

Crystal Chemistry of Manganese containing Perovskites related to Calcium Aluminate Cements

S. Stöber and H. Pöllmann

Martin - Luther Universität Halle, Institut für Geowissenschaften und Geographie, Mineralogie/Geochemie, Halle (Saale), Germany (stefan.stoeber@geo.uni-halle.de)

With the improvement of iron rich CAC cement properties due to intergrinding and sintering of Mn - secondary raw materials and cement raw meal, perovskite phases contain significant concentrations of Mn³⁺/Mn⁴⁺ ions, dependent on the oxygen fugacity (f_{O_2}). Brownmillerite phases, structurally described as oxygen deficient perovskites, can compensate certain amounts of Mn⁴⁺ due to incorporation of additional oxygen, but will become unstable and dissolve into Alumina rich Iron - Manganese - Brownmillerites $Ca_2(Al,Mn,Fe)O_{5+d}$ [3] and Perovskite $Ca(Mn,Ti,Fe)O_{3-d}$.

Beside the typical layer sequence of tetrahedra (t) - octahedra (o) in brownmillerite type structure, different stacking sequences can be stabilised due to the variation of f_{O_2} . These structures are built up of different sequences like oo or too. In order to investigate these phases, samples with the chemical compositions $CaFeO_{3-d}$ - $CaMnO_{3-d}$ - $CaTiO_3$ were synthesised either as powders by sol - gel methods or as single crystals. The crystal structures were refined using neutron diffraction techniques at the BENSC E6 of the Helmholtz - Centre Berlin for Materials and Energy, the manganese valences were determined by iodometric titration. The valence state of iron was determined by Mössbauer - spectroscopy. The phases with the chemical composition $Ca(Fe,Mn,Ti)O_{3-d}$ with ABO_3 type structure crystallise predominately in space group Pnma. With the incorporation of trivalent iron the space group changed to I4/mcm and finally into Pm3m. The phase transition is also dependent on the temperature level, which was proofed by high temperature XRD

Phase with the chemical composition $Ca_3(Fe,Mn,Ti)_3O_{8+d}$ ($n = 3 A_3B_3O_{8+d}$) [1], [2] were only synthesised purely in a narrow range as long as enough iron filled the tetrahedrally coordinated sites in the crystal structure.