

## MS14-P15 Mineral-like phases in the MO–CdO–As<sub>2</sub>O<sub>5</sub>–H<sub>2</sub>O system ( $M^{2+} = \text{Mg, Mn, Fe, Co, Ni, Cu, Zn}$ )

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In order to understand the mobility of the As<sup>5+</sup> 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<sub>2</sub>O<sub>5</sub>–H<sub>2</sub>O ( $M^{2+} = \text{Mg, Mn, Fe, Co, Ni, Cu, Zn}$ ) 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)<sub>2</sub>, As<sub>2</sub>O<sub>5</sub> and metal-bearing salts has revealed three new compounds: Cd<sub>4.75</sub>Ni<sub>0.25</sub>(AsO<sub>4</sub>)<sub>2</sub>(AsO<sub>3</sub>OH)<sub>2</sub>·4H<sub>2</sub>O (1), Cd<sub>0.75</sub>Co<sub>2.75</sub>(AsO<sub>4</sub>)<sub>2</sub>(HAsO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>AsO<sub>4</sub>)<sub>0.5</sub> (2) and Cd(Zn<sub>0.75</sub>Cd<sub>0.25</sub>)(AsO<sub>3</sub>OH)<sub>2</sub>·2H<sub>2</sub>O (3). Their structures were determined by single-crystal X-ray diffraction. 1 is a cadmium analogue of the mineral miguelromeroite, Mn<sub>2</sub>H<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O [4]. It crystallise monoclinic (s.g. C2/c,  $a = 18.375(4)$ ,  $b = 9.5395(19)$ ,  $c = 9.977(2)$  Å,  $\beta = 96.19(3)^\circ$ ,  $V = 1738.6(6)$  Å<sup>3</sup>,  $Z = 4$ . 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,  $\beta = 113.23(3)^\circ$ ,  $V = 930.1(3)$  Å<sup>3</sup>,  $Z = 4$ ). 3 represents previously unknown structure type. It is triclinic (s.g. P1,  $a = 6.8700(10)$ ,  $b = 7.513(2)$ ,  $c = 8.275(2)$  Å,  $\alpha = 84.68(3)$ ,  $\beta = 82.48(3)$ ,  $\gamma = 82.79(3)^\circ$ ,  $V = 418.82(16)$  Å<sup>3</sup>,  $Z = 2$ ) and is composed of edge-linked octahedral chains running parallel to [101]. The chains contain Cd<sub>12</sub>O<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub> and (Zn<sub>2</sub>/Cd<sub>2</sub>)O<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub> octahedral pairs sharing opposite edges, which are further interconnected via AsO<sub>3</sub>OH<sup>2-</sup> 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.

**Keywords:** cadmium arsenates, 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

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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.

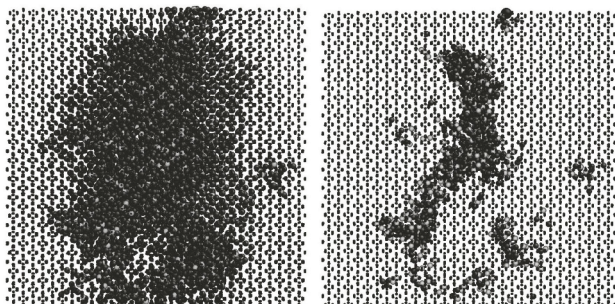
The **purpose** of the present work was to investigate the mechanisms of formation of a cascade of atomic displacements in the structure of zircon due to the alpha-decay under the action of recoil nuclei.

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<sup>3</sup> 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.



**Figure 1.** Radiation damage, produced by 20 keV Th recoil in zircon at the peak of the damage (left column) and after structure relaxation (right column).

**Keywords:** radiation resistance of minerals, semiempirical interatomic potential method, molecular dynamics method, computer simulation of the structure and properties of the crystal, Frenkel defects

## MS14-P17 Nanoscale structure refinement of pyroxenes using precession electron diffraction tomography

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The precession electron diffraction (PED) technique [1] has been originally developed for structure determination at a submicrometer scale in a transmission electron microscope (TEM). The resulting intensities keep dynamical in nature, due to electron multiple scattering, but are more closely correlated with the structure factor values with respect to the non-precised intensities, which is crucial for structure solution and refinement [2]. Since, many structures have been solved using PED, recently combined with the tomographic acquisition of 3D electron diffraction data (PEDT) [3]. Even more recently, a full structure refinement method based on PEDT data and dynamical calculations of diffracted intensities has been successfully proposed [4].

In the field of mineralogy, the sensitivity of PED data to structure factors can be used to refine cations fractionation on specific sites with mixed occupancies. This gives access to the ordering parameter of structures such as Fe<sup>2+</sup> and Mg bearing pyroxenes. Ordering phenomena being time and temperature dependent, we get quantitative information concerning the thermal history and closure temperature of diffusion processes in the hosting rocks. The present study concerns the application of the full structure dynamical refinement method on natural pyroxenes from various origin, including (Fe<sup>2+</sup>,Mg)SiO<sub>3</sub> orthopyroxene (already studied thanks to a 2D zone-axis approach [5]) and (Fe<sup>2+</sup>,Mg,Ca)SiO<sub>3</sub> clinopyroxene. The refinement of 3D electron diffraction data against dynamical calculations enables the estimation of the (Fe,Mg) occupancies on M1 and M2 sites of the structures with a good precision, the refined values being closed to those deduced from XRD experiments at the grain scale. We will discuss on the accuracy and sensitivity of the method and on its potential application in the field of geothermometry using local analysis of terrestrial or extra-terrestrial pyroxene bearing rocks.

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