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Anion Diffusion Processes in O- and N-Mayenite Investigated by Neutron Powder Diffraction

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Abstract. The crystal structure of mayenite (ideal composition: $Ca_{12}Al_{14}O_{33}$) consists of a (disordered) calcium-aluminate framework comprising 32 of the 33 oxygen anions. It contains large open cages, 1/6 of them being filled randomly by the remaining "free" oxygen which is available for diffusion and very high ionic conductivities. This extra-framework oxygen could be substituted by nitrogen, opening up possibilities for a pure nitrogen ionic conductor. From high temperature neutron powder diffraction experiments, data analysis employing difference Fourier methods and anharmonic Debye-Waller factors and comparing pure O-mayenite with partly exchanged N/O-mayenite it is concluded that oxygen diffusion proceeds via jump-like processes, intimately coupled to relaxations of Ca and involving exchange of the "free" oxygen with framework oxygen, while nitrogen diffusion appears to proceed via an interstitial process.

1 Introduction

Mayenite, with nominal composition $Ca_{12}Al_{14}O_{33}$, has recently attracted much attention for technological applications, *e.g.*, as transparent conductive oxide, as catalyst for the combustion of volatile organic compounds or, of main interest here, as a highly efficient oxygen ionic conductor [1]. These materials properties are related to its particular crystal structure, which may be described as a nanoporous cubic structure (space group $I\bar{4}3d$, $Z = 2$, $a = 11.98$ Å). 64 of the 66 oxygen ions per unit cell are assumed to be fixed in a Ca-Al-O framework forming 12 "cages", 5-6 Å in diameter. The remaining two oxygen ions, called "free" or "extra-framework" oxygen, are randomly distributed inside 1/6 of the cages. The high mobility of these oxygen ions has been related to large 'windows' (~3.7 Å in diameter) made up of

6-membered rings between these cages (Fig. 1). The “free” oxygen can be substituted selectively by other anions such as fluoride, chloride, hydroxide or hydride, as well as electrons, forming electrides. As a new approach we have successfully substituted it by nitrogen, therewith opening up possibilities for a pure nitrogen ionic conductor.

More recent structure determinations [2,3] have shown that the structure is more adequately described as a relatively stable aluminate framework consisting of 8-membered rings of AlO_4-tetrahedra with disordered Ca and “free” O distributed within. In particular, it is concluded that Ca is displaced towards the centre of the cage by about 0.5 Å, if this cage is occupied by the “free” oxygen as illustrated in Fig. 1. In this contribution it is shown that valuable information about the diffusion properties of these materials can be obtained from high temperature neutron powder diffraction experiments comparing pure oxygen and (partly) nitrogen exchanged samples by analysing the data using difference Fourier methods and anharmonic contributions to the Debye-Waller factor.

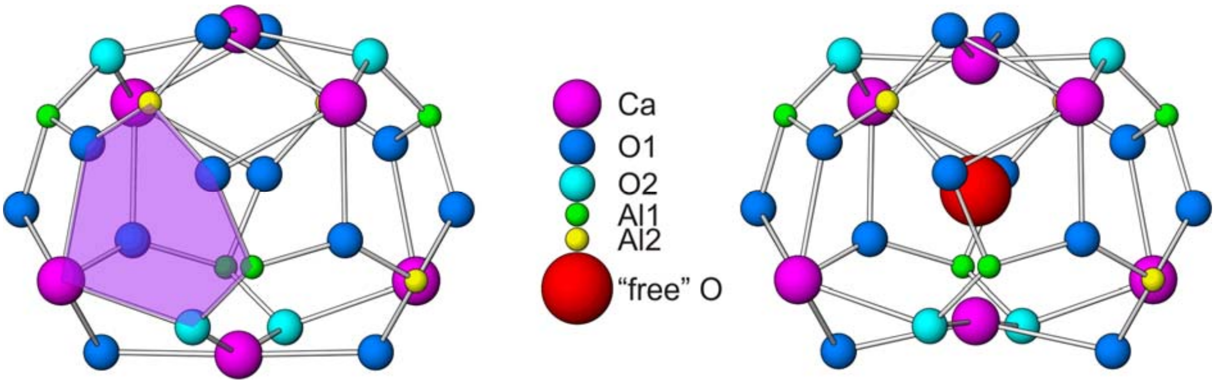

Fig. 1: Sketch of an empty (left) and filled (right) cage of mayenite (atom sizes arbitrary, *i.e.* not scaled to relative ionic radii). Note the displaced positions of the two Ca atoms on the middle axis. One “window” connecting two adjacent cages formed by a six atom ring (Ca-O1-Al2-O1-Al1-O2) is highlighted in the left drawing.

2 Methods and Materials

Pure oxygen containing samples (called O-mayenite in the following) were synthesized by a solid state route from $CaCO_3$ and Al_2O_3 by repeated heating in air up to 1350 °C and homogenization in an agate mortar. Nitrogen exchanged samples were obtained by ammonolysis of these samples at 950 °C for 10 h. For the latter sample (called N/O-mayenite in the following) chemical analysis by hot gas extraction revealed a nitrogen content of 0.55 wt.%, which is less than that expected for a complete exchange of all “free” oxygen (0.68 wt.%). However, the true composition cannot be determined from this value, since mayenite samples usually contain an excess of anions over the stoichiometric composition. For our O-mayenite a composition $Ca_{12}Al_{14}O_{33.57}$ was determined from the refinement of the occupancies at room temperature using the neutron powder data [2]. This excess is due to the presence of peroxide, superoxide and hydroxide species, as meanwhile confirmed by Raman measurements and chemical analysis (presence of hydrogen). Similarly, for N containing samples the presence of amides, imides, etc. can be expected. Unfortunately, a refinement of the occupancies for the N/O-sample does not help, since the replacement of 3 O^{2-} by 2 N^{3-} as suggested by charge balance leads to roughly the same total scattering length $b_{av} = n(O)b_O +$

$n(\mathrm{N})b_\mathrm{N}$, because the ratio $b_\mathrm{N}/b_\mathrm{O}$ is accidentally about 3/2 (b_O = 5.803 fm, b_N = 9.40 fm). From the refinement, however, again resulting in an overall excess occupancy, it can be concluded that the N/O-sample contains both O and N, although the exact ratio could not be determined. N is probably present mainly in the form of NH_2^- as found for a fully exchanged pure N-mayenite sample for which preliminary results are available, but only at room temperature so far. In spite of these slight uncertainties, from a comparison of the results for O- and N/O-mayenite the specific behaviour of nitrogen can be deduced at least qualitatively. The excess anions in O-mayenite disappear at high temperatures leading to a stoichiometric composition above 700 °C [2], whereas the occupancy stays constant for O/N-mayenite up to 1050 °C, *i.e.*, the assumed species are present up to high temperatures.

Neutron powder experiments were carried out at the diffractometer SPODI at the FRM2 in Garching [4] at various temperatures up to 1050 °C using a wavelength of 1.548 Å and a high-temperature niobium furnace. In this paper results are presented only for the highest temperatures, where diffusion is most prominent and therefore “seen” best. Full details for all measurements will be presented elsewhere. Data analysis was performed with the Rietveld option of Jana2000 [5] and in-house programs. It was found that our samples contained small amounts of side phases which were included in the fits: O-mayenite 5.1 wt.-% of $\mathrm{Ca_9Al_6O_{18}}$, O/N-mayenite 5.5 wt.-% of $\mathrm{CaAl_2O_4}$ and N-mayenite 4.6 wt.-% of $\mathrm{Ca_9Al_6O_{18}}$.

For interstitial diffusion processes, the *average* structure will show a continuous distribution of the ions along their diffusion pathway. This can be described by the probability density function (PDF), which is determined by a Fourier inversion of the Debye-Waller factor which in turn can be derived from the measured Bragg intensities. To allow more general forms of the PDF anharmonic terms have to be included. At sufficiently high temperatures (no static disorder, no correlation) diffusion may be considered as the migration of individual ions within a smooth effective (single or one particle) potential (OPP). Then the corresponding PDF follows Boltzmann statistics. The valleys in this potential landscape define the diffusion pathways and the saddle points designate the barriers to migration, which can be compared with otherwise determined activation energies. For more details about this type of analysis, see, *e.g.*, ref. [6].

For interstitialcy diffusion processes, *i.e.*, when regular lattice sites are involved and some metastable positions may be occupied transiently, the above procedure is often less effective, and it is better to introduce corresponding extra (split) positions. Alternatively (and always), one may visualise the pathways of the diffusing ions by determining residual (scattering length) densities using difference Fourier methods. Due to uncertainties of the phases (depending on the actual structure model used in the structure refinement) and series termination effects, usually only relatively strong residual densities can be interpreted confidently.

3 Results and Discussion

3.1 O-Mayenite

The diffusion properties of pure O-mayenite have already been discussed in [2]. Therefore, here only a brief summary and some additional remarks are given for comparison. Fig. 2 shows the residual scattering density as obtained from difference Fourier analysis, after inclusion of the framework atoms only, in a section through the cage. The “free” O is clearly located (shown in red colour) in the middle of the cage, but considerably smeared out with maxima shifted sideward from the centre of the cage. In addition, there are residual densities which can unequivocally be assigned to split positions of Ca (in purple). As elaborated in

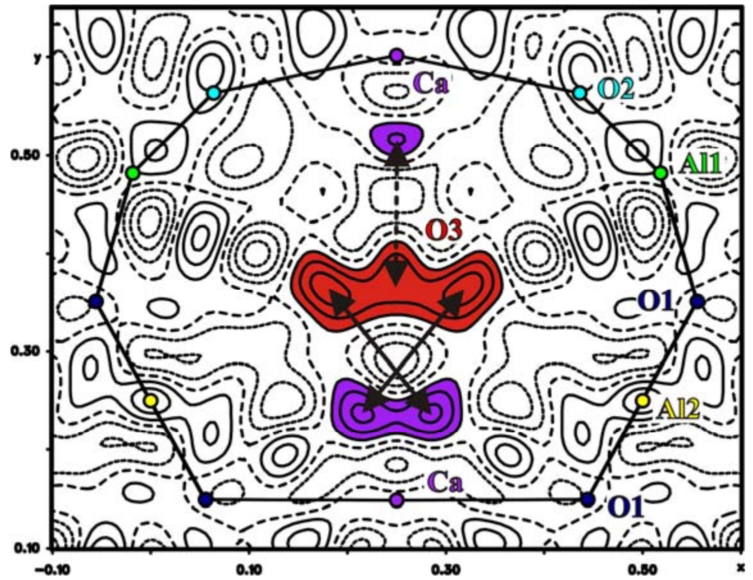

Fig. 2: Difference Fourier plot of a *xy*0-section through the cage surrounding a "free" anion position. It shows the residual scattering density in O-mayenite at 1050 °C after subtraction of all framework atoms. The arrows indicate the assumed Ca-O pairs (the dashed arrow is equivalent by the $\bar{4}$ symmetry present at the centre of the cage).

more detail in [2] these positions are occupied, if, and only if, this cage is occupied by O at the same time (*cf*. Fig. 1). The crosswise distances between Ca and O, as indicated by the arrows in Fig. 2, are about 2.4 Å which is similar to the bond length in CaO, *i.e.*, the Ca-O pairs adopt a bond-like character. This means that the "free" oxygen is not really "loosely bound" as often claimed in the literature. A jump of O leaving the cage is accompanied by a relaxation of Ca into its original position. Further relaxations of other atoms in the cage wall are conceivable, but the limited quality of the powder data (as compared to single crystal data) did not allow extracting such finer details of the relaxation processes unambiguously. This coupled process has to be taken into account in any theoretical modelling of the diffusion in mayenite.

All attempts to determine the complete diffusion pathway itself, assuming an interstitial process, by performing anharmonic refinements did not lead to reasonable results, *i.e.* no continuous density between adjacent "free" O positions can be detected. This was confirmed in further difference Fourier maps as shown, *e.g.*, in the sections through and perpendicular to the 6-membered ring connecting two cages (Fig. 3). Hence it has to be concluded that diffusion takes place via an interstitialcy type process involving exchange of the "free" oxygen with framework oxygen. This finding is in excellent agreement with recent *ab initio* model calculations [7]. Some, but not all, of the remaining residual densities in the difference Fourier maps (Figs. 2 and 3) could be identified with transiently occupied, metastable positions (see also Fig. 11 of Ref. [2]), in fair agreement with the predictions of [7], again, however, the significance of them did not warrant any definite conclusions [2].

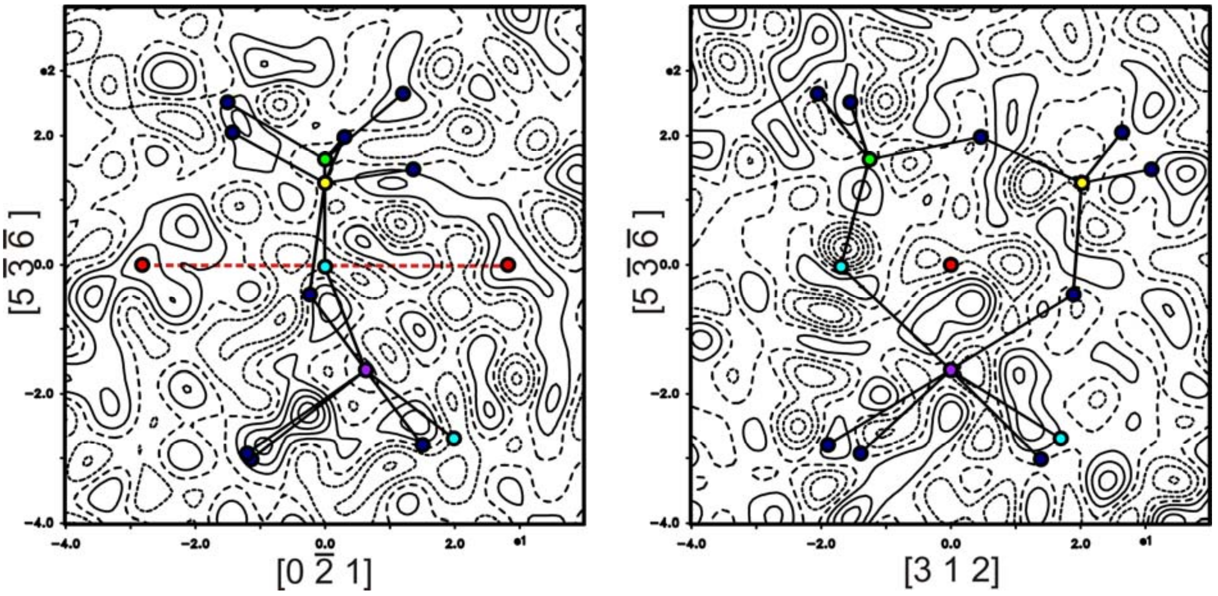

Fig. 3: Difference Fourier maps at 1050 °C showing two "free" anion positions (connected by the dotted red line) in adjacent cages (left) and perpendicular section through the centre of the 6-membered ring between two cages (right).

3.2 N/O-Mayenite

It is important to note that test refinements of the occupancies of framework oxygen did not reveal any significant amount of nitrogen absorbed in the framework. This already rules out a similar exchange process of N with the framework as found for O in O-mayenite, *i.e.*, all nitrogen remains located within the cages. As mentioned, however, some additional oxygen must be present and nitrogen probably appears mainly in the form of NH_2^-, *i.e.*, the following densities have to be interpreted as averages over all these species. Nevertheless, the striking differences in comparison with O-mayenite can safely be attributed to the particular behaviour of nitrogen. Fig. 4 shows the same difference Fourier section as Fig. 2. One may discern similar features with regard to the side maxima, but somewhat weaker and further smeared out. On the other hand, there is an additional strong maximum at the centre of the cage. It is

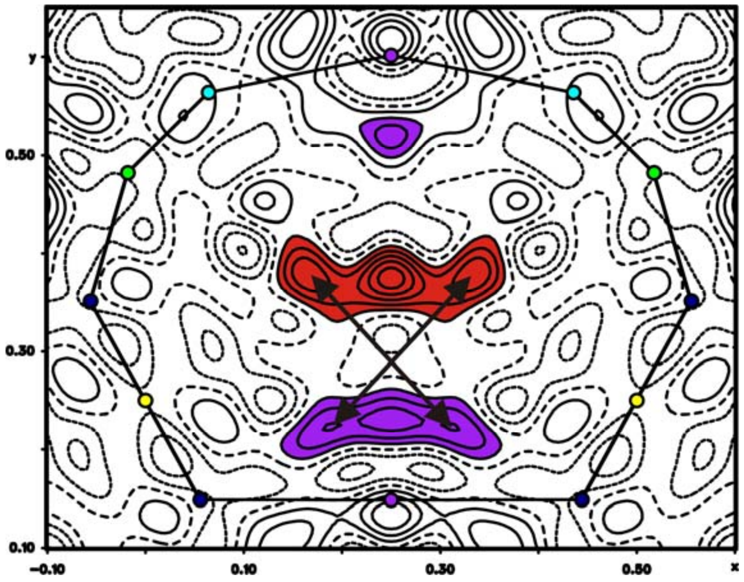

Fig. 4: Difference Fourier plot of the same section as in Fig. 2 showing the residual densities of N/O-mayenite at 1050 °C. The arrows indicate the same Ca-O correlation as in O-mayenite and the middle peak is assigned to N.

then straightforward to associate the former feature with the remaining oxygen, behaving just as in pure O-mayenite, and the extra maximum with nitrogen, again probably in the form of NH_2^-. Although the presence of the hydrogenated species is dictated by the refined excess occupancy, hydrogen ions could not be detected directly, because the corresponding (negative, $b_H = -3.74$ fm) *average* scattering density is too low, probably due to orientational disorder.

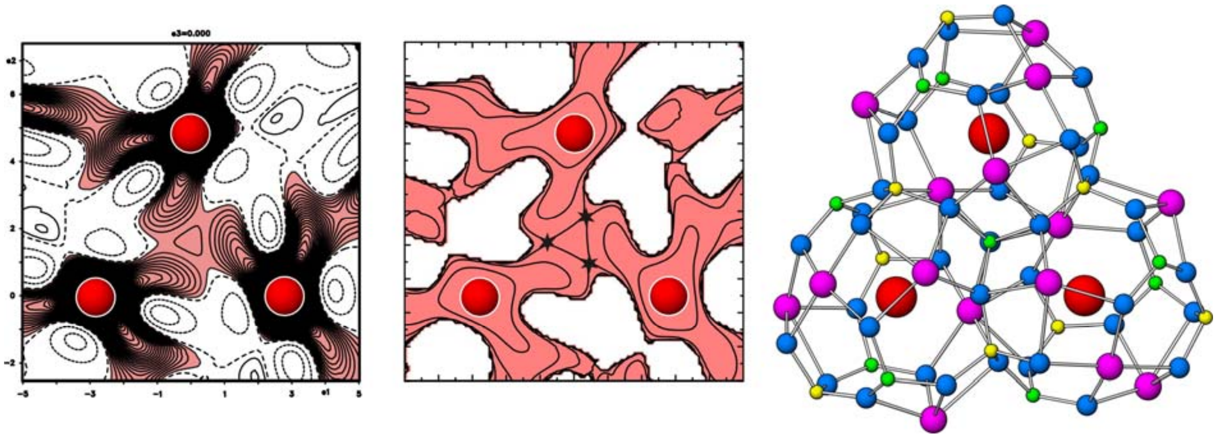

Fig. 5: PDF (left) and OPP (middle) plots of N/O-mayenite at 900 °C showing a section through three adjacent cages (perpendicular to [111]). The corresponding view of the structure is shown on the right for comparison. In the OPP, potential lines are drawn in steps of 100 meV. The positions of the saddle points in the OPP (potential barriers) are marked by stars.

Another feature of N/O-mayenite different from O-mayenite is that here continuous densities were suggested from various difference Fourier maps, which could be better confirmed through refinements of anharmonic contributions to the Debye-Waller factor. The results for the two highest temperatures, 900 °C and 1050 °C, were principally very similar, but those for 900 °C were more significant on statistical grounds, because of slightly better data quality and more concentrated densities at the lower temperature. Therefore the PDFs and OPPs for 900 °C are shown in Fig. 5 in a section perpendicular to [111] comprising three cage centres. As seen, the pathway is not straight directly from one site to the next, but curved approaching an Al-O edge of the 6-membered ring. The apparent potential barrier of ≈ 0.3 eV at the saddle point in the potential, indicated by a star in the OPP, is certainly too low, when compared with activation energies obtained from preliminary conductivity measurements (about 1 eV [8]). This is to be expected, if the PDF at the barrier position is assumed to be due to nitrogen alone, while that at the average (equilibrium) position is composed of an average over all anions, in particular oxygen. Therefore, these results can be taken as convincing evidence, that nitrogen diffusion is mainly governed by an interstitial process.

4 Conclusions

Definite and reliable conclusions could only be derived for pure O-mayenite. Diffusion proceeds via a jump-like process involving exchange of the “free” oxygen with framework oxygen, intimately coupled to large relaxations of nearest neighbour Ca ions and probably weaker ones of other ions of the cage walls. This rather complicated diffusion process may be understood by the very long jump distance (about 5.6 Å between adjacent cage centres) and the high charge of O^{2-}. Although the results for N/O-mayenite should be interpreted with some care, there is convincing evidence that nitrogen diffusion proceeds via an interstitial process on a curved pathway, while oxygen in this material behaves as in pure O-mayenite.

This difference may simply be understood by the larger ionic size of nitrogen, in particular, in its hydrogenated form. This reduces the bonding character to Ca, and therewith the relaxation of Ca, and also prohibits even transient bonding within the framework. Moreover, the reduced charge of NH_2^- greatly facilitates diffusion of these species. To obtain more quantitative results for the nitrogen diffusion (*e.g.*, true values for the potential barrier) it is necessary to investigate fully exchanged pure N-mayenite. Such work is currently underway. In any case, the results presented here are very encouraging suggesting that a pure nitrogen ionic conductor can be synthesised opening up many interesting new applications (N gas sensor, ammonia synthesis, etc.).

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