MS14-P15 Mineral-like phases in the MO–CdO–As_2O_5–H_2O system (M^{2+} = Mg, Mn, Fe, Co, Ni, Cu, Zn)

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In order to understand the mobility of the As^{5+} in the environment, one has to investigate structural features and stabilities of 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 arsenates in the MO-CdO-As_2O_5-H_2O (M^{2+} = 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 arsenates from this system have been observed and structurally investigated [1-3]. The low temperature hydrothermal reactions of $Cd(OH)_2$, As_2O_5 and metal-bearing salts has revealed three new compounds: $Cd_{4.75}Ni_{0.25}(AsO_4)_2(AsO_3OH)_2{\cdot}4H_2O$ (**1**), $Cd_{0.75}Co_{2.75}(AsO_4)_{1.5}(HAsO_4)(H_2AsO_4)_{0.5}$ (**2**) and $Cd(Zn_{0.75}Cd_{0.25})(AsO_3OH)_2{\cdot}2H_2O$ (**3**). Their structures were determined by single-crystal X-ray diffraction. **1** is a cadmium analogue of the mineral miguelromeroite, $Mn_5H_2(AsO_4)_4{\cdot}4H_2O$ [4]. It crystallise monoclinic (s.g. $C2/c$, a = 18.375(4), b = 9.5395(19), c = 9.977(2) Å, b = 96.19(3)°, V = 1738.6(6) Å³, Z = 4. **2** is isotypic to the alluaudite-like Cd-arsenates described in [3] (s.g. $C2$, a = 11.981(2), b = 12.485(3), c = 6.7661(14) Å, b = 113.23(3)°, V = 930.1(3) Å³, Z = 4). **3** represents previously unknown structure type. It is triclinic (s.g. $P\bar{1}$, a = 6.8700(10), b = 7.513(2), c = 8.275(2) Å, a = 84.68(3), b = 82.48(3), g = 82.79(3)°, V = 418.82(16) Å³, Z = 2) and is composed of edge-linked octahedral chains running parallel to [$\bar{1}$01]. The chains contain $Cd1_2O_8(H_2O)_2$ and $(Zn2/Cd2)_2O_8(H_2O)_2$ octahedral pairs sharing opposite edges, which are further interconnected *via* AsO_3OH^{2-} tetrahedra 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.* References: [1] Cooper, M.A. & Hawthorne, F.C. (1996) Can. Mineral. 34, 623-630 [2] Effenberger, H. (2002) Z. Kristallogr. Suppl. Iss. 19, 85 [3] Stojanović, J., Đorđević, T., Karanović, Lj. (2012) J. Alloy. Compd. 520, 180-189 [4] Kampf, A.R. (2009) Am. Mineral. 94, 1535-1540.

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

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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 Å^3 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 CHEBYSHEV.

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.