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Systematic Study of Structural Instabilities in $REMO_3$ Series Compounds by First Principles Calculations

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Compounds having chemical formula of ABO_3 often exhibits so called perovskite structures, which are one of the most popular targets in the field of materials science and engineering. There are rather few compounds having ideal cubic perovskite structure under ordinary conditions. Many of perovskite compounds undergo structural phase transitions with the change of external parameters of temperature or pressure and have distorted structures. These phase transitions in compounds are often characterized and understood in terms of soft phonon modes. Soft phonon mode refers to an instable lattice vibrational mode in crystals. Softening and condensation of instable mode brings small atomic displacement into a crystal structure, lowering the symmetry of the crystal below the transition point. For instance, a soft optic mode at the Brillouin zone center Γ point causes ferroelectric transitions, as in the case of $BaTiO_3$. On the other hand, soft mode at the zone boundary *R* point brings rigid rotation of oxygen octahedra. One example is $LaAlO_3$, which undergoes cubic to rhombohedral transitions at temperature around 800 K.

Recent advances in computational technique enable us to determine full phonon dispersion from first principles. Such first principles method should provide a powerful tool for the systematic investigations of soft phonon modes, which drive structural phase transitions in compounds. Here we report our application of the method to the issue of general behavior of phonon instability in perovskite type oxides and related compounds. We have chosen a series of $REMO_3$ (RE=rare earth, M=Al, Ga, In) compounds as a target for the systematic theoretical investigation of soft mode behavior. Crystal structures of these compounds show systematic variation with the change in the A site and the B site cation species. Thus they provide good model materials for a systematic study of structural changes and phase transitions behaviors.

First we investigated pressure effect on the soft mode behaviors in these perovskite type compounds. Concerning the pressure effect on the structural phase transitions associated with soft phonon modes, an empirical "general rule" has been established [1]. The rule tells that the instability of the cubic perovskite structure decreases for zone center transitions and increases for zone boundary transitions (ZBT) with pressure in general. However, the rule has been challenged by a recent high pressure experiment that revealed that $LaAlO_3$ undergoes pressure induced rhombohedral to cubic transition [2]. In the present study, we have made a theoretical approach on the issue employing the first principles projector augmented wave (PAW) method based on density functional theory (DFT). In addition to the conventional static total energy calculations, we have computed phonon states by the direct method. The calculated phonon dispersion curves of cubic $LaAlO_3$ at equilibrium volume is shown in FIG.1. A soft mode with an imaginary frequency emerges at the Brillouin zone boundary *R* point, telling that the compound is instable against the rotational displacements of the oxygen octahedra. Thus, examining phonon dispersion relations gives information on the structural instabilities and possible structural deformations. We performed a series of calculations with changing volume to investigate the soft mode behavior under pressures. The calculated results well reproduced the experimental observations including the phase transition pressure and the pressure dependence of phonon frequencies. Our calculations also verified the compound's exceptional behavior that the cubic phase is stabilized under pressure. From the further systematic calculations on a series of $REAlO_3$ and $REGaO_3$ compounds, we found that the behavior is not peculiar to $LaAlO_3$ but rather ubiquitous among many compounds (FIG. 2). A good correlation between the tolerance factor and the instability is found among aluminates and gallates. Such new findings should provide a clue for a more general understanding of the soft mode behavior under pressures [3].

As another subject of our systematic investigation on the structural properties of $REMO_3$ series compounds, we picked up the issue of ferroelectricity in the hexagonal $LuMnO_3$ type compounds. The structure appears in some rare earth gallates and indates as a competing phase against the perovskite structure. This type of structure recently has attracted much attention due to the rise of isostructural $YMnO_3$ and $REMnO_3$ families as multiferroic systems [4]. Although extensive studies have been made on these compounds, origin of their ferroelectricity is still controversial and no systematic way to enhance their properties has been found yet. From our calculations on gallates and indates compounds, we found some trend in the structural and ferroelectric properties with rare earth elements. The knowledge may give directions for controlling properties of this emerging class of ferroelectrics.

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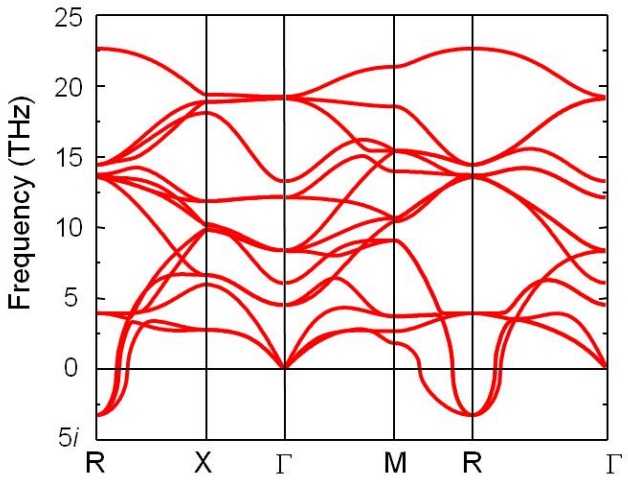

FIG. 1. Calculated phonon dispersion relation of $LaAlO_3$ in cubic perovskite phase

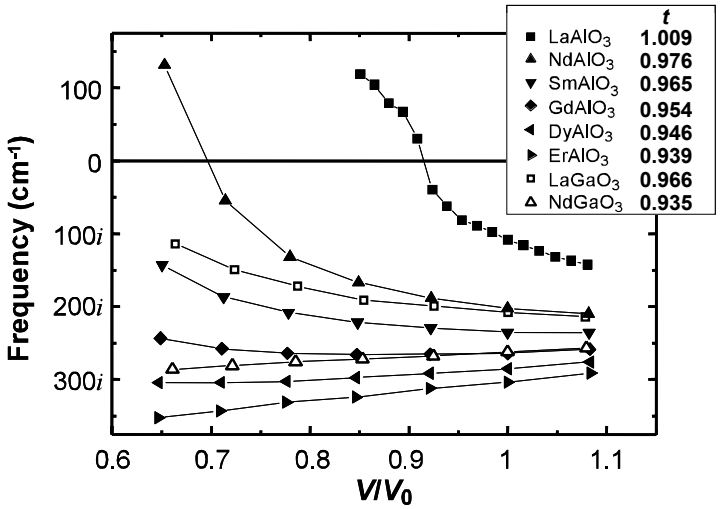

FIG. 2. Frequencies of *R* point soft mode versus normalized volume for various compounds