MS14-P15 Mineral-like phases in the MO–CdO–As₂O₅–H₂O system (M²⁺ = Mg, Mn, Fe, Co, Ni, Cu, Zn)

Tamara Đorđević¹, Sabrina Gerger¹, Ljiljana Karanović²

1. Institut für Mineralogie und Kristallographie Universität Wien Althanstr. 14 1090 Wien Austria
2. Faculty of Mining and Geology, Laboratory for Crystallography, Dušina 7, 11000 Belgrade, Serbia

email: tamara.djordjevic@univie.ac.at

In order to understand the mobility of the As⁵⁺ in the environment, one has to investigate structural features and arsenic compounds that occur as the result of natural and technological processes. The synthesis of mineral analogues that are stable over geological time scales could lead to increased stability of waste bearing phases. Having this in mind, the arsenites in the MO-CdO-As₂O₅-H₂O system (M²⁺ = Mg, Mn, Fe, Co, Ni, Cu, Zn) system have been studied by means of the single-crystal X-ray diffraction and vibrational spectroscopy. Up to now only four arsenites from this system have been observed and structurally investigated [1-3]. The low temperature hydrothermal reactions of Cd(OH)₂, As₂O₅ and metal-bearing salts has revealed three new compounds: Cd₃⁺Ni₂⁺(AsO₅), (AsO₅OH), 4H₂O (I), Cd₃⁺Co₂⁺(AsO₅), (H₂AsO₄)₂(H₂AsO₄) (2) and CdZn₂⁺Cl₂(AsO₅), (AsO₅OH), 2H₂O (3). Their structures were determined by single-crystal X-ray diffraction. I is a cadmium analogue of the mineral miguelmeroite, Mn₂⁺H₂(AsO₅), 4H₂O [4]. It crystallizes monoclinic (s.g. C₂/f, a = 18.375(4), b = 9.5395(19), c = 9.977(2) Å, β = 96.19(3)°, V = 1738.6(6) Å³, Z = 4). 2 is isotopic to the alluvaudite-like Cd-arsenites described in [3] (s.g. C₂, a = 11.981(2), b = 12.485(3), c = 6.7661(14) Å, β = 113.23(3)°, V = 930.1(3) Å³, Z = 4). 3 represents previously described strunite type. It is triclinic (s.g. P by 1, a = 6.8700(10), b = 7.513(3), c = 8.2757(2) Å, a = 84.68(3), b = 82.48(3), c = 82.79(3)°, V = 418.82(16) Å³, Z = 2) and is composed of edge-linked octahedral chains running parallel to [101]. The chains contain Cd₁₁O₆(H₂O), and Zn₂Cd₂O₆(H₂O) octahedral pairs sharing opposite edges, which are further interconnected via AsO₄OH⁴⁻ tetrahedral sharing common vertices and intralayer hydrogen bonds. The layers are positioned parallel to the (010) plane and connected only by interlayer hydrogen bonds. The infrared spectra were measured for all three compounds. The OH stretching frequency is in good agreement with the observed O−O distances. Financial support of the Austrian Science Foundation (FWF) (Grant V203-N19) is gratefully acknowledged.


Keywords: cadmium arsenites, hydrothermal synthesis, crystal structure, infrared spectroscopy

MS14-P16 MD study of radiation damage in zircon in connection with the problem of utilization of high-level waste

Oleksii Hrechanivskyi¹, Vadim Urusov²

1. Institute of Geochemistry, Mineralogy and Ore Formation of NAS of Ukraine
2. Moscow State University, Moscow, Russia

email: grechanovsky@gmail.com

Vitrification, or immobilization of nuclear wastes into glass, is the most widespread method of their treatment. However, the service life of such matrices is no longer than 30–40 years. An alternative to vitrification of nuclear wastes is utilization of high-level waste (HLW) in ceramic matrices and materials.

Many authors have considered zircon as a matrix for the disposal of nuclear fuel and weapons-grade plutonium. However, over the geological time, the alpha-decay of uranium and thorium atoms has brought about a damage of the structure of zircon and its transition from the crystalline state to the X-ray amorphous (metamict) state.

The purpose of the present work was to investigate the mechanisms of formation of a cascade of atomic displacements in the structure of zircon due to the alpha-decay under the action of recoil nuclei.

The radiation damage in zircon was investigated by the method of molecular dynamics (MD). This method consists in calculating trajectories of the motion of all atoms involved in a system on the basis of Newton’s second law. As a recoil nucleus for a zircon nanofragment of 400×400×400 Å³ in size containing about 5 million atoms, we used the knock-on atom of thorium (analogue of the recoil atom) with the energy of 20 keV. As the program for the MD modeling, we used the program complex DL_POLY. The computer calculations were fulfilled on the supercomputer SKIF MSU CHEBSHEV.

The calculations carried out showed that the motion of the knocked-on thorium atom with the energy of 20 keV results in its impact with other atoms of the system. These atoms are displaced from the equilibrium positions, begin to move, and, in turn, displace other atoms. This process results in the formation of the atomic displacement cascade (fig. 1).

Close overlap of three atomic displacement cascades was also studied using the MD simulation method. Results show that the number of Frenkel pairs increases nearly linearly with number of such cascades. The number of formed Frenkel pairs of Zr and O (taking into account their content in zircon) less, than in the case of Si atoms.

In whole obtained results show that in zircon every alpha-decay of radioactive elements results in the origin of amorphous area. These results also indicate that most correct model of zircon amorphization is the direct impact model of amorphization.