

DISORDER AND DIFFUSION IN MAYENITE

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Mayenite, nominally $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, a component of calcium aluminate cements, has recently attracted enormous attention for novel technological applications, e.g. as transparent conductive oxide, as catalyst for the combustion of volatile organic compounds or as oxygen ionic conductor. These exciting properties are related to its peculiar crystal structure consisting of a calcium-aluminate framework, comprising 32 of the 33 oxygen anions. The remaining oxygen is distributed over 1/6 of large cages within the framework. It is considered to move freely through large openings between adjacent cages and can be substituted by a number of other anions including electrons. However, the true structure is heavily disordered and usually non-stoichiometric due to the presence of extra anions. The materials properties can be modified by substitutions on the anion and cation lattice. In this contribution we report on the real structures with respect to their disorder and diffusion behaviour for pure oxygen mayenite as well as samples doped with nitrogen and iron.

Four samples with nitrogen contents of 0 (O-mayenite), 0.55, 1.00 and 1.27 wt.% N were prepared via a solid state route and subsequent ammonolysis. In the sample with 0.55 wt.% N only part of O was substituted by N (O/N-mayenite). Two iron doped samples with 0.1 and 2.5 mol% Fe were synthesised via a sol-gel route. All samples were investigated by neutron and synchrotron X-ray powder diffraction up to 1050°C. Data were analysed by the Rietveld method including anharmonic Debye-Waller factors and by difference Fourier methods. At ambient temperature O-mayenite contains O_2^- and OH^- , N-doped samples NH_2^- , while the sample with the higher Fe content was free of extra radicals. In O- and N-mayenite the extra species are lost under vacuum conditions above ca. 700°C, whereas O/N-mayenite retained NH_2^- up to high temperatures. Diffusion of oxygen proceeds via a jump-like interstitialcy process involving exchange of the "free" oxygen with framework oxygen, coupled to relaxations of Ca ions [1]. In contrast, in O/N-mayenite the mobile anion NH_2^- diffuses via an interstitial process [2]. The heavy disorder found for the Fe doped sample promises very large ionic conductivities.

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References

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