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# Abstract

Layered titanium-oxypnictides, $A$Ti$_2$Pn$_2$O [$A$ = Na$_2$, Ba, (SrF)$_2$, (SmO)$_2$; $Pn$ = As, Sb, Bi], have the common undistorted structure, including Ti$_2$O-plane that leads to quasi two-dimensional (2D) electronic structures. Recently, Kageyama's group (Kyoto Univ. Japan) has synthesized BaTi$_2$Sb$_2$O and reported its superconductivity with the transition temperature, $T_c$ = 1.2 K. Guloy's group (USA) has also synthesized Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O individually and reported its superconductivity with $T_c$ = 5.5 K. Followed by their pioneering works, similar kinds of compounds, BaTi$_2$Bi$_2$O, BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O, BaTi$_2$(Sb$_{1-x}$Sn$_x$)$_2$O, Ba$_{1-x}$K$_x$Ti$_2$Sb$_2$O, and Ba$_{1-x}$Rb$_x$Ti$_2$Sb$_2$O, have been synthesized to get superconductivities, achieving the current highest $T_c$ around 6.1 K. Although they are not high-$T_c$ superconductors, they have been still studied because there has been a puzzle between experiments and theoretical predictions on the structural phase transition at low temperature. The layered titanium oxypnictides show anomalies attributed to charge density wave (CDW) in resistivity and magnetic susceptibility at low temperature. Subedi predicted that $\sqrt{2}\times\sqrt{2}\times1$ superstructure is realized at low temperature by using *ab initio* phonon calculation for BaTi$_2$Sb$_2$O in 2013. However, such a superstructure had not been detected for a long time even by intensive diffraction experiments. Recently, Frandsen *et al.* have reported a four-fold symmetry breaking for BaTi$_2$As$_2$O and BaTi$_2$Sb$_2$O by using neutron diffraction (ND). Based on the result, they argued that the strucutural transition in the layered pnictides oxide could be attributed to *exotic* mechanism such as intra-unitcell nematic CDW detected cuprtes and iron-arsenides superconductors, because the four-fold symmetry breaking cannot be predicted *ab inito* phonon calculation for BaTi$_2$Sb$_2$O. On the other hand, Davies *et al.* have detected $2\times2\times1$ superstructure for Na$_2$Ti$_2$As$_2$O and $2\times2\times1$ one for Na$_2$Ti$_2$Sb$_2$O by using single-crystal X-Ray diffraction (XRD) in 2016. They concluded the structural transition is caused by *conventional* electron-phonon mechanism, which is completely contradicted to the conculsion by Frandsen *et al.* Thus, the mechanism of the structural transion in layered titanium-oxypnictides is still under intensive discussion.

Unfortunetely, the aforementioned experimental results have been interpreted only by the phonon calculation for BaTi$_2$Sb$_2$O so far. On the other hand, the previous experimental and theoretical studies revealed that electronic properties such as band structure and Fermi surface are governed not only by Ti-3$d$ orbital but also by $Pn$-$p$ orbital. Therefore, the structural transiton should be also discussed based on a comprehensive phonon calculation for $A$Ti$_2$$Pn$$_2$O [$A$ = Na$_2$, Ba, $Pn$ = As, Sb, Bi]. In this thesis, I performed a comprehensive phonon calculation for BaTi$_2$$Pn$$_2$O [$Pn$ = As, Sb, Bi] and Na$_2$Ti$_2$$Pn$$_2$O [$Pn$ = As, Sb] to reveal the relation between a type of pnictogen and the structural transion. For BaTi$_2$As$_2$O, I provide a new theoretical prediction, by which the above discrepancy is resolved without any unconventional explanation. Phonon dispersions and changes of nesting vectors in Fermi surfaces are clarified to lead to orthorhombic $2\times2\times1$ superstructure for BaTi$_2$As$_2$O that is completely consitetent with the experimentally observed one by Frandsen. On the other hand, there is still descripancy for BaTi$_2$Sb$_2$O and BaTi$_2$Bi$_2$O that the predicted tetragonal $2\times2\times1$ superstructures are inconsittent with the experimental one (Sb), or have not been detected so far (Bi). I also applied *ab initio* phonon analysis for Na$_2$Ti$_2$$Pn$$_2$O ($Pn$ = As, Sb), and found a clear contrast between the cases with lighter/heavier pnictogen in comparisons with experiments. The result completely explains the experimental structure at low temperature, $C2/m$ for $Pn$ = As, within the conventional charge density wave, while there arise discrepancies when the pnictogen gets heavier. Our phonon calculation predicts that a *Cmce* polymorph is more stable than the experimentally observed superstructure (*Cmcm*) for $Pn$ = Sb. The trend is again consistent with BaTi$_2$$Pn$$_2$O ($Pn$ = As, Sb, Bi), where the phonon calculation could explain experiments only for $Pn$ = As, but not for the other heavier $Pn$. It might be a general tendency also applicable to the layered titanium-oxypnictides that the hevier $Pn$ induces the discrepancy between experiments and calculations.

To reveal the origin of discrepancy, I focus on the height of $Pn$ toward Ti$_2$O plane in layered titanium-oxypnictides. This is because the tendency toward electronic correlation is well captured by a trend of $h$, a vertical distance between Fe layer and $Pn$ or $Ch$ in iron arsenide superconductors that have similar electronic structures to our layered titanium-oxypnictides. Based on quantitative analysis according to the previous study, I revealed that Ti-As bonding is more covalent than Ti-Sb one, and the distance of Ti-$Pn$ (the height of $Pn$ toward Ti$_2$O plane) governs the covalency as well as electronegativity in layered titanium-oxpnictides. Our analysis could support the correlation effect gets more enhanced for Sb than As in layered titanium-oxypnictides. I currently believe that the present discrepancy could be attributed to the electronic correlation effects that are not taken into consideration at the GGA-PBE level. If the discrepancy is attributed to the electronic correlation as I suggest, calculation using exchange-correlation functional beyond GGA such as GGA+$U$ and hybrid functionals is necessary to reproduce the experimentally observed superstructures of $Pn$ = Sb, Bi. This is a promissing future work.


Keywords, Layered titanium-oxypnictides, Superconductivity, Strucutural transition, DFT, Phonon calculations