

**AB INITIO SIMULATION OF THE ELECTRONIC STRUCTURE  
OF ZIRCON (ZrSiO<sub>4</sub>) AND QUARTZ (SiO<sub>2</sub>)**

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Zircon, ZrSiO<sub>4</sub>, is the widespread natural mineral that usually concentrates uranium and thorium. It is characterized by an extremely high resistance to chemical and physical degradation. Recently zircon has been proposed as the prospective material for the immobilization of plutonium. For the industrial applications as waste forms, it is important to develop the microscopic model of the radiation damage of zircon including the atomic and electronic structure of metamict (amorphous) and heterogeneous (ZrSiO<sub>4</sub>+SiO<sub>2</sub>+ZrO<sub>2</sub>) areas of the mineral.

*Ab initio* quantum-chemical cluster calculations of ZrSiO<sub>4</sub> electronic structure were carried out using the MO LCAO discrete-variation X<sub>α</sub>-method. Zircon was simulated by the clusters [Si<sub>5</sub>Zr<sub>6</sub>O<sub>44</sub>]<sup>44-</sup> and [Zr<sub>5</sub>Si<sub>6</sub>O<sub>44</sub>]<sup>44-</sup> containing the central tetrahedron SiO<sub>4</sub> and the central dodecahedron ZrO<sub>8</sub>, respectively. The comparative analysis of the electronic structure of SiO<sub>4</sub> tetrahedra in zircon and those in alpha-quartz has been performed on the base of the cluster models [Si<sub>5</sub>Zr<sub>6</sub>O<sub>44</sub>]<sup>44-</sup> (for zircon) and [Si<sub>5</sub>O<sub>16</sub>]<sup>12-</sup> (for quartz). When constructing the clusters, the following structural features of the minerals have been taken into account: (1) the isolated SiO<sub>4</sub> tetrahedra in ZrSiO<sub>4</sub> and polymerized ones in SiO<sub>2</sub>; (2) the three-fold coordination of oxygen atoms (<sup>III</sup>O) in ZrSiO<sub>4</sub> and two-fold coordination of oxygen atoms (<sup>II</sup>O) in SiO<sub>2</sub>; (3) the [001] edge-connected chains of Zr and Si polyhedra in zircon; (4) the nonequivalence of the connection of ZrO<sub>8</sub> dodecahedra in [100] and [001] directions of zircon.

For the energy spectrum of both minerals, electronic configurations, effective charges of atoms, total and deformation electron density maps have been calculated. It was shown that the energetic and spatial electron density distributions for <sup>III</sup>O and <sup>II</sup>O atoms differed noticeably. In particular, the <sup>III</sup>O<sub>2s</sub>, 2p spectrum is characterized by a smaller width that may be explained as the result of increasing ionicity and decreasing of the oxygen orbitals hybridization in zircon as compared with quartz. It was supposed that the higher chemical stability of zircon was due to the peculiarities of the electronic structure of <sup>III</sup>O atoms. Using the spatial integrating of the electron density in the clusters the effective charges of atoms have been calculated. Their values were the following: Q<sub>Si</sub> = 2.51 e, Q<sub>Zr</sub> = 2.78-2.87 e, Q<sub>O</sub> = -1.28 e in zircon, Q<sub>Si</sub> = 2.57 e, Q<sub>O</sub> = -1.24 e in quartz. The larger Q<sub>Si</sub>-value in quartz as compared with zircon indicates the more covalent character of the Si-O bonding in the latter mineral. This is a result of increasing covalent mixing of Si3s, 3p and O2p states in isolated SiO<sub>4</sub> tetrahedra of zircon. It was established that the Zr-O bonding features differed in [100] and [001] directions of zircon. It was shown that the theoretical results were in the good agreement with the experimental data of optical spectroscopy and XPS.

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