

High-pressure Polymorphs of LaHO with Anion Coordination Reversal

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Supporting Information Placeholder

ABSTRACT: Two novel high-pressure polymorphs of lanthanum oxyhydride have been successfully predicted and stabilized under pressure. When reacted at 3 GPa, the fluorite structure of LaHO with anion-centered tetrahedral (HLA₄/OLA₄) geometry is transformed to the PbCl₂-type structure involving coordination number increase of H⁻ to five (HLA₅ square pyramids). Upon further application of pressure to 5 GPa, LaHO changed into the anti Fe₂P-type structure. Interestingly, the 5 GPa phase contains tetrahedral HLA₄ and square-pyramidal OLA₅ geometry, meaning coordination switching, as confirmed by *ab initio* calculations. The structural analysis shows that this unprecedented phenomenon is enabled by higher compressibility of hydride anion and emphasizes its potential in the search for new high-pressure forms of hydride-based materials.

High-pressure synthesis offers an access to new compounds that exhibit novel chemical and physical functions.¹ Among high-pressure polymorphs, the most well-known is diamond which finds a wide variety of applications. Application of pressure to a ferromagnetic α -Fe induces a structural transition to ε -Fe and leads to superconductivity at low temperature.² Furthermore, meta-stable superhydrides exhibit high- T_c superconductivity under megabar pressures: H₃S at $T_c = 203$ K³ and LaH₁₀ at $T_c = 260$ K.⁴

High-pressure polymorphs have structures with higher density, and this is enabled, for example, by forming closest-packed arrays of atoms (e.g., hexagonal closed packed (hcp) ε -Fe vs body-centered cubic α -Fe) and by altering bonding character (e.g., diamond vs graphite). In ionic compounds, high pressure often leads to an increase of coordination number.⁵ In the first case for instance, the transformation from NaCl-type to CsCl-type structures involving a coordination change of 6 to 8 occurs in binary halides,⁶ oxides,⁷ chalcogenides,⁸ and intergrowth compounds.⁹ Similarly, tetrahedrally coordinated SiO₂ have various high-pressure forms such as rutile-type phase with octahedral coordination¹⁰

Recent studies on oxyhydrides have revealed novel properties (e.g., hydride conductivity and heterogeneous catalysis) associated with unique features of the hydride anion, such as lability and high polarizability.^{11–16} Our study on SrVO₂H revealed that the V–H–V distance decreases twice as large as the V–O–V distance, indicating that H⁻ anion is extraordinary compressible.¹⁷ The size flexibility of H⁻ was then exploited to enable a novel anion order-disorder transition in LnHO.¹⁸ For Ln = Sm–Er with smaller ionic radii (R_{Ln}), LnHO adopts the anion-disordered fluorite structure. Since the O²⁻ anion becomes gradually under-bonded with increasing R_{Ln} (i.e., application of negative *chemical* pressure), anion ordering takes place for Ln = La–Nd (Figure 1a), where H⁻ anions are expanded to form a larger HLn₄ tetrahedron, resulting in a smaller OLn₄ tetrahedron. Based on this result, we hypothesized that the application of external pressure to the anion-ordered LnHO induces anion-disorder. However, we unexpectedly obtained two polymorphs which exhibit unprecedented anion coordination reversal.

Since the previously used metathesis synthesis (Ln₂O₃ + CaH₂ → 2LnHO + CaO)^{18,19} is unsuitable for a high-pressure setup, we employed a direct reaction using a cubic anvil apparatus, as used in the synthesis of perovskite-based oxyhydrides.^{20,21} Lanthanum sesquioxide and lanthanum hydride in a molar ratio 1:1 were mixed, pressed up to 1, 3 and 5 GPa, heated at 900 °C for 1 hour. The synchrotron X-ray diffraction (SXRD) profile (Figure 2a) showed that the sample prepared at 1 GPa is the same as the ambient LaHO phase with the anion-ordered fluorite structure (Figure 1a).²² The cell parameters of $a = 8.0765(2)$ Å and $c = 5.7257(2)$ Å are quite close to those of reported. This phase will be denoted as α -LaHO by analogy with predicted CaF₂ polymorphs.²³ α -LaHO contains three independent lanthanide sites, all in eightfold (H × 4, O × 4) and nearly cubic environments.²² As reported previously, from the anion-centered viewpoint, both anions lie in tetrahedral environments, but with distinct volumes of 8.15 Å³ for HLA₄ and 7.39 Å³ for OLA₄.

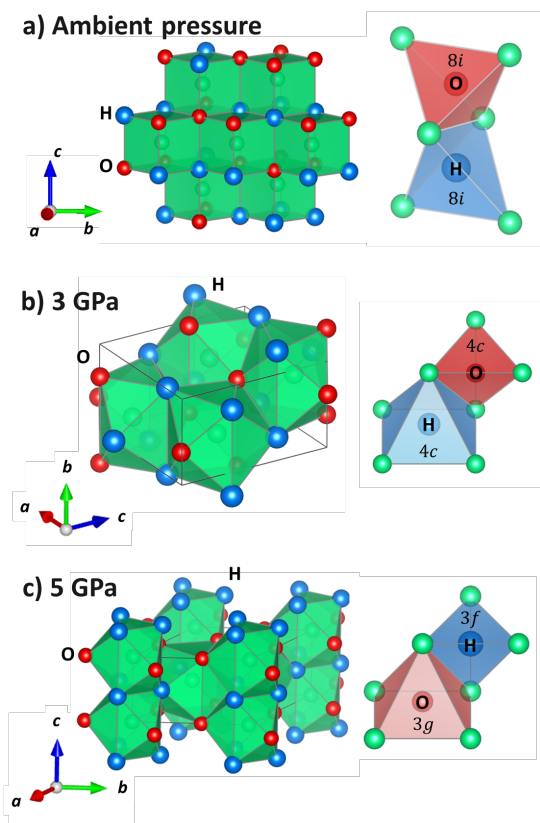
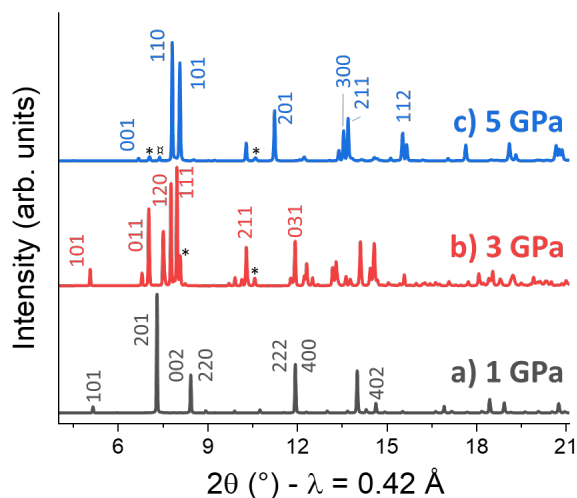


Figure 1. Crystal structures (a) α -LaHO at ambient pressure (and 1 GPa) crystallizing in the anion-ordered fluorite structure ($P4/nmm$) with LaO_4H_4 local coordination,²² (b) γ -LaHO ($Prma$) at 3 GPa with LaO_4H_5 and (c) δ -LaHO ($P\bar{6}2m$) at 5 GPa with LaO_5H_4 . The right panels represent the coordination geometry around the hydride and oxide anion, (a) HLa_4 and OLa_4 , (b) HLa_5 and OLa_4 , (c) HLa_4 and OLa_5 . Red, blue and green spheres



denote O, H and La atoms, respectively.

Figure 2. SXR D patterns of LaHO synthesized at 900 °C under a pressure of (a) 1 GPa, (b) 3 GPa and (c) 5 GPa. Unreacted precursors peaks are denoted by * for La_2O_3 and \square for LaH_3 .

By applying pressure up to 3 GPa, a completely different SXR D pattern (Figure 2b) is obtained, which can be indexed by

an orthorhombic cell of $a = 6.41 \text{ \AA}$, $b = 3.92 \text{ \AA}$ and $c = 7.08 \text{ \AA}$, except for small impurity peaks. A similar unit cell is found in compounds with the PbCl_2 -type structure (space group $Pnma$) such as CaH_2 ($a = 5.95 \text{ \AA}$, $b = 3.61 \text{ \AA}$, $c = 6.85 \text{ \AA}$),²⁴ SrH_2 , BaH_2 and CaF_2 at 9.5 GPa.²⁵ The cation arrangement in the PbCl_2 structure is given by a distorted hcp, with anions in tetrahedral (ClPb_4) and square-pyramidal (ClPb_5) coordination. Synchrotron/neutron Rietveld refinements successfully converged to the agreement factors of $R_{\text{Bragg}} = 3.51\%/3.40\%$ and $R_{\text{wp}} = 11.1\%/4.64\%$ (Table S1) when oxide and hydride anions were placed, respectively, at the four- and five-coordinated site (Figure 1b). The neutron refinement shows that the anion occupancies stayed at 1. Bond valence sum (BVS) calculation using tabulated parameters²⁶ yielded $\text{La} = +3.30(1)$, $\text{O} = -2.19(1)$ and $\text{H} = -1.11(1)$, which is in good agreement with their formal valences. We call the 3 GPa phase as γ -LaHO by analogy with CaF_2 polymorphs.²³ As for multiple anion system, M. Glätzle *et al.* recently reported that LnOF oxyfluorides ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}$) adopt the PbCl_2 -type structure when synthesized under pressure (11 GPa).²⁷

The observed pressure-induced transition ($\alpha \rightarrow \gamma$) in LaHO is understandable from various angles. Firstly, the density increases by 5% from 5.54 to 5.82 g/cm^3 . Secondly, the cation-coordination increases from 8 ($\text{H} \times 4$, $\text{O} \times 4$) to 9 ($\text{H} \times 5$, $\text{O} \times 4$) and La^{3+} cations adopt a more closely-packed (hcp) arrangement. Regarding the anion, only the hydride increases its coordination number from 4 to 5. Note also that the OLa_4 tetrahedral volume reduces only slightly (6.94 \AA^3). The increased coordination in H^- (not in O^{2-}) is in line with the fact that a structural modification under pressure takes place in general by imposing a distortion to atoms with weaker bonds.²⁸ Here the La-H bonding should be weaker than La-O in terms of valence (-1 vs -2) and the average bond distance (2.52 \AA vs 2.44 \AA for α phase). The pressure-induced α - γ transition in LnOF ²⁷ can also be understood in the same manner. The important difference, however, is that LnOF requires a much higher pressure of 11 GPa to stabilize the γ form. Much lower critical pressure in LaHO (3 GPa) could be ascribed to weaker bond strength for La-H than La-F, as demonstrated in fluorides, chlorides and hydrides with transition metals.²⁹

In parallel to the experimental approach, *ab initio* random structure searching (AIRSS)^{31,32} has been performed on LaHO at different pressures, similarly to the approach taken for the high pressure phases of group-II difluorides.³² The CASTEP cod³³ was employed to perform the structural optimizations through the density functional PBEsol.³⁴ Structure files containing the full computational details are provided in Supporting Information. The results obtained confirm our experimental observations where the PbCl_2 structure type was identified as a stable denser structure compared to fluorite.

When the synthesis pressure was further increased to 5 GPa, we again encountered a drastic change in the X-ray diffraction pattern. The new pattern (Figure 1c) was indexed by a hexagonal cell ($a = 6.17 \text{ \AA}$, $c = 3.60 \text{ \AA}$). Literature search has revealed that the Fe_2P -type structure ($P\bar{6}2m$) is a candidate. Although US_2 ,³⁵ USe_2 ,³⁵ BaCl_2 ,³⁶ and BaI_2 ³⁷ adopt this structure, oxides, fluorides and hydrides are not known to date. For anions, we initially placed O^{2-} and H^- , respectively, at a tetrahedral ($3f$) and square-pyramidal ($3g$) site, as observed in the γ -phase (3 GPa), but this resulted in poor agreement (see the neutron refinement in Figure S2). A remarkable improvement has been obtained when the two anionic sites were swapped, giving $R_{\text{Bragg}} = 4.72\%/2.65\%$ and $R_{\text{wp}} = 6.74\%/3.28\%$ for synchrotron/neutron data (Figure 1c, Table S2). Neither anti-site (H/O) disorder nor anion deficiency was observed. Remarkably, this structure (δ -LaHO) has been included in the structures predicted by AIRSS (Table S3, Figure S4).

One can also justify the second transition from γ -LaHO to δ -LaHO by the density increase from 5.82 to 6.54. However, the most distinct feature of this transition is the reversed coordination environment around the anions: HLa₅ and OLa₄ in γ -LaHO change into HLa₄ and OLa₅ in δ -LaHO. As far as we are aware, the reduction in coordination number by pressurization (HLa₅ \rightarrow HLa₄) has never been reported. We believe the hydride compressibility plays a predominant role in this coordination reversal. In fact, HLa₄ tetrahedra are significantly compressed from 8.15 to 6.6 Å³ ($\gamma \rightarrow \delta$; 19%), three times greater than OLa₄ tetrahedra with a compression from 7.39 to 6.94 Å³ ($\alpha \rightarrow \delta$; 6%). The BVS calculations for δ -LaHO show a reasonable value of -1.7 for oxide, but the value of -1.8 for hydride is much higher than that of the γ phase. The apparent over-bonded H⁻ merely implies a difficulty in evaluating BVS for hydride with the ability to flexibly change its size.¹⁷

LaH_{2.3} with the fluorite structure is phase-segregated into LaH_{2+x} and LaH at 10 GPa.³⁸ This fact underlines the role of multiple anions with distinct compressibility for the realization of anion-coordination reversal. We believe that this concept can be extended to other oxyhydrides and more generally hydride-fluorides and hydride-nitrides. Since high pressure phases of CaF₂ have been theoretically predicted to be excellent ionic conductors,^{23,32} α -LaHO, γ -LaHO and δ -LaHO may also be a potential candidate for hydride conductors, possibly after introduction of appropriate anion vacancy by aliovalent cation substitution. Higher pressure study is also of great interest. AIRSS searches on LaHO up to 100 GPa has predicted a further transition to a hexagonal (*P6₃mmc*) structure with HLa₅ bipyramidal and OLa₆ octahedral coordination (Figures S5, S6).

ASSOCIATED CONTENT

Supporting Information

Experimental details including synthesis methods, materials characterization and additional data are given in supporting information.

The Supporting Information is available free of charge on the ACS Publications website.

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Anion coordination reversal
Higher H^- compressibility

