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# Mössbauer spectrum of high-pressure synthesized ilmenite-type $FeGeO_3$

**T. Fujii · D. Nakatsuka · M. Nakanishi · J. Takada · T. Yoshino**



**Abstract** Ilmenite-type $FeGeO_3$ was prepared by high-pressure synthesis technique using a Kawai-type multi-anvil apparatus at 23.5 GPa and 500 °C. The effects of post annealing on the high-pressure synthesized samples were investigated by XRD analysis, Mössbauer spectroscopy and SQUID-magnetization measurements. The subsequent annealing after the high-pressure synthesis was effective to improve the crystallinity and increased the crystallite size of the ilmenite-type $FeGeO_3$. The room temperature Mössbauer spectrum was composed of sharp paramagnetic doublets assigned to $Fe^{2+}$. The well-crystallized ilmenite-type $FeGeO_3$ showed typical antiferromagnetic behavior with the Néel temperature of 79 K, while the as-prepared sample without annealing demonstrated the superparamagnetic characteristics with larger magnetization.

**Keywords** Ilmenite-type $FeGeO_3$ · High-pressure synthesis · Antiferromagnetism · Mössbauer spectroscopy

## 1 Introduction

$FeGeO_3$ crystallizes in a clinopyroxene structure with the space group C2/c at ambient conditions and decomposes at high pressures and temperatures. Under the very limited conditions above 23 GPa and below 700 °C, it transforms into an ilmenite structure with $R\overline{3}$ [1]. Due to the metastability of ilmenite-type $FeGeO_3$, it was hard to obtain the

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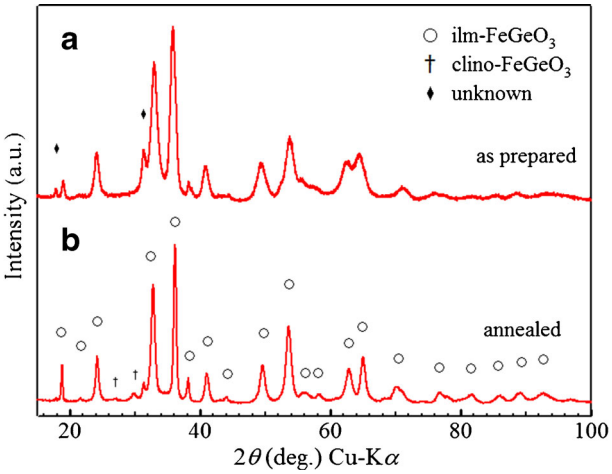


**Fig. 1** XRD patterns of high-pressure synthesized samples at 23.5 G Pa at 500 °C: **a** before and **b** after the annealing in vacuum at 500 °C for 96 h

well-crystallized sample. Recently we have successfully prepared well-crystallized ilmenite-type $FeGeO_3$ by using high-pressure synthesis and subsequent annealing at 500 °C for 96 h [2]. The subsequent thermal annealing could affect the rearrangement of both cations and anions transforming into the ilmenite structure and release the residual strains therein. In this paper, we report the effects of subsequent annealing on high-pressure synthesized $FeGeO_3$. The structural, electronic and magnetic properties of ilmenite-type $FeGeO_3$ before and after the annealing were investigated by XRD analysis, Mössbauer spectroscopy and SQUID-magnetization measurements.

## 2 Experimental

Ilmenite-type $FeGeO_3$ was prepared by a high-pressure synthesis technique from laboratory-synthesized clinopyroxene-type $FeGeO_3$. The clinopyroxene-type $FeGeO_3$ powders were sealed in an Au capsule and placed in the center of a cylindrical BN sleeve surrounded by an octahedral pressure medium (MgO+5% $Cr_2O_3$) with a $TiB_2$ heater. The sample was compressed to 23.5 GPa and then heated at 500 °C for 4 h in a Kawai-type multi-anvil apparatus using tungsten-carbide cubic anvils with a 46-mm-edge-length [3]. After releasing both temperature and pressure, the high- pressure synthesized sample was placed in an evacuated quartz tube and annealed at 500 °C for 96 h.

Crystal structures of obtained samples were investigated by X-ray diffraction (XRD) with monochromatic Cu-K$\alpha$ radiation. Chemical states of Fe ions in $FeGeO_3$ were characterized by conventional transmission Mössbauer spectroscopy at room temperature with a 925 MBq $^{57}$Co/Rh source. The velocity scale and isomer shift (IS) of Mössbauer spectra were calibrated by a $\alpha$-Fe foil at room temperature. Temperature dependent magnetic properties were studied by using a superconducting quantum interference device magnetometer (SQUID) between 5 and 300 K. In zero-field-cooling (ZFC) magnetization measurement, the sample was first cooled down to 5 K without applied magnetic field and then the magnetization was measured from 5 to 300 K in the applied magnetic field of 200 Oe. While

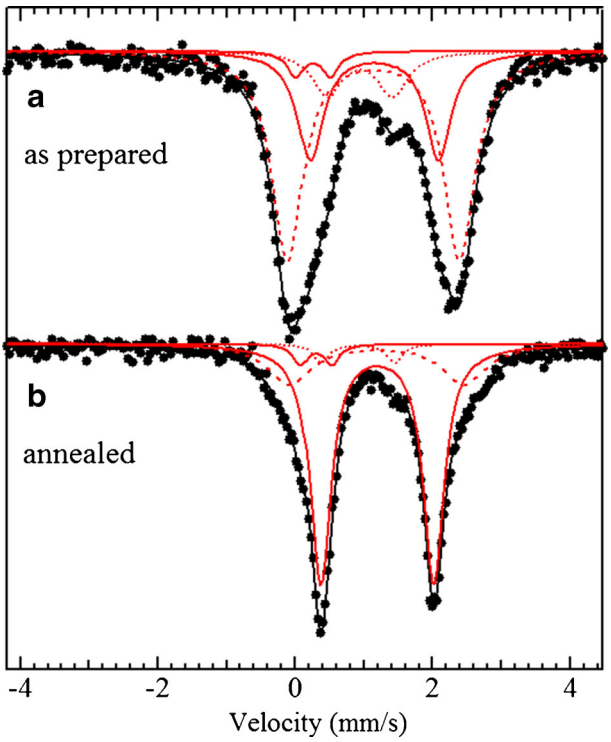


**Fig. 2** Room temperature Mössbauer spectra of high-pressure synthesized samples: **a** before and **b** after the annealing. The lines indicate the individual iron components tabulated in Table 1

in the field-cooled (FC) magnetization measurement, the magnetization was measured from 300 to 10 K with the applied magnetic field of 200 Oe.

## 3 Results and discussion

Figure 1 shows the XRD patterns of the high-pressure synthesized samples before and after the annealing. The as-prepared sample pressed at 23.5 GPa had a broad XRD pattern characteristic to ilmenite structure, though small unknown peaks were detected. The XRD pattern indicated the formation of ilmenite-type $FeGeO_3$ after applying the high-pressure. The hexagonal lattice constants of the as-prepared ilmenite-type $FeGeO_3$ were calculated to be a = 5.068 and c = 14.03 Å, which were nearly consistent with those in literature (a = 5.051, c = 14.09 Å) [1]. After the subsequent annealing at 500 °C for 96 h, the XRD peaks assigned to the ilmenite-type $FeGeO_3$ became increasingly sharper and well-resolved. The lattice constants showed the slight change to a = 4.968 and c = 14.13 Å. The increase in c/a ratio with releasing pressure was observed in the compressed ilmenite ($FeTiO_3$) crystals as well [4]. The crystallite size by the Scherrer's formula was increased to from 10 to 15 nm. Moreover unknown XRD peaks were almost vanished, but very small impurities assigned as clinopyroxene-type $FeGeO_3$ were presented in turn. The annealing process was confirmed to improve the crystallinity of the ilmenite-type $FeGeO_3$.

**Table 1** Fitted Mössbauer parameters obtained from the spectra in Fig. 2

| As prepared | IS (mm/s) | QS (mm/s) | FWHM(mm/s) | Area (%) |
|---|---|---|---|---|
| Doublet 1 | 1.15 ± 0.00 | 2.51 ± 0.02 | 0.55 ± 0.01 | 59.4 ± 1.5 |
| Doublet 2 | 1.15 ± 0.00 | 1.87 ± 0.02 | 0.45 ± 0.02 | 25.5 ± 1.2 |
| Doublet 3 | 0.94 ± 0.02 | 0.96 ± 0.03 | 0.51 ± 0.05 | 11.4 ± 0.6 |
| Doublet 4 | 0.26 ± 0.02 | 0.50 ± 0.04 | 0.28 ± 0.04 | 3.6 ± 0.5 |
| Annealed | IS (mm/s) | QS (mm/s) | FWHM(mm/s) | Area (%) |
| Doublet 1 | 1.25 ± 0.02 | 2.54 ± 0.05 | 0.82 ± 0.09 | 17.7 ± 1.2 |
| Doublet 2 | 1.19 ± 0.01 | 1.65 ± 0.04 | 0.39 ± 0.06 | 72.8 ± 1.1 |
| Doublet 3 | 0.65 ± 0.02 | 1.65 ± 0.07 | 0.54 ± 0.02 | 5.1 ± 0.6 |
| Doublet 4 | 0.25 ± 0.03 | 0.37 ± 0.07 | 0.37 ± 0.04 | 4.4 ± 0.8 |

Figure 2 shows the room temperature Mössbauer spectra of ilmenite-type $FeGeO_3$ before and after the annealing. The spectra were fitted with four paramagnetic doublet components to reproduce the observed ones. The fitted parameters are tabulated in Table 1. According to the IS values, both spectra were mostly assigned to the absorption of $Fe^{2+}$ states as expected from the formal charge of iron in $FeGeO_3$. Only a small amount of $Fe^{2.5+}$ ions (Component 3) and $Fe^{3+}$ ions (Component 4) contaminated the spectra. One of the possibilities presenting the conterminous components in $FeGeO_3$ was formation of oxidized particles or layers on $FeGeO_3$ in air. Moreover, the clinopyroxene- type $FeGeO_3$ was known to be decomposed into spinel phase at high pressure conditions [1]. However it is very hard to make quantitative discussions basing on the XRD phase identifications, because the samples contained non- or extremely- poor-crystalline components even after the subsequent annealing [2]. By the way, the spectrum of as-prepared $FeGeO_3$ mainly consisted of a broad doublet component (Component 1) with larger quadrupole splitting (QS). The broadness and larger QS indicate the highly distorted structure of the as-prepared sample. The poor crystallinity of the as-prepared sample is confirmed by XRD. While the spectrum of the post-annealed sample consists of a sharp paramagnetic doublet (Component 2) with the moderate QS value of 1.65 mm/s, besides the spectrum shows broad tailing peaks attributing to the contaminants. From a crystallographic view point, the ilmenite structure possesses unique octahedral $Fe^{2+}$ sites with the higher site symmetry [4, 5]. It is reasonable to assume the ilmenite-type $FeGeO_3$ showed one paramagnetic doublet with the moderate QS.

Figure 3 shows the temperature dependent magnetization curves of ilmenite-type $FeGeO_3$ sample before and after the annealing. The ZFC and FC magnetization curves of the as-prepared sample showed large splitting at low temperature. Obtained behavior was typical for nanosized magnetic materials, so-called superparamagnetism [6]. The FC curve was increased progressively with decreasing the temperature, while the ZFC curve showed a maximum. The temperature corresponding to the maximum in the ZFC curve was related to the average blocking temperature. On the other hand, as for the annealed sample, both ZFC and FC magnetization curves showed sharp peaks at 79 K. This profile evidently indicated that the antiferromagnetic transition occurred at that temperature. The ilmenite-type $FeGeO_3$ was concluded to show the typical antiferromagnetic behavior with the Néel temperature ($T_N$) of 79 K. The large magnetization observed in the FC curve for the as prepared sample could be attributed to uncompensated surface spins in antiferromagnetic nanocrystals [7].

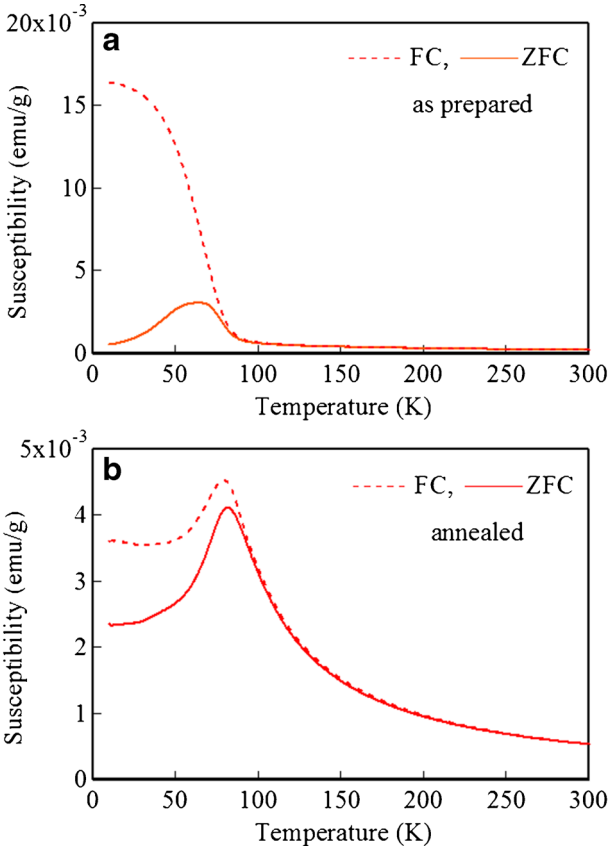


**Fig. 3** Temperature dependence of magnetic susceptibility of high-pressure synthesized samples in both ZFC and FC processes: **a** before and **b** after the annealing

## 4 Conclusions

Well-crystallized ilmenite-type $FeGeO_3$ was successfully synthesized by the subsequent annealing at 500 °C for 96 h after the high-pressure synthesis at 23.5 GPa at 500 °C for 4 h. The annealing process proceeded the crystallization of the ilmenite-type $FeGeO_3$ and increased the grain size of 1.5 times larger than that of the as-prepared sample. The broad Mössbauer spectra of $Fe^{2+}$ states with larger QS changed sharp profiles without further oxidization. The well-crystallized ilmenite-type $FeGeO_3$ was concluded to show the typical antiferromagnetic behavior with the $T_N$ of 79 K, while the as-prepared sample showed superparamagnetic behaviors.

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