1200°C.

sub-spectrum, which might be related with the interaction between iron ions in the garnet and ones in the cobalt ferrite. However, absorption spectra of the ferrite powders mixed and annealed at various temperatures were different from the spectrum in Fig. 3(a). As shown in Fig. 3(b), the Mössbauer spectrum of the powder annealed at 1000°C had the sub-spectra of the cobalt ferrite and a very small amount of the garnet subspectra, which meant the small portion of garnet crystallized. The annealing temperature was not large enough to make the garnet powder. The spectra had an extra sub-spectrum related with the interaction between iron ions of different ferrite powders. The sub-spectrum was located on the second

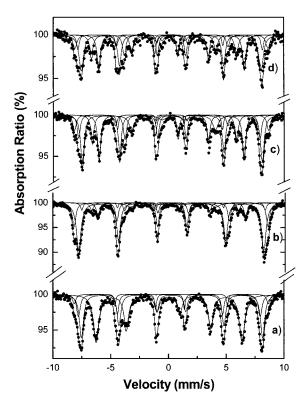


Fig. 3. Mössbauer spectra for a) the mixed powder and ferrite powders annealed at b) 1000°C and c) 1200°C, and d) 1400°C.

left-side peaks of the spectra in Figs. 3(c) and (d). The sub-spectrum was originated from the separation of the sub-spectrum for 24(d) sites into two sub-spectra. It is believed that the interaction occurred between the grain surfaces of the cobalt ferrite and the garnet located closely. However, there was no evidence for cobalt and yttrium ions to be misplaced on unwanted sites. If any, more complicate absorption spectra might be expected. The absorption area ratio of iron ion sites related with the interaction is shown in Table 1 as a function of annealing temperature. The annealing temperature yielded the increase of the area ratio, which were related with the interaction. However, the ratio did not increase more than

Table 1. Variation of the absorption area ratio for the $(CoFe_2O_4)_{0.5}(Y_3Fe_5O_{12})_{0.5}$ powders annealed at $1200^{\circ}C$ and $1400^{\circ}C$ and the mixed powder.

Annealing Temperature	Cobalt-ferrite		YIG		
	a-site	b-site	a-site	d-site	
			·	(d- site	d'-site)
(-)	area ratio (%)				
1400	11.05	9.47	37.09	21.44	20.95
1200	10.47	9.46	35.12	24.39	20.56
Mixed	15.27	5.39	33.08	46.26	

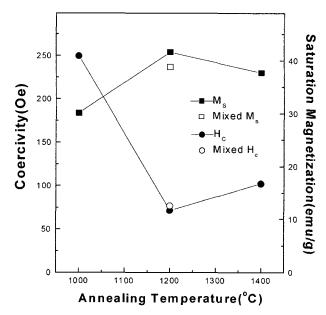


Fig. 4. Saturation magnetization and coercivities for the powders as a function of annealing temperature and for the mixed powder.

the certain amount. It is because when raw materials for two different ferrite powders were mixed and annealed at a certain temperature, raw chemicals became completely the cobalt ferrite and the garnet powders and two ferrite powders aggregated. The cobalt ferrite and the garnet were simply located closely with each other and if any ions were inter-diffused into unexpected sites, their amount might be very small enough to be ignored.

The magnetic properties of annealed powders were determined at room temperature by using a vibrating sample magnetometer. The result of the measurement for the ferrite powders is shown in Fig. 4. The small saturation magnetization and the large coercivity of the powder prepared at 1000°C were related to the growth of the cobalt ferrite. Even though the powder was annealed at 1000°C, the temperature was too low to crystallize the garnet powder completely, as shown in Fig. 1(a). The annealed powder consisted of cobalt ferrite and unformed chemicals (α -Fe₂O₃ and Y₂O₃). The remains made the saturation magnetization small, however, the high coercivity was related with the hard magnetic material, the cobalt ferrite. The powders prepared at 1200°C had the similar saturation magnetization and the coercivity regardless of the preparation method. The saturation magnetization of the pure cobalt ferrite and the garnet was 75.8 emu/g and 27.3 emu/g, respectively. The

powders prepared at 1200°C had 41.6 emu/g, which was very close to the calculated saturation magnetization (40.5 emu/g). It means that the interaction between the cobalt ferrite and the garnet powder did not have an important role for their magnetic properties.

4. Conclusion

The results of XRD and Mössbauer measurements, and SEM observation indicated that when chemicals for structurally different ferrite powders annealed together, raw chemicals became one of ferrite powders, which had a lower crystallization temperature and others grew later. And then the particles aggregated and formed large grains of ferrite powders. There was no evidence of cobalt ions replaced with iron ions or Y ions in garnet powders or Y ions located with Fe or cobalt sites in cobalt ferrites. If any small portion of ions were misplaced on another ferrite powder sites, the amount of the misplacement would be too small to be observed using XRD, Mössbauer spectroscopy and VSM. And the interaction between the cobalt ferrite and the garnet identified using the Mössbauer spectroscopy was too small to change their macroscopic magnetic properties. To make a new form of a ferrite powder, it might be necessary to anneal the mixed powder with an extremely high temperature.

Acknowledgements

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