Synthesis and structural properties of clinopyroxenes of the hedenbergite CaFe\(^{2+}\)Si\(_2\)O\(_6\) - aegirine NaFe\(^{3+}\)Si\(_2\)O\(_6\) solid-solution series

GÜNTHER J. REDHAMMER*\(^{(1)}\), GEORG AMTHAUER\(^{(2)}\), WERNER LOTTERMOSER\(^{(2)}\) and WERNER TREUTMANN\(^{(3)}\)

\(^{(1)}\) Institute of Crystallography, RWTH Aachen, Jägerstr. 17/ 19, D-52056 Aachen, Germany

\(^{(2)}\) Institute of Mineralogy, University of Salzburg, Hellbrunnerstr. 34, A-5020 Salzburg, Austria

\(^{(3)}\) Institute of Mineralogy, Philipps-Universität, Hans-Meerweininstr., D-35032 Marburg/Lahn, Germany

Abstract: Clinopyroxenes along the solid solution hedenbergite-aegirine \(\text{M}^2_2\text{Ca}^{2+1-x}\text{Na}^+x\text{M}^1 \text{Fe}^{2+1-x}\text{Fe}^{3+x}\text{Si}^2\text{O}\text{_6}\) were synthesized using hydrothermal techniques at 4 kbar. Different temperatures and redox conditions were used to determine optimum synthesis conditions and the stability range of individual compositions in the T - log \(f\text{O}_2\) field. Synthesized samples were characterized using microprobe analysis, X-ray powder diffraction and Mössbauer spectroscopy at 298 K and 80 K. The structure was refined in the \(\text{C}_2\text{/c}\) space group by means of the Rietveld method.

Along the solid-solution series between hedenbergite \((a_0 = 9.8448(6)\text{ Å}, b_0 = 9.0296(6)\text{ Å}, c_0 = 5.2452(4)\text{ Å}, \beta = 104.813^\circ)\) and aegirine endmembers \((a_0 = 9.6547(6)\text{ Å}, b_0 = 8.7941(8)\text{ Å}, c_0 = 5.2944(4)\text{ Å}, \beta = 107.398^\circ)\), the changes in unit cell dimensions show significant deviations from linearity. Mean and individual M1-O distances decrease linearly from hedenbergite to aegirine; mean M2-O and T-O distances do not change significantly, whereas individual length may vary. While in hedenbergite the coordination of the M2 site is 6+2, it is 4+4 in aegirine. The Mössbauer spectra of the solid-solution endmembers display narrowly split resonance absorption lines with hyperfine parameters typical for Fe\(^{2+}\) \((\delta = 1.18\text{ mm/s}, \Delta = 2.25\text{ mm/s at 298 K})\) and Fe\(^{3+}\) \((\delta = 0.38\text{ mm/s}, \Delta = 0.30\text{ mm/s at 298 K})\). Fe occupies only the M1 site. The Fe\(^{2+}\) resonance absorption is somewhat broadened in the 80 K spectra of the solid solution, which is due to a distribution of quadrupole splittings.

Key-words: hedenbergite, aegirine, Rietveld refinement, Mössbauer spectroscopy.

Introduction

Hedenbergite CaFe\(^{2+}\)Si\(_2\)O\(_6\) (hd) and aegirine NaFe\(^{3+}\)Si\(_2\)O\(_6\) (ae) are chain silicates belonging to the group of clinopyroxenes, general formula \([5-8]\text{M}^2_2\text{M}^1_4\text{T}_2\text{O}_6\). Both compounds are widespread in nature and usually found in magmatic and metamorphic rocks, aegirine for instance in intrusive and volcanic rocks, hedenbergite in skarns. Hedenbergite and aegirine form a complete solid solution and naturally occurring intermediate minerals of this series are denoted as aegirine and aegirine-augite (Morimoto, 1988).

Clinopyroxenes have monoclinic symmetry and generally crystallize in space group \(\text{C}_2\text{/c}\). The crystal structure is shown in Fig. 1. Ca\(^{2+}\) and Na\(^+\) ions occupy the strongly distorted 8-fold coordinated M2 polyhedra, iron occupies the regular M1