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Sol-gel synthesis and dilute magnetism of nano MgO powder doped with Fe

Kiyoshi Nomura · Souichirou Taya · Atsushi Okazawa · Norimichi Kojima

Abstract Mg oxides doped with 1 % ^{57}Fe were prepared by a sol-gel method, and annealed at various temperatures. Nano-size Mg oxides were characterized by Mössbauer spectrometry, magnetization and XRD measurements. The crystalline size of MgO increases with increase of annealing temperature. Samples annealed at 600 °C and 800 °C gave only doublet peaks of paramagnetic Fe^{3+} in Mössbauer spectra although Fe^{3+} doping into MgO induced a distorted structure and showed weak ferromagnetism. It is considered that the magnetic property is due to defect induced magnetism by doping Fe^{3+} into MgO. For a sample heated at 1000 °C, it is found from low temperature Mössbauer spectra that Fe^{3+} species are located at the core and shell of fine $MgFe_2O_4$ grains and diluted in MgO matrix.

Keywords MgO doped with Fe · Mössbauer · Mg ferrite nano powder · dilute magnetism

1 Introduction

Ferromagnetic semiconductors with a large band gap are expected as spintronics materials since it is suggested that the semiconductors with the larger band gap show the higher Curie temperature [1]. Many researchers have studied semiconductors doped with transition metals and theoretical models in order to understand dilute ferromagnetism [2]. Oxide semiconductors doped with dilute magnetic ions give transparent and magnetic films. For example, Co- or Fe-doped TiO_2 films show ferromagnetism at room temperature (RT) [3].

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Authors have engaged in a study on dilute magnetism using especially SnO_2 and $Sn(Sb)O_2$ doped with ^{57}Fe because the band gap of SnO_2 is 3.6 eV [4, 5]. We need to take an attention whether or not the doped metal ions are precipitated as fine particles although the nano-size precipitated magnetic dots are useful as application of spintronics. It is often reported that the magnetic moment is enhanced when the doping rate of magnetic ions decreases. Many researchers are interested in the phenomena as a basic problem.

On the other hand, oxide insulators such as HfO_2, CaO, Al_2O_3, and ZrO_2 also show sometimes weak ferromagnetism, and a magnetic defect of nano particles has been discussed [6]. Authors have also studied the magnetic properties of Al_2O_3 and ZrO_2 doped with dilute metal ions [7, 8], and found that diamagnetic oxide insulators such as Al_2O_3 and YAG ($Y_3Al_5O_{12}$) show ferromagnetic behavior when doping rate of Fe^{3+} decreased [7, 9]. MgO is also a diamagnetic insulator with a large band gap (7.8 eV) and is used as a thin insulate layer between ferromagnetic layers. Magnetism is not expected in simple sp oxide like MgO. Recently, theoretical study on polaronic distortion and Mg-vacancy-induced magnetism in MgO suggest the possibility of ferromagnetism in hole-doped MgO [10]. It is also reported that chemically synthesized nano-scale MgO shows defect-induced magnetism [11]. The strange magnetism of Mg oxides is reviewed by M. Stoneham [12]. It is important to study on the doping effect of dilute Fe in MgO. We have synthesized dilute Fe-doped MgO powders by a sol-gel method. Dilute Fe-doped Mg oxides and the precipitated nano-size Mg ferrites in MgO are characterized by Mössbauer spectrometry.

2 Experimental details

a) Fe-doped MgO powders were synthesized by a sol-gel method. The initial solution with nominal composition was prepared by mixing the appropriate molar ratios of 0.5 M Mg solution and 0.01 M ^{57}Fe solution. The mixed solution was added by citrate acid and ethylene glycol, and heated at around 90 °C. The obtained gel was heated at 250 °C for 2 h and at 550 °C for 30 min. The crushed samples were annealed at various temperatures for 3.5 h. The nominal composition ratios of Mg and Fe oxides are given with atomic percentages (%).

b) Crystal structures and crystalline sizes were analyzed by XRD using Cu X-ray. Bulk magnetic properties (M-H curves) were measured at RT by a vibration sample magnetometer (VSM). Chemical states of ^{57}Fe involved in MgO were characterized by ^{57}Fe Mössbauer spectroscopy. Doppler velocities were calibrated at RT using α-Fe foil. Some samples were measured at low temperatures using a cryostat without vibration.

3 Results and discussion

XRD patterns of 1 % ^{57}Fe-doped Mg oxides synthesized by a sol-gel method show a cubic structure of MgO as shown in Fig. 1. XRD peaks of $MgFe_2O_4$ were not detected for samples heated at less than 800 °C, but the trace peaks were observed for a sample heated at 1000 °C. The lattice parameters of MgO are $a = 0.4232$ nm, 0.4227 nm, 0.4217 nm, and 0.4220 nm for the samples heated at 550 °C, 600 °C, 800 °C, and 1000 °C for 3.5 h, respectively. The decrease of lattice parameters means that Fe^{3+} ions are incorporated into well crystal of MgO because the ionic radius of Fe^{3+} (0.0785 nm) with six coordinated oxygen atoms is smaller than that of Mg^{2+}(0.086 nm). The lattice parameter (0.4220 nm) of MgO for the sample heated at 1000 °C slightly increased, compared to that for the sample heated at

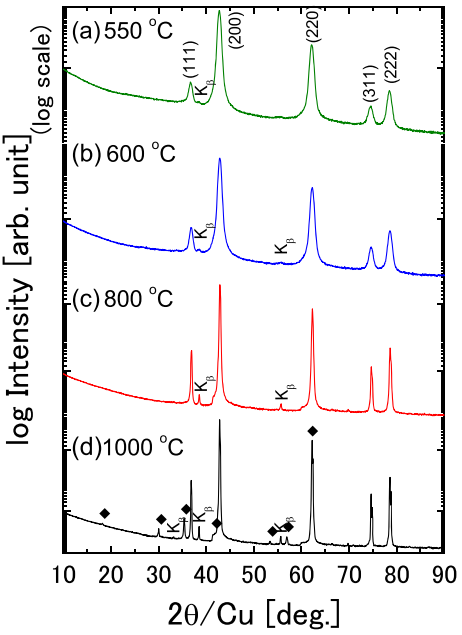

Fig. 1 X-ray diffraction patterns of 1 % ^{57}Fe doped Mg oxides, preheated at 550 °C for 0.5 h and annealed at 550, 600, 800, and 1000 °C for 3.5 h in air atmosphere

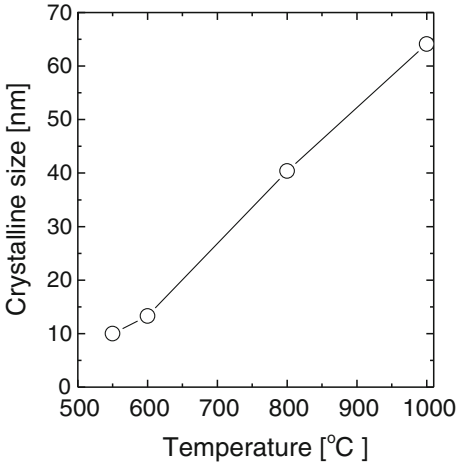

Fig. 2 Temperature dependence on crystalline size of 1 % Fe doped MgO, preheated at 550 °C for 0.5 h and annealed at 550, 600, 800, and 1000 °C for 3.5 h in air atmosphere

800 °C, which is considered to be due to dilution of Fe doped in MgO with precipitation of fine $MgFe_2O_4$. The crystalline size of MgO itself increased with the increase of annealing temperatures up to 1000 °C as shown in Fig. 2.

M-H curves of the samples annealed at various temperatures are shown in Fig. 3. After heating at 1000 °C, the M-H curve showed relatively strong ferromagnetism. The saturation magnetization was 0.4 μ_B/Fe, and the coercivity was 85 Oe. The large magnetic hysteresis is clearly due to partial precipitation of ferrimagnetic $MgFe_2O_4$. When samples were annealed in low vacuum condition of 10^{-4} torr, the crystalline size of MgO was almost similar to that heated in air atmosphere. The crystalline size of MgO was not so strongly affected by different atmosphere, but by annealing temperature.

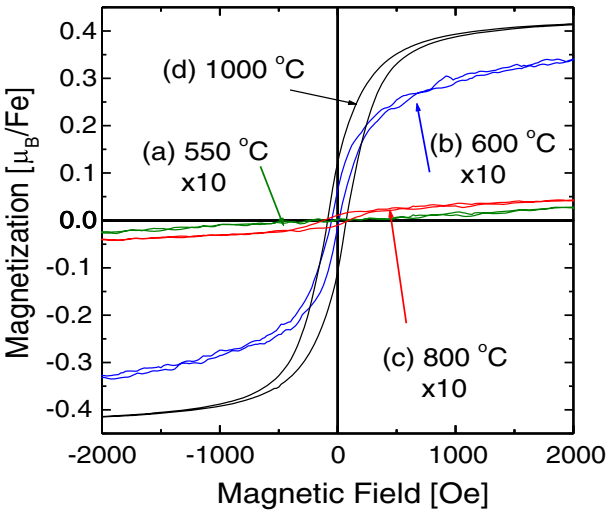

Fig. 3 Magnetization curves at RT for 1 % Fe doped MgO, preheated at 550 °C for 0.5 h and annealed at 550, 600, 800, and 1000 °C for 3.5 h in air atmosphere

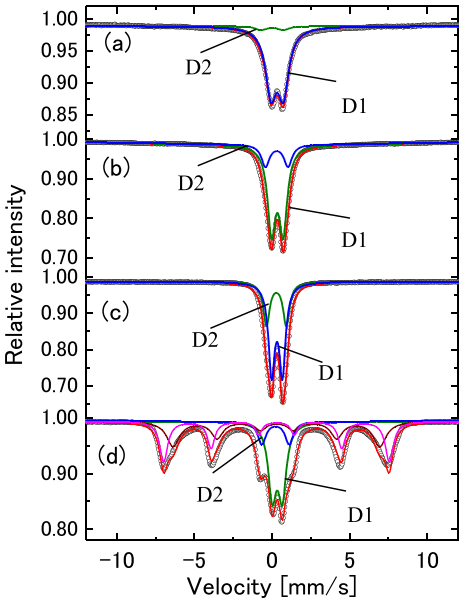

Fig. 4 4 Mössbauer spectra at RT for 1 % Fe doped MgO annealed at 550 °C for 0.5 h, crushed and annealed at 550, 600, 800, and 1000 °C for 3.5 h in air atmosphere

^{57}Fe Mössbauer spectra of the samples annealed at various temperatures are shown in Fig. 4. Two kinds of doublets were observed for the samples heated until 800 °C. The Mössbauer parameters are as follows; D1: isomer shift (IS) = 0.33 mm/s, quadrupole splitting (QS) = 0.66 mm/s, D2: IS = 0.29 mm/s, QS = 1.19 mm/s. The full width at half maximum (Γ) of doublet became small, such as 0.85, 0.64, and 0.49 mm/s for samples annealed at 550 °C, 600 °C, and 800 °C, respectively. The intensity of D1 and D2 increased with the increase of annealing temperature. They suggest that Mössbauer–Lamb factors

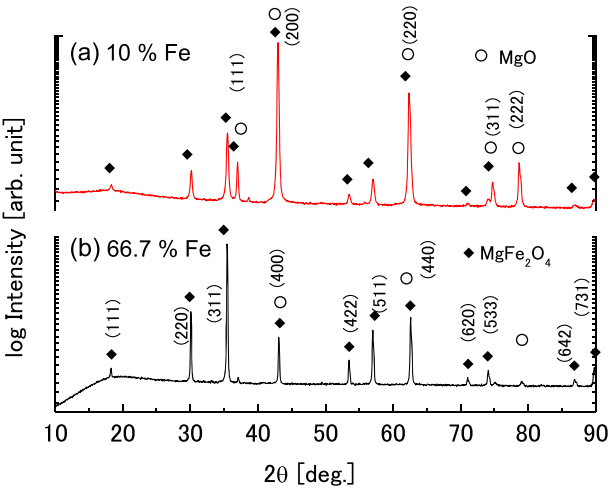

Fig. 5 XRD patterns of **a** 10 % Fe doped MgO and **b** 66.7 % Fe and 33.3 % Mg mixed oxides

increase due to well crystalline MgO, and that Fe^{3+} ions are strongly trapped at Mg site of MgO. Doublet D1 is considered to be due to Fe^{3+} substituted at the Mg site in MgO. Doublet D2 with small *IS* and large *QS* is due to paramagnetic Fe^{3+} species located in a more distorted lattice or vicinity to defects. Especially the intensity of D2 increased with increase of annealing temperature. It is considered that the amount of Fe^{3+} occupied at the more distorted sites increased because the compact crystal was formed.

It is noted that samples heated below 800 °C showed only paramagnetic doublets although the weak ferromagnetization hysteresis was observed in M-H curves. The doublets are considered to be due to paramagnetic species of Fe^{3+} incorporated in crystalline MgO with around 64 nm in a diameter. The results of XRD showed that the crystallinity is poor for the sample annealed at 600 °C and well for the sample annealed at 800 °C. FWHM of doublet peaks became narrow for the sample heated at 800 °C. It suggests that the defect-induced ferromagnetism may appear for the samples heated below 800 °C.

Mössbauer spectrum of the sample heated at 1000 °C was first decomposed into at least two kinds of sextets (M1 and M2). The magnetic fields are 45.1 T and 41.3 T due to Fe^{3+} species occupied at tetrahedral A and octahedral B sites in $MgFe_2O_4$, respectively. These parameters are similar to those obtained by N. Pailhe et al. [13]. However, fitting curves were not always better as shown in Fig. 4 (d). By the way, Mössbauer analysis of the nanocrystalline and non-equilibrium ferrite has recently been reviewed by V. Sepelak et al. [14]. Thereby, the disordered magnetic moments in shell of $MgFe_2O_4$ grains give the reduction of magnetic field. The magnetic sextets with tailing can be further decomposed into four sextets, which correspond to each pair of core and shell of fine grains, respectively. (see Fig. 9) On the other hand, for the samples annealed in vacuum condition (10^{-4} torr), single peak of Fe^{2+} in MgO was observed as an additional peak although the intensity of sextets due to $MgFe_2O_4$ decreased relatively. IS value of Fe^{2+} is corresponding to that of FeO.

In order to confirm the assignment of Mössbauer subspectra, stoichiometric $MgFe_2O_4$ (66.7 % Fe and 33.3 % Mg) and 10 % Fe-doped Mg oxides were prepared by the same method, and annealed at 800 °C. XRD patterns and M-H curves are shown in Figs. 5 and 6, respectively. XRD patterns of 10 % Fe-doped Mg oxides show cubic MgO and inverse spinel $MgFe_2O_4$ although 66.7 % Fe- and 33.3 % Mg-mixed oxides become almost $MgFe_2O_4$

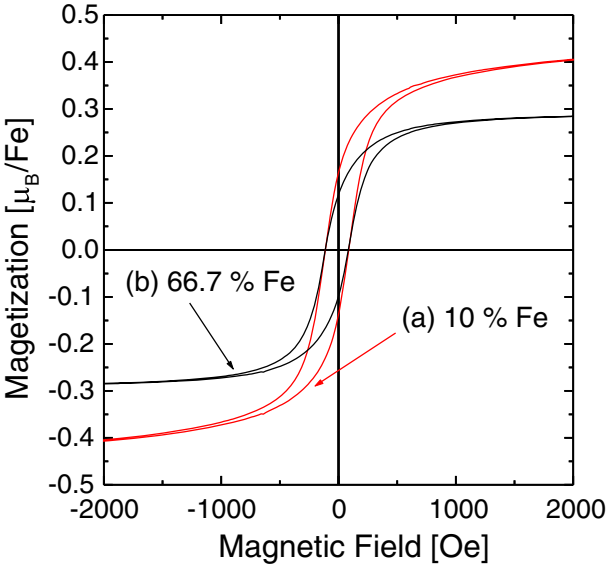

Fig. 6 Magnetization curves at RT for **a** 10 % Fe doped MgO and **b** 66.7 % Fe and 33.3 % Mg mixed oxides, annealed at 800 °C

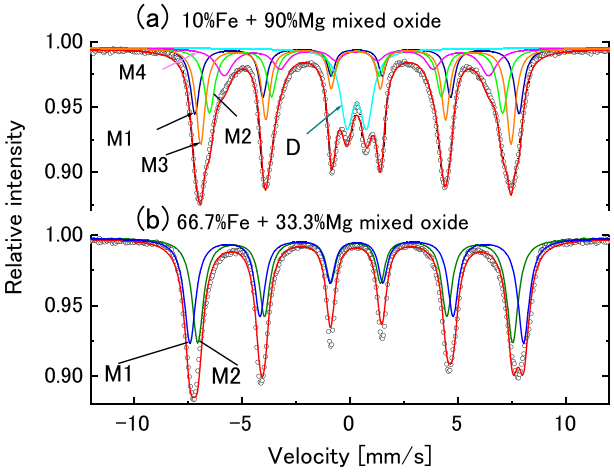

Fig. 7 Mössbauer spectra at RT for **a** 10 % Fe doped Mg oxides and **b** 66.7 % Fe and 33.3 % Mg mixed oxides, annealed at 800 °C

crystal powder as expected. Lattice planes, (200) and (220), of MgO are consistent with (400) and (440) of $MgFe_2O_4$. Both oxide compounds fit together well and coexist. As shown in Fig. 6, the saturation magnetization of 10 % Fe-doped MgO was larger than that of nearly pure $MgFe_2O_4$ although the crystalline size (29 nm) of the former was smaller than that of the latter (64 nm). This is based on antiparallel spin orientation of Fe at site A and site B of inverse spinel. The difference refelects the bulk magnetic property. Mössbauer spectra of these samples are shown in Fig. 7. The sample of nearly pure $MgFe_2O_4$ shows two

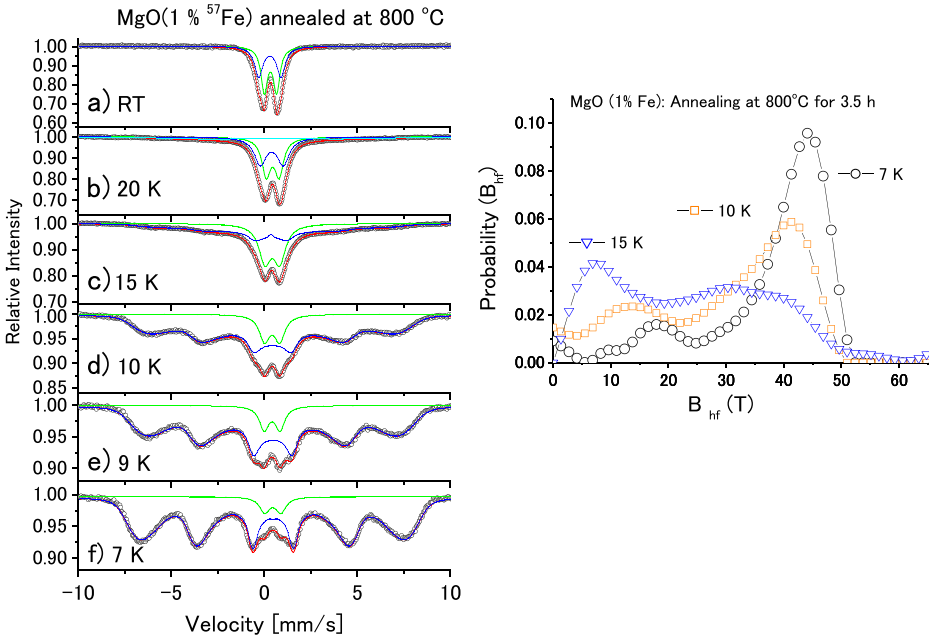

Fig. 8 Low temperature Mössbauer spectra (*left*) and hyperfine distribution (*right*) of 1 % Fe doped MgO annealed at 800 °C for 3.5 h in air atmosphere

sextets with almost the same area intensity and sharp peaks, which are clearly assigned to tetrahedral site A and octahedral site B of inverse spinel $MgFe_2O_4$, respectively. 10 % Fe-doped Mg oxide showed broad sextets, which could be decomposed into four sextets for the core and shell of the precipitated Mg ferrite.

The shell of inverse spinel shows spin canting tending to reduce the inner magnetic field, and sometimes different population of Fe occupied at site A and site B. Therefore, the powder of Mg ferrite with small crystalline size (29 nm) showed the large magnetic hysteresis. The non-equilibrium cation distribution in $MgFe_2O_4$causes the increase of magnetization.

Mössbauer spectra of 1 % ^{57}Fe-doped MgO samples heated at 800 °C and at 1000 °C were measured at low temperatures as shown in Figs. 8 and 9, respectively. In the case of the sample heated at 800 °C, the magnetic broad peaks appeared under 20 K in addition to the paramagnetic peaks. Some magnetic hyperfine distributions are shown in Fig. 8 right. The average hyperfine fields increase with decreasing the measuring temperature, whereas the doublets' intensity of paramagnetic Fe^{3+}decreases. Mössbauer parameters at 7 K are as follows; D1: $IS = 0.45$ mm/s, $QS = 0.87$ mm/s, $\Gamma = 0.67$ mm/s, Area intensity = 5.5 %, M1: $B_{hf} = 44$ T at maximum peak of hypertine distribution, Average $< B_{hf} >=$ 37.9 T, $IS = 0.46$ mm/s, $2\varepsilon = -0.02$ mm/s, $\Gamma = 0.68$ mm/s, Area intensity = 94.5 %. The broad magnetic peaks cannot be clearly decomposed into two sextets such as site A and site B of Mg ferrite, and so may reduce in slowly magnetic relaxation of dilute Fe-doped MgO. The peaks are a little different from temperature dependence Mössbauer spectra of the super-paramagnetic particles of $MgFe_2O_4$ [15].

In the case of the sample heated at 1000 °C, RT Mössbauer spectrum are composed of four components of the core and shell of Mg ferrite as shown in Table 1. The crystalline size of Mg ferrite is less than that of the precipitated Mg ferrite in 10 % Fe-doped MgO (29 nm) .

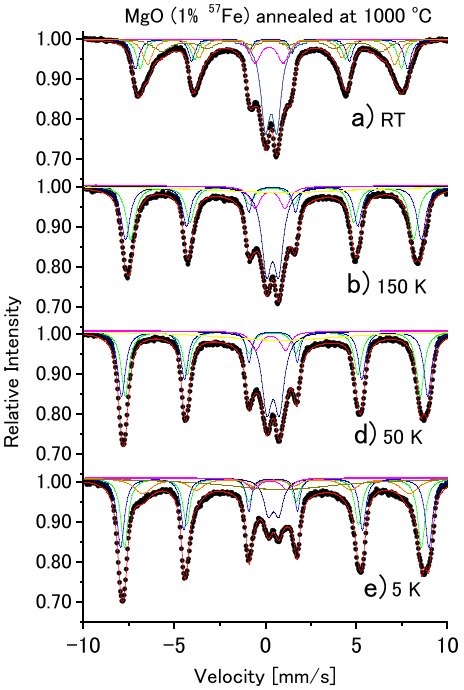

Fig. 9 Low temperature Mössbauer spectra of 1 % ^{57}Fe doped MgO annealed at 1000 °C for 3.5 h in air atmosphere

Table 1 Mössbauer parameters of 1 % ^{57}Fe doped MgO, annealed at 1000 °C for 3.5h in air atmosphere

	B_{hf} (T)	*IS*(mm/s)	2ε (mm/s)	Γ(mm/s)	Area Int.%	Assignment
a) RT /Comp.						
M1	46.4T	0.31	0.05	0.48	15.5%	Site A in Core $MgFe_2O_4$
M2	44.5T	0.28	0.04	0.48	15.5%	Site B in Core $MgFe_2O_4$
M3	42.1T	0.30	0.04	0.65	17.9 %	Site A in Shell $MgFe_2O_4$
M4	37.4T	0.31	0.05	1.26	16.2 %	Site B in Shell $MgFe_2O_4$
D1	-	0.31	0.63	0.59	25.7 %	MgO(Fe)
D2	-	0.20	1.56	0.74	9.2 %	MgO(Fe)
e) 5K /Comp.						
M1	52.5T	0.47	0.09	0.49	27.9 %	Site A in $MgFe_2O_4$
M2	50.6T	0.40	0.02	0.49	28.2 %	Site B in $MgFe_2O_4$
M3′	45.2T	0.47	0.20	1.52	19.5 %	MgO(Fe)
M4′	26.3T	0.72	0.17	2.1	11.4 %	MgO(Fe)
D1	-	0.46	0.57	0.63	8.5 %	MgO(Fe)
D2	-	0.33	1.93	1.0	5.8 %	MgO(Fe)

On cooling to 150 K, the decomposed four sextets at RT are developed into two sextets with high intensity although the peak intensity of paramagnetic doublets is rather unchanged. It is clear that this is due to the developed magnetic field in shell domain of Mg ferrite grains. At 5 K, the broad sextet component and relaxation peaks reappeared with

decreasing the peak intensity of paramagnetic doublets. The magnetic field (45.2 T) of the broad sextet is smaller than that of Mg ferrite (site A: 52.5 T, site B: 50.6 T), and similar to the magnetic relaxation observed in Mössbauer spectra measured at less than 20 K for the sample heated at 800 °C. Thus, the micro magnetic structures are composed of several kinds of components; the tetrahedral site A and octahedral site B of $MgFe_2O_4$ and the diluted Fe-doped MgO.

4 Summary

Diluted Fe-doped Mg oxides were prepared by a sol-gel method and the nano structures were identified mainly by Mössbauer spectrometry. It is found that 1 % Fe-doped MgO samples annealed below 800 °C show dilute ferromagnetism due to the distorted structure of MgO. However, when 1 % Fe-doped MgO samples are annealed at high temperatures around 1000 °C, the fine grains of $MgFe_2O_4$ are easily precipitated in MgO because the crystal lattice of $MgFe_2O_4$ and MgO fit together well. It is concluded that the magnetic structures of crystalline grains consist of several components: the core and shell of Mg ferrite and the dilute Fe-doped MgO. The crystalline sizes of MgO can be easily controlled by heating temperatures and the grain sizes of Mg ferrite precipitated at high temperatures could be controlled by doping rates of Fe.

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