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Lithium and Rare-Earth Oxides Studied by Density Functional Theory

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Rare-earth metal oxides (ReO) have potential applications in various fields ranging from CMOS technology to Li-Ion batteries. Various unique properties, like the possibility to grow epitaxial REO on Si substrates and their combination to form alloys or superlattices [1] allows experimentally a variation in structure as well as properties of such layers. Despite the recent progress only limited knowledge exists concerning the lithium rare-earth oxides compounds.

The treatment of the rare-earth metals in density functional theory (DFT) enforces a special treatment of the correlated *f*-electrons which is handled in the exchange-correlation by using an LDA+U approach, details can be found in [2]. This is tested carefully for the structural, vibrational, dielectric and electronic properties of the rare-earth oxides.

First, the thermodynamic stability of Li-rare-earth-oxygen compounds is investigated by DFT. All experimentally known crystal structures within the group of Li-rare-earth oxides are used as the starting point for the determination of the thermodynamic stable crystal phases. Each rare-earth element forms a stable compound together with Li and oxygen stable against the separation into the single oxides. It is found that $LiReO_2$ is the most common stoichiometry of the stable crystals, e.g. for Re = Sc, Y, Gd, and Lu. An exception is La where a defect crystal structure $La_4Li_2O_7$ is found the most energetically favourable. The crystal is build up from spacegroup 139 (*I*4/*mmm)* with ¼ of the oxygen atoms removed. The interaction between the oxygen vacancies results in a strong tendency for ordering.

Second, the stability is investigated focusing on alloying between La and Lu compounds in comparison to Gd. Since the stable phases for La and Lu differ by varying the concentration in the respective crystal structures a crystal transformation is expected. However, the DFT calculations predict that in the intermediate range none of the commonly known crystal structures is stable allowing for a tuning by varying experimentally the stoichiometry.

Third, the Li diffusion kinetics in rare-earth oxides is studied. The ReO are found thermodynamically stable against Li. Together with their high electronic band gap exceeding 5 eV, a potential to act as a solid state electrolyte is investigated. A possible intermixing, experimentally demonstrated for La_2O_3 and Lu_2O_3 or arranging them as superlattices allows a variation in the lattice parameter. The diffusion pathways and diffusion energetic is calculated showing that the variable lattice parameter also influences the diffusion of Li.

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References:

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