

Single-crystal X-ray diffraction and temperature dependent ^{57}Fe Mössbauer spectroscopy on the hedenbergite-aegirine $(\text{Ca},\text{Na})(\text{Fe}^{2+},\text{Fe}^{3+})\text{Si}_2\text{O}_6$ solid solution

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ABSTRACT

Synthetic samples with different chemical compositions along the hedenbergite–aegirine $(\text{CaFe}^{2+}\text{Si}_2\text{O}_6\text{--NaFe}^{3+}\text{Si}_2\text{O}_6)$ solid-solution series have been investigated by single-crystal X-ray diffraction and ^{57}Fe Mössbauer spectroscopy. All compounds show $C2/c$ symmetry, both at 298 K and at low temperature (100 K). The structural changes within the hedenbergite–aegirine series are dominated by the M1 site while the M2 site plays a minor role. Replacement of Fe^{2+} by Fe^{3+} increases the polyhedral distortion of the M1 site and causes an increased repulsion between neighboring M1 sites. The changes in M1-site geometry also induce distinct alterations within the kinking state of the tetrahedral chains, but the changes in tetrahedral bond lengths and angles are small. In addition to the single-crystal X-ray diffraction experiments, a large number of synthetic samples were investigated by ^{57}Fe Mössbauer spectroscopy at 298 K and, for three selected compositions, between 80 and 700 K. Here, substantial line broadening of the Fe^{2+} resonance absorption was observed as an aegirine component is substituted. Two different groups of local distortion environments were observed for Fe^{2+} within the solid-solution series, which change relative proportions and numeric value of the quadrupole splitting as a function of chemistry and temperature. This line broadening cannot be ascribed to discrete next-nearest-neighbor (NNN) configurations of Ca and Na as has been done in the literature. Above ~250 K, additional resonance absorption appears in the spectra of samples with aegirine components between 20 and 75 mol%. This absorption gains intensity with increasing temperature, while the ^{57}Fe hyperfine parameters approach values intermediate between Fe^{2+} and Fe^{3+} . This effect is ascribed to fast electron delocalization between Fe^{2+} and Fe^{3+} at elevated temperature.

Keywords: Synthesis, crystal structure, Mössbauer spectroscopy, hedenbergite–aegirine series, clinopyroxenes