



Keywords: Chevkinite group, composition, phase transition, oxidation state, high pressure, annealing

MS14-P6 Characterization of Mn octahedral molecular sieves by electron diffraction and Rietveld refinement

Enrico Mugnaioli¹, Enrico Mugnaioli¹, Michael Gregorkiewitz¹,
Mauro Gemmi², Marco Merlini³

1. Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Università degli Studi di Siena, Siena, Italy
2. Center for Nanotechnology Innovation@NEST, Istituto Italiano di Tecnologia, Pisa, Italy
3. Dipartimento di Scienze della Terra 'A. Desio', Università degli Studi di Milano, Milan, Italy

email: enrico.mugnaioli@unisi.it

Manganese is an extremely versatile element due to its multiple oxidation states. Tunneled octahedral manganese oxides are found in nature as alteration products in mineralized rocks. Their structures are characterized by channels walled by edge-sharing MnO_6 octahedra and hosting different ionic species (Na, K, Ba...). Small differences in manganese oxidation state are associated with a wide structural variety of framework connectivity and pore sizes [1].

Tunneled manganese oxides belong to the group of octahedral molecular sieves (OMS), due to their open framework structures recalling the better-known tetrahedral molecular sieves, i.e. zeolites. In the last years OMS raised an increasing interest for their electronic properties. While tetrahedral frameworks are typically electronic insulators, OMS are mixed electronic/ionic conductors. The octahedrally coordinated elements in OMS frameworks have easily accessible 3d orbitals. Oxidation state and band gap are structurally related and depend on position and coordination of the extra-framework ions. Manganese tunneled oxides find advanced applications in gas sensing, heterogeneous catalysis, batteries and supercapacitors [2]. Moreover, manganese OMS exhibit electric and magnetic transitions at relatively high temperatures and show a superconductive behavior connected with charge-ordering of framework and extra-framework atoms [3].

A systematic structure characterization of manganese OMS is hampered by difficulty in growing single crystals and achieving pure synthetic products. In this contribution we present the structure investigation of several natural and synthetic manganese OMS, combining X-ray powder diffraction, transmission electron microscopy and electron diffraction tomography [4]. The frameworks of unknown structures were determined ab-initio by direct methods, and extra-framework ion positions were identified during structure refinement. Intermediate phases occurring during the synthesis were tracked by thermal analysis and structurally characterized. Finally, order-disorder transitions of extra-framework atoms, eventually associated with superstructure modulations, were investigated by cryo-controlled experiments.

- [1] Pasero, M. (2005). *Rev. Mineral. Geochem.* **57**, 291–305.
- [2] Wei, W. *et al.* (2011). *Chem. Soc. Rev.* **40**, 1697–1721.
- [3] Sato, H. *et al.* (1999). *Phys. Rev. B* **20**, 12836–12841.
- [4] Mugnaioli, E. *et al.* (2009). *Ultramicroscopy* **109**, 758–765.

Keywords: manganese oxide, Rietveld refinement, electron diffraction, phase transition

MS14-P7 Size-controlled synthesis of a mordenite type zeolite from organic template free initial gel

Yuri A. Kalvachev¹, Totka D. Todorova¹

1. Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences

email: kalvachev@clmc.bas.bg

One of the widely used zeolite minerals mordenite has chemical formula $\text{Na}_8(\text{H}_2\text{O})_{24}[\text{Al}_8\text{Si}_{40}\text{O}_{96}]$. Its structure is characterized by 12-membered and 8-membered rings running along the c axis, and another 8-membered rings running along the b axis; these channels accommodate extraframework cations and water molecules. The mineral, especially synthetic varieties, has many industrial applications such as isomerization catalysts. The structure has an orthorhombic unit cell ($a = 18.1 \text{ \AA}$, $b = 20.5 \text{ \AA}$, and $c = 7.5 \text{ \AA}$) with topological space group symmetry Cmcn.

This study reports on the hydrothermal synthesis of mordenite crystals without an organic template and on the characterization of resulting crystals, as the ultimate goal has been to decrease the crystal size. Two synthesis approaches have been applied. The first one involved subjecting a standard initial gel $18\text{SiO}_2 : \text{Al}_2\text{O}_3 : 1.24\text{K}_2\text{O} : 1.21\text{Na}_2\text{O} : x\text{H}_2\text{O}$ to hydrothermal crystallization for a period of 2 to 7 days ($x=600, 280$ and 22.5). The second approach included the usage of seeds employing the same initial gel composition. The crystals growth kinetics of mordenite at a different seed content (1, 2 and 5 wt. %) has been studied. The seed-assisted process enabled us to synthesize mordenite crystals of submicrometric range. Particle size distribution of the resulting products strongly depends on the water content in the initial gel and on the amount of added seed. It has been found that seed concentration and water content in the initial gel are the key factors influencing the crystallization time and the physicochemical properties of crystalline products. Six hours is the shortest time in which zeolite mordenite with high crystallinity is obtained.

Acknowledgments. The authors acknowledge the financial support from the operational programme “Human Resources Development” within project BG051PO001-3.3-06-0027.

Keywords: Nanozeolites, Mordenite, Hydrothermal synthesis, Seed-mediated synthesis