Advances on the LiCl salt flux method and the preparation of phase pure $La_{2-x}Nd_xLiHO_3$ ($0 \leq x \leq 2$) oxyhydrides

Øystein Slagtern Fjellvåg,[*a] Kristin Hubred Nygård,[a] Ponniah Vajeeston,[a] and Anja Olafsen Sjåstad[*a]

[a] Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, P. O. Box 1033, N-0315 Oslo, Norway.

E-mail: o.s.fjellvag@smn.uio.no; a.o.sjastad@kjemi.uio.no

Experimental:

The oxyhydrides $La_{2-x}Nd_xHO_3$ ($0 \leq x \leq 2$) were prepared from the binary oxides La_2O_3 (Molycorp 99.99 %) and Nd_2O_3 (Molycorp 99.9 %). Prior to synthesis, the oxides were dried at 1100 °C for 12 hours and transferred directly into an argon filled glove box (MBraun) to avoid hydration. LiCl and KCl (both Sigma-Aldrich 99.0 %) were dried at 585 °C before transferred into the glove box. Stoichiometric amounts of the binary oxides together with a 1:4 excess of LiH (Sigma-Aldrich, 95 %) was grinded together with 100 mass % salt (with respect to the reactants) inside the glove box. The mixture was transferred to a tantalum crucible and sealed in a stainless-steel ampoule. The samples were heated at temperatures between 375 and 800 °C. Excess LiCl and LiH were removed by washing with methanol. Note: All experiments must be evaluated with respect to safety. Care must be taken when working with metal hydrides as they react vigorously with water and air. A detailed description is given elsewhere.[1-2]

Home-laboratory XRD measurements were performed on a Bruker AXS D8 Discover instrument with Cu $K_{\alpha1}$ radiation from a Ge(111) Johansen monochromator in Bragg-Brentano geometry. The mass percent of the different phases were quantified by Rietveld refinements. The Rietveld refinements were carried out in TOPAS V5.[3-4] Six background parameters was used to fit the background and a Thomson-Cox-Hasting to fit the peak shape. The structure was not refined, but obtained from literature.[2]

Neutron diffraction were carried out at room temperature at the two-axis powder diffractometer PUS at the JEEP II reactor at Institute for Energy Technology (IFE), Kjeller, Norway, with a wavelength of 1.55434 Å. The Rietveld refinements were carried out in TOPAS V5.[3-4] A eight polynomial background function was used and a Thompson-Cox-Hastings pseudo-Voigt peak shape. Lanthanum and neodymium were restricted to have the same atomic position and thermal displacement parameters. Structural information from the refinements are given in Table 1.

Table 1: Crystallographic data of $LaNdLiHO_3$ in space group *Immm* [a = 3.5265(3) Å, b = 3.7248(2) Å, and c = 12.8099(8) Å] from neutron diffraction.

Atom	Wycoff	x	y	z	Occupancy	B_{ISO}
La	4i	0	0	0.36254(12)	0.5	0.09(4)
Nd	4i	0	0	0.36254(12)	0.5	0.09(4)
Li	2a	0	0	0	1	0.40(16)
H	2b	0.5	0	0	1	1.39(11)
O1	4i	0	0	0.17706(17)	1	0.64(4)
O2	2d	0.5	0	0.5	1	0.64(4)

Thermogravimetric (TG) measurements were performed by heating powder samples under a 50 % O_2 in N_2 atmosphere (both 99.999 %, Praxair) and measuring the mass change as a function of temperature using a Netzsch STA 449 F1 Jupiter instrument. All samples were heated at 10 °C min^{-1} up to 800 °C, where the temperature was held for 120 min. The sample mass was 10.0 ± 1.0 mg for all measured samples and the “flex tangent” method were used to find the decomposition temperature. The buoyancy effect was corrected by subtracting a blank reference scan at exactly the same conditions.

Computational details:

Total energies were calculated by the projected augmented plane-wave (PAW) implementation of the Vienna *ab initio* package (VASP).[5-6] All these calculations were performed with the Perdew, Burke, and Ernzerhof (PBE)[7] exchange correlation functional with the Hubbard parameter correction (GGA+U), following the rotationally invariant form.[8-9] An effective U values of 7.5 eV and 6.2 eV was used for the La and Nd, respectively. The ground-state geometries were determined by minimizing stresses and Hellman-Feynman forces using the conjugate-gradient algorithm with force convergence < 10^{-3} eV $Å^{-1}$. Brillouin zone integration was performed with a Gaussian broadening of 0.1 eV during all relaxations. 512 k-points in the whole Brillouin zone for the structure with a 600 eV plane-wave cutoff were found sufficient to ensure the required accuracy. The k-points were generated using the Monkhorst-Pack method with a grid size of 8×8×8 for structural optimization. A similar density of k-points and energy cutoffs were used to estimate total energy as a function Nd concentration in $La_{2-x}Nd_xLiHO_3$ solid solutions. For the initial structure generation the structural data for La_2LiHO_3 and Nd_2LiHO_3 are taken from ICSD database and we used the *ab initio* random searching structure (AIRSS)[10] method to generate possible model structures for the chosen Nd substitution in La_2LiHO_3 matrix coupled with VASP calculations. Iterative relaxation of atomic positions was stopped when the change in total energy between successive steps was < 1 meV/cell. The heat of formation (ΔH) is calculated using the following equation

$$\Delta H = E_{total}^{\mathrm{La(2-x)NdxLiHO3}} - [E_{bulk}^{LiH} + (2-x)\, E_{bulk}^{La2O3} + xE_{bulk}^{Nd2O3}]$$

where $E_{total}^{\mathrm{La(2-x)NdxLiHO3}}$, E_{bulk}^{LiH}, E_{bulk}^{La2O3}, and $xE_{bulk}^{Nd2O3}$are the total energy of the bulk $La_{2-x}Nd_xLiHO$ (in *Immm*), LiH (in *Fm-3m*), La_2O_3(in *P-3m1*) and Nd_2O_3 (in *P-3m1*), respectively.

A frozen phonon calculation was applied to the supercells using the phonopy program to obtain the phonon dispersion curve and phonon density of states.[11] An atomic displacement of 0.0075 Å was used with a symmetry consideration to obtain the force constants for the phonon calculations. The displacements in opposite directions along all possible axes were incorporated in the calculations to improve the precision. The force calculations were made using the VASP code with the supercell approach (with GGA+*U* correction) and the resulting data were imported into the Phonopy program. The dynamical matrices were calculated from the force constants, and phonon density of states (DOS) curves were computed using the Monkhorst-Pack scheme.[12] Phonon calculations for La_2LiHO_3 and Nd_2LiHO_3 is given in Figure S1 and S2. As no negative vibrational frequencies are encountered, the calculated compounds are considered stable. Phonon calculations was also carried out for Sm_2LiHO_3 with basis in an optimized structure based the structure of La_2LiHO_3. The phonon dispersion and DOS is given in Figure S3. Negative phonon frequencies are encountered for this compound, thus it is considered unstable.

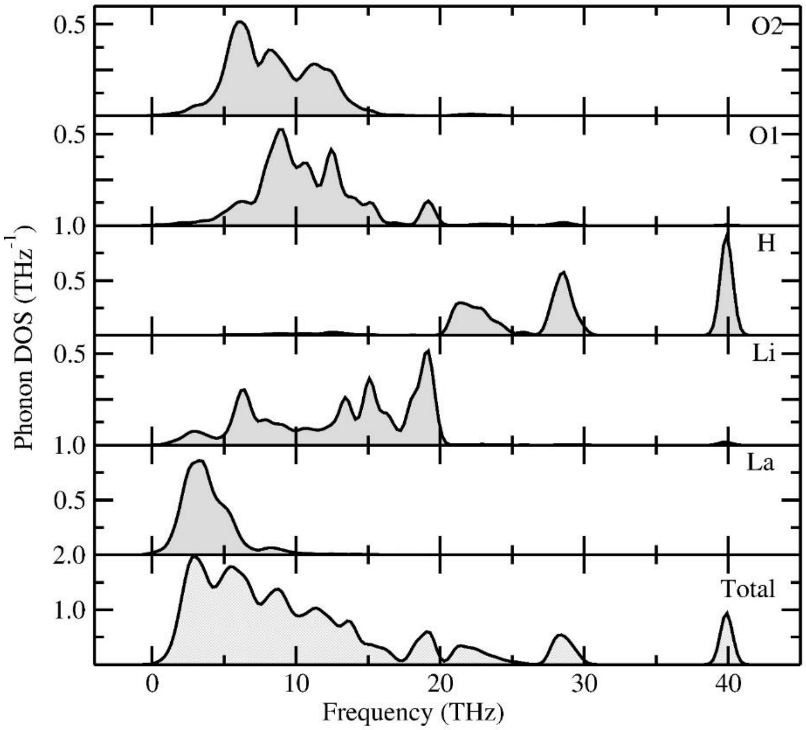

Figure S1: Calculated total and site projected phonon density of states (PDOS) for La_2LiHO_3.

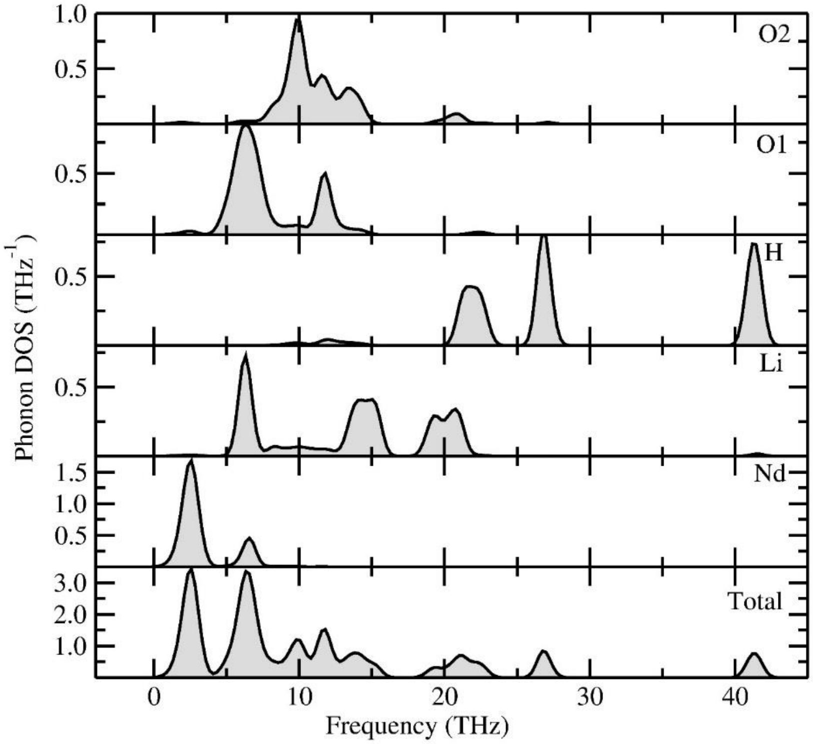

Figure S2: Calculated total and site projected phonon density of states (PDOS) for Nd_2LiHO_3.

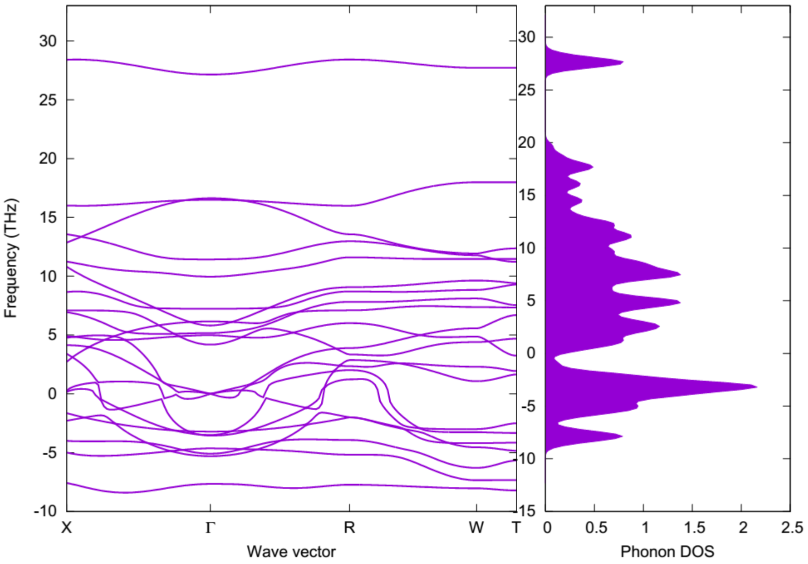

Figure S3: Calculated phonon dispersion and density of states (DOS) of Sm_2LiHO_3. The structural model is based on the crystal structure of orthorhombic La_2LiHO_3. Phonons with negative frequencies are encountered, therefore the compound is considered to be unstable.

References:

1. Schwarz, H., *Neuartige Hydrid-Oxide der Seltenen Erden: Ln2LiHO3 mit Ln = La, Ce, Pr und Nd*. Karlsruhe, 1991.

2. Fjellvåg, Ø. S.; Armstrong, J.; Sławiński, W. A.; Sjåstad, A. O., Thermal and Structural Aspects of the Hydride-Conducting Oxyhydride La2LiHO3 Obtained via a Halide Flux Method. *Inorg. Chem.* **2017,** *56*, 11123-11128.

3. Bruker-AXS *TOPAS V5: General profile and structure analysis software for powder diffraction data, Bruker AXS, Karlsruhe, Germany.*, 2013.

4. Coelho, A., TOPAS and TOPAS-Academic: an optimization program integrating computer algebra and crystallographic objects written in C++. *Journal of Applied Crystallography* **2018,** *51*, 210-218.

5. Kresse, G.; Furthmüller, J., Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996,** *54*, 11169-11186.

6. Kresse, G.; Furthmuller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **1996,** *6*, 15-50.

7. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996,** *77*, 3865.

8. Liechtenstein, A. I.; Anisimov, V. I.; Zaanen, J., Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators. *Phys. Rev. B* **1995,** *52*, R5467-R5470.

9. Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Szotek, Z.; Temmerman, W. M.; Sutton, A. P., Electronic Structure and Elastic Properties of Strongly Correlated Metal Oxides from First Principles: LSDA + U, SIC-LSDA and EELS Study of UO_2 and NiO. *Phys. Status Solidi A* **1998,** *166*, 429-443.

10. Chris, J. P.; Needs, R. J., Ab initio random structure searching. *Journal of Physics: Condensed Matter* **2011,** *23*, 053201.

11. Togo, A.; Oba, F.; Tanaka, I., First-principles calculations of the ferroelastic transition between rutile-type and SiO_2 at high pressures. *Phys. Rev. B* **2008,** *78*, 134106.

12. Monkhorst, H. J.; Pack, J. D., Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976,** *13*, 5188-5192.