MERIT Internship report

MERIT 3rd

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Date

June 13, 2017–August 31, 2017

Place

High Pressure Group, National Institute for Materials Science

Activity

In this internship, sample synthesis and crystal structure evaluation were carried out in order to perform bulk synthesis of mixed anion compounds using belt type high-pressure equipment in NIMS High Pressure Group. A belt type synthesizer is a combination of a pair of upper and lower anvils made of cemented carbide and a cylinder (belt) in a hydraulic high pressure press. It is possible to realize a high pressure of 10 GPa (100,000 atm). Furthermore, by passing an electric current between the upper and lower anvils, the heater inside the cell can be heated to as high as 2000 °C.

Using this method, we attempted to synthesize mixed anion compounds, which is the theme that I am engaged in university. Mixed anionic compounds are often metastable under normal pressure as opposed to compounds containing single anion (e.g., oxides). Therefore, a special method such as synthesis under high temperature and high pressure is adopted. In fact, the oxyhalide Sr_2NiO_3X (X = Cl, F) containing Ni (III) was synthesized for the first time using a belt type synthesizer of a receiving institution (Tsujimoto, Y. *et al.*, *Inorg. Chem.* 2013, **52**, 10211-6.). In this project, we conducted experiments aimed at RNiO$_2$F (R = La, Nd), which I first obtained as a thin film.

Synthetic experiments were first carried out using RF_3, R_2O_3, NiO as the starting materials at a pressure of 2-4 GPa and a temperature of 800-1600 ° C. As a result, only a mixture of ROF and NiO was obtained. Since these substances are less dense than the target material (perovskite type RNiO$_2$F), experiments were carried out under a higher pressure of 5-10 GPa. As a result, *R*OF underwent a phase transition from the monoclinic to the orthorhombic phase, and no reaction with NiO was observed.

Since the high pressure phase of *R*OF is larger in density than the perovskite phase, we considered that it is difficult to obtain $RNiO_2F$ from these starting materials. In particular, considering the fact that NiO did not change after high-pressure treatment, poor reactivity of NiO with *R*OF was speculated. Therefore. R_2NiO_4 was added to the starting mixture, and further experiments were carried out. However, R_2NiO_4 decomposed after the reaction, and again a mixture of ROF and NiO was obtained. Other synthesis experiments were conducted under conditions of excess fluorine by adding fluorocarbon polymer (polyvinylidene fluoride, $[CH_2CF_2]_n$). Thermal decomposition of the polymer provided excess fluorine source. Unfortunately, we could not obtain perovskite type $RNiO_2F$. From these results, it is expected that the thermodynamical stability of *R*OF is extremely high, so that there was no temperature / pressure condition that $RNiO_2F$ can exist stably. Therefore, in order to obtain this compound as a bulk, it is considered that devising of a further synthetic route is necessary.

I deal with thin film samples using pulsed laser deposition method at university, and have almost no experience of handling bulk samples. In this internship project, I gained valuable opportunities to experience technologies that cannot be touched by ordinary research, or make discussions with people who are studying with different ideas. Although I could not necessarily get the results I expected, this project will be a great wealth in the future life.

Acknowledgments

I would like to express my gratitude deeply to Dr. T. Taniguchi in NIMS, who kindly accepted me as an internship student, and Dr. H. Miyakawa who gave me a detailed coaching in experiments. Also, I thank other staff in the High Pressure Group for having scientific discussions with me. I also sincerely thank Prof. Tetsuya Hasegawa, my supervisor, for introducing this internship, Prof. K. Ishizaka, and MERIT staff who provided such valuable opportunities.