

**⁵⁷Fe MÖSSBAUER SPECTROSCOPIC INVESTIGATIONS ON THE
BROWNMILLERITE SOLID SOLUTION SERIES $\text{Ca}_2(\text{Fe}_{2-x}\text{Al}_x)\text{O}_5$**

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Brownmillerite $\text{Ca}_2\text{FeAlO}_5$ is one of the four main components of portland cement clinkers. For $\text{Ca}_2(\text{Fe}_{2-x}\text{Al}_x)\text{O}_5$, there is a complete solid solution between $\text{Ca}_2\text{Fe}_2\text{O}_5$ (mineral name srebredolskite) and $\text{Ca}_2\text{Al}_2\text{O}_5$ up to $x = 1.36$ at ambient conditions (REDHAMMER et al., 2004 and references therein). Using ceramic sintering and slow cooling of the melt, 32 different samples between $x = 0.00$ and 1.36 have been synthesized. Besides the investigation by powder and single crystal X-ray diffraction, most of the samples were investigated by ⁵⁷Fe Mössbauer spectra at room and elevated temperatures also.

At room temperature pure $\text{Ca}_2\text{Fe}_2\text{O}_5$ exhibits two magnetically ordered subspectra, which can be assigned to ferric iron on both the octahedral (O) and the tetrahedral (T) sites. The ratio O : T corresponds to the ideal 1 : 1 ratio. Both sites show unusual large quadrupole splittings of -1.471(5) mm/s for the tetrahedral and +1.514 mm/s the octahedral site respectively. The internal magnetic field at the probe nucleus is 42.8(1) and 50.4(1) Tesla, values typical for ferric iron. The main component V_{zz} of the electric field gradient at the octahedral site spans up an angle of 85° with the direction of the internal magnetic field, whereas it is oriented at 90° to V_{zz} at the tetrahedral site. In situ heating experiments have shown that the Néel - temperature in pure $\text{Ca}_2\text{Fe}_2\text{O}_5$ is 450 °C. Exchanging ferric iron by aluminum causes an increasing complexity of the spectra. Besides one spectrum for ferric iron on (O), two subspectra for tetrahedrally coordinated ferric iron can be resolved, which only differ in the size of the internal magnetic field. Additionally, the incorporation of aluminum causes the spectra to become successively more relaxed and data evaluation becomes highly difficult. Increasing aluminum content causes the Néel temperature to decrease. For samples with $x = 1.10$ only paramagnetic two line spectra are revealed at room temperature. The Al/Fe distribution has been determined both, from the Mössbauer data and the single crystal intensity data. For low aluminum contents, they show a distinct preference of aluminum for the tetrahedral site. Above a $2/3$ filling of the tetrahedral site with aluminum, additional Al is equally distributed over both sites. Within the complete solid solution series, the quadrupole splitting for both the (O) and the (T) sites slightly increases linearly, suggesting somewhat more distorted crystallographic sites in the high aluminum containing samples.

References

REDHAMMER, G.J., TIPPELT, G., ROTH, G. & AMTHAUER, G. (2004): Am. Mineral., **89**: 405-420.