A comparative *ab initio* thermodynamic study of oxygen vacancies in oxide perovskites: role of phonons

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Perovskite oxides like $SrTiO_3$ ($BaZrO_3$, $LaGaO_3$ etc) belong to the most prominent functional materials with numerous applications. All such oxides are materials with a considerable band gap, reveal ABO_3-type cubic perovskite structure but differ with respect to the existence of ferroelectric phase transition. The oxygen vacancy V_o is a very common defect in these and related materials, controlling mass transport and other device properties, e.g. permeation membranes and solid oxide fuel cell cathodes. We performed detailed *ab initio* thermodynamic study of V_o in these materials with a focus on a role of phonons in the Gibbs free formation energy and its temperature dependence.

Using a hybrid Hartree-Fock (HF)-DFT method combined with LCAO basis set as implemented in CRYSTAL computer code [1] and a periodic supercell approach [2], the atomic and electronic structure and phonon properties of oxygen vacancies were calculated and compared in the mentioned materials. It is shown that use of hybrid functionals is vital for a correct reproduction of not only defects basic properties but also Raman phonon modes [3]. The Gibbs free formation energy of V_o and its considerable temperature dependence was compared for the mentioned oxides. The importance of supercell effects for the Gibbs free formation energy of V_o is discussed. The major factors determining defect behavior in the mentioned oxides and the degree of electron distribution around the oxygen vacancy were identified.

We have used the polarizability model [4] in order to calculate the temperature dependence of soft phonon mode in $SrTiO_3$. It is, therefore, shown that the temperature dependence of soft phonon mode is important for correct calculations of defect formation energies.

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