



New synthetic microporous zirconosilicate and its structural relations with the mineral parakeldyshite

Нов синтетичен микропорест цирконосиликат и структурните му взаимоотношения с минерала паракелдишит

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Zirconium containing minerals are scarcely distributed in nature and generally their formation is attributed to hydrothermal alkaline conditions. The most recent statistics of the IMA Commission on New Minerals, Nomenclature and Classification shows that among the zirconium-containing minerals, zirconosilicates form the largest class (73 of the total number of 94 mineral species). The ZrO_6 polyhedra in the structures of the known so far natural and synthetic zirconosilicates do not show tendency to condensation. That is why the lowest Si:Zr ratio is 2 and as occurring in the structures of zirconium pyrosilicates keldyshite $(Na,H)_2ZrSi_2O_7$, parakeldyshite $Na_2ZrSi_2O_7$ and khibinskite $K_2ZrSi_2O_7$. Synthetic analogs of the three minerals have already been obtained in laboratory conditions. It has been reported that these crystal structures possess large cavities where the alkali cations are situated, however, neither of the structures exhibits ion exchange properties.

In the process of investigation of the system $Na_2O : ZrO_2 : SiO_2 : H_2O$ at $200^\circ C$ we obtained a new compound with the same chemical composition as parakeldyshite. The XRD and DTA-TG analyses showed that its structure is different and that this new compound contains water molecules of zeolitic type. This contribution includes information about the crystal structure of that new compound and its relation to that one of the mineral parakeldyshite. The stoichiometric and topological similarity of the described structures to nine more compounds with general chemical formula $A_{2(3)}MT_2O_7$ ($A=Na, K; M=Si, Zr, Sc, Lu; T=Si, Ge, P$) is discussed. It is pointed out that the newly synthesized microporous zirconosilicate is the only water containing material from the studied series. It was also found that unlike parakeldyshite the sodium ions of the studied compound could easily be exchanged for barium and strontium.

The title compound $Na_2ZrSi_2O_7 \cdot H_2O$ was structurally characterized by electron and X-ray powder diffraction and the results show monoclinic crystal lattice $C2/c$, $a = 5.476(1)$; $b = 9.420(1)$; $c = 13.129(1)\text{\AA}$; $\beta = 92.89(1)^\circ$. There is a close similarity of the cell parameters and the powder diffraction pattern to those ones of the synthetic $Na_3ScSi_2O_7$ ($Pbnm$, $a = 5.354$; $b = 9.347$; $c = 13.098\text{\AA}$). Although there is no direct group-subgroup relationship between the $Pbnm$ and $C2/c$ space groups, both are subgroups of $Cmcm$ which allows using of suitably modified atomic coordinates of $Na_3ScSi_2O_7$ as a starting structural model for Rietveld refinement carried out with the program GSAS ($R_{wp} = 8.26\%$; $\chi^2 = 3.45$). Water content was obtained from the DTA-TG analyses and confirmed by the structure refinement. The crystal structure consists of layers built of ZrO_6 octahedra and SiO_4 tetrahedra, the latter forming condensed Si_2O_7 pyrogroups by connection Fig. 1. The two sodium ions and water molecules are

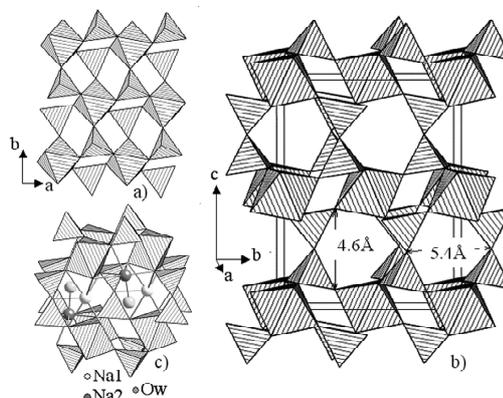


Fig. 1. Crystal structure of the title compound: a) α -ZrP type layer; b) 3D framework; c) channels and cavities

Table 1.

Compound Reference code	Crystal lattice (lattice parameters in Å; angles in °, volume in Å ³)	FD*
K ₃ LuSi ₂ O ₇ (CC412528)	P6 ₃ /mmc, a=b=5.1160(10), c=13.8883(6)	15.292
K ₃ ScSi ₂ O ₇ (CC413432)	P6 ₃ /mmc, a=b=5.6065(1), c=13.6420(4)	16.157
SiP ₂ O ₇ (CC75116)	P6 ₃ , a=b=4.7158(3), c=11.917(1)	26.14
Na ₃ ScSi ₂ O ₇ (CC20120)	Pbnm, a=5.354(3), b=9.347(4), c=13.089(4)	18.32
Na ₂ ZrSi ₂ O ₇ ·H ₂ O This study	C12/c1, a=5.4715(4), b=9.4111(6), c=13.0969(8), β=92.85(1)	17.85
K ₂ ZrGe ₂ O ₇ (CC88843)	C12/c1, a=9.9619(2), b=5.5578(1), c=12.9555(3), β=105.169(1)	17.33
K ₂ ZrSi ₂ O ₇ (CC20100) Khibinskite	P112 ₁ /b, a=9.54, b=14.26, c=5.6, γ=116.516	17.60
Na ₂ ZrGe ₂ O ₇ (CC20402) synthetic Parakeldyshite	P-1, a=5.630(1) Å, b=6.677(2), c=9.108(5), α=70.60(4) β=88.85(4) γ=87.04(2)	18.6
Na ₂ ZrSi ₂ O ₇ (CC24866) Parakeldyshite	P-1, a=6.66(3), b=8.83(4), c=5.42(2) α=92.75 β=94.25 γ=72.33	19.82
NaZrSi ₂ O ₆ (OH) (CC20186) Keldyshite	P-1, a=9.0(1), b=5.32(2), c=6.96(3) α=92.0(1), β=116.0(1), γ=88.0(1)	19.97

* FD – framework density = number of framework cations per 1000 Å³

placed in cavities and channels set up respectively within and between the layers.

We noted stoichiometric and structural similarities of the studied compound with triclinic parakeldyshite and orthorhombic Na₃ScSi₂O₇. A search within the crystallographic databases has shown nine more compounds adopting similar structural topology. In the Table 1 they are arranged according to the symmetrical hierarchy. The basic building units for all of them are M octahedra and T tetrahedra. Two types of composite building units were defined **M2T6** for the first five compounds listed in the table and **M2T4** for the rest of them. The CBUs experience different degree of distortion and accordingly the layers show various symmetries, being highest in the case of K₃LuSi₂O₇ and lowest for NaHZrSi₂O₇ (keldyshite). Those differences additionally influence the way of the three-dimensional arrangement of the layers. The first seven compounds contain two symmetrically related layers per unit cell, while the rest three – only one.

Na₂ZrSi₂O₇·H₂O undergoes two phase transformations upon heating. The first low-temperature one connected with the dehydration process passes without energetic changes and converts the monoclinic Na₂ZrSi₂O₇·H₂O into the orthorhombic Na₂ZrSi₂O₇ (Fig. 2). The process is reversible as evidenced by the rehydration of Na₂ZrSi₂O₇ heated to 400° C, however, water content restoration goes slower as compared to that one in the common zeolitic compounds. The dehydrated sample recovers all the water molecules and its monoclinic structure after 10 days exposure at permanent humidity. The second high-temperature transformation is a typical first-order phase transition resulting in the formation of triclinic parakeldyshite-like compound (Fig. 2). Unlike the first transformation the second one is irreversible and does not allow hydration of the compound. The newly formed framework locks the sodium ions thus precluding the ion-exchange properties of the structure.

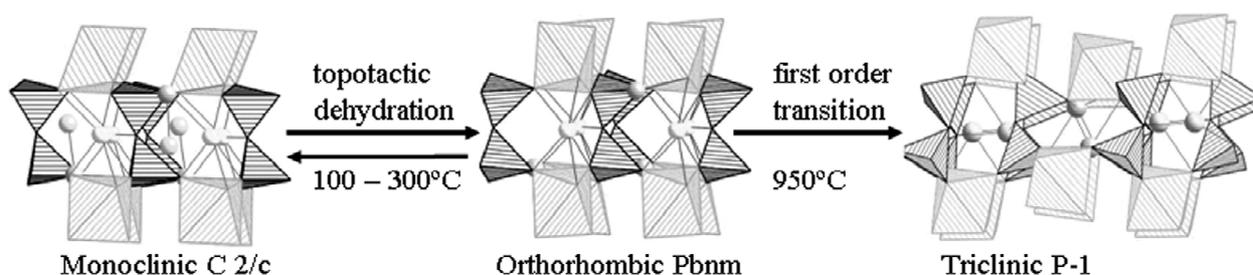


Fig. 2. Temperature-induced transitions of the studied compound