A Mössbauer effect study of Fe$^{3+}$ bearing $\gamma$-Fe$_2$SiO$_4$

LI Zhe (李哲)$^1$, I. Shinno$^2$, YE Danian (叶大年)$^1$, FU Pingqiu (傅萍秋)$^3$
& ZHANG Yueming (张月明)$^3$

1. Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China;
2. Graduate School of Social and Cultural Studies, Fukuoka 810, Japan;
3. Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

Correspondence should be addressed to Li Zhe (email: lizhe@igcas.ac.cn)

Received January 18, 2000

Abstract  Three synthetic Fe$^{3+}$ bearing $\gamma$-Fe$_2$SiO$_4$ were analyzed using electron probe method, and the Mössbauer spectra of the samples at 298 K, 150 K, and 95 K were measured. Each spectrum at three temperatures is composed of two doublets. These two doublets are assigned to Fe$^{2+}$ in the octahedral sites and Fe$^{3+}$ in the tetrahedral sites, respectively. Site occupancies were determined. The results show that Fe$^{3+}$ and a small amount of Si$^{4+}$ are in the tetrahedral and octahedral sites, respectively. The average bond lengths of the octahedral and tetrahedral sites were calculated according to the equations primarily given by Hill et al., O'Neill and Navrotsky and modified by the authors. Furthermore, the octahedral and tetrahedral bond lengths were used to calculate cell parameters and oxygen parameters. In addition, Fe$^{3+}$ line broadening in the Mössbauer spectra of Fe$^{3+}$ bearing $\gamma$-Fe$_2$SiO$_4$ were interpreted by using the next nearest neighbor effects.

Keywords: Fe$^{3+}$ bearing iron silicate spinel, Mössbauer effect, bond lengths, cell parameters, oxygen parameters, next nearest neighbor effects.

The spinel form of magnesium-iron orthosilicate, (Mg, Fe)$_2$SiO$_4$, is believed to be one of the most abundant minerals in the mantle’s transition zone. The olivine-spinel phase transition and crystal structure of silicate spinel have been extensively investigated for understanding possible phase transformations and crystal chemistry of the orthosilicate. Since Ringwood$^{[1]}$ first synthesized the spinel polymorph of Fe$_2$SiO$_4$, the spinel polymorphs Ni$_2$SiO$_4$, Co$_2$SiO$_4$, and Mg$_2$SiO$_4$ were also successfully synthesized$^{[2-5]}$. The determinations of the crystal structures of the spinel polymorphs of Fe$_2$SiO$_4$, Ni$_2$SiO$_4$, and Co$_2$SiO$_4$ were carried out by some authors. Morimoto et al.$^{[6]}$ first investigated the crystal structure of three polymorphs of Co$_2$SiO$_4$, and determined that 3.1 ± 0.8 percent of the silicon atoms are in the octahedral sites in $\gamma$-Co$_2$SiO$_4$. In the same year, Yagi et al.$^{[7]}$ determined the crystal structure of the spinel form of Fe$_2$SiO$_4$ and Ni$_2$SiO$_4$. They found that 2.3 ± 1 and 0.5 ± 1.2 percent of the silicon atoms are octahedrally coordinated in $\gamma$-Fe$_2$SiO$_4$ and $\gamma$-Ni$_2$SiO$_4$, respectively. Ma$^{[8]}$ studied the cation distribution in $\gamma$-Ni$_2$SiO$_4$, and found that 8 ± 1 percent of the silicon atoms occupy the octahedral sites. Fu et al.$^{[9]}$ studied $\gamma$-Fe$_2$SiO$_4$ by using the X-ray diffraction and the Mössbauer effect, and cell parameters and oxygen parameters were determined. Choe et al.$^{[10]}$ measured in situ Mössbauer spectra of
iron silicate spinel $\gamma$-$Fe_2SiO_4$, using a diamond anvil cell at pressures up to 16 GPa and room temperature. More recently, O’Neill and McCammon\cite{11} determined the Fe$^{3+}$ content in $\gamma$-$Fe_2SiO_4$ by using the M"ossbauer spectroscopy.

In the present work, the electron probe analyses and the M"ossbauer studies of Fe$^{3+}$ bearing $\gamma$-$Fe_2SiO_4$ were carried out. Site occupancies were deduced based on the M"ossbauer analyses. In the M"ossbauer study the important trend is to establish relationships between the crystal structure and the M"ossbauer parameters, and to deduce the crystal structure parameters based on the M"ossbauer analysis. Therefore, the average bond lengths of the octahedral and tetrahedral sites, cell parameters and oxygen parameters were calculated by using the equations given by Hill et al.\cite{12} and O’Neill and Navrotsky\cite{13} and modified by the authors in this study. Since the oxygen parameter and cell parameter can be used to completely describe the structure of spinel, the crystal structure parameters of Fe$^{3+}$ bearing $\gamma$-$Fe_2SiO_4$ were completely given without the traditional X-ray single crystal experiment. These parameters are coincident with the general change trend of the average bond lengths proposed by Ye et al.\cite{14} for phase transformation of olivine-silicate spinel under high pressure and high temperature. In addition, these parameters were also compared with that of iron silicate spinel $\gamma$-$Fe_2SiO_4$ obtained using X-ray single crystal method, and it is in good agreement with the prediction. Finally, the next nearest neighbor effects were used to explain Fe$^{3+}$ line broadening in the M"ossbauer spectra of Fe$^{3+}$ bearing $\gamma$-$Fe_2SiO_4$.

1 Experimental

Fe$^{3+}$ bearing $\gamma$-$Fe_2SiO_4$ was synthesized using a 6-6 II stage anvil high-pressure apparatus actuated with a 3000 ton oil press. At first, Fe$^{3+}$ bearing $\alpha$-$Fe_2SiO_4$ were synthesized using this apparatus, then they were used as the starting material for the synthesis of Fe$^{3+}$ bearing $\gamma$-$Fe_2SiO_4$ in this study. The synthetic experiments were given by Fu et al.\cite{9} in detail.

The single phases of Fe$^{3+}$ bearing $\gamma$-$Fe_2SiO_4$ were checked by using X-ray powder diffraction method, and no impurities were found in these samples. The chemical components of these samples were analyzed by using Cameca SX51 electron probe microanalyzer. The electron microprobe analyses were carried out on six representative crystals for each sample.

The M"ossbauer spectra of Fe$^{3+}$ bearing $\gamma$-$Fe_2SiO_4$ at 298 K were obtained using a constant-acceleration M"ossbauer spectrometer (Elsint Model MDF-N-5) in conjunction with a 1024 channel analyzer (MCA 1000). The spectra at 150 K and 95 K were measured with a constant-acceleration M"ossbauer spectrometer (Austin Science Association) in conjunction with a 1024 channel analyzer (ORTEC 7700). The measurements at low temperatures were made with an OXFORD Instrument 41074 cryostat, which is capable of changing temperature in the range of 77—300 K, using liquid nitrogen, with a temperature variation of 0.1 K. The temperatures were monitored with a calibrated copper-constantan thermocouple. A $^{57}$Co source with about 5 mCi in a palladium matrix was used in the M"ossbauer measurements. The velocity was calibrated by using