Packing schemes of cavities in selected clathrasils and zeolites and the analogous packings of atoms in crystal structures

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ABSTRACT

Sizes of cavities and their packing schemes in selected zeolites and clathrasils were studied by means of least squares fitting of circumscribed spheres to them. Resulting packing of spheres of different diameters was analyzed by the coordinates of their centers, their volumes and sphericity, and interpreted by comparison with analogous packings of atoms in inorganic compounds and alloys. The topology is described qualitatively as “negative” structures formed by the cavities.

Melanophlogite and dodecasils 3C and 1H are all clathrasils with isolated cavities. They all have pentagonal dodecahedral [512] cages, associated with other cavity types. The packing of cavities in melanophlogite is analogous to the packing of atoms in the structure of Cr2Si, where the Cr atoms formicosahedra around the Si sites. Dodecasil 3C has a cubic arrangement of [512] cages, which is described as ABC stacking of kagome nets and its cavity packing is an analog to the packing scheme of atoms in the cubic Laves phase MgCu3. Dodecasil 1H has an arrangement of [512] cages in an AA stacking of kagome nets and is analogous to the alloy structure type CaZn3. Edingtonite and natrolite are built from two types of cavities, tetragonal scalenohedra and [86] cavities. The [86] cavities have different shape and packing in the two structures. In paulingite, the largest cavity, a large rhombicuboctahedron [412684] with a diameter of 11.02 Å is in a body centered configuration. It is interspaced by six other types of cavities with diameters from 5.10 to 8.20 Å, arranged in a complex pattern. In this structure, there are three non-intersecting channel systems. Their cavity arrangements mimic sodalite and a modified ReO3 structure. The cubic structure of sodalite has only one type of cavity, a truncated octahedron [416] with a diameter of 6.41 Å, arranged in a body-centered packing analogous to α-Fe. Chabasite has a rhombohedral packing of elongate cavities [416284], whereas Linde Type A has [416] and [416284] cavities in a CsCl-type arrangement. The cavity representation used here gives a clear picture of cavities and interconnections even for complicated cases.

Keywords: Clathrates, zeolites, functional cavities, cavity packing, alloys

INTRODUCTION

Zeolites are crystalline substances with a structure consisting of a framework of interconnected tetrahedra, containing open cavities in the form of channels and interconnected cages. Clathrates have a similar framework, but with cages isolated from each other in terms of cation mobility and exchange.

Several classifications have been proposed and/or used in describing these micro- to mesoporous structures. The universally used classification is in fact a listing of topologically identical structures by the International Zeolite Association (e.g., Meier and Olson 1992; Meier et al. 1996) by means of three-letter codes (Table 1). Breck (1974) introduced a classification by means of “secondary building units”—characteristic groups of tetrahedra that are present in several structure types. A modification of this classification for mineralogical purposes is given by Gottardi and Galli (1985). Its detailed use was made by Armbruster and Gunter (2001). A classification scheme using cage types is yet another approach used by Smith (1988) and for clathrasils by Gies (1991). These classifications as well as more detailed investigations of selected groups (e.g., van Koningsveld and Gies 2004) are typically concerned with detailed total or local configurations of the silicate framework. In the present work, we attempt a different approach, studying the packing schemes, size ratios, and interconnection (contacts) of functional cages in selected zeolites and clathrasils. Topology of these “negative” structure elements is then compared with the topology of atoms or atom groups in alloys and other compounds.

EXPERIMENTAL METHODS

The functional cages in the zeolites and clathrasils were approximated by a sphere, least-squares fitted to the atoms defining the cage. This calculation, based on the approach of Balić-Žunić and Makovicky (1996), also yields coordinates of a centroid of the cage, i.e., a point with the least variation of the distances to the cages vertices. The resulting sphere radius and sphere volume are the estimates of the cage size in this scheme. These calculations were performed using computer program IVTON (Balić-Žunić and Vicković 1996), in a version adapted to polyhedra with a high number of vertices.

In the analysis, we used several types of volumes characterizing the cages.

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