

**FIRST-PRINCIPLES INVESTIGATION OF STRUCTURAL,
ELASTIC, ELECTRONIC AND THERMAL PROPERTIES OF
RARE-EARTH TITANATE AND HAFNATE OXIDES**

By

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ABSTRACT

We performed first-principles calculations based on density functional theory on a wide range of Ln_2TiO_5 compositions ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}$ and Y) in order to systematically investigate their structural, elastic, electronic and thermal properties. At low temperature, these compounds crystallize in orthorhombic structures with $Pnma$ symmetry, and the calculated equilibrium structural parameters agree well with experimental results.

In order to understand rare-earth hafnium oxide solid solutions $\text{Dy}_x\text{Hf}_{1-x}\text{O}_{2-x/2}$ with fluorite structures, we further investigated the $\text{HfO}_2\text{-Dy}_2\text{O}_3$ binary system in different composition ratio by first-principles calculation within the projector-augmented wave (PAW) method and the generalized gradient approximation (GGA) to the exchange-correlation functional. The structural, electronic, elastic, and thermal properties were studied in detail for $\text{Dy}_x\text{Hf}_{1-x}\text{O}_{2-x/2}$ ($x = 0.5, 0.67, \text{ and } 1$), corresponding to $\text{Dy}_2\text{Hf}_2\text{O}_7$, Dy_2HfO_5 and sesquioxide Dy_2O_3 . We adopted a methodology to reduce the number of site-occupancy configuration by taking advantage of the symmetry of Dy_2HfO_5 (Fd3m, 227) in modeling the site disorder of Dy_2HfO_5 bulk material.

A complete set of elastic parameters, such as elastic constants, Hill's bulk moduli, Young's moduli, shear moduli, and Poisson's ratio, were calculated to investigate ductility and anisotropy of Ln_2TiO_5 and $\text{Dy}_x\text{Hf}_{1-x}\text{O}_{2-x/2}$. All Ln_2TiO_5 and $\text{Dy}_x\text{Hf}_{1-x}\text{O}_{2-x/2}$ are ductile in nature. Analysis of densities of states and charge densities suggests that the oxide bonds are highly ionic. The nature of chemical bonding has been analyzed to explain the elasticity and anisotropy of Ln_2TiO_5 and $\text{Dy}_x\text{Hf}_{1-x}\text{O}_{2-x/2}$. Thermal properties including the mean sound velocity, Debye temperature and minimum thermal conductivity were obtained from the elastic constants