Temperature dependence of the hyperfine parameters of synthetic
$P2_1/c$ Mg-Fe clinopyroxenes along the MgSiO$_3$-FeSiO$_3$ join

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ABSTRACT

Transmission $^{57}$Fe Mössbauer measurements were acquired in the temperature range 11–745 K from a suite of nine synthetic Ca-free $P2_1/c$ Mg-Fe clinopyroxenes (cpx) along the MgSiO$_3$-FeSiO$_3$ join. The paramagnetic Mössbauer spectra (MS) consist of one doublet produced by Fe$^{2+}$ ions at an almost regular octahedral M1 site and a second doublet at a more distorted octahedral M2 site. The temperature dependencies of the Fe$^{2+}$ center shifts were fit to equations derived from the Debye model for the lattice vibrations, allowing the determination of the characteristic Mössbauer temperatures for the two Fe sites. The temperature variations of the M1 and M2 quadrupole splitting $\Delta E_Q(T)$ are consistent with the higher distortions of the M2 octahedra. Applied-field MS revealed that the principal component of the electric field gradient, $V_{zz}$, is positive, implying a tetragonal compression of both octahedral sites. The crystal-field model was used to analyze $\Delta E_Q(T)$ and to calculate the energy gaps $\Delta_1$ and $\Delta_2$ of the first excited electronic states within the 3D orbital term, both at M1 and M2. The various physical quantities derived from the MS are discussed in terms of the Fe/(Fe + Mg) ratio.

INTRODUCTION

Ca-poor Mg-Fe pyroxenes are important components of the Earth’s crust and upper mantle. They exhibit both orthorhombic and monoclinic symmetries depending on the external conditions of pressure and temperature (e.g., Woodland and Angel 1997). The crystal structure of all pyroxenes can be described in terms of alternating tetrahedral and octahedral layers that lie parallel to the (100) plane. Within the tetrahedral layer, each SiO$_4$ tetrahedron shares two corners with adjacent tetrahedra to form infinite chains parallel to the c axis. The octahedral layer contains two sixfold-coordinated sites for Fe$^{2+}$ and Mg$^{2+}$, denoted as M1 and M2.

The high-pressure $C2/c$ polymorph relevant for the upper mantle is non-quenchable (Angel et al. 1992; Hugh-Jones et al. 1994). Thus in-situ Mössbauer measurements at high pressure are needed, as reported by McCammon and Tennant (1996) on FeSiO$_3$. Their spectra were collected at room temperature (RT), whereas variable-temperature Mössbauer spectroscopy (MS) provides important information on lattice temperatures, electronic structures and distortions of the iron sites. Variable-temperature MS studies are only mentioned in literature for orthopyroxenes (e.g., Lin et al. 1993; Regnard et al. 1987; Sinha et al. 1993; Van Alboom et al. 1993, 1994). For a better understanding of the other polymorphs in the MgSiO$_3$-FeSiO$_3$ system, it is useful to extend this variable-T work to the low-pressure $P2_1/c$ structures. The object of this study is to extend the results of Angel et al. (1998) on Ca-free $P2_1/c$ clinopyroxenes to more temperatures and to extend the results of Eeckhout et al. (2000) to more compositions.

EXPERIMENTAL METHODS

Clinopyroxenes of nine different compositions between the end-members MgSiO$_3$ ($X_{Fe} = 0.00$) and FeSiO$_3$ ($X_{Fe} = 1.00$) were synthesized in a multi-anvil press operating at 10 GPa and 1200 °C. The duration of the multi-anvil experiments was 10 hours in the 1000 ton uniaxial split-sphere press (Hymag 1000, samples H819, H750, H1089, and H1090) and 12 hours in the 1200 ton press (Sumitomo UHP 1200, samples U1853, S2102, U1850, U1847, and U1848). For the samples $X_{Fe} = 0.092(3)$, 0.193(5), and 0.469(23) a 70% $^{57}$Fe-enriched synthesized fayalite was used, whereas for the other compositions the $^{57}$Fe enrichment was 20%. More details about the synthesis procedure and conditions are provided by Eeckhout et al. (2000).

Our samples were synthesized under conditions in which the $C2/c$ pyroxene polymorph is stable, but reverts to the $P2_1/c$ structure upon quenching. The formation of single-phase $P2_1/c$ clinopyroxene was confirmed by powder X-ray diffraction (XRD) using a Siemens D5000 diffractometer. Chemical analyses were performed by electron microprobe. The results of the syntheses are summarized in Table 1.

Mössbauer spectra (MS) were collected in transmission geometry. A $^{57}$Co(Rh) source was driven by a constant-acceleration, triangular waveform. For absorber preparation the Mg$_{1-x}$Fe$_x$SiO$_3$ powders were diluted with boron nitride and the mixture was sealed in a boron nitride capsule. The absorber temperature was varied between 11 K and 745 K. MS with 512