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LETTER

Letter: On the classification and standardization of zeolite crystal structures: telling apart the ACO from the GIS and MER framework types

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Received 1st November 2001, Accepted 7th January 2002
First published as an Advance Article on the web 25th January 2002

A number of zeolite-type frameworks (ACO, APC, APD, ATT, DFT, GIS, MER)[1] exhibit close structural similarities among themselves because of their similar building schemes of linked 8-rings in one plane, interconnected by one-dimensional crankshaft units (**c** and **cc** units in ref. 2) as shown in Fig. 1.

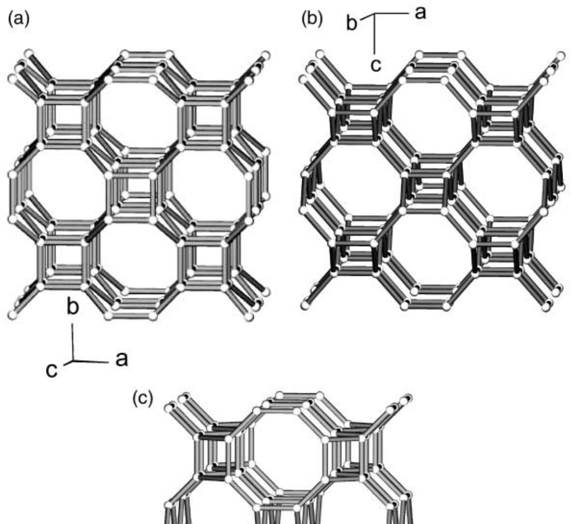

Fig. 1 Projections of the ACO, GIS, and MER-type framework structures in similar orientations and sections in their highest possible topological symmetry. a) The framework structure of the ACO-type framework in space group $Im\bar{3}m$ simulated by DLS refinements.[7] b) The framework structure of the GIS-type framework of tetramethylammonium gismondine[9] in space group $I4_1/amd$. c) The framework structure of the MER-type framework of the average structure of synthetic merlinoite[10] in space group $I4/mmm$. Only the part of the unit cell corresponding to the ACO and GIS-type structures is shown. The face-diagonal **a** + **b** of MER corresponds to 2 × **c** in GIS and to 2 × **a** (or 2 × **b**) in ACO.

Consequently, their lattice constants are either similar or closely related by simple relationships which makes it difficult to correctly identify these compounds by diffraction experiments alone.

In a recent paper[3] on the use of HF as mineralizer in hydrothermal and organothermal syntheses of Me^{2+}-substituted aluminophosphates, among others a gismondine-type phase (framework type code GIS) was described and its crystal structure was determined. Its chemical composition was given in ref. 3 as $Co_{0.84}Al_{0.16}PO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.5H_2O$ and its space group as $I\bar{4}2m$. The atoms P and (Co, Al) are tetrahedrally coordinated by oxygen atoms. The highest symmetry which can be attained by a tetrahedral framework of GIS-topology is space group $I4_1/amd$.[1] Any lower symmetry observed for this type of framework must correspond to a subgroup of $I4_1/amd$.[4] However, space group $I\bar{4}2m$ is clearly not a subgroup of space group $I4_1/amd$ since the diagonal mirror plane of $I\bar{4}2m$ is not present in $I4_1/amd$.[4]

The basic nets of tetrahedral frameworks are distinguished and classified by determining their topological properties. In particular the coordination sequence of the coordination tetrahedra surrounding a central tetrahedron and the vertex symbol enumerating the rings of coordination tetrahedra around a central tetrahedron are diagnostic for a given topology of a framework.[1] We calculated the coordination sequences and vertex symbols of the two tetrahedral sites of this phase[3] using the program ZeoTsites[5] and obtained for the coordination sequence (among T-atoms only) for the first 10 coordination shells the values 4 9 19 35 52 72 100 131 163 201 and the vertex symbol $4 \cdot 8_2 \cdot 4 \cdot 8_2 \cdot 4 \cdot 8_2$ for both of them. These values obviously do not correspond to those of a GIS-type framework (4 9 18 32 48 67 92 120 150 185 and $4 \cdot 4 \cdot 4 \cdot 8_2 \cdot 8 \cdot 8$), but are instead identical to those of the ACO-type framework.[1,6]

Actually, the chemical composition given for the framework of the ACO-type compound in ref. 6 ($Co_{0.89}Al_{0.11}PO_4 \cdot 0.5C_2H_8N_2 \cdot 0.25H_2O$) is very similar to that in ref. 3, as are the unit cell constants. The space group is the same. After proper standardization,[7] that is a shift of 0.5 in the *c*-direction and transformation of the atomic coordinates by 1 0 0/0 −1 0/0 0 1, the mean deviation of the framework atoms of the two compounds is only 0.04 Å.

Interestingly, there exists also a pure cobalt phosphate with a framework of type ACO.[8] Its composition is $CoPO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.25H_2O$, but it crystallizes in space group $P2_12_12_1$, with a doubling of the unit cell volume. This symmetry can be derived as a subgroup of index 8 from $I\bar{4}2m \longrightarrow I222 \longrightarrow P2_12_12 \longrightarrow P2_12_12_1$, where the last symmetry reduction involves a doubling of the *c*-cell constant. In ref. 8 the framework type is described as similar to MER.[1] In fact, both the coordination sequence and the vertex symbol correspond to the ACO-type. The reduction in symmetry relative to $I\bar{4}2m$ is most likely related to the fact that atom O(7) which is bridging between atoms Co(2) and P(4) is also weakly bonded to Co(1) (2.47 Å) and Co(4) (2.78 Å), thus, effectively giving Co(1) and Co(4) coordinations which are best called 4 + 1. Similar

DOI: 10.1039/b110001g

coordinations exceeding the usual tetrahedral coordination have repeatedly been observed in microporous aluminium phosphates.

Fig. 1 illustrates the differences between the ACO, GIS and MER-type frameworks. Despite their similarities the topologies of their underlying nets are clearly different as can be easily verified by comparing their coordination sequences and vertex symbols. The same result can be obtained by strictly standardizing unit cell settings and atomic parameters as defined in ref. 7.

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