An external field applied $\text{MFe}_2\text{O}_4$ (M=Mn, Mg) nanoparticles with Mössbauer spectroscopy.

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I. Introduction
The ferrite magnetic nanoparticles have long been studied due to the scientific and technological interest, which can be used in catalysts, high density magnetic storage and biosensors [1-3]. Recently, the magnetic properties of nanoparticles have been reported because the novel properties in a few nanometer sizes [3]. Specially, spinel ferrites, $\text{MFe}_2\text{O}_4$ (M=Mn, Co, Ni, Cu, Zn, etc.) were interested in not only a recording media, microwave device as the general application, but also hyperthermia, target drug delivery, and the magnetic resonance imaging (MRI), which used the novel properties in a few nanometer sizes [4].

II. Experiments
The transition metal doped ferrites, $\text{MFe}_2\text{O}_4$ (M=Mn, Mg) samples were prepared by a HTTD methods [2]. Manganese(II) acetylacetonate $[\text{Mn(CH}_3\text{COCH=C(O-)CH}_3\text{)}_2]$, Magnesium acetate tetrahydrate $[\text{Mg(CH}_3\text{CO}_2\text{)2 4H}_2\text{O}]$, and iron(III) acetylacetonate $[\text{Fe(CH}_3\text{COCH=C(O-)CH}_3\text{)}_3]$ were used as starting materials to prepare $\text{MFe}_2\text{O}_4$ (M=Mn, Mg) powder samples. Manganese acetylacetonate and Magnesium acetate tetrahydrate with 1,2-Hexadecanediol were mixed with iron(III) acetylacetonate in phenyl ether and benzyl ether, respectively. The mixture was heated up to 200 °C to clearly dissolve and uniformly disperse the nanoparticles, and maintained for 30 min. under Ar atmosphere. It reheated up to 260 ~ 300 °C and maintained for 1 h to form the $\text{MFe}_2\text{O}_4$ nanoparticles, because the reaction allows ferrite nanoparticles to be easily isolated during the chemical reaction between byproducts and the ether solvents. Then, it cooled down to room temperature (RT). The crystal structures of the samples were examined by x-ray diffraction patterns with Cu Kα radiation ($\lambda = 1.5406$ Å). Magnetic measurements were performed by vibrating sample magnetometer (VSM). The hyperfine interaction between the Fe (i.e. the magnetic field at the nucleus) and its environment in the crystal lattice was characterized by Mössbauer spectroscopy, which used conventional spectrometer with a $^{57}\text{Co}$ source in a rhodium matrix.

III. Results and Discussion
X-ray diffraction was used to confirm the crystal structure and crystallographic parameters of the samples. An analysis of XRD patterns for $\text{MFe}_2\text{O}_4$ (M=Mn, Mg) have a cubic spinel structure (space group $Fd\bar{3}m$) with the lattice constants $a_0 = 8.418 \pm 0.001$, and $8.332 \pm 0.001$ Å, respectively. The particle size for the samples calculated using Scherrer equation, which has the value of 6 nm.

The hysteresis loops were measured using VSM with maximum applied field 1.5 T at RT, which the typical superparamagnetic behavior was observed in the samples. The magnetization ($M_s$) is 37.8 emu/g and for $\text{MnFe}_2\text{O}_4$, and 53.9 emu/g for $\text{MgFe}_2\text{O}_4$, respectively, which shows almost zero coercivity ($H_c$) value. The Mössbauer spectra of the samples were taken at RT and 4.2 K with applied field 4.8 T, to understand localized nearest neighbor effects on effective field, as shown in Fig. 1 and 2. The Mössbauer spectra of the samples were analyzed by a least-squares fitting to two hyperfine sextets of the following model, $\text{(M}_{x}\text{Fe}_{1-x})_A[\text{M}_{1-x}\text{Fe}_{x}]\text{BO}_4$ (M=Mn, Mg), where the subscripts A and B denote the tetrahedral sites and octahedral sites, respectively. According to the isomer shifts at 4.2 K for the A and B sites of the samples, the valence state of Fe ions is $3^+$, relative to the Fe metal. An analysis of Mössbauer spectra at 4.2 K with applied field shows that the area ratio of the A and B sites are 3 : 7 for $\text{MnFe}_2\text{O}_4$, respectively, and are 4 : 6 for $\text{MgFe}_2\text{O}_4$. It could explain that $\text{MFe}_2\text{O}_4$ (M=Mn, Mg) follows the model, $\text{(M}_{0.6}\text{Fe}_{0.6})_A[\text{M}_{0.4}\text{Fe}_{1.4}]\text{BO}_4$, and $(\text{M}_{0.2}\text{Fe}_{0.8})_A[\text{M}_{0.8}\text{Fe}_{1.2}]\text{BO}_4$.