

Compression Behavior Studies on Ammonium Molybdophosphate (AMP)

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1. Introduction

The recent event at the Fukushima Daiichi nuclear power plant (NPP), Japan, has emphasized the criticality of radiological monitoring and decontamination and confinement actions for radionuclides released into the atmosphere, land and water surfaces. Because of their long half-life, activities of ^{135}Cs and ^{137}Cs in various environmental compartments would either be monitored to evaluate mobility, or isolated if Cs sequestration occurs above national or international guidelines [1].

Evaporation, precipitation, extraction, adsorption, ion-exchange methods have been considered as the remediation for radiocesium in aqueous radioactive wastes. Among them, the ion-exchange technique has outstanding efficiency for removal cesium and ion-exchange properties of ammonium molybdophosphate (AMP) have been known for a long time [2]. AMP has shown its noticeable qualities in selectivity of Cs and stability in acid solutions [3].

Though many meaningful results are reported in AMP every year, its pressure behavior is not well known yet. In this study, compression behavior of AMP was observed by using diamond anvil cell (DAC) and synchrotron high-energy and -flux X-ray beam.

2. Materials and Experimental Methods

2.1 Sample powder preparation

AMP sample showing yellow color was purchased from ACS reagent grade from Sigma-Aldrich (ideally, its chemical formula is $\text{H}_{12}\text{Mo}_{12}\text{N}_3\text{O}_{40}\text{P}\cdot x\text{H}_2\text{O}$, Fig. 1). Structural characterization of AMP was performed at the beamline 10-2 at the SSRL (Stanford Synchrotron Radiation Lightsource) and its structure model is shown in Fig. 1.

2.2 High-pressure experiments

A cylindrical type diamond anvil cell (DAC) with two opposed diamonds supported by tungsten-carbide plates was used for the high pressure experiments. The powdered sample was loaded into a 400 μm diameter and less than 150 μm thick sample chamber. A few ruby spheres of ~ 20 μm diameter were added as a pressure gauge. Subsequently, methanol and ethanol 4:1 mixture solution (labeled ME41), and silicone oil were added as hydrostatic pressure-transmitting medium (PTM). The pressure at the sample in the DAC was measured by detecting the shift of R1 emission line of included ruby spheres (precision: ± 0.05 GPa). The pressure was calculated using the equation below (1):

$$P = A/B [1 + (\Delta\lambda / \lambda_0)] B \quad (1)$$

Changes in the unit cell lengths and volume were derived from a series of whole profile fitting procedures using the GSAS suite of programs.

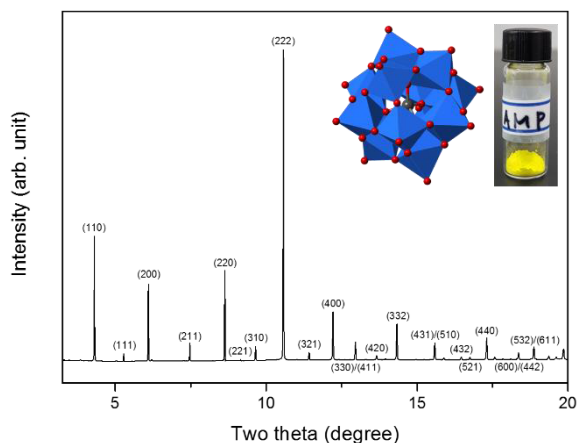


Fig. 1. Structure model and X-ray powder diffraction pattern of AMP.

3. Results and Discussion

3.1 Under methanol-ethanol pressure medium

The XRD patterns and unit-cell volume changes of AMP upon increase pressure up to 6.0(1) GPa have been exhibited in Fig. 2. At around 1.0(1) GPa, the peak splitting of most hkl peaks are observed ((211) peak is emphasized in grey bar in Fig. 1) with

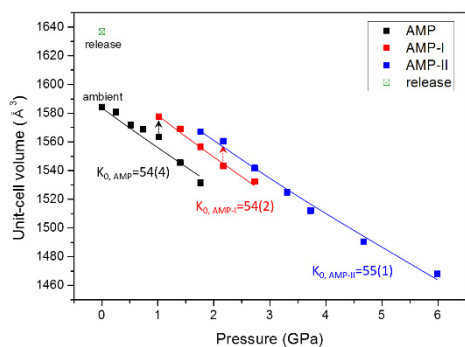
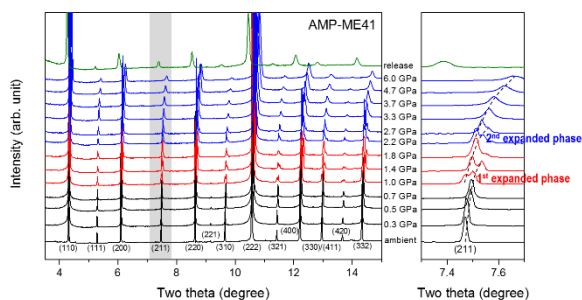


Fig. 2. X-ray powder diffraction pattern of AMP up to 6.0 GPa under ME41 PTM condition (up) and the unit-cell volume contraction as function of pressure (down).

volume expansion by ca. 0.9%. Subsequently, the X-ray powder diffraction pattern of AMP reveals a slight 1.1% volume expansion at 2.2(1) GPa again. According to the bulk modulus calculation, ambient phase, the 1st and the 2nd expanded phases of AMP have the similar values which is around 54, interestingly. These expanded phases are taken place due to the insertion of PTM molecules into the interlayered space of AMP. The unit-cell volume of the AMP after pressure release is ca. 3.3% larger than that of ambient AMP.

3.1.1 Under silicone-oil pressure medium. In the presence of non-penetrating silicone oil, the diffraction peak shifts indicated by the dashed line in Fig. 2 reveal a contraction of the unit-cell volume up to 10.1(1) GPa. The bulk modulus of AMP under silicone oil PTM is 24(3) until 2.1(1) GPa. In the post region of pressure, the unit-cell volume contraction hardly occur up to 10.1(1) GPa with 276(27) bulk modulus which is the largest measured in our experiments. Above 6.0(1) GPa, the diffraction peaks gradually disappear indicating pressure induced amorphization, but slightly re-crystallization to the original phase was found after pressure. Compared to AMP under ME41 PTM, there was no evidence of any unit-cell volume expansion in the presence of non-penetrating silicone oil PTM.

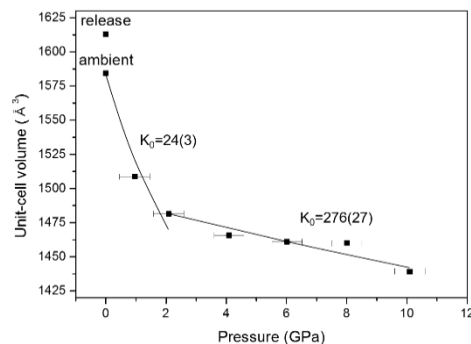
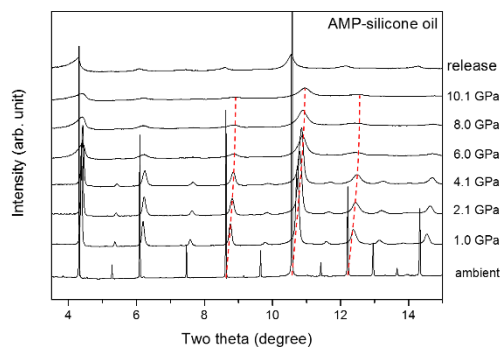


Fig. 3. X-ray powder diffraction pattern of AMP up to 10.1 GPa under silicone oil PTM condition (up) and the unit-cell volume contraction as function of pressure (down).

4. Conclusions

In summary, we have demonstrated the compression behavior of AMP in the methanol-ethanol mixture and silicone oil medium. Upon pressure increase under mixture PTM, the unit-cell volume expansions occur, indicating pressure induced insertion of PTM molecules into the AMP interlayer.

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