Study on transition metal chalcogenide intercalation chemistry through in-situ X-ray diffraction

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Many layered transition metal chalcogenides show intriguing properties related to quantum behaviors. Intercalation chemistry has been a longstanding approach not only to modify those properties, but also to synthesize new layered-structure materials. To achieve intercalation, hydrothermal or solvothermal method is effective method for high-throughput synthesis as different intercalates can work under similar conditions with a one-pot reaction. Although the approach has been widely applied in synthesis, the mechanism for such chemical process has not been sufficiently investigated. The reactants are usually contained within a Teflon-cup sealed by a stainless-steel autoclave, which is completely a black box. One hydrothermal or solvothermal reaction at a time can only be evaluated after restoring it to the ambient condition, while what happens during the reaction is largely unknown. To solve such a problem, in-situ X-ray diffraction at 17-BM at Argonne National Laboratory is an optimal technique since it can provide the diffraction data of the reaction system when the reaction is processing. A clearer understanding of the mechanism of the solvothermal reaction will facilitate designing more suitable synthesis conditions for the aimed intercalated metal chalcogenide with unique physical properties. We have achieved both hydrothermal and solvothermal (with ethylenediamine and 1,2-diaminopropane) conditions at 17-BM through a quartz tube (1/8" in diameter) and a syringe pump, to study the reaction process to form several intercalated MCh (M = Fe, Co; Ch = S, Se). Beyond our early expectation, the crystallization step of the final product could be within an hour, which is much shorter than the time we usually set for the hydrothermal/solvothermal reactions (3 to 6 days). Through the analysis of the contour plots and the refinements of the diffraction data, several interesting intermediate phases have also been observed in each reaction. In the hydrothermal reaction to form ammonia intercalated FeS, for instance, major reflections can be indexed to a space group of P4/nmm with a = 3.88 Å and c = 9.92 Å. What is more intriguing, for the reaction time of about 24 hr, the ex-situ product (I4/mmm a = 3.68 Å and c = 15.02 Å) was never reported before. Furthermore, the intermediate phase was never recovered during ex-situ studies even with short reaction times. This indicates that the intermediate phase is a precursor to the final product, but it is only stable in hydrothermal conditions with high basicity.

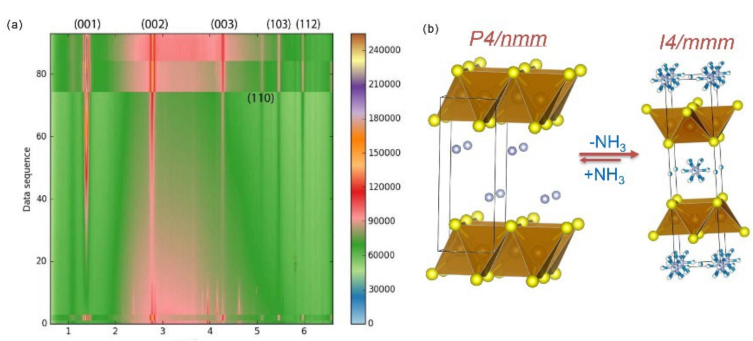

Figure 1