First-principles investigation of high-pressure phase transition and piezoelectric properties in LiNbO$_3$

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LiNbO$_3$ is one of the popular ferroelectric material belongs to space group *R3c*. Due to the tolerance factor, LiNbO$_3$ cannot form stably the simple perovskite structure under the ambient condition. Recently, we predicted the crystal structures and transition mechanism of high-pressure phase of LiNbO$_3$ [1], which were not completely elucidated by experimental study [2]. Revealed structures were NaIO$_3$-type structure (*Pnma*) as room temperature high-pressure phase and apatite-like structure (*P6$_3$/m*) as high temperature high-pressure phase. It should be noted that the NaIO$_3$-type structure is closely related with the popular GdFeO$_3$-type perovskite structure. The only difference between these structures is that A-site position and B-site position is inter-exchanged. On the other hand, KNbO$_3$ can form well-known ferroelectric tetragonal phase (*P4mm*). This shows that different size of A-site distinguishes the stable crystal structure between LiNbO$_3$ and KNbO$_3$. Therefore, if LiNbO$_3$ lattice is expanded by external pressure, it can be expected *R3c-P4mm* phase transition might occur. In this study, we investigated the piezoelectric properties of LiNbO$_3$ with various hypothetical crystal structures by the method of density functional perturbation theory, and possible phase transition mechanism will be discussed.

First-principles calculations were performed by utilizing Vienna Ab-initio Simulation Package (VASP) [3]. Hypothetical crystal structures were constructed and their relative phase stability was investigated by calculating pressure-relative enthalpy (P-ΔH) curve under the specified pressure. Piezoelectric stress constant e_{ij} was calculated by the method of density functional perturbation theory (DFPT), and elastic constant C_{ij} was calculated by finite difference method. Piezoelectric strain constant $d_{\alpha j}$ was obtained as $d_{\alpha j} = s_{jk}e_{\alpha k}$, where s_{jk} is the elastic compliance tensor.

Fig. 1 shows relative enthalpy changes for each phase with respect to the enthalpy of LiNbO$_3$ structure (*R3c*) as a function of the pressure. Three phases shown in positive pressure region (Fig. 1(a)) has no piezoelectricity because of centrosymmetry. On the other hand, as expected, negative pressure plays favorable role to stabilize phases. Especially, *P4mm* phase becomes most stable among prerovskite phases below -4 GPa. In addition, *R3m* and *Amm2* phases also become more stable than *R3c* phase above -9 GPa. These structures are connected with *P4mm* phase by common subgroup *Cm* and *Pm* symmetries, respectively. Moreover, we found displacement along instable mode at R-point phonon of *Pm3m* phase gives *R3c* phase, which is paraelectric phase of LiNbO$_3$. Therefore, these phases are expected to work as bridging phases in *R3c-P4mm* transition. Although *R3c-P4mm* phase transition becomes possible at -6 GPa, accidental increase of the lattice constant of *P4mm* phase was occurred at -6 GPa due to breaking of Nb-O bond along polarization axis. However, ferroelectricity of *P4mm* phase is stable because large Li off-centering with respect to cubic *Pm3m* phase gives exceedingly large energy gain (~0.2 eV/f.u.). Fig. 2(a) shows the changes of

piezoelectric stress constant e_{33} of *R3c* and *P4mm* phases as a function of the pressure. e_{33} of *R3c* phase continuously decreases at positive pressure region and reversely increases at negative pressure region. Interestingly, e_{33} of *R3c* phase increases as negative pressure increases, while reverse case is observed for *P4mm* phase. Negative pressure introduces more free volume, which should enhance the coupling between strain and displacement. On the other hand, such lattice expansion weakens orbital hybridization between Nb-O. The same discussion can explain the dependences of C_{33} and d_{33} on the pressure. Divergence behavior of *P4mm* phase near -5 GPa is originated in the small C_{33}. Finally it should be mentioned that electromechanical coupling factor of *P4mm* phase was predicted to be ~79 % at 0 GPa, which is about 3 times larger than that of *R3c* phase. Present results suggest that phase instability has a crucial role for large electromechanical coupling as discussed in $PbTiO_3$ [5].

References

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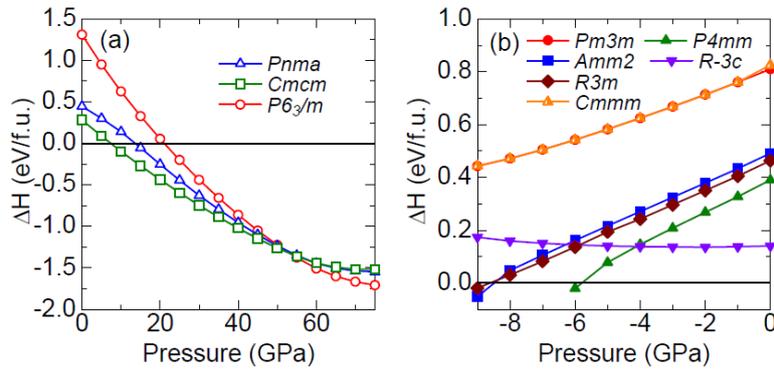[5] J.Frantti, Y. Fujioka, and R. M. Nieminen, J. Phys. Chem. Lett., B 111, 4287 (2007)

FIG. 1. Pressure-relative enthalpy curves for the various phases at (a) positive pressure region and (b) negative pressure region. Relative enthalpy was defined as the difference between enthalpy of the one phase and that of *R3c* at each pressure.
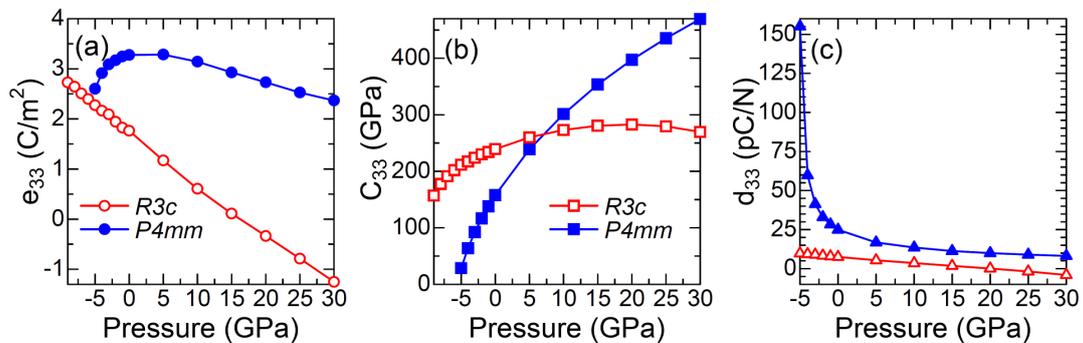

FIG. 2. (a) Piezoelectric stress constant e_{33}, (b) elastic constant C_{33}, (c) piezoelectric strain constant d_{33} of R3c and P4mm phase as a function of the pressure.