Preparation and Diffraction Studies of Layered Manganese Oxides

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Introduction and Motivation

What is a rechargeable battery?

A battery is made up of at least one electrically-charged cell which converts stored chemical energy into electrical power. Batteries provide voltage and capacity. When an electrochemical reaction occurs in a battery and electrochemical energy is produced, chemical changes occur in the battery. If one can reverse those chemical changes by charging the battery, then the battery is rechargeable. This reversal of the chemical changes must be efficient enough that it can be repeated thousands of times.

Properties of a good electrode for a rechargeable battery
- Good oxidizing and reducing agent
- Large storage capacity
- High power and energy density
- Good electrical conductivity
- High reactivity
- Reversible
- Safe
- Stable
- Inexpensive
- Environmentally friendly
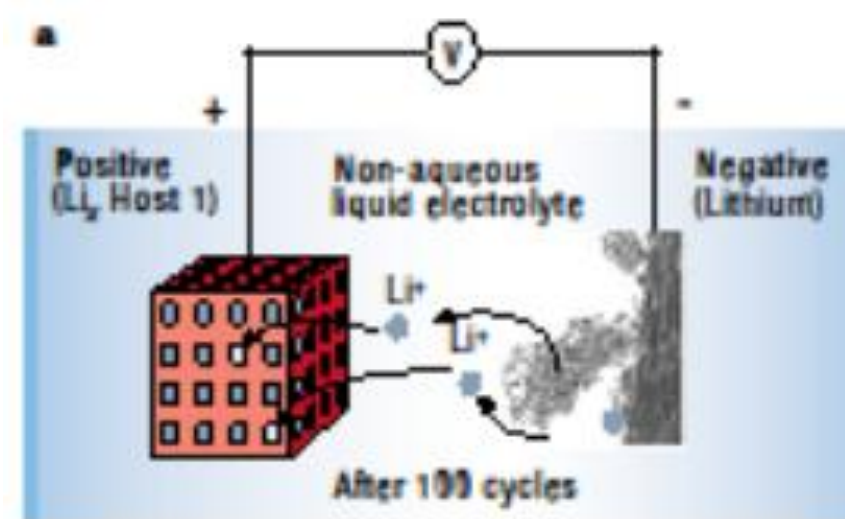
Schematic diagram of a rechargeable $LiCoO_2$ battery. From J.M. Tarascon and M. Armand, *Nature*, 414 (2001) 359.

Why manganese oxides?

- Transition metal compounds are good electrodes because they have several oxidation states—can easily be oxidized and reduced
- Manganese has ten known oxidation states.
- Many different tunnel structure frameworks can be formed from layered manganese oxide frameworks.
- Layered sodium manganese oxide phases: $MnO_2 \cdot H_2O \cdot Na_2O$ (vernadite), $Na_4Mn_{14}O_{27} \cdot 9H_2O$ (birnessite), $Na_y MnO_2 \cdot xH_2O$ (buserite), $\alpha\text{-}NaMnO_2$, $\beta\text{-}NaMnO_2$, $Na_{0.44}MnO_2$, and $Na_2Mn_3O_7$
- Birnessite is useful because when metal ions are placed between the layers of birnessite, they can easily be removed by an acid or exchanged for other cations—can be used to make tunnel structure frameworks

$\beta\text{-}NaMnO_2$ $\beta\text{-}MnO_2$ $Na_4Mn_{14}O_{27} \cdot 9H_2O$, birnessite


$\alpha\text{-}NaMnO_2$
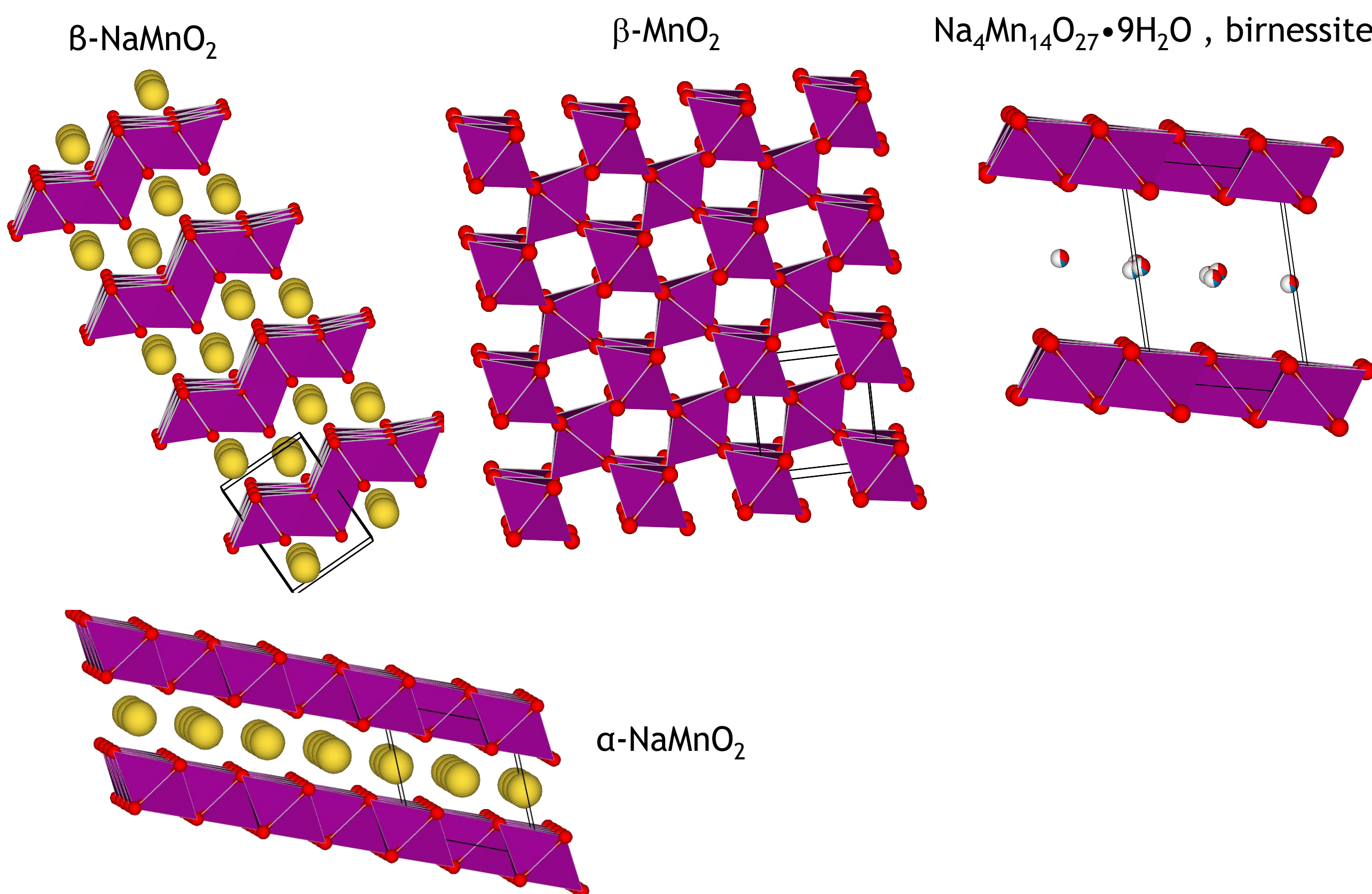
What is diffraction?

About Diffraction
- Diffraction is the scattering of a beam of particles when it comes in contact with a material. If the material is crystalline, we observe Bragg reflections.
- We use X-rays and neutrons for diffraction because they have the right wavelengths for inter-atomic spacing.

Bragg's Law
- $n\lambda = 2d\sin\theta$
- Equation relating the perpendicular distance between two planes in a crystal (the d-spacing of the planes) and the scattering angle between the incident and outgoing X-ray or neutron beam
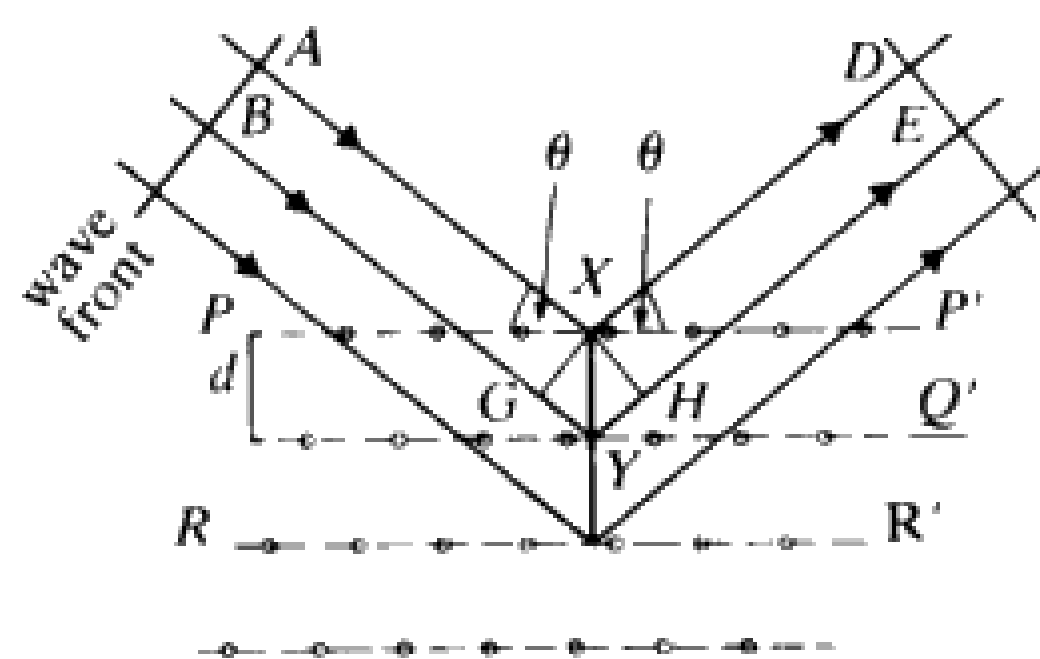
Derivation of Bragg's Law. From The University of Oklahoma Chemical Crystallography Lab: http://xrayweb.chem.ou.edu/notes/crystallography.html

Rigaku Ultima III X-ray Diffractometer

Experimental

We focused our research on synthesizing birnessite. In doing so, we used various different reaction conditions. We created birnessite from an aqueous solution of NaOH and solid Mn_2O_3 in an oven and from aqueous solutions of NaOH, $Mn(NO_3)_2$, and H_2O_2 without heat. De-intercalation describes the process by which an atom is removed from a crystal lattice without destroying the prior framework structure. We performed de-intercalation experiments with $\alpha\text{-}NaMnO_2$ and I_2 crystals in acetonitrile and ethanol (both dried over 3Å molecular sieves) at room temperature and solvothermally with the following conditions: exposed to air and water, exposed to air but not water, air-free but exposed to water, and air and water free. Neutron experiments were performed previously on $\alpha\text{-}NaMnO_2$ to explore the magnetism on this layered material.

Results

X-ray diffraction
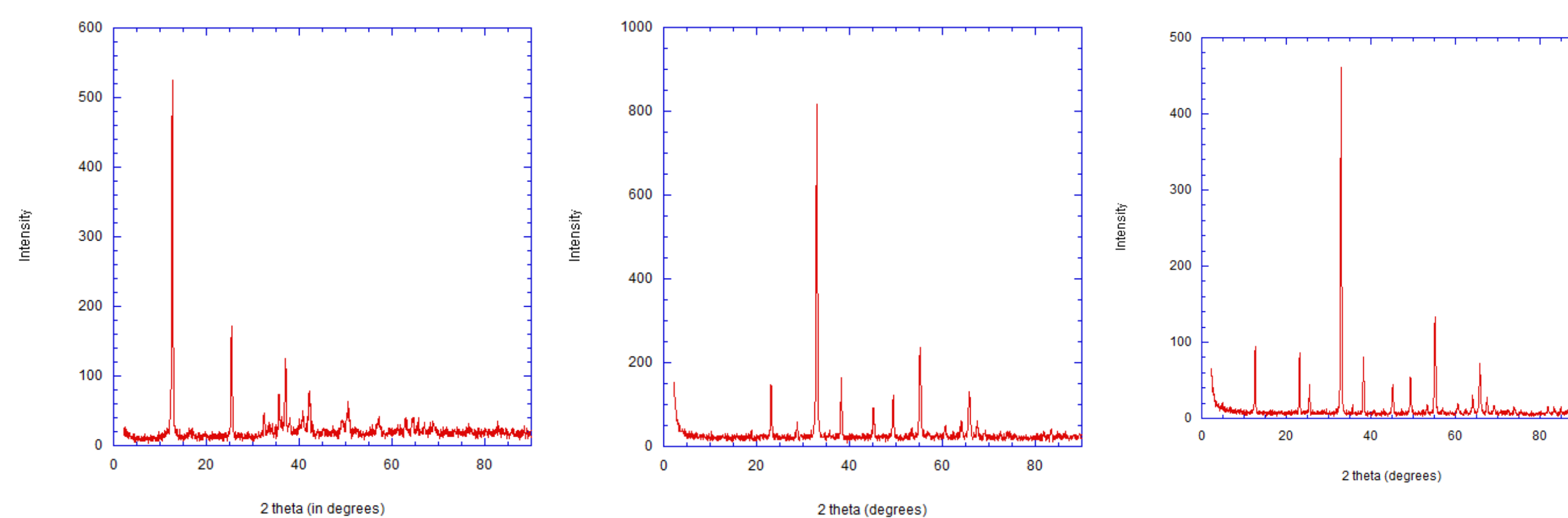
X-ray powder diffraction pattern from de-intercalation of air and water exposed $\alpha\text{-}NaMnO_2$ with acetonitrile and I_2 crystals at room

X-ray powder diffraction pattern for the Mn_2O_3 that we used in our experiments.

X-ray powder diffraction pattern from synthesis with Mn_2O_3 and NaOH.
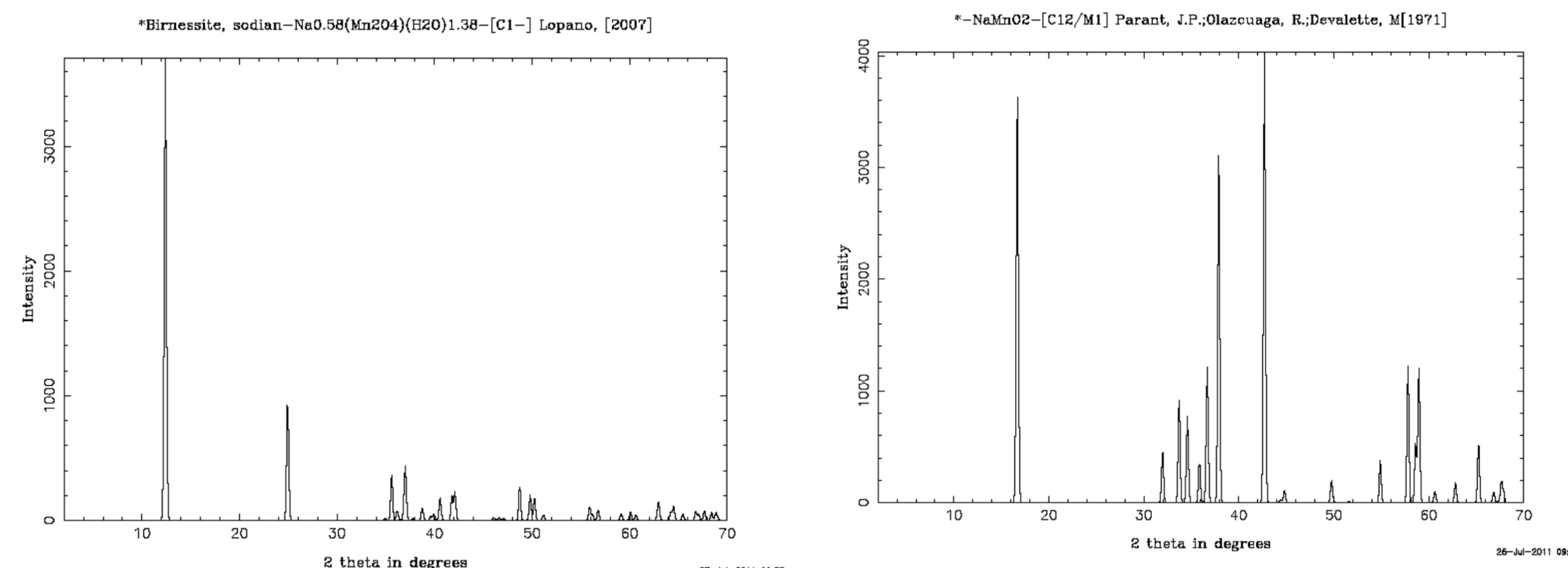
Calculated X-ray powder diffraction pattern for $\alpha\text{-}NaMnO_2$. From J.P. Parant, R. Olazcuaga, M. Devalette, C. Fouassier, P. Hagenmuller, Sur Quelques Nouvelles Phases de Formule Nax Mn O2 (X<1), *Journal of Solid State Chemistry*, 3 (1971) 1.

Calculated X-ray powder diffraction pattern for $Na_{0.58}Mn_2O_4 \cdot 1.38H_2O$ birnessite. From C. L. Lopano, P.J. Heaney, J. E. Post, J. Hanson, S. Komarneni, Time-resolved structural analysis of K- and Ba-exchange reactions with synthetic Na-birnessite using synchrotron X-ray diffraction, *American Mineralogist*, 92 (2007) 380.

In a powder diffraction pattern, the d-spacing of the planes in a crystal determine the spacing between Bragg peaks. The type of atoms in a sample and their arrangement on the crystal planes determine the intensity of the Bragg peaks. As evident from the above diagrams, the substance that we synthesized from Mn_2O_3 and NaOH was a mixture of birnessite and Mn_2O_3. The Bragg's peak at 2θ=12.65° corresponds to birnessite, while the peak at 2θ=23.15° corresponds to Mn_2O_3. The peak at 2θ=25.50° corresponds to birnessite, while all of the Bragg's peaks thereafter correspond to Mn_2O_3. The air and water exposed $\alpha\text{-}NaMnO_2$ that was de-intercalated with acetonitrile and I_2 crystals at room temperature seems to be pure birnessite. All of its Bragg's peaks correspond to the calculated peaks for birnessite. None of its peaks correspond to those of its constituent $\alpha\text{-}NaMnO_2$.

Thermogravimetric analysis
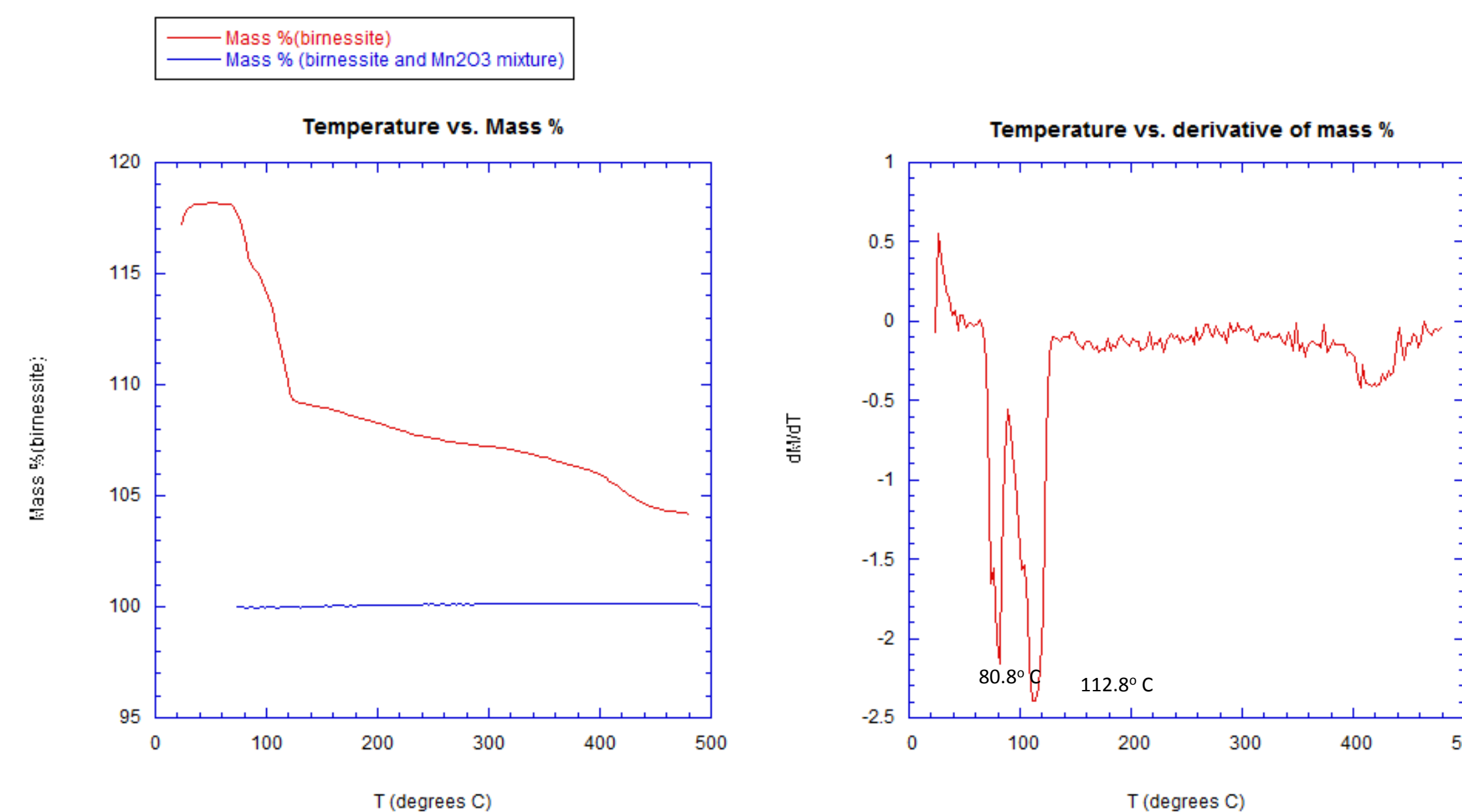
Thermogravimetric analysis of temperature vs. mass % of the air and water exposed $\alpha\text{-}NaMnO_2$ that we de-intercalated with acetonitrile and I_2 crystals and mass % of our synthesized mixture of birnessite and Mn_2O_3.

Thermogravimetric analysis of temperature vs. derivative of mass % of our de-intercalated $\alpha\text{-}NaMnO_2$.

Results cont.

These graphs are of the mass % changes of two different samples that we tried to convert to birnessite. In red is the mass change for the air and water exposed $\alpha\text{-}NaMnO_2$ that we de-intercalated with I_2 (in acetonitrile) and in blue, our hydrothermally synthesized mixture of birnessite and Mn_2O_3. The derivative dM/dT shows how the mass of the de-intercalated compound changes with increasing temperature. Clearly, the two peaks indicate mass loss upon increasing temperature as acetonitrile and possibly water escape, while the hydrothermally synthesized sample remains at a constant mass because solvent was not involved in its formation.

Neutron diffraction on $\alpha\text{-}NaMnO_2$
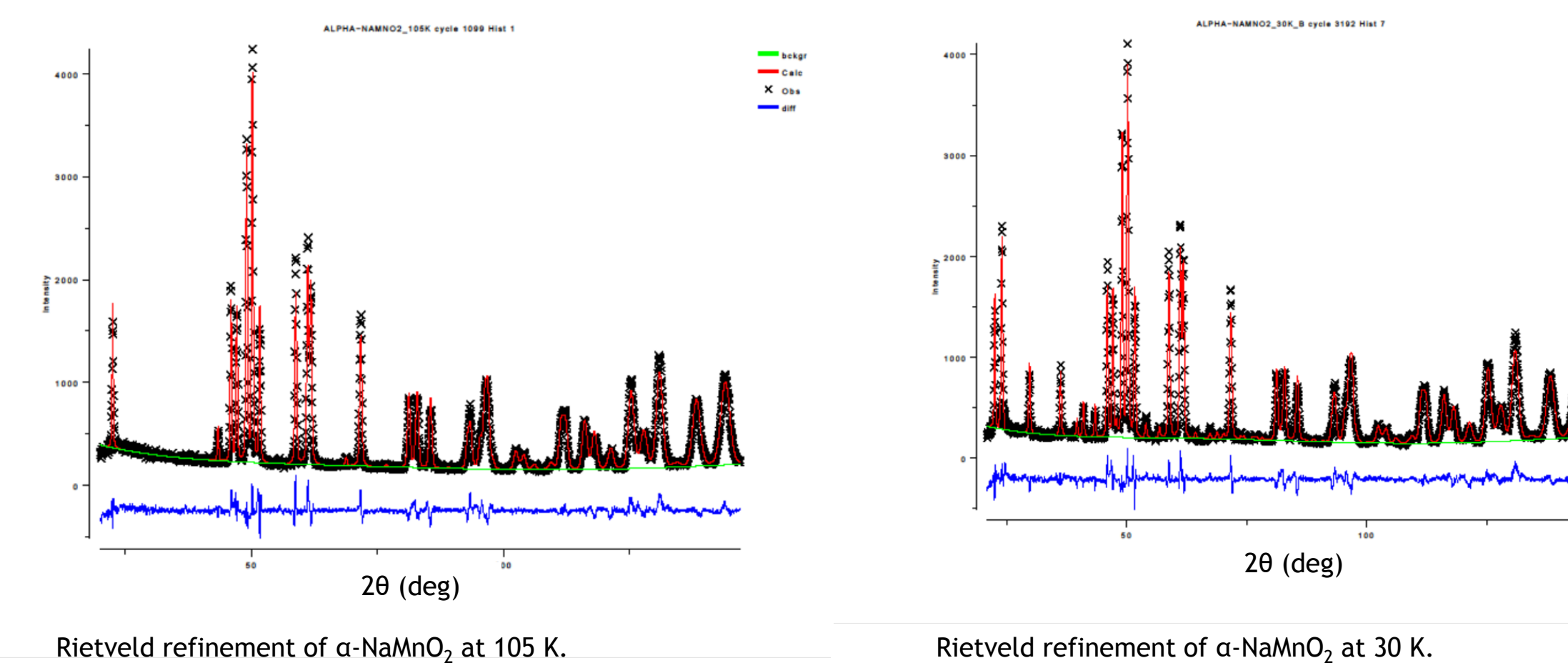
Rietveld refinement of $\alpha\text{-}NaMnO_2$ at 105 K.

Rietveld refinement of $\alpha\text{-}NaMnO_2$ at 30 K.
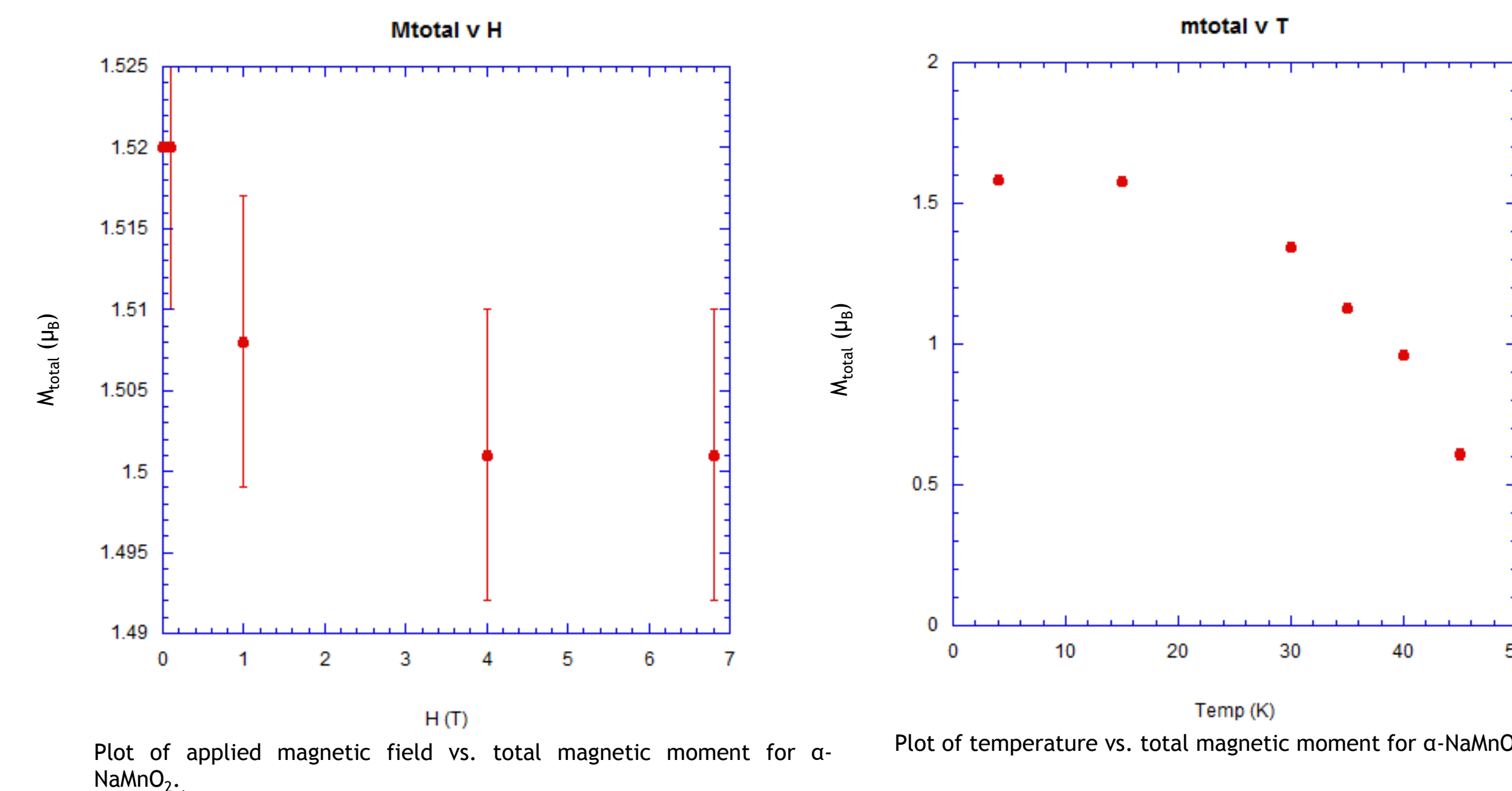
Plot of applied magnetic field vs. total magnetic moment for $\alpha\text{-}NaMnO_2$.

Plot of temperature vs. total magnetic moment for $\alpha\text{-}NaMnO_2$.

$\alpha\text{-}NaMnO_2$ has a magnetic ordering temperature of 45 K. Below this temperature, $\alpha\text{-}NaMnO_2$ has a magnetic moment in the x and z directions. As shown by the above Rietveld refinements, magnetic peaks are visible at 30 K, but not at 105 K. Rietveld refinement is a least-squares method of optimizing the total powder pattern fitting between data and its model. In a Rietveld refinement, we try to minimize the differences between the raw data and the model of the data. In particular, we try to minimize χ^2 and the residual R. The graphs above summarize that while the total magnetic moment of $\alpha\text{-}NaMnO_2$ does not change with applied magnetic field within accuracy, it does decrease with increasing temperature.

Conclusions and Future Work

We found that the best way to produce birnessite was through air and water exposed de-intercalation of $\alpha\text{-}NaMnO_2$ with acetonitrile. We found that synthesis of Mn_2O_3 and NaOH was another way to produce some birnessite (although some Mn_2O_3 remained unreacted). Synthesis of NaOH, $Mn(NO_3)_2$, and H_2O_2 yielded an amorphous solid, while the other de-intercalation experiments yielded other manganese oxide phases. As for $\alpha\text{-}NaMnO_2$, the substance is magnetic below 45 K. Its total magnetic moment decreases as temperature is increased and remains constant as the outside applied magnetic field changes.
A next step in this research is to react birnessite with organic precursors and observe the structural changes that occur. In the future, we can also use our TGA data to dehydrate birnessite. We would also like to perform neutron scattering experiments on all our birnessite compounds to determine chemical stoichiometry accurately, and determine its magnetic ordering.

Acknowledgements