Nature of the Monoclinic to Cubic Phase Transition in the Fast Oxygen Ion Conductor La₂Mo₂O₉ (LAMOX)

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Abstract: La₂Mo₂O₉ (LAMOX) is a fast oxygen ion conductor which shows high oxygen ion conductivities comparable to those of yttria-sabilized zirconia (YSZ). LAMOX is subject to a structural phase transition from the nonconductive monoclinic form to the highly conductive cubic form at about 580 °C. The origin of the conductivity in cubic LAMOX has been suggested to be due to a "disorder" in the O sublattice without any insight into the real distribution of the oxygen ion. In this paper, thanks to the application of the neutron atomic pair distribution function (PDF) analysis, we provide evidence that the local structure of the cubic polymorph of LAMOX is exactly the same of that of the monoclinic phase, thus indicating that the structural phase transition is actually a transition from a static to a dynamic distribution of the oxygen defects. This work represents the first application of the atomic-pair distribution function analysis to the study of an oxygen fast-oxide ion conductor and clearly indicates that a more reliable and detailed description of their local structure, particularly in the highly conductive phases, can lead to a better comprehension of the structure–property correlation, which is the starting point for the design of new and optimized functional materials.

Fast oxygen ion conductors represent important technological materials due to their use in the field of solid-state ionics and in particular as electrolytes in solid oxide fuel cells (SOFC).[1] Currently the most commonly used materials are those based on ZrO_2 oxide, usually stabilized in its highly conducting cubic form by aliovalent doping such as with Y_2O_3.[2,3] However, the use of yttria-stabilized zirconia (YSZ) is limited by its low oxygen mobility below 1000 °C. As a consequence, the need for new materials with analogous conductivities, i.e., in the range of 10^{-1} S cm^{-1}, at lower temperatures (600–700 °C) is highly desirable in order to make them technologically useful. A strong contribution in this respect has been recently given by the discovery of a new oxygen ion conductor material of formula $La_2Mo_2O_9$, also known as LAMOX.[4]

This compound exhibits a first-order phase transition from the nonconductive monoclinic phase (α) to the highly conductive cubic phase (β) at around 580 °C[4] with the latter phase having an ionic conductivity of 6×10^{-2} S cm^{-1} at 800 °C. The structure of the low-temperature phase was not solved at the time of the LAMOX discovery due to its great complexity and was only solved by I. R. Evans et al. in 2005.[5] This resulted in

one of the most complex oxide structures reported up to now with 312 crystallographically independent atoms. On the basis of the atoms' arrangement in the α-form it was proposed that the structure of the β-phase corresponds to a time average version of the room-temperature monoclinic structure.[5] The structure of the cubic form was proposed in 2000 by Lacorre[6] and then revised in 2001 by the same authors.[7] This was determined by means of neutron diffraction and led the authors to propose a model where two of the three available oxygen sites (O2 and O3) are partially occupied and characterized by huge atomic displacement parameters (up to $B_{eq} \sim 20$ Å^2 for the O3 site). The presence of a strong modulation in the neutron diffraction patterns of the conducting β-phase of LAMOX led to the conclusion that a strong static disorder of oxygen atoms occurred in this phase[6] which was considered to be the source of the high oxygen mobility. However, the use of a probe of the average structure like neutron diffraction in presence of a significant diffuse scattering will not reveal all the details of this complex compound leading to a loss of structural details which may be of great importance to understand the underlying conduction mechanism.

In order to get further insight into the structural features of the La₂Mo₂O₉ α- and β-phases, test the available models for both, and try to better understand the correlation between the

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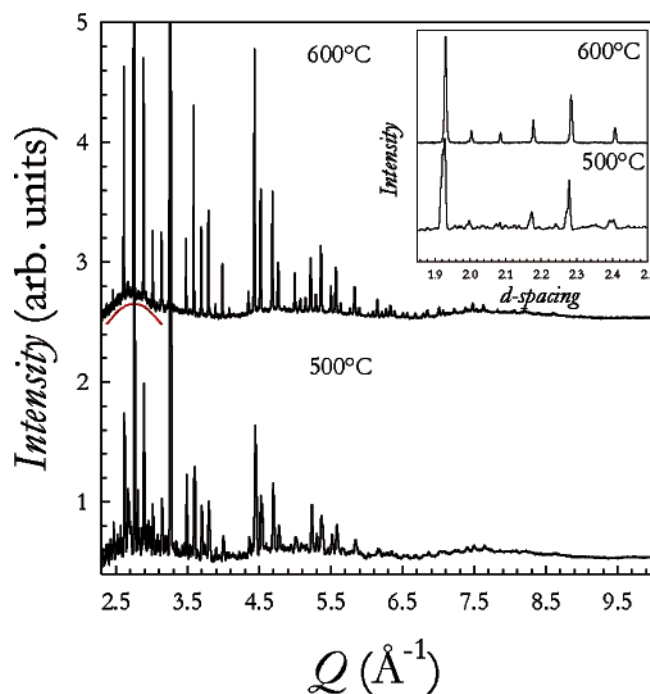
Figure 1. Time-of-flight neutron diffraction patterns of La$_2$Mo$_2$O$_9$ at 500 °C (lower part) and 600 °C (upper part). The inset shows a small part of the pattern on an expanded scale for both temperatures for comparison.

monoclinic and cubic polymorphs, we looked at both the short and long range order in this compound. This was accomplished by means of the atomic pair distribution function (PDF) analysis of time-of-flight neutron data collected on the α-phase (at 500 °C) and β-phase (at 600 °C) of LAMOX. The power of the PDF analysis in obtaining information on the short range order in complex materials is well proven.[8,9] The strength of the technique comes from the fact that it takes all the components of the diffraction data (Bragg peaks and diffuse scattering) into account and thus reveals both the longer range atomic order and the local deviations from it. In particular, due to the significant diffuse scattering found in the LAMOX neutron patterns, we expect that a PDF analysis could help in getting a more complete picture of its structural characteristics.

Figure 1 compares a selected region of the LAMOX time-of-flight neutron patterns at 500 °C (lower part) and 600 °C (upper part) as a function of Q, the magnitude of the momentum transfer. The 500 °C pattern is fully compatible with the monoclinic reference structure[5] while the 600 °C pattern is in total agreement with the cubic reference structure.[7] In the inset of Figure 1 we show a very small part of the neutron patterns in order to highlight the differences in the crystal structure between the two samples. As can be seen, the monoclinic sample (lower part) presents several splittings of the analogous single peaks in the pattern of the cubic sample (upper part), and in addition, it is characterized by the presence of several very low-intensity superstructure peaks which are absent in the data at 600 °C. Finally, in the pattern of the cubic sample (main part of Figure 1) we underline with a red curve the peculiar undulation of the diffuse background which is peaked at around 3 Å^{-1}. This has been previously connected to the presence of

short range order in the oxygen sublattice for distances around 2.5 Å,[6,7] namely around the shortest O−O distance. We remark that in all the previous structural studies carried out on the LAMOX compound the information contained in the diffuse scattering was totally neglected being this peculiar background simply fitted and subtracted from the neutron diffraction patterns.

From the experimental data presented above we extracted the PDFs of the monoclinic (500 °C) and cubic (600 °C) LAMOX through the procedure described in the Experimental Section. Figure 2A shows the two experimental PDFs overlapped in the r-range extending to 20 Å together with the difference curve calculated by subtracting the PDF of the 500 °C data from the PDF of the 600 °C data. The comparison of the data sets clearly reveals that the PDFs of the monoclinic and cubic samples are substantially identical over the range investigated. This result implies that the local structure of the two polymorphs of LAMOX is the same, as opposed to the average structures, which are markedly different (see Figure 1). Figure 2B indicates the expected change to the PDF if the local structure really changes from the monoclinic to the cubic phases. The two curves in Figure 2B were calculated from the monoclinic[5,10] and cubic[6] models with all parameters the same except for the cell parameters and atomic positions. This is provided to help develop an intuitive feeling about how large the changes in the PDF would be at this phase transition if the two phases were fully ordered. Clearly, the observed changes are much smaller than predicted.

Moreover, the use of physically reasonable thermal factors, taken from the monoclinic model, to calculate the PDF of the cubic structure leads to very sharp peaks in the PDF in contrast to the peak shape of the experimental PDF. This result is the first indication that the static disorder of the monoclinic structure, which is represented by the 216 oxygen atoms possessing different and unique atomic positions, is in a sense replaced in the cubic phase by a distribution of the oxygen ions which is locally the same as in the monoclinic phase but no longer long-range ordered. The loss of long-range order would allow the structure to become dynamic, consistent with increased ionic conductivity though our current diffraction data do not separate the static and dynamic components explicitly.

Figure 3 shows the result of the fitting procedure carried out on the experimental PDFs. Figure 3A shows the fit of the monoclinic model[5] to the 500 °C data. The fitting parameters were the scale factor, the lattice constants (a, b, c, and γ), and the dynamic correlation factor (δ) which takes into account the correlated motion between atom pairs. Red, blue, and black lines represent, respectively, the calculated PDF, the experimental PDF, and the difference curve. The "goodness of fit" indicator (R_{wp}) of this fit is 14.7%, corresponding to a very good agreement between the experimental and calculated PDFs,[11] even without refining atomic positions. In Figure 3B we show the fit of the same monoclinic model to the 600 °C data (cubic LAMOX). As can be appreciated, the modeling of the experimental PDF of the cubic LAMOX by means of the monoclinic

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(10) In the calculation of the PDFs, we used in both structures a single adp value for each kind of atom, i.e., La, Mo, and O. In particular, the values used have been taken from the monoclinic structure[5] and averaged over the thermal factors of each site. The U values used were 0.0152, 0.010, and 0.0253 Å^2 for the La, Mo, and O sites, respectively.
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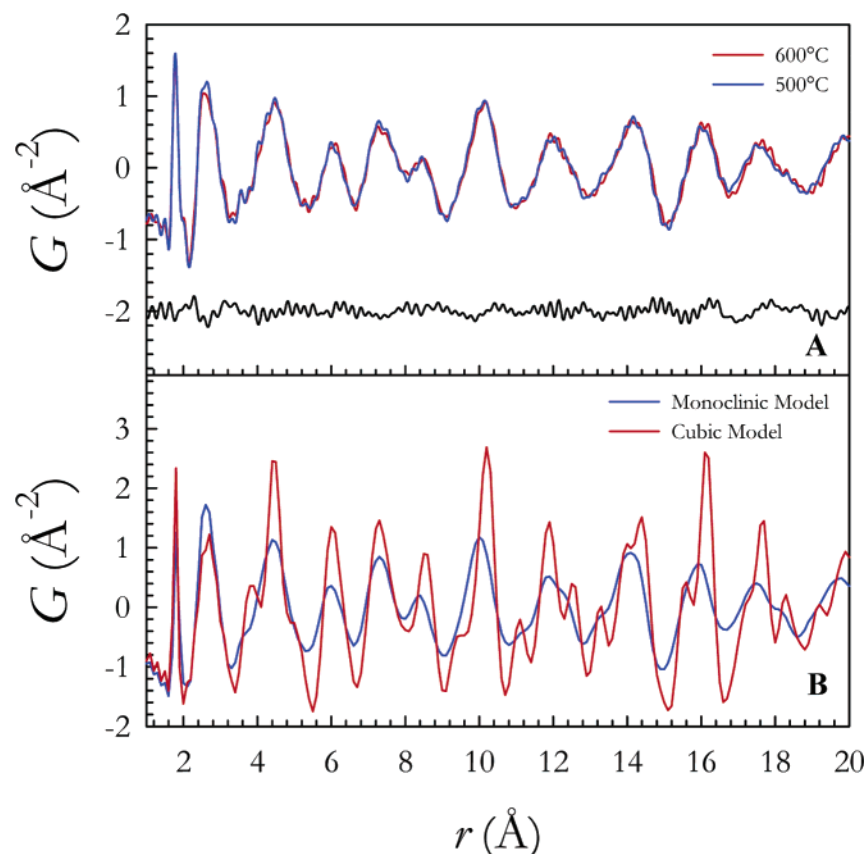
Figure 2. (A) Comparison between the experimental PDFs of LAMOX at 500 °C (blue line) and 600 °C (red line) and their difference (black line). (B) Comparison between the calculated PDFs of LAMOX from the monoclinic (blue line) and cubic (red line) models. Details about the calculated PDFs are in the text.

model leads to a very good agreement between the two with a R_{wp} of 15.5%.

Finally, in Figure 3C we show the result of a fit of cubic LAMOX carried out using the cubic model.[7] One of the peculiarities of this model is the presence of large atomic displacement parameters (U), particularly for the O2 ($U_{equiv}=0.085$ Å²) and O3 ($U_{equiv}=0.233$ Å²) sites. In order to "test" the cubic model against the experimental cubic sample in the same way as before for the monoclinic model, we refined the same parameters used in the previous fits, i.e., the scale factor, the lattice constant, and the dynamic correlation factor. From the results plotted in Figure 3C, it is clear that the cubic model described in the current literature is inappropriate for describing the experimental PDF of the cubic LAMOX, particularly for r < 10 Å. The R_{wp} has now increased to 38.4%.

The inclusion of the atomic positions and atomic displacement parameters as variables in the fit of the cubic model to the 600 °C data leads to a much better agreement between the experimental and calculated cubic LAMOX (R_{wp} 20.0%), as shown in Figure 4. The final structural parameters obtained from this fit are reported in Table 1 and compared to those determined from a Rietveld refinement of the same sample, which agree with the available structural description of the cubic polymorph of LAMOX. As can be appreciated, there are several significant differences between the two data sets, particularly for the Mo coordinate, the *y*-coordinate of O2, and the overall position of the O3. Finally, with the only exception of the Mo, the atomic displacement parameters of all the atoms are lower, in particular for the O3 atom, even though all of them remain quite high.

We note that a possible extension of this model to also include the refinement of the atom occupancies leads to meaningless results for the O1 position (always bigger that 1.2). More reliable results with reference to the occupancies may be obtained by extending the fit of the PDF to a higher *r*-range. In this case, the final fit results are closer to those obtained from the Rietveld refinement, particularly for the atomic displacement parameters and the occupancies, since we are now looking at the average structure of the sample.

The results presented so far have shown that the average structures for the LAMOX compound at 500 °C and at 600 °C are different and, in particular, monoclinic at the first temperature and cubic at the second. However, a striking feature of the PDFs of the two phases is that by crossing the phase transition the local structure does not substantially change, as exemplarily shown in Figure 2A. These results strongly support a scenario in which the structural phase transition from the α- to the β-phase is a transition from a long-range ordered to a, presumably dynamic, short-range ordered distribution of the oxygen defects while preserving the monoclinic local structure. In particular, the monoclinic phase presents a Mo–O environment of variable coordination, namely 4, 5, and 6, which, by considering the oxygen sharing pattern, become 3.73, 4.77, and 4.94.[5] In the cubic phase the "average" Mo–O coordination number is 4.5. The peculiar nature of the $\alpha \rightarrow \beta$ phase transition is the local change (with time) of the Mo–O coordination environment due to the migration of the oxygen ions through a vacancy mechanism. An average probe such as the neutron diffraction well describes the long-range static distribution of
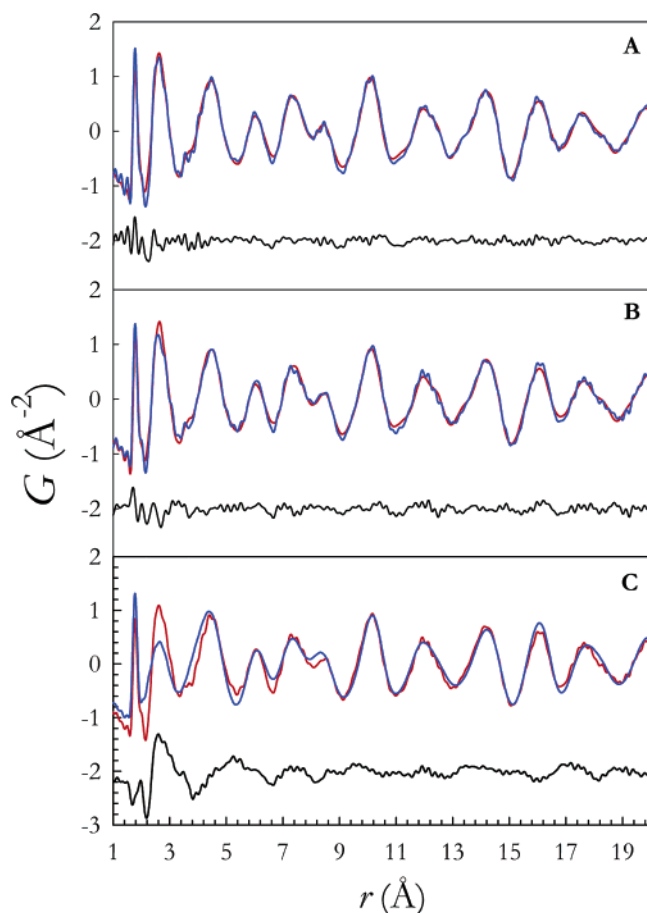
Figure 3. (A) Fit of the experimental PDF of LAMOX at 500 °C with the monoclinic model (red, blue, and black lines represent, respectively, the calculated PDF, the experimental PDF, and the difference curve in all the three panels). (B) Fit of the experimental PDF of LAMOX at 600 °C with the monoclinic model. (C) Fit of the experimental PDF of LAMOX at 600 °C with the cubic model. In all the refinements, the starting model was from the published structure in the literature,[5,6] and the parameters fitted in the refinement were scale factor, dynamic correlation factor, and lattice constants.

the oxygen ions in the monoclinic phase, but fails in describing the dynamic distribution in the cubic phase. In this last case all this information is found in the diffuse scattering due to the short-range order which is clearly visible in the neutron pattern of the sample at 600 °C. Since this information is not used in the traditional Rietveld refinement of the neutron diffraction patterns, the only way to deal with the oxygen sublattice is by introducing large values of the atomic displacement parameters for the oxygen ions, as done in the available models describing the cubic structure by means of neutron diffraction.[6,7] The consequence on the calculated PDF of the huge thermal factors is a smearing of the oxygen atom density leading to a poor description of the local structure (see Figure 3C).

The power of the PDF analysis, which makes use of the total scattering function, is nicely probed in the present case. The PDFs of LAMOX at 500 and 600 °C are substantially identical showing that on the local scale the structure, in both cases, is monoclinic. The use of the cubic model to refine data at 600 °C has been proven to be possible (see Figure 4), but even in the case of a real-space refinement including all the scattering components, the final result is a cubic structure where the large atomic displacement parameters compensate for the dynamic distribution of the atoms and the inability to precisely define
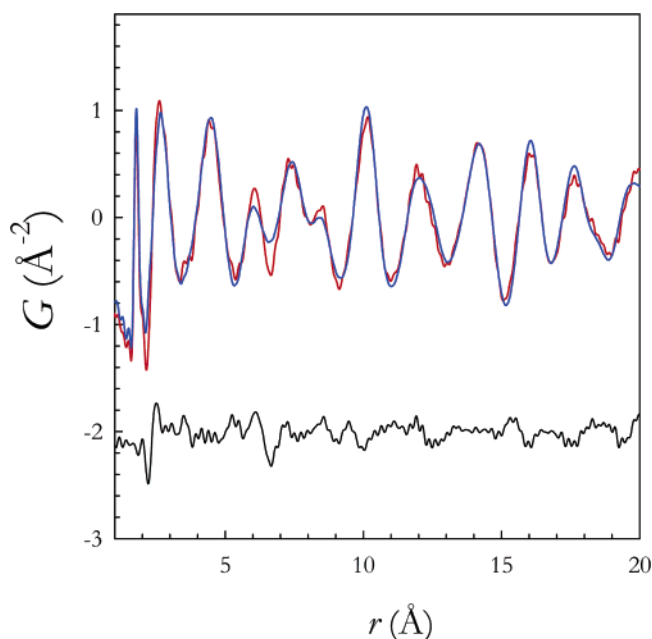
Figure 4. Fit of the experimental PDF of LAMOX at 600 °C with the cubic model (red, blue, and black lines represent, respectively, the calculated PDF, the experimental PDF, and the difference curve). The fit was carried out in the same way as those shown in Figure 3, but the atomic positions and atomic displacement parameters were allowed to vary.

Table 1. Fit Results for the Rietveld Refinement of the Cubic LAMOX and for the PDF Fit Represented in Figure 4, i.e., Carried out by Using the Cubic Model

parameter	Rietveld refinement	fit of Figure 4
lattice parameter (Å)	7.21788(8)	7.2220(3)
La, x	0.8543(3)	0.8575(2)
U_{iso}	0.065(7)	0.1004(8)
Mo, x	0.1682(2)	0.1754(2)
U_{iso}	0.057(6)	0.0750(4)
O1, x	0.3147(4)	0.3103(2)
U_{iso}	0.093(3)	0.0578(6)
O2, x	0.9933(5)	0.9859(2)
O2, y	0.1875(9)	0.1615(3)
O2, z	0.3438(5)	0.3455(2)
U_{iso}	0.088(4)	0.0614(5)
O3, x	0.894(1)	0.9830(3)
O3, y	0.698(6)	0.7531(3)
O3, z	0.553(1)	0.4950(3)
U_{iso}	0.33(3)	0.0310(7)
R_{wp} (%)	2.99	18.7

their position. However, it is clear by comparing Figures 3C and 4 that the total scattering method allows for a better description of the cubic sample with the cubic model, even though it also ends, like in the Rietveld refinement, with high thermal factors which are not simply due to the dynamics of the oxygen migration but to some deficiencies in the model. The cubic model does not correctly capture the geometry of the oxygen ion coordination and is lacking in describing the O-occupancies in the short range. This can be understood if we compare the U values of LAMOX with other fast oxygen-ion conductors such as YSZ. For example, a time-of-flight study of YSZ[12] at 767 °C determined a U_{iso} for the O atoms of 0.018 Å^2. Even for higher temperatures the U values are always significantly lower than those of O atoms in LAMOX. It should be noted that the highest adp (atomic displacement parameter)

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pertains to the Mo which is the ion most involved in the oxygen diffusion through a change in its coordination environment.

The main result presented so far, i.e., the equivalence of the local structure in the monoclinic and cubic phases, is of great importance since it demonstrates that what is usually considered as a "disordered oxygen distribution" actually has a well-defined local structure which is the same as in the monoclinic phase but dynamic. As it has been suggested by Evans and co-workers, the structure of the oxide ion conducting phase corresponds to a time-averaged version of the monoclinic phase.[5] However, in the present work we took a step further in elucidating the correlation between the α- and β-phases of LAMOX by directly showing this relationship through the PDF analysis. This understanding allows us to consider different possible oxygen ion conduction paths in the conducting β-phase of LAMOX by considering, as a starting point, the monoclinic structure. A possible proposal of this conduction mechanism may be done on the basis of the Mo−O coordination environment as is found in the monoclinic phase. It is plausible that the conduction mechanism involves the migration of an oxygen ion from a Mo−O polyhedron with a higher coordination number toward an oxygen vacancy on another Mo−O polyhedron. Interestingly, it is possible to follow a path in the monoclinic structure which involves distances from an O belonging to a first "donor" Mo−O polyhedron to the Mo of another "acceptor" Mo−O polyhedron of about 5.6 Å (Mo−O−V_O−Mo). This distance is exactly the one separating two Mo atoms belonging to two different polyhedra that are connected by two oxygen atoms each belonging to a separate polyhedron and with a partial O-occupancy, i.e., for example, Mo−O2−O3−Mo. This result suggests that when the LAMOX transforms from the α- to the β-phase the oxygen starts "jumping" from a Mo−O group to the next Mo−O group leading to, on average, two sites with partial occupancy (what is seen from the average probe) that are actually sites within a polyhedron with a well-defined coordination which is changing with time.

In conclusion, we have provided the first application of the atomic-pair distribution function analysis to the study of an oxygen fast-oxide ion conductor of actual interest in the SOFC community. Our results have shown that a clear and reliable description of the local atom arrangement in the LAMOX structure can only be achieved through the application of a local probe such as the PDF. This allowed us to directly determine that the transition from the monoclinic to the cubic phase of LAMOX is a transition from a static to a dynamic distribution of the oxygen defects while preserving the monoclinic local structure. The application of the PDF analysis to the solid-state ionic materials can allow a more detailed description of their local structure, particularly in the highly conductive phases, and leads to a better comprehension of the structure−property correlation, which is the starting point for the design of new and optimized functional materials.

Experimental Section

$La_2Mo_2O_9$ has been prepared by conventional solid-state reaction by mixing stoichiometric amounts of high purity La_2O_3 and MoO_3 powders (Aldrich >99.9%) into ethanol in an agate mortar, compressing, and then heating at 500 °C for 24 h, then at 700 °C for another 24 h and finally at 900 °C for 60 h, during which the sample undergoes regrounding twice. Phase purity was checked by means of room-temperature X-ray powder diffraction (XRPD) patterns acquired with a Bruker D8 Advance diffractometer.

Neutron powder diffraction measurements were carried out on the NPDF[14] diffractometer at the Lujan Center at Los Alamos National Laboratory. A 10 g sample of LAMOX powder was packed in a cylindrical vanadium tube and measured from 300 to 750 K. Data were processed to obtain the PDFs using PDFgetN,[13] and the structural modeling was carried out using the program PDFFIT2.[11]

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