In Situ X-ray Study of Lithiated Pyrolusite

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Introduction: Pyrolusite (β-MnO₂) is reported to have the well-known rutile structure. The structure can accommodate topochemically up to 0.2 Li atoms per Mn atom [1]. ⁶Li and ⁷Li MAS NMR and neutron powder diffraction studies have been done on this system to locate the Li⁺ ions in the lithiated pyrollusite structure. More information concerning the impurities that coexist with this compound is necessary in order to refine the structure with the neutron data.

Methods and Materials: On heating, pure pyrollusite shows a phase transformation to Mn₂O₃ at around 550 °C [2]. In our experiment, we collected synchrotron x-ray data over a wide temperature range to observe the phase transformation for both pyrollusite and the lithiated pyrollusite compound.

Results: Figure 1 shows the in situ x-ray synchrotron powder diffraction patterns of the host, pyrollusite. The temperature was ramped from room temperature to 730 °C over 80 minutes. A clear-cut phase transformation from pyrollusite (β-MnO₂) to Mn₂O₃ is seen at around 550 °C. Figure 2 shows the diffraction patterns of the lithiated pyrollusite. The temperature was ramped from room temperature to 730 °C over 120 minutes, and was cooled down. In this figure, more than 5 different phases are observed. We are especially interested in the phase that disappears above 100 °C. Variable temperature ⁶Li MAS NMR studies are now in progress to characterize this phase.

Conclusions: In our in situ synchrotron x-ray diffraction study of lithiated pyrollusite compound, we found an interesting impurity phase that coexists with the host pyrollusite structure at room temperature but disappears on heating above 100 °C. In contrast, pyrollusite contains no impurities and undergo clear-cut phase transformation to Mn₂O₃ at 550 °C.


Figure 1. Time-resolved, in situ X-ray synchrotron powder diffraction patterns of pyrollusite. The temperature was ramped from room temperature to 730 °C over 80 minutes.

Figure 2. Time-resolved, in situ X-ray synchrotron powder diffraction patterns of lithiated pyrollusite. The temperature was ramped from room temperature to 730 °C over 120 minutes, and was cooled down to room temperature over 120 minutes.