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STRUCTURES OF INORGANIC COMPOUNDS

Structure of Selenium and Tellurium Clusters in Cavities of Na*X* Zeolite

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Abstract—The structure of Na*X* zeolite crystals with the Se and Te atoms incorporated into the structure from their vapors has been studied. It is shown that selenium atoms form clusters in the shape of six- and four-membered rings located in the cuboctahedral cavities of the structure framework. Single Se_2 molecules are located in large cavities, whereas Te atoms form four-membered rings located in cuboctahedra. Large cavities are occupied by two alternating configurations of Te atoms forming either a chain consisting of 16 links or an eight-membered ring. © *2000 MAIK "Nauka/Interperiodica".*

One of the methods for obtaining systems of nanometer particles widely used in electronics and optics is the synthesis of semiconductor clusters in zeolite cavities. The regular arrangement of such clusters set by the structure of the zeolite matrix allows one to study these clusters by well-developed diffraction methods.

We had the aim to determine the structure and positions of semiconductor selenium and tellurium clusters formed in the cavities of Na*X* zeolite during adsorption of Se and Te vapors. Earlier [1], we obtained and studied single crystals of the zeolite catalyst Te/Na*X* containing tellurium ions coordinated with sodium ones. Two positions of tellurium ions were established. One is located at the center of a cuboctahedron (1.3 tellurium ions per unit cell), whereas the other, in a large cavity (3.7 tellurium ions per unit cell).

The synthesis of semiconductor clusters in Na*X* was performed by the modified multistage method suggested elsewhere [1]; in this method, the last stage was changed—the Na*X*(Te) crystals were treated in a hydrogen flow. In the synthesis of clusters from vapors, the initial matrices were single crystals of Na*X* zeolite of the octahedral shape with a 0.17 mm-long edge and the dehydrated unit-cell composition $Na_{92}Al_{92}Si_{100}O_{384}$ [2]. Because of a small number of available single crystals, the crystals for the X-ray diffraction study were treated together with the fine-crystalline (0.005–0.010) fraction of Na*X* zeolite in the vapors of a semiconductor element. In each cycle of the synthesis, we used 100 mg of fine-crystalline zeolite and several single crystals dehydrated by heating to 400°C mixed with the dried Se or Te powder in the weight ratios 7 : 1 and 6 : 1, respectively. The obtained Na*X* + Se mixture in a sealed ampoule was heated for 24 h at 400°C and then for 24 h at 225°C. The Na*X* + Te mixture was heated for 48 h at 540°C. As a result of the procedure, the synthesized crystals acquired the orange [Na*X*(Se)] or the brown [Na*X*(Te)] color. To prevent possible dehydration, the synthesized crystals were coated with lacquer films. As the X-ray powder diffraction and other X-ray diffraction experiments showed, the treatment of zeolite crystals in the Se and Te vapors leads to a certain degradation of the zeolite lattice—more pronounced for Na*X*(Te) than for Na*X*(Se).

The unit-cell parameters determined on a diffractometer are 25.06(1) Å for a crystal treated in selenium vapors and 25.14(1) Å for a crystal treated in tellurium vapors. The space group for both crystals was determined to be *Fd*3 and coincided with the space group of the initial Na*X* crystals.

The intensity measurements were performed on an automated triple-crystal diffractometer operating in the mode of a normal beam (MoK_α-radiation, graphite monochromator). However, the integrated intensities were estimated by the well-known algorithm used in the profile analysis [3]. The intensities obtained were corrected for polarization and kinematic factors; no absorption correction was introduced. Altogether, the intensities of 330 nonzero nonequivalent reflections were measured for Na*X*(Se) and 256 for Na*X*(Te) crystals. In the following calculations, we used 307 and 236 reflections with $I \geq 3\sigma(I)$, respectively. The initial model structure consisted solely of the framework atoms [2]. The positions of the non-framework atoms were determined from the difference electron-density maps and the intermediate LSM refinements by the AREN-90 complex of programs [4] and the modified version of the ORFLS program [5]. The atomic factors of neutral atoms [6] and the Cruickshank weighting scheme were used [7]. The positions of all the atoms were refined in the isotropic approximation. The final values of the reliability factors were $R = 0.051$, $wR = 0.055$ and $R = 0.097$, $wR = 0.104$ for the Na*X*(Se) and

Atomic coordinates, isotropic thermal parameters, occupancies *p*, and multiplicities *N* of the atomic positions

Atom	*p*/*N*	*x*/*a*	*y*/*a*	*z*/*a*	*B*, A^2
Na*X*(Se)					
Si	1	0.9470(2)	0.0350(2)	0.1248(2)	1.00(7)
Al	1	0.9460(2)	0.1237(2)	0.0367(2)	.81(7)
O(1)	1	0.8940(4)	0.9991(5)	0.1103(4)	2.0(4)
O(2)	1	0.9974(4)	0.9994(4)	0.1441(4)	1.2(2)
O(3)	1	0.1806(5)	0.0747(5)	0.2811(5)	2.1(3)
O(4)	1	0.9268(4)	0.0725(5)	0.1752(5)	1.8(3)
SeI'*a*	5.9(4)/32	0.0574(6)	0.0574(6)	0.0574(6)	4.8(5)
SeI'*b*	4.0(5)/32	0.072(1)	0.072(1)	0.072(1)	6.7(9)
SeII'	4.0(5)/32	0.166(2)	0.166(2)	0.166(2)	9(2)
SeII	8.2(7)/32	0.2363(4)	0.2363(4)	0.2363(4)	3.2(4)
Se(1)	3.8(6)/48	0.125	0.125	0.037(2)	9(1)
Se(2)	6.9(6)/96	0.274(2)	0.303(2)	0.279(2)	8(1)
Se(3)	7.1(8)/96	0.092(2)	0.155(2)	0.448(2)	7(1)
Se(4)	3.3(6)/96	0.509(4)	0.238(3)	0.356(3)	5(2)
Se(5)	2.9(7)/96	0.418(41)	0.285(4)	0.306(4)	6(2)
Na(1)	4.4(6)/16	0	0	0	1.1(7)
Na(2)	3(2)/32	0.231(3)	0.231(3)	0.231(3)	2(2)
Na*X*(Te)					
Si	1	0.9476(4)	0.0349(3)	0.1234(6)	.7(2)
Al	1	0.9456(4)	0.1223(6)	0.0368(4)	1.2(3)
O(1)	1	0.895(1)	0.999(1)	0.107(1)	2.0(6)
O(2)	1	0.995(1)	0.996(1)	0.144(1)	1.2(5)
O(3)	1	0.181(1)	0.072(2)	0.284(1)	3.0(7)
O(4)	1	0.929(2)	0.074(2)	0.174(2)	4.6(8)
TeI'	4.1(5)/32	0.079(2)	0.079(2)	0.079(2)	5(1)
TeII'	4.4(6)/32	0.186(2)	0.186(2)	0.186(2)	5(2)
Te(1)	10.2(7)/96	0.490(2)	0.491(2)	0.386(2)	4.5(7)
Te(2)	3.4(5)/32	0.403(2)	0.403(2)	0.403(2)	6(2)
Te(3)	4(1)/96	0.046(6)	0.067(6)	0.438(7)	9(4)
Te(4)	3.9(5)/48	0.125	0.125	0.817(3)	4(1)
Te(5)	5.0(8)/96	0.279(4)	0.026(4)	0.852(4)	6(2)
Te(6)	3.1(6)/32	0.436(2)	0.436(2)	0.436(2)	7.(3)
NaII	33(3)/32	0.232(1)	0.232(1)	0.232(1)	5.3(8)
NaI	3(1)/16	0	0	0	1(3)

Na*X*(Te) crystals, respectively. The atomic coordinates and the isotropic thermal factors are listed in table.

A three-dimensional framework of *X* zeolite consists of cuboctahedra arranged according to the tetrahedral law and connected by hexagonal prisms. In *X* zeolite there are three types of the cavities—those having the shapes of hexagonal prisms and cuboctahedra and the so-called large cavity in the shape of a truncated cuboctahedron. The notation used for the main sites of non-framework atoms corresponds to the generally used nomenclature.

One of the difficulties usually encountered in the determination of the zeolite structures with large voids is the nonunique interpretation of the electron-density maxima. If the corresponding positions are occupied only partly, they can be filled statistically with atoms of different kinds (the mixed positions). One can often observe the splitting of a position into several new ones located close to one another around the initial position

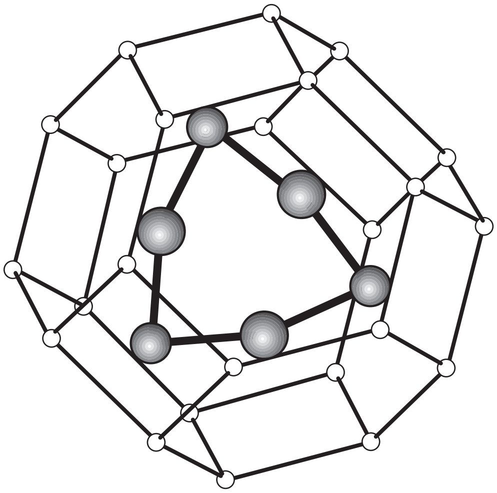

Fig. 1. Six-membered ring formed by Se atoms inside a cuboctahedron.

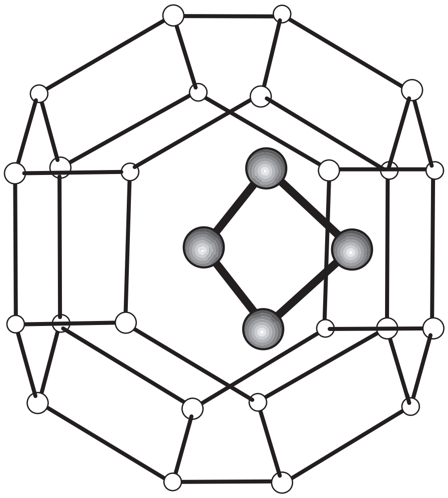

Fig. 2. Four-membered ring formed by Se or Te atoms inside a cuboctahedron.

with the atoms located only in one of these new positions.

The comparison of interatomic distances and valence angles in the aluminosilicate frameworks of the zeolites studied here and the *d*-Na*X* zeolite [2] shows that the zeolite framework is rather stable. Upon crystal treatment in selenium or tellurium vapors, the Si–O–Al angles changed by values not exceeding 5.6°, whereas the (Si, Al)–O bond lengths changed within 0.03 Å. The maximum changes in the structure are associated with the redistribution of the nonframework atoms.

Crystal structure of Na*X*(Se). In the Na*X*(Se) zeolite, the highest occupancy is observed for position I' in the cuboctahedral cavity split into positions I'*a* and I'*b*. The refinement shows that the total occupancy of both positions corresponds to 9.9 Se atoms. Position II' in dehydrated Na*X* is empty. Upon crystal treatment in selenium vapors, this position had the maximum electron density corresponding to the presence of four Se atoms.

In addition to the electron-density maxima in positions I' and II', a new electron-density maximum due to Se(1) is observed opposite the four-membered ring on the twofold axis which was not observed for the initial Na*X* zeolite [2]. The SeI'*a*–Se(1), 2.45(1) Å and the SeI'*b*–SeII' 2.38(4) Å distances are close to the Se–Se 2.37 Å distance in the eight-membered Se_8 rings [8].

The electron microscopy studies showed [9] that the distribution of the Se atoms incorporated into mordenite corresponds to the formation of Se clusters in some unit cells, whereas some other unit cells remain empty. The set of consistent interatomic distances for the crystal studied also leads to a conclusion that selenium atoms have a tendency to be combined inside the cavities and are not statistically distributed over the whole crystal volume. The analysis of the electron-density maxima allows us to state that inside cuboctahedra, alternating differently oriented six- and four-membered rings are formed by the SeI'*a*–Se(1) and SeI'*b*–SeII' atoms (Figs. 1, 2). It should also be emphasized that the occupancies of the corresponding positions agree quite well with this model.

The analysis of the additional electron-density maxima inside the large cavity in Na*X*(Se) zeolite allows us to identify them as the superposition of three crystallographically nonequivalent positions of Se_2 molecules, with each of them being multiplied by the symmetry elements. The Se–Se distances are 2.12(10) and 2.21(6) Å, which is in good agreement with the Se–Se 2.18 Å length in a Se_2 molecule determined by the electron diffraction method in vapors [10].

Crystal structure of Na*X*(Te). The maximum in position I' inside a cuboctahedron in the Na*X*(Te) structure is noticeably displaced to the cuboctahedron center in comparison with its position in Na*X* zeolite, whereas maximum II' is displaced toward the six-membered “window” between the cuboctahedron and the large cavity. These displacements result in a distance between the maxima equal to 2.72(4) Å. The almost equal weights of the maxima in the positions I' and II' and the distance Te–Te 2.72(4) Å (intermediate between the Te–Te 2.56 Å [11] in a Te_2 molecule and the Te–Te 2.86 Å in the Te crystal) lead to the assumption that both positions are occupied with Te atoms which may form a corrugated Te_6-ring similar to that shown in Fig. 2. The large cavity has two alternative configurations of Te atoms forming a ring and a chain, respectively (for a clearer representation, see Figs. 3 and 4). The eight-membered ring (Fig. 3) is formed by three crystallographically independent Te(1), Te(2), and Te(3) atoms multiplied by the symmetry operations. The bond length ranges within 2.72–3.07 Å, the

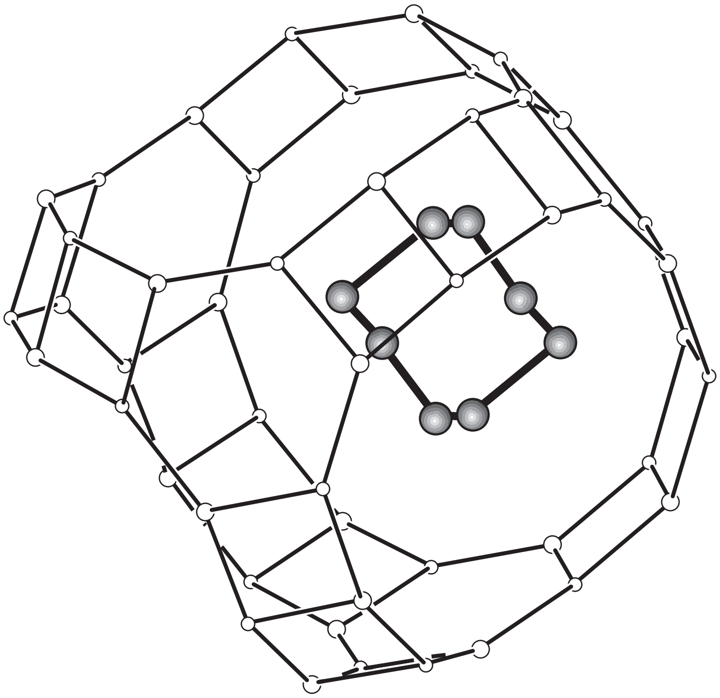

Fig. 3. Eight-membered ring formed by Te atoms in a large cavity.

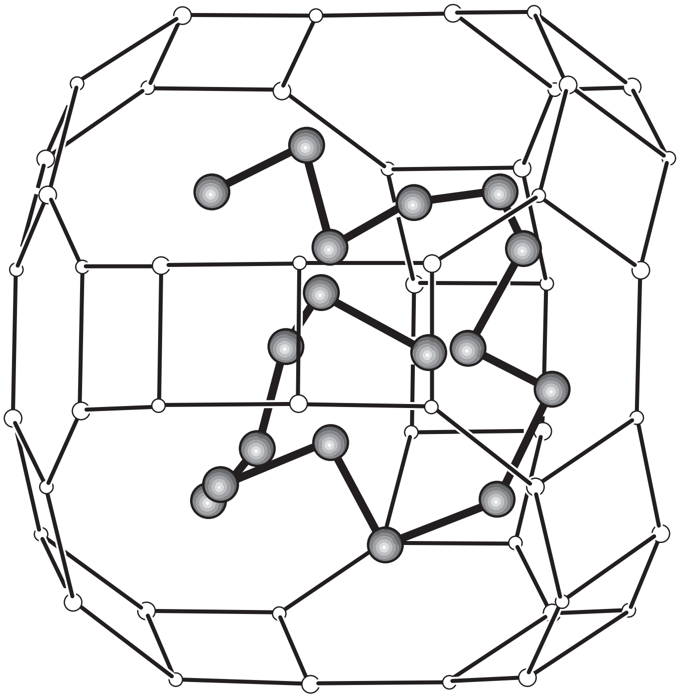

Fig. 4. Fragment of Te-chain in a large cavity.

valence angle ranges within 89.5°–140.3°. It is seen from Fig. 4 that the chain consists of 16 links formed by three other crystallographically nonequivalent atoms, Te(4), Te(5), and Te(6), multiplied by the symmetry operations. The chains in the neighboring cavities can be connected. The Te–Te bond lengths in the chain range within 2.63–2.72 Å, the valence angles, within 95.2°–135.7°. All the atoms in the chain and in the ring are spaced by the distances exceeding 3.11 Å from the framework atoms.

Similar to *d*-Na*X*, the main cationic position II in a large cavity is completely filled with Na atoms. The coordinates of this position agree with the analogous coordinates in *d*-Na*X*, which indicates that position II is filled solely with Na atoms. Comparing the data obtained in [1] with the results obtained in the present study, we draw the following conclusions. Unlike the data in [1], where the total number of Te atoms per unit cell was determined to be five, the total number of Te atoms per unit cell determined in the present study equals 38. Contrary to [1], in our case, Te atoms are combined to form charged clusters in the form of six-membered rings located in cuboctahedra and eight-membered rings or chains located in the large cavity.

We believe that the 16.5 h treatment of Na*X*(Te) crystals in the [1] reducing atmosphere of the hydrogen flow at 475°C leads to the formation of Te^{2-} ions separated from the negatively charged aluminosilicate–oxygen framework by the tetrahedral groupings of Na^+ ions. Such groupings are located in cuboctahedra and large cavities. The aluminosilicate frameworks described in [1] and determined in the present study have similar structures.

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