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In Situ Time-resolved XRD during Manganese Oxide Nano-particle Synthesis

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Beamline(s): X7B

Introduction: The field of nano particle preparation has been motivated by the observation that new and useful chemical and physical characteristics that are significantly different from the bulk materials can be obtained in this way [1]. The understanding of the preparation of other materials such as zeolites has been facilitated by in situ X-ray powder diffraction measurements [2,3] and we have applied this technique to nano-particle synthesis. Manganese oxide minerals have been shown to have a wide range of structures that have economic and environmental significance [4]. There have been several studies on the formation of nano-crystalline manganese oxides including the formation of nano-fibers [5]. Recently, it has been shown that single-crystal nano-rods of α -MnO₂ can be prepared by a liquid phase comproportionation method [6]: $3\text{MnSO}_4 + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$

Methods and Materials: Manganese (II) sulfate hydride ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) and potassium permanganate (VII) (KMnO_4) were dissolved in distilled water at room temperature. This solution was added to a capillary cell (Fig. 1) and pressurized to 50 psi using Nitrogen. A sample heater was programmed to heat the sample isothermally or in ramping mode. Fig. 2 shows the results of a run in the isothermal mode where the sample was heated to 115°C in 5 minutes and then held at that temperature.

Results: The initial diffraction pattern (not shown) is that of an amorphous solution; the layered manganese oxide (Birnesitte) forms rapidly (Fig.2) and is further transformed to α -MnO₂ (Hollandite) in 20 minutes.

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References:

[1]. Alivisatos, A. P. *J. Phys. Chem.* 100, 13226(1996).

[2]. Norby, P.; Christensen, A. N.; Hanson, J. C. *Inorg. Chem.*, 38, 1216(1999).

[3]. Norby, P.; Hanson, J. *Catalysis Today*, 39, 301(1998).

[4]. Post, J. E. *Proc. Natl. Acad. Sci. USA*, 96, 3447(1999).

[5]. Xai, G. G.; Tong, W.; Tolentino, E. N.; Duan, N.-G.; Brock, S. L.; Wang, J.-Y.; Suib, S. L.; Ressler, T. *Chem. Mater.*, 13, 1585(2001).

[6]. Wang, X.; Li, Y. *Chem. Comm.*, 764 (2002).

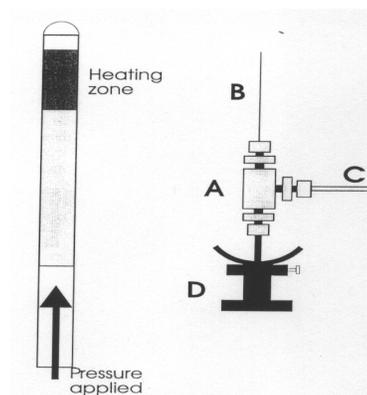


Fig. 1. Capillary cell and goniometer mount.

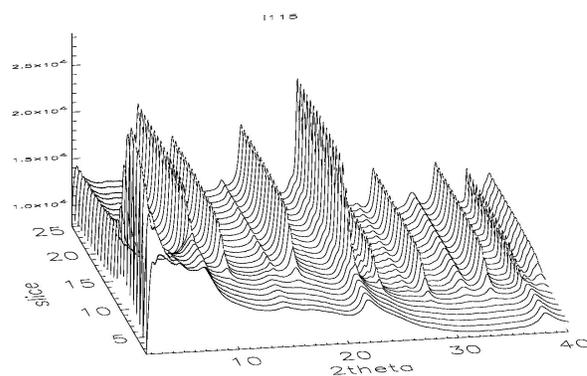


Fig 2. In situ time-resolved pattern (3.3min/slice).