Abstract No. klei552

Time-resolved Ion-exchange Experiments of Microporous Lithosilicate RUB-29

M. Kleinsorge, S-.H. Park, J.B. Parise (SUNY, Stony Brook) and J.C. Hanson (BNL)
Beamline(s): X7B

Introduction: Based upon the ion-exchange property of recently discovered lithosilicate RUB-29 ($Cs_{14}Li_{24}[Si_{72}Li_{18}O_{172}]*14H_2O$) resulted from our previous ion-exchange experiments [1], we have explored to find replaceable mono- (Ag^+, Li^+, Na^+) and bivalent (Ca^{2+}, Mg^{2+}, Zn^{2+}) cations for Cs and Li cations of RUB-29. The modification and characterization of the ion-exchanged RUB-29 materials may give an insight into possible technical applications of these in ion exchange and gas absorption branches. On the other hand, to manufacture structurally and chemically stable H-forms of RUB-29 is a very relevant prerequisite for another application of the material as a potential catalyst.

Methods and Materials: For each run of ion exchange experiment with a variety of solutions ($AgNO_3$, LiCl, NaCl, $CaCl_2$, $Mg(NO_3)_2$ and $ZnCl_2$) a powder sample of as-synthesized RUB-29 was packed in a thin quartz capillary with a diameter of 0.7 mm. The ion-exchange experiments were performed at room temperature (RT) and 80°C in a continuous flow of each solution variously concentrated between 0.01 and 5.0 M. The ammonium exchanges of as-synthesized RUB-29, Mg-RUB-29 and Na-RUB-29 were conducted in the presence of 0.1M ~ 1M NH_4NO_3 solutions at RT. Structural changes accompanying each ion-exchange run were monitored using in situ synchrotron X-ray (λ = 0.9273Å) diffraction techniques with translating imaging plate [2]. The structure analysis was carried out using a Rietveld analysis program GSAS [3].

Results: Based on obtained time-resolved synchrotron X-ray powder pattern from the ion-exchanges conducted here, the best ion exchange effect was observed by using 0.1M ~1M NaCl and 0.1M $Mg(NO_3)_2$ solutions. In the case of Na- and Mg exchanges, the exchange rate was improved by increasing temperature from RT to 80°C. The replacement of Ag^+ cations was observed only at 80°C. Among bivalent cations, Mg^{2+} cations can be more readily incorporated into RUB-29 channels than Zn^{2+} cations although both cations possess a similar ionic radius. No ion exchange effect of RUB-29 using a $CaCl_2$ solution was observed, so far. The time-resolved X-ray diffraction data while ammonium exchange of Na-RUB-29, Mg-RUB-29, and as-synthesized RUB-29 showed that all these materials can be effective ion exchange matrix for ammonium exchange to produce H-RUB-29. All ammonium exchange experiments were finished within 10~15 min. without serious sample hydrolyzing. Structure refinements of Na-, Mg-, and NH_4-RUB-29 revealed no change in space group symmetry of these materials from the original space group I222 for as synthesized RUB-29 material. However, full structure refinements of ion exchanged RUB-29 materials showing a good agreement to the calculated model with corresponding experimental data was unsuccessful using the obtained synchrotron X-ray powder diffraction data. This was mainly due to the larger number of structural parameters (> 330) and high degree of peak overlap. For these reasons, we necessitated to use synchrotron X-ray single crystal data. A series of single crystal Na-exchange RUB-29 experiments was performed, and, thereafter, synchrotron X-ray single crystal data of Na-RUB-29 were collected. This resulted structure model of Na-RUB-29 with varying degree of Na-exchange has been suggested [4]. Structure refinements of Mg- and NH_4-RUB-29 are now in progress using a combined method of synchrotron X-ray single crystal with high-resolution neutron powder diffraction data.

Acknowledgments: We acknowledge financial support from the NSF via DMR-0095633.

References:

[1] S-.H. Park, J.B. Parise, H. Gies, H. Liu, C.P. Grey, B.H. Toby, J. Am. Chem. Soc. 2000, 122, 11023-11024
[2] J.B. Parise, C.L. Cahill, Y.J. Lee, Can. Mineral. 2000, Vol. 38, 777-800.
[3] A.C. Larson, B. Von Dreele, GSAS: General Structure Analysis System, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
[4] S-.H. Park, M. Kleinsorge, C.P. Grey, J.B. Parise, J. Solid State Chem., submitted

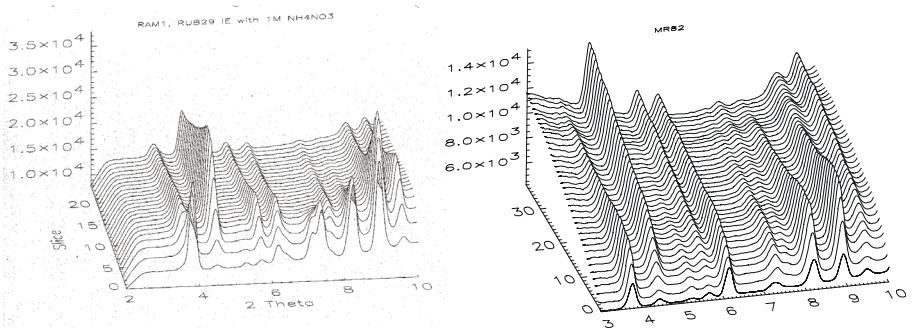

Fig.1. In situ synchrotron X-ray powder diffraction pattern (λ = 0.9274 Å) obtained while ammonium at RT (Fig. 1-a) and magnesium at 80°C (Fig. 1-b) exchanges of as-synthesized RUB-29 at X7B of BNL.