Structures and properties of variously doped Mayenite investigated by neutron and synchrotron powder diffraction

H. Boysen[1,*], I. Kaiser-Bischoff[1], M. Lerch[2], S. Berendts[2], A. Börger[3], D. M. Trots[4,5], M. Hoelzel[5,6], A. Senyshyn[5]

[1] LMU, Department f. Geo. und Umweltwissenschaften, Sektion Kristallographie, Theresienstr. 41, 80333 München, Germany
[2] TU Berlin, Institut für Chemie, Straße des 17. Juni 135, 10623 Berlin, Germany
[3] TU Braunschweig, Institut für Physikalische und Theoretische Chemie, Hans-Sommer-Straße 10, 38106 Braunschweig, Germany
[4] HASYLAB, Notkestrasse 85, 22607 Hamburg, Germany
[5] TU Darmstadt, Institute of Materials Science, Petersenstr. 23, 64287 Darmstadt, Germany
[6] TUM, Forschungsneutronenquelle FRM-II, 85747 Garching, Germany
[*] boysen@lmu.de

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Abstract. Mayenite ($Ca_{12}Al_{14}O_{33}$) is a promising new ionic conductor. This is related to its particular crystal structure, consisting of a calcium-aluminate framework, comprising 32 of the 33 oxygen anions. The remaining "free" oxygen is distributed over 1/6 of large cages in the framework and may diffuse through large openings between adjacent cages. The structure is heavily disordered involving displacements of Ca cations and the presence of extra anions like O_2^-, O_2^{2-}, O^- and OH^-, which are released at high temperatures under vacuum conditions. The "free" oxygen has been substituted by nitrogen, opening up possibilities for a pure nitrogen ionic conductor. Material properties can be modified by doping on the cation sites. Detailed structure determinations with respect to disorder and ionic diffusion were carried out by neutron and X-ray synchrotron powder diffraction. At high temperatures diffusion of oxygen proceeds via a jump-like process involving exchange of "free" oxygen with framework oxygen, coupled to relaxations of the Ca ions. In contrast, nitrogen diffuses as NH_2^- via an interstitial process. Fe doping leads to samples free of extra anions, larger disorder and promises higher ionic conductivities at high temperatures.

Introduction

Mayenite, of nominal composition $Ca_{12}Al_{14}O_{33}$, known as a major component of calcium aluminate cements, has recently attracted renewed attention for modern technological applications, e.g. as transparent conductive oxide, as catalyst for the combustion of volatile organic compounds or as oxygen ionic conductor. These properties can be related to its particu-

lar crystal structure (space group $I\bar{4}3d$, a = 11.98 Å) [1, 2] consisting of a calcium-aluminate framework comprising 32 of the 33 oxygen anions. The remaining "free" oxygen is distributed over 1/6 of large cages in the framework and is thought to diffuse through large openings between adjacent cages. The true structure is heavily disordered [3, 4] involving displacements of Ca cations and the presence of extra anion species O_2^-, O_2^{2-}, O^- and OH^-. The extra-framework oxygen can be exchanged by other anions opening up possibilities for new anionic conductors. Material properties can further be modified by doping on the cation sites. Here we present detailed structure determinations related to the disorder and diffusion properties as a function of composition and temperature by high temperature neutron and X-ray powder diffraction experiments. The results demonstrate that rather fine structural details, as revealed by anharmonic contributions to the Debye-Waller factor and by difference Fourier methods, can reliably be deduced from the high quality powder data nowadays available at modern neutron and synchrotron sources. Information about the amount of hydrogen in the samples can be drawn from the incoherent scattering contribution to the background.

Experimental

Pure oxygen mayenite samples were synthesized via a solid-state route. Nitrogen doped samples with 0.55, 1.00 and 1.27 wt-% N were obtained from these by ammonolysis, iron doped samples with 0.1 and 2.5 mol-% Fe via a sol-gel route. Neutron measurements were carried out at the powder diffractometer SPODI at the FRM2 (Garching) using a wavelength of λ = 1.548 Å and a Nb vacuum resistance furnace up to 1050 °C. Synchrotron X-ray measurements were done at instrument B2 at HASYLAB (Hamburg) with λ = 0.49324 Å and a graphite furnace up to 900 °C. The data were analysed by the Rietveld method including anharmonic Debye-Waller factors and by difference Fourier methods with JANA2000 [5]. All samples contained small amounts of side phases whose weight fractions were determined from the refinements and are summarized in table 1.

Table 1. Phase analysis of samples.

O (pure)	4.98(11) % $Ca_3Al_2O_6$	Fe (2.5)	5.47(10) % $CaAl_2O_4$
O/N (0.55)	5.71(14) % $Ca_3Al_2O_6$	N (1.27)	6.28(10) % $CaAl_2O_4$

Results

O-Mayenite
The results for pure O-mayenite have already been published in [3] and are briefly summarized here for comparison. The as synthesized sample shows an excess of oxygen with composition $Ca_{12}Al_{14}O_{33.5}$, which is explained by the presence of extra species O_2^-, O_2^{2-}, O^- and/or OH^-. Two of these, peroxide and hydroxide groups, could be identified by difference Fourier synthesis as shown in figure 1(left). This assignment, i.e. ignoring other minima and maxima, is validated by "correct" O-O and O-H distances, respectively. Note that the O_2^{2-} anion is oriented along the larger extension of the cage, while OH^- point towards the neighbouring Ca. The sample becomes stoichiometric at high temperatures under the vacuum conditions of the used furnace. The loss of H is evidenced by a reduction of the incoherent background (see below). Above ca. 900 °C atomic displacement parameters (ADP's) become extremely large (U_{iso} around 0.3 Å^2) indicating the delocalization and diffusion of the free oxygen. Difference Fourier maps (calculated with empty cage) show two maxima located

off-centre of the cage (figure 1, right). The additional maxima represent split Ca positions, also located off the $\bar{4}$ axis running vertically through the cage. It is then straight forward to assume that Ca atoms are shifted away from their normal positions when the cage is occupied by an O ion. This means that Ca-O bonds are formed instantaneously (the distances indicated by the arrows in figure 1 (right) agree with the normal Ca-O bond distances of 2.4 Å), i.e. the "free" oxygen is not "loosely bound" as anticipated in the early literature and the diffusion has to be considered as a coupled Ca-O process. Since no continuous density could be found between adjacent cages and from further indications of transiently occupied metastable positions it can be concluded, that oxygen diffuses via an exchange with framework oxygen, i.e. an interstitialcy process. All these findings are in excellent agreement with theoretical ab initio calculations [6].
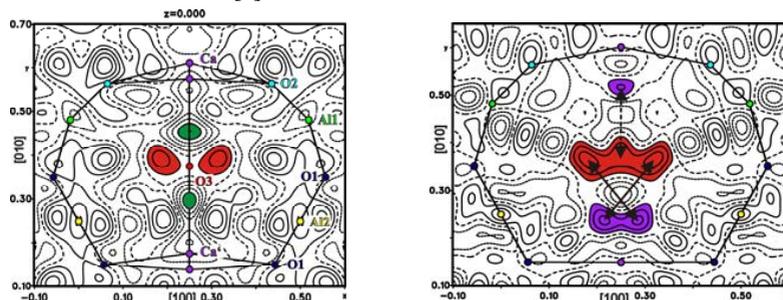

Figure 1. Difference Fourier maps of O-mayenite at room temperature after inclusion of O in the centre of the cage and split Ca position (left) and at 1050 °C after refinement with empty cage (right).

O/N-Mayenite

The formal replacement of 1 O^{2-} by 2/3 N^{3-} leads to a composition $Ca_{12}Al_{14}O_{32}N_{0.67}$, i.e. 1/9 of cage positions should be occupied. In the first sample (0.55 wt.% N) only part of the oxygen was substituted by nitrogen. Again there is over-occupancy of the cage position, probably due to additional species $NH^{2-}$and/or NH_2^-, but only a slight decrease with temperature. A concomitant decrease of the background indicates the loss of some but not all hydrogen. The multitude of different species did not allow a clear assignment. However, in contrast to O-mayenite, a continuous density distribution between adjacent cages was found from anharmonic refinements at high temperatures. This is interpreted as an interstitial diffusion process of N, probably in the form of NH_2^--groups (see below). Further details can be found in [7].

N-Mayenite

The sample with 1.00 wt.% N was measured only at room temperature. Difference Fourier maps revealed residual positive and negative densities (figure 2). The highlighted ones may be assigned to N and H, respectively. Refinement resulted in a ratio 1:2 of the occupancies and "correct" N-H distances. Therefore part of the nitrogen is present as NH_2^--groups, supporting the assumption of interstitially diffusing amide anions in O/N-mayenite (see above). The sample with 1.27 wt.% N also shows an over-occupancy, which decreases to stoichiometric values above 700 °C. The almost complete loss of hydrogen is again confirmed by a reduction of the incoherent background. Very large U_{iso}'s are again found at high temperatures (e.g. 0.25 Å^2 at 900 °C), but, unfortunately, no clear conclusions about the un-

derlying diffusion properties of the remaining N^{3-}-ions could be drawn so far from neither anharmonic refinements nor difference Fourier analyses.
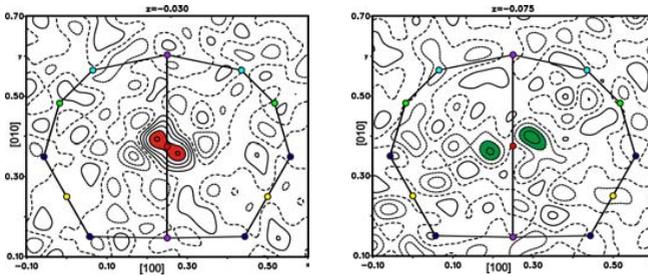

Figure 2. Difference Fourier maps of N-mayenite at room temperature at two sections through minima and maxima of highlighted residual peaks (after inclusion of nominal amount of N in the cage).

Fe-Mayenite

The sol-gel synthesized sample doped with 2.5 mol-% Fe (which replaces Al) shows a stoichiometric composition, more or less (see below) independent of temperature, i.e. it contains no appreciable amounts of additional species. A very low content of hydrogen is confirmed by the much lower background as compared to the other samples (see figure 4 below). The O density is considerably smeared out already at room temperature (figure 3, left) and not really detectable above 900 °C (figure 3, right), confirmed by an unrealistically large U_{iso} of about 0.5 Å^2 (which also implies large uncertainties on the refined occupancies). This complete smearing, i.e. the extremely low local densities prohibited so far to determine reliable diffusion path ways. The sample with 0.1 mol.% Fe still contained hydrogen and behaved similar to pure O-mayenite. This means that there must be a certain threshold above which Fe inhibits the inclusion of unwanted extra anions.
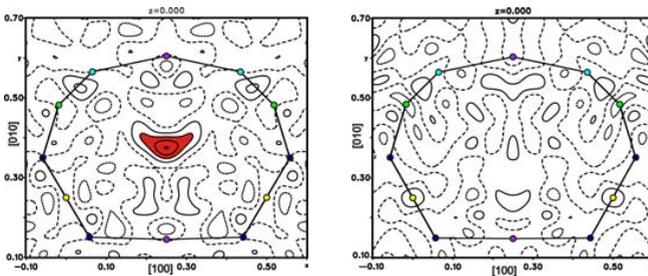

Figure 3. Difference Fourier maps of Fe-mayenite at room temperature (left) and at 1050 °C (right), after refinement with empty cage.

Estimation of hydrogen content

The strong incoherent scattering cross section of protons leads to a large background in neutron powder diagrams. By proper scaling with the scale factor of the Bragg intensities it is possible to determine at least approximately the amount of hydrogen in the sample. However, this requires to consider carefully other sources of background such as thermal diffuse scattering, multiple scattering, etc. This has been done before for the simple case of glassy carbon [8] and will be developed further for more demanding cases like this. Here we use only some qualitative arguments to estimate the gain and loss of hydrogen.

Figure 4 shows a comparison of three samples. Apart from the clearly lower hydrogen content of the Fe doped sample (see above) one may notice the different form of the low angle

part between O- and N-mayenite. This might be related to the different bond states of hydroxide and imide/amide, respectively, but this has to be explored further more carefully.
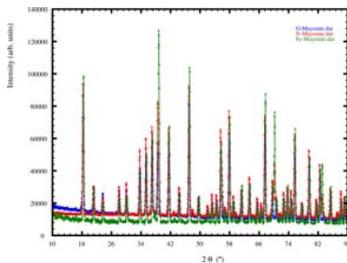

Figure 4. Comparison of neutron powder diagrams of O (blue)-, N (red)- and Fe (green)- mayenite at room temperature. The data were normalized to the first (mayenite) peak. Larger intensity differences are due to texture effects of the Nb peaks arising from the furnace.

Thermal expansion

The thermal expansion of four samples has been followed by synchrotron measurements at instrument B2, whose OBI image plate allows rapid data collection. The results of heating/cooling cycles are shown in figure 5. The lattice constants of all samples show "normal" linear increase up to about 400°C. At higher temperatures expansion increases more strongly. For O-mayenite this is due to the loss of extra anion species in agreement with previous reports that both OH^- and active oxygen species (O_2^-, O^-), contract the unit cell when they are clathrated into the mayenite cages. Then, as expected, after cooling to room temperature the lattice constant of O-mayenite is larger than initially. At ambient conditions those of the N-doped samples increase with nitrogen content and Fe-mayenite also has a larger lattice constant. These findings can simply be explained by larger ionic radii. However, in contrast to O-mayenite, thermal expansion in N-mayenite samples is retarded between 800 – 900°C, due to loss of nitrogen, which is not recovered and consequently leads to smaller lattice constants at room temperature after cooling. In O/N-mayenite the smaller losses of extra anions lead to an almost reversible behaviour. That of Fe-mayenite is similar, but less pronounced, as in N-mayenite, which might be due a possible change of the Fe oxidation state.
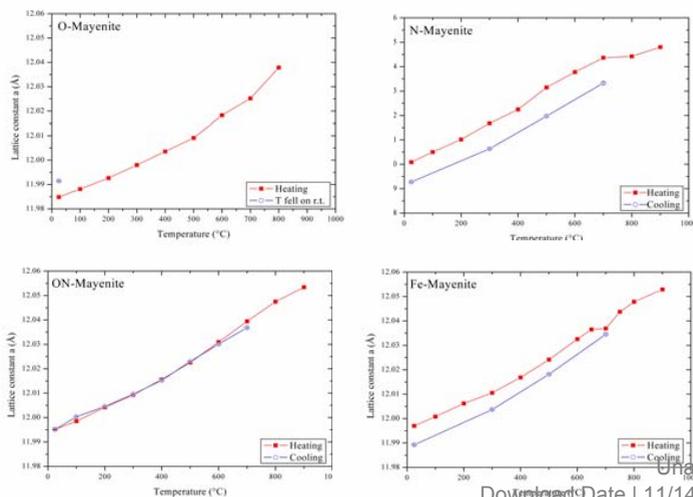

Figure 5. Temperature dependence of lattice constants of O-, O/N-, N- and Fe-mayenite during heating and cooling (only one point for O-mayenite due to a failure of the furnace).

Discussion and conclusions

O-Mayenite synthesized via a solid-state route contains extra anions, of these OH^- and O_2^- could be substantiated from neutron powder diffraction data. The excess anions are lost at high temperatures under vacuum conditions. This change is irreversible as evidenced by larger lattice constant after heating/cooling. Oxygen diffusion proceeds via a jump-like process involving exchange of "free" oxygen with framework oxygen, coupled to relaxations of the Ca ions. Test refinements proved that no nitrogen is incorporated into the framework of N-doped samples. Possible excess anions are imide and/or amide, NH_2^- was substantiated. Again they are lost at high temperatures and the process is irreversible under vacuum conditions. Nitrogen diffuses (probably) as NH_2^- via an interstitial process. This may be related to the larger radius and lower valence if compared with O^{2-} exhibiting interstitialcy behaviour. The situation for pure N^{3-} is not clear at the moment. Of technical importance is the observation that the incorporation of extra anions is suppressed by doping with iron. Fe-mayenite shows large disorder already at room temperature and extreme delocalisation at high temperatures. This points towards very high anionic conductivity (to be verified).

The results presented in this paper demonstrate the power of neutron powder diffraction for the elucidation of disorder and diffusion effects in crystals. However, it has to be admitted that very subtle details, like e.g. an unambiguous detection of intermediate metastable positions during the diffusion processes or of the very low local densities at high temperature, requires even higher quality single crystal data. It should also be noted that attempts to disentangle the various species by combined neutron and synchrotron refinements did not lead to unambiguous results, because they were very sensitive to the oxidation state used for the different ions in the X-ray case. Hence, extreme care should be taken when trying to deduce occupancies from X-ray data.

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