m14.o03

Manganese oxide tunnel structures determined with TEM

J. Hadermann[a], A.M. Abakumov[b], L. Gillie[c], O. Perez[c], C. Martin[c], M. Hervieu[c], G. Van Tendeloo[a]

[a] EMAT, University of Antwerp, Belgium, [b] Moscow State University, Russia, [c] ISMRA-CNRS Caen, France. E-mail: joke.hadermann@ua.ac.be

Keywords: structure determination, transmission electron microscopy, incommensurate structures

Complex manganese oxides A_xMnO_2 (x < 1) show a tendency to form complex tunnel structures. The major structural unit of the tunnel walls is a rutile-type chain of edge sharing MnO_6 octahedra. A variety of structures arises due to the ability of these chains to form double and triple chain blocks by sharing octahedral edges. We will present the structure determination of three such tunnel compounds with approximately the same A/Mn ratio, $SrMn_3O_6$ [1], $CaMn_3O_6$ and $Sr_{0.9}Mn_3(O,F)_6$, where the shape of the channels and the ordering pattern of the A-cations vary. We have solved their structures with transmission electron microscopy (TEM) and then refined them from XRD and/or NPD data. The HREM images taken along the direction of the tunnel propagation clearly show that the three compounds have different shapes of tunnels. In the case of $SrMn_3O_6$ the tunnel structure is of a "figure-of-eight" shape. The electron diffraction patterns of $SrMn_3O_6$ show satellite reflections due to an incommensurate modulation caused by the ordered Sr-distribution over the available positions in the tunnels, only 67% of the tunnel sites are filled with cations. This ordering also affects the positions of the oxygen, making one Mn-O distance substantially longer, resulting in a pyramidal instead of an octahedral coordination for some of the Mn-cations. Local areas were found with a range of different modulations, corresponding to slightly different Sr-contents. Although it has nominally the same composition as $SrMn_3O_6$, the $CaMn_3O_6$ structure contains smaller six-sided tunnels comparable to those of $CaFe_2O_4$. Each tunnel comprises a single string of the Ca-cations in which every third A-position is vacant. The empty sites in neighbouring Ca-strings are shifted relative to each other by one repeat period along the *c*-axis of the $CaFe_2O_4$ subcell giving rise to a monoclinic distortion. The analysis of the Mn-O distances allows to speculate that there is Mn^{+3}/Mn^{+4} charge ordering with the Mn^{+4} cations located near the cation vacancies in the A-sublattice. Introducing fluorine into the anion sublattice drastically changes the connectivity scheme of the octahedral strings. The $Sr_{0.9}Mn_3(O,F)_6$ compound shows large todorokite-type 3x3 channels in which four Sr strings are placed. The electron diffraction patterns show satellite reflections indicating a composite structure with two different repeat periods for the Sr- and octahedral sublattices due to the ordering of Sr in the tunnels. Replacing Sr by Ca or adding F to the compound thus results in different structures, which will be compared and discussed.

[1] L.J. Gillie, J. Hadermann, O. Pérez, C. Martin, M. Hervieu, E. Suard, *J. Solid State Chem.* 177 (2004) 3383-3391.

m14.o04

Deformed Penrose Tilings

T.R. Welberry[a], A.G. Beasley[a] and Bernd Sing[b]

[a] Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia, and [b] Fakultät für Mathematik, Universität Bielefeld, Universtätstrasse 25, 33615 Bielfeld, Germany. E-mail: welberry@rsc.anu.edu.au

Keywords: quasicrystals, Penrose tiling, deformed model sets

In a recent study [1] using Monte Carlo (MC) simulation of a model quasicrystal it was shown that the kinds of local distortions that result from 'size-effect'-like relaxations are in fact very similar to some mathematical constructions called 'deformed model sets' [2-4]. Of particular interest is the fact that it has been proven that these deformed model sets are pure 'point diffractive', i.e. they give diffraction patterns that have sharp Bragg peaks and no diffuse scattering. It should be noted that the MC simulations in [1] themselves gave diffraction patterns displaying some diffuse scattering but this can be attributed to the fact that the simulations by their very nature did include a certain amount of randomness. Examples of 'deformed model sets' on the other hand may be constructed by *simple prescription* and hence contain *no randomness*. In this case the diffraction patterns then show no diffuse scattering. In this paper we demonstrate that simple deformed model sets can be constructed, based on the simple Penrose rhomb tiling, by using deformations which are defined in terms of the local (nearest neighbour only) environment of each vertex (site). The resulting model sets are all topologically equivalent to the Penrose tiling (same connectedness), are perfectly quasicrystalline but show an enormous variation in the Bragg peak intensities. This has particular significance in terms of the determination of quasicrystal structure. While it may not be possible to decorate the two types of tiles in a tiling model in a way that will reproduce observed Bragg peak intensities the added possibility of local deformations means that numerous additional adjustable parameters are available when trying to make the fit. For the examples described here, which are based on nearest-neighbour environments, 12 deformation parameters may be chosen independently. If more distant neighbours are taken into account further sets of parameters may be defined.

[1] Sing, B. and Welberry, T.R. Deformed Model Sets and Distorted Penrose Tilings. *Zeitschrift für Kristallographie,* In press (2006).
[2] Baake, M. and Moody, R.V. Pure point diffraction. *J. Non-Cryst. Solids.* 334-335, 77-82 (2004).
[3] Baake, M. and Sing, B. Kolokoski (3,1) is a (deformed model set. *Canad. Math. Bull.* 47, 168-190 (2004).
[4] Baake, M. and Lenz, D. Deformation of Delone dynamical systems and pure point spectrum. *J. Fourier Anal. Appl.*, 11, 125-150 (2005).