MITT.ÖSTERR.MINER.GES. 151 (2005)

APERIODIC ORDER OF TETRAHEDRAL CHAINS IN $CA_2FE_2O_5$ AT HIGH TEMPERATURES

Krüger, H. & Kahlenberg, V.

Institut für Mineralogie und Petrographie, Universität Innsbruck, Innrain 52, A-6020 Innsbruck
e-mail: Hannes.Krueger@uibk.ac.at

The basic building units of brownmillerite type structures are perovskite-like layers of corner sharing $(Fe,Al)O_6$-octahedra and *zweier* single chains of $(Fe,Al)O_4$-tetrahedra. A three-dimensional framework is formed by alternating stacking of octahedral layers and sheets of tetrahedral chains. WOERMANN et al. (1968) performed DTA experiments on $Ca_2Fe_2O_5$, showing two weak reversible thermal effects at 430°C and 690°C respectively. Magnetic measurements using ^{57}Fe Moessbauer spectroscopy and neutron diffraction (TAKEDA et al.,1968) revealed, that $Ca_2Fe_2O_5$ is an antiferromagnet and that the first thermal effect corresponds to the Néel temperature of the material. For temperatures above 690°C contradictory results have been reported. SHIN et al. (1979) proposed, that $Ca_2Fe_2O_5$ has *Pnma* symmetry up to 1100°C. BERASTEGUI et al. (1999) performed a Rietveld analysis on HT powder neutron diffraction data. They refined the stucture in space group *Imma*, introducing disorder of the tetrahedral chains. This disorder describes each tetrahedral chain as either left- (L) or right-handed (R) with the same probability. New HT single crystal X-ray diffraction experiments at 800°C revealed, that $Ca_2Fe_2O_5$ forms a incommensurately modulated structure adopting superspace group *Imma(00γ)s00*, with *q=0.588*. The modulation affects the sequence of R or L orientated tetrahedral chains within the layer, breaking the lattice periodicity along *c*. This is modelled with crenel occupation modulation functions for the tetrahedral Fe, as well as for the interconnecting oxygen atom. The same type of modulation was firstly described by LAMBERT et al. (2002) for commensurate phases in the system $Ca_2Co_{2-x}Al_xO_5$.

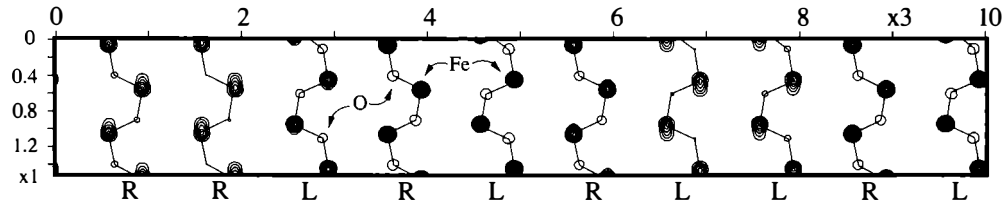

Fig. 1: Physical space section at x2=0.25, t=0 of the four-dimensional F_{obs}-synthesis showing the modulated sequence of R/L tetrahedral chains.

References

WOERMANN, W., EYSEL, W. & HAHN, T. (1968): Proceed. 5th Int. Symp. Chem. Cem., I, 54.

TAKEDA, T., YAMAGUCHI, Y., TOMIYOSHI, S., FUKASE, M., SUGIMOTO, M. & WATANABE, H. (1968): J. Phys. Soc. Japan, 24, 446.

SHIN, S., YONEMURA, M. & IKAWA, H. (1979): Bull. Chem. Soc. Japan, 52, 947.

BERASTEGUI, P., ERISKSSON, S.-G. & HULL, S. (1999): Mater. Res. Bull. 34(2), 303.

LAMBERT, S., LELIGNY, D., GREBILLE, D., PELLOQUIN, D. & RAVEAU, B. (2002): Chem. Mater., 14, 1818.