

Phase Transformations in Ln_3TaO_7 : A First-Principles Study

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Pure and doped lanthanoid tantalates Ln_3TaO_7 (Ln = lanthanoid) with a Weberite-type structure are of interest for a range of applications, including photocatalysis [1], gas sensor electrodes, and magnetic devices [2]. Doped La_3TaO_7 has also been shown to exhibit reasonable oxide ion conductivities, making it a potential electrode material for solid oxide fuel cells and electrolyzers [3]. These compounds are known to undergo various phase transformations at different temperatures depending on the size of the lanthanoid ion. Several experimental studies have reported that, in general, for lanthanoids larger than Ho^{3+} , the crystal structures can be thought of as a distorted fluorite-related Weberite structure, with ordered arrays of oxide vacancies and Ln^{3+} and Ta^{5+} ions partitioned into seven- and six-coordinated sites, respectively. There is still some uncertainty about the precise crystal symmetries exhibited by each compound at room temperature [1,2,4], although in general La and Pr systems are reported to possess $Ccmm$ (= $Cmcm$) symmetry, while systems with smaller ions belong to space group $C222_1$. The chief difference between these structures is the tilting of the TaO_6 octahedra, either around the $[100]$ axis in $Cmcm$ or $[010]$ axis in $C222_1$. Figure 1 compares the $Cmcm$ and $C222_1$ structures of Nd_3TaO_7 , which have been observed to coexist at room temperature [2], by way of example.

To further identify the thermodynamically stable forms of each compound, in this study we systematically investigated the relative stabilities of orthorhombic phases of Ln_3TaO_7 , where Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb and Y, derived from first-principles calculations. These were carried out using the projector-augmented wave method within density functional theory, as implemented in the VASP code [5]. The general gradient approximation used for the exchange-correlation functional with Perdew-Burke-Ernzerhof parameterization. [6]. A plane-wave cutoff of 520 eV, with a k -point mesh for Brillouin zone sampling of primitive cells, based on the Monkhorst-Pack scheme [7], of $3 \times 5 \times 5$. An energy convergence of less than 1 meV per formula unit (f.u.) was achieved. Lattice constants and internal coordinates were fully optimized until residual Hellmann-Feynman forces were smaller than 2.5×10^{-3} eV/f.u.

Our calculations confirm that the stability of the $C222_1$ phase increases as the Ln ion decreases, as shown in Fig. 2, consistent with experimental trends, and confirming that this is the thermodynamically stable phase at 0 K. In the case of the lanthanoids proper, this relationship is close to linear. For La_3TaO_7 , the energy difference is within the uncertainty limit of the calculations, so that the $Cmcm$ phase is expected to be stable even at low temperatures, in line with experimental observations. Future work will compare the stabilities of disordered fluorite structures to the ordered $C222_1$ phase for small lanthanoid ions (e.g., Ho and Er).

References

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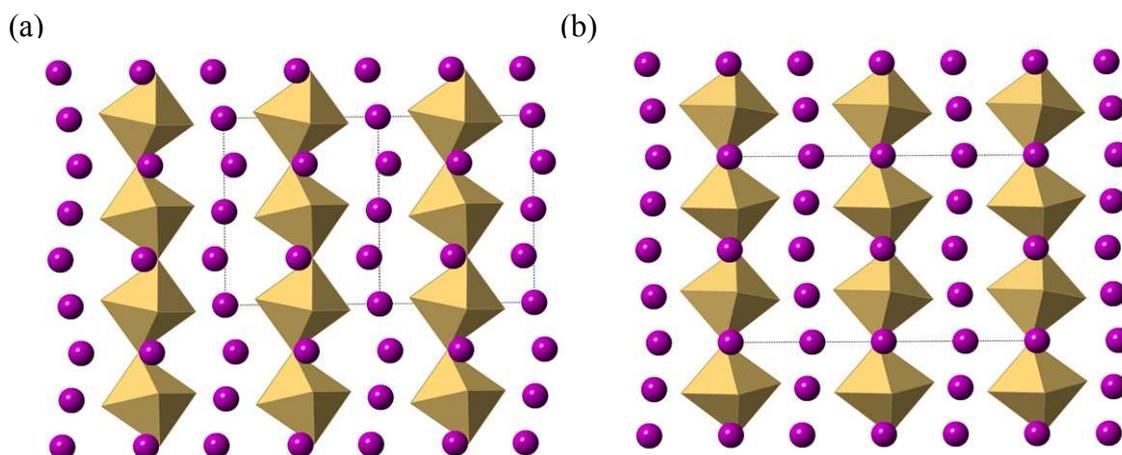


FIG. 1. Orthorhombic phases of Nd_3TaO_7 viewed down $[110]$: (a) space group $Cmc2_1$, and (b) space group $C222_1$. Balls represent Nd and octahedra TaO6 groups. The dashed lines demarcate a single unit cell in each case.

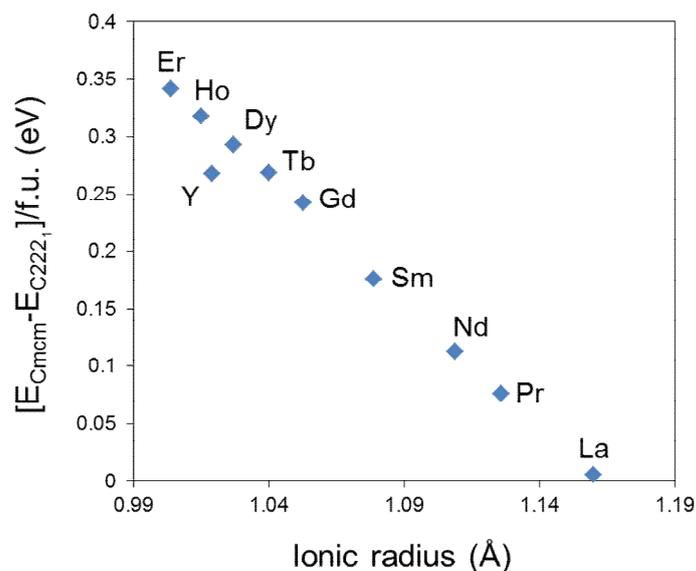


FIG. 2. Difference in lattice energies per formula unit for orthorhombic and tetragonal structures of Ln_3TaO_7 ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$ or Y) as a function of Ln ion radius.