

Mössbauer study on the antiferromagnetic FeO synthesized under high pressure

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Abstract Mössbauer study and magnetic measurements were carried out on the stoichiometric FeO, prepared with the high pressure (~ 5.5 GPa) synthesis technique. Well known defects (Koch-Cohen clusters) in FeO are detected even in the stoichiometric specimen, prepared at high temperatures.

Keywords FeO · High pressure synthesis · Mössbauer spectroscopy

1 Introduction

A series of 3d mono oxides, MO (M = Mn, Fe Co and Ni), have a simple NaCl crystalline structure and their electronic states have been investigated intensively for long time. In the case of FeO and CoO, one or two electrons exist in the degenerated $d\varepsilon$ orbitals due to the regular octahedral ligands. Co-existence of the spin-orbit interaction, because of only the partial quenching of the orbital angular momentum ($S = 2$ and $L = 1$), and the Jahn-Teller effect with both T_{2g} and E_g type of the lattice distortion bring about a complex situation [1, 2].

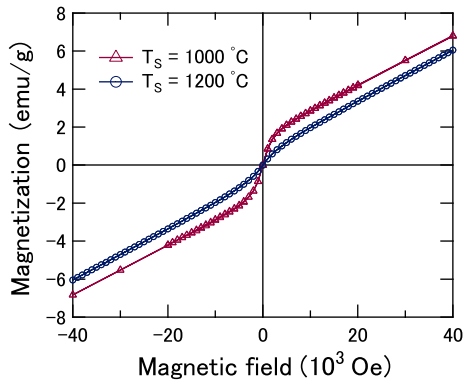
Difficulty in the sample preparation makes the experimental investigation of fundamental properties of FeO difficult. Stoichiometric compound cannot be synthesized at ambient pressure. Instead one obtains Fe_XO with $X \lesssim 0.96$. Lattice defects introduced by this non-stoichiometry are reported to form a cluster structure (Koch-Cohen cluster) [3].

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Fig. 1 Magnetization curves for the FeO samples prepared under high pressure and high temperature



It was reported that stoichiometric FeO can be achieved by disproportionation of Fe_xO at 225 °C [4]. However, formation of the ferromagnetic Fe_3O_4 is inevitable in this case and the magnetic investigation of FeO is impossible [5].

Synthesis of the stoichiometric FeO can be achieved by the preparation of the specimen under high pressure [6]. In this study, we performed Mössbauer and magnetic studies on the stoichiometric FeO prepared with the high pressure synthesis technique. It is disclosed that the Koch-Cohen cluster does exist even in this case, especially when the reaction temperature is high.

2 Experimental procedure

Samples were synthesized using a modified belt-type high pressure and high temperature apparatus installed in the National Institute of Materials Science (NIMS) [7]. The starting material was prepared by mixing α -Fe and Fe_2O_3 powder with the atomic ratio of Fe : O = 1 : 1, approximately 0.4 g in total, and was sealed in a Pt capsule. The capsule was heated up to $T_s = 1000$ °C and 1200 °C under 5.5 GPa for 1 h. Total composition of the specimen can be expected unchanged.

Powder X-ray diffraction of the synthesized samples revealed that they are in an NaCl type single phase and no trace of other compounds was detected. Magnetization measurements were carried out with a conventional SQUID magnetometer. Mössbauer spectra were recorded on a conventional constant acceleration spectrometer at room temperature. The velocity scale and isomer shift were calibrated relative to α -Fe at room temperature and line widths (FWHM) of 0.27 mm/s for the outer lines of α -Fe were obtained. Data were analyzed using a commercially available analysis program, MossWinn Ver.3.

3 Result and discussion

The magnetization curves recorded at room temperature are shown in Fig. 1. They are linear to the applied fields in a range between 10 kOe and 40 kOe. However, small amounts of ferromagnetic components are clearly seen in both magnetization curves. Assuming that the residual ferromagnetic parts are composed of α -Fe, the

Fig. 2 Inverse susceptibility plotted against temperature for the $T_s = 1000\text{ }^\circ\text{C}$ sample

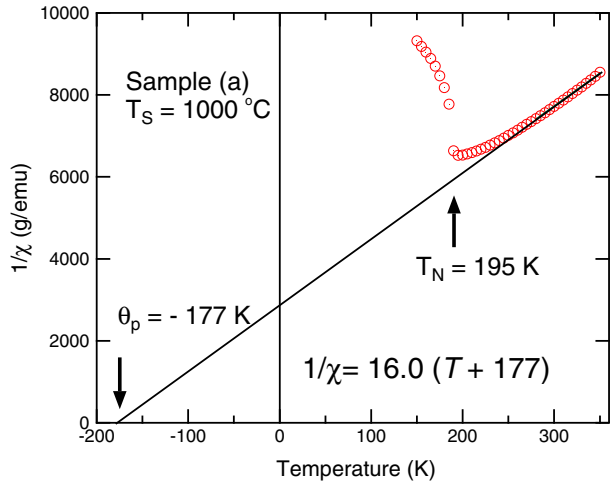
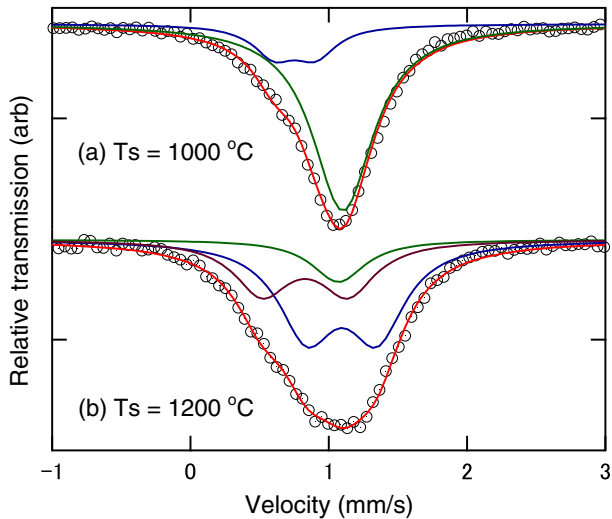


Fig. 3 Mössbauer spectra recorded at room temperature for FeO samples prepared under high pressure and high temperature. The reaction temperatures are (a) $T_s = 1000\text{ }^\circ\text{C}$ and (b) $T_s = 1200\text{ }^\circ\text{C}$. Fitting parameters are summarized in Table 1



amounts are estimated to be 0.69 at % for the $T_s = 1000\text{ }^\circ\text{C}$ sample and 0.24 at % for the $T_s = 1200\text{ }^\circ\text{C}$ sample, respectively. From this result, higher reaction temperature may bring lower concentration of ferromagnetic components.

Paramagnetic susceptibilities can be deduced from the linear parts. Figure 2 shows the inverse susceptibility plotted against temperature for the $T_s = 1000\text{ }^\circ\text{C}$ sample. T_N was about 195 K and the paramagnetic Curie temperature, θ_p , was estimated as -177 K . According to the Curie constant, the effective magnetic moment, μ_{eff} , was determined as $5.68\ \mu_B$. This amplitude fits to the case of angular momentum of $S = 2$ and $L = 1$, [1] though the temperature range of the measurement cannot be considered wide enough. It is noted that the ferromagnetic components in the samples were less temperature dependent.

Table 1 Mössbauer parameters for FeO spectra at 298 K

Sample	T_s (°C)	Site	IS ^a (mm/s)	QS (mm/s)	LW (mm/s)	Area (%)
(a)	1000	Fe ²⁺ :A	1.088		0.536	82.0
		Fe ²⁺ :B	0.755	0.297	0.370	18.0
(b)	1200	Fe ²⁺ :A	1.070		0.469	12.5
		Fe ²⁺ :B	1.094	0.507	0.496	56.0
		Fe ²⁺ :C	0.828	0.620	0.481	31.5

^arelative to Fe metal

Mössbauer spectra recorded at room temperature are shown in Fig. 3. The sharper spectrum was observed for the $T_s = 1000$ °C sample, compared with that prepared at $T_s = 1200$ °C. The spectrum for the $T_s = 1000$ °C sample can be fit to the combination of a major singlet, about 80 % of the absorption, and an additional minor doublet (Fig. 3a). No significant absorption due to magnetite was observed, in contrast to the previous reports [4, 5]. The singlet can be attributed to the Fe²⁺ ions in a cubic environment without defects and the doublet Fe²⁺ in defect sites. The isomer shift of the singlet is about 1.08 mm/s. This value is comparable to the isomer shift of Fe_{0.861}O (1.05 mm/s) but larger than that reported for FeO containing small amount of Cr³⁺ ions [8].

On the other hand, the spectrum for the sample prepared at $T_s = 1200$ °C is more complex and at least two kinds of Fe sites with lower symmetry are responsible for doublets in the spectrum. It is noted that the fitting is not unique and many models have been proposed [9]. This result suggests that the number of Fe defects are larger in the sample prepared at $T_s = 1200$ °C. We have to conclude that the stoichiometric FeO without lattice defect has not been synthesized yet. However, high pressure synthesis can produce specimens which have less defect sites than those produced under ambient pressure conditions. We expect that the stoichiometric FeO without defects can be synthesized in near future.

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