Summary of thesis:

Antiperovskite Oxide $Sr_{3-x}SnO$: Discovery of Superconductivity and Its Evolution with Deficiency

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In this thesis, we report the discovery of a new class of oxide superconductors, the antiperovskite oxides [1], and optimize the condition for synthesis of superconducting $Sr_{3-x}SnO$ [2]. We clarify the dependence of superconductivity on deficiency x in $Sr_{3-x}SnO$ [3], and theoretically propose the possibility of topological superconductivity even in deficient samples [1, 4]. Antiperovskite oxides A_3BO (A = Mg, Ca, Sr, Ba, Yb, Eu; B = Si, Ge, Sn, Pb) have recently been demonstrated to exhibit Dirac electronic dispersion near the Γ point in the Brillouin zone based on first-principles calculations. Charge balance in this class of material, assuming a typical A^{2+} and O^{2-} valences, leads to $(A^{2+})_3(B^{4-})(O^{2-})$, where the B ions have an unusual 4- state.

Such negative valance ions are consistent with theoretical calculations. Furthermore, antiperovskite oxides with heavier elements have been predicted as topological crystalline insulators, due to the inversion of the conduction d band of A^{2+} and the valance p band of B^{4-}. Finding of superconductivity emerging in such an unusual electronic state would be quite interesting, and an important step towards understanding of superconductivity in topologically nontrivial materials.

To this goal, we synthesized various antiperovskite oxides, including Ca_3SnO, Ca_3PbO, Sr_3SnO, and Sr_3PbO. These antiperovskite oxides are air sensitive, so we developed various techniques to handle them during measurements that minimize their exposure to air.

Finally, we discovered the first superconductivity among the antiperovskite oxides in the hole-doped $Sr_{3-x}SnO$ [1], with evidences of zero resistivity and diamagnetic Meissner signal below the critical temperature T_c of 5 K. The initial synthesis method used suffered from uncontrolled evaporation of Sr and it was difficult to quantify the exact composition needed for superconductivity.

We overcame this hurdle by modifying various parameters and optimized the synthesis of $Sr_{3-x}SnO$ [2]. With the optimized synthesis, we successfully tuned the amount of the strontium deficiency, and the volume fraction of the superconductivity at 5 K reached up to 100% with the optimal deficiency of around x = 0.5 [3]. We

calculated band structures of various “$Sr_{2.5}SnO$” and found that the shape of the bands are not altered significantly by the Sr deficiency, but the chemical potential is shifted substantially [4]. Interestingly, this compound exhibits double superconducting transitions with the T_c’s of about 5 and 1 K, as observed in the zero field AC susceptibility measurements [3]. These T_c’s at 5 and 1 K do not change significantly as a function of x. Mössbauer spectra provide some evidence for a Sn^{4-} state in $Sr_{3-x}SnO$, which is the first macroscopic evidence for 4- metal ions in antiperovskite oxides.

Furthermore, an unusual paramagnetic Meissner effect was observed in some $Sr_{3-x}SnO$ samples. The NMR results reveal unusual $1/T_1$ behavior for stoichiometric non-superconducting samples, which may originate from Dirac nature of Sr_3SnO.

We believe these results push $Sr_{3-x}SnO$ and antiperovskite oxides in general as strong candidates for investigation of interesting physics. The superconductivity realized in $Sr_{3-x}SnO$ makes this class of materials a candidate for future investigation of topological superconductivity.

[1] M. Oudah, A. Ikeda, J. N. Hausmann, S. Yonezawa, T. Fukumoto, S. Kobayashi, M. Sato, and Y. Maeno., Superconductivity in the antiperovskite Dirac-metal oxide $Sr_{3-x}SnO$, *Nature Commun.*, 7, 13617-1-6 (2016); DOI:10.1038/ncomms13617.

[2] J. N. Hausmann, M. Oudah, A. Ikeda, S. Yonezawa, and Y. Maeno, Controlled synthesis of the antiperovskite oxide superconductor $Sr_{3-x}SnO$. *arXiv preprint arXiv*:1712.09484, 2017.

[3] M. Oudah, J. N. Hausmann, S. Kitao, A. Ikeda, S. Yonezawa, M. Seto, and Y. Maeno, Evolution of Superconductivity with Sr-Deficiency in Antiperovskite Oxide $Sr_{3-x}SnO$, *Phys. Rev. Lett.*, Submitted Jan.4, 2018.

[4] A. Ikeda, T. Fukumoto, M. Oudah, J. N. Hausmann, S. Yonezawa, S. Kobayashi, M. Sato, C. Tassel, F. Takeiri, H. Takatsu, H. Kageyama, and Y. Maeno, Theoretical band structure of the superconducting antiperovskite oxide $Sr_{3-x}SnO$, *Physica B: Condensed Matter*, Accepted, 2017; DOS:10.1016/j.physb.2017.10.089.