Report on MERIT Long-term Overseas Dispatch

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I stayed at the group of Prof. Philip Lightfoot in the school of chemistry, St. Andrews University, United Kingdom from 6/1/2015 to 27/3/2015. They study novel magnetic and ferroelectric materials based on solid state chemistry. My purpose of this stay is learning their unique synthetic methods and structural analysis and discovering novel materials. I have been especially interested in their study on novel transition metal oxfluorides using solvothermal technique.

Physical properties of transition metal oxides generally depend on elements, valence, coordination environment, and connectivity of the coordination polyhedra. In oxfluorides, two types of anions, oxide and fluoride anions, coordinate to a transition metal cation, which enable variety of the coordination environments. For example, there are a lot of ways of replacing some of the octahedrally coordinated oxide ions by fluoride ions. They should show rich structural and physical properties depending on the coordination environments.

They have developed solvothermal synthesis of transition metal oxfluorides, in which metal sources are reacted in a solvent at 100-200°C. It has mainly two advantages over conventional solid state synthesis. Using solvents, single crystals are more accessible. Moreover, metastable compounds could be obtained in the low temperature reactions. One of the features of their synthesis is using an ionic liquid, 1-ethyl-3-methylimidazolium-bistrifluoro-methylsulfonylimide ([EMIM]Tf_2N), as a solvent as well as conventional water or ethylene glycol. The use of ionic liquids in a synthesis is relatively new and regarded as a promising method. Another feature of their synthesis is adding templates in the reactions, which are usually small and chemically stable organic molecules. Interestingly, templates seem to control the connectivity of the coordination polyhedra and dimensionality of the products. Successful example of the method is a layered material $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$ synthesized from VOF_3 (metal source), $C_7H_{13}N$ (template), and [EMIM]Tf_2N

(solvent), in which V^{4+} ions (S = 1/2) form kagome lattice. This material has attracted much attention in the field of frustrated magnetism, which is my research interest. While the idea of the synthesis is simple, rational choices of metal sources, templates, and solvents from infinitely many combinations and the knowledge of structural analysis are required for efficient material discoveries.

To obtain novel oxfluorides with frustrated lattices of Mo^{5+} (S = 1/2) or Ni^{2+} (S = 1) ions, I tried reactions with different combinations of metal sources, templates, and solvents. As a result of 120 reactions, 3 structures of new molybdenum oxfluorides have been successfully solved by single crystal X-ray diffraction experiments and structural analyses. One of the new materials has a quite rare defect-ordered double-perovskite structure ($AA'BB'X_6$-type), in which defects in the A-sites show a layered order. Although it is not a frustrated magnet, it is structurally interesting and ion conductivity through defect sites could be expected. I hope to publish a short joint paper on this compound in the future.

During the stay, I had an opportunity of a talk in the condensed matter seminar in the school of physics in the university. Moreover, I attended several talks and final presentations of the undergraduate students. Making the most of staying in UK, I visited solid state chemistry groups in the University of Oxford and University of Edinburgh. I was permitted to make a talk on my study and look around the laboratories there. The discussions and meetings with the professors and their students made this stay more valuable.

I deeply appreciate Prof. Philip Lightfoot for accepting my stay even though we have not met before. I have learned a lot on structural chemistry and structural analysis from his discerning advices based on deep knowledge of inorganic materials and crystallography. I thank Cameron Black, a talented chemist and a very nice Scottish guy, helping me arranging the stay and experiments. I would like to utilize the solvothermal techniques learned from him for my future studies. I was able to have full weekends thanks to his lectures on Scottish cultures. I enjoyed collaborating with Irene Munaò, a skilled crystallographer and a cheerful Italian girl, on single crystal X-ray diffraction experiments and structural analyses. I thank Dr. Lucy Clarke giving me useful advises on the ionothermal synthesis and helping me kindly the stay in UK. I thank Charlotte Dixon welcoming me with energy in the lab. I also thank Lauren, Rebecca, Mike, Wenjiao, Sam, Lewis, Daniel and everyone I met in the school of chemistry for accepting and helping the stay. Working in the international and lively group made me grow. I am grateful for Prof. Simon Clarke and Prof. Mike Hayward in the University of Oxford and Prof. Paul Attfield in the University of Edinburgh and their group members for warmly welcoming my visit. Finally, I am deeply grateful for the MERIT program, Prof. Kazushi Kanoda, and Prof. Zenji Hiroi for permitting and supporting such a great opportunity of this stay.