

CRYSTAL CHEMISTRY OF LOW SYMMETRY VESUVIANITES FROM KHARMANKULSKIY AND MONETNAYA DACHA MINES (URALS, RUSSIA)

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Introduction



Vesuvianite is a complex mineral with a range of crystal chemical phenomena arising due to so-called 'rod polytypism' [1-3]. Its general formula looks like $X_{18}[X^*Y]_{12}T_2Z_{10}O_{66}(OH,F)_6$ where X, X' = Ca, Na, K, (are sevenfold to ninefold coordinated), Mn; Y = Al, Mg, Fe²⁺, Fe³⁺, Ca, Ti, Cr, Mn, Zn (has octahedral coordination); Y' = Mg, Al, Fe²⁺, Fe³⁺, Cu (has square-pyramidal coordination); Z = Si, Al (has tetrahedral coordination) In the structures of 'high' vesuvianites (space group P4/nnc), rods are disordered, whereas in the structures of 'low' vesuvianites (space groups P4/n and P4nc), there is an ordered arrangement of rods.

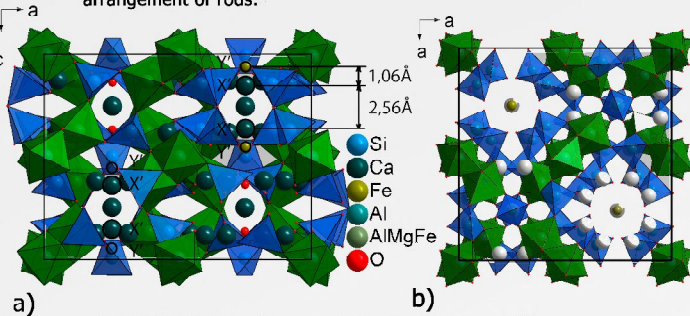
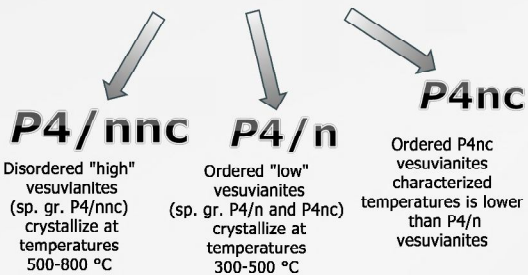


Fig.1 (a) Projection of the vesuvianite structure down [100]; (b) projection of the vesuvianite structure down [001]; Total occupation positions X' and Y' is equal 1.

"High" and "low" vesuvianite



Diffraction of "high" and "low" vesuvianites

Three types of glide violating reflections were distinguished (1) hk0 with h + k = 2n + 1; (2a) 0kl with k + l = 2n + 1; (2b) hhl with l = 2n + 1. Type 1 violates the n glide plane perpendicular to the fourfold axis, type 2a violates the n glide plane in (100), and type 2b violates the c glide plane in (110). Occurrence of type 1 reflections excludes space groups P4/n and P4/nnc and suggests P4nc. Observation of reflections of type 2, a,b excludes P4nc and P4/nnc leading to space group P4/n.



Fig.2 reconstruction of reciprocal space 010 for sample from Monetnaya dacha

Samples was taken from collections of Mineralogical Museum of St. Petersburg State University (fig.3 a,b).

The crystals of vesuvianite selected for data collection was studied using a Bruker SMART APEX X-ray and a Stoe IPDS diffractometers (MoK α X-radiation) equipped with a CCD and Image Plate type area detector accordingly. The unit-cell parameters were refined using least-squares techniques. The SHELXL program package was used for all structural calculations [4]. The chemical composition was studied by the wave-length dispersion spectrometry using a Cameca MS-46 electron microprobe. I

The unit-cell parameters for sample from Kharmankulskiy mine are as following: a = 15.621(1), b = 11.877(1) Å, V = 2898.6(3) Å³. Crystal chemical formula can be written as Ca_{18.84}Mg₇₅Fe₈₁Al_{8.55}Si_{17.32}O_{67.12}(OH)₆. The structure of examined sample was refined in the P4/nnc, P4/n or P4nc space groups with the R-indices equal to 0.093, 0.012 and 0.034, respectively. However, the P4/nnc and P4/n models corresponded to a high number of systematic absence violations, whereas the number of violations for the P4nc was essentially smaller. It is noteworthy that the P4nc space group is quite rare for 'low' vesuvianites [3,5,6].

For sample vesuvianite from Monetnaya Dacha (Middle Ural, Russia) crystal structure is refined in the space group P4/n to R1 = 0.038 on the basis of 6091 independent reflections with I > 2 σ I. Attempts to refine the structure in the space group P4/nnc resulted in significantly higher R1 of 0.072, whereas 981 reflections violated systematic absence conditions for the group. Chemical composition studied using Cameca electron microprobe is as following MS-46 (wt. %): SiO2 37.92, TiO2 1.23, Al2O3 16.72, MgO 2.39, CaO 37.05, FeO 4.17, MnO 0.52, total 100.00. Empirical formula calculated on the basis of Si = 18 is Ca_{18.84}Mg_{1.69}Fe_{2.1}Ti_{0.44}Mn_{0.21}Al_{9.35}Si₁₈O₆₈(OH)_{9.41}O_{0.59}*

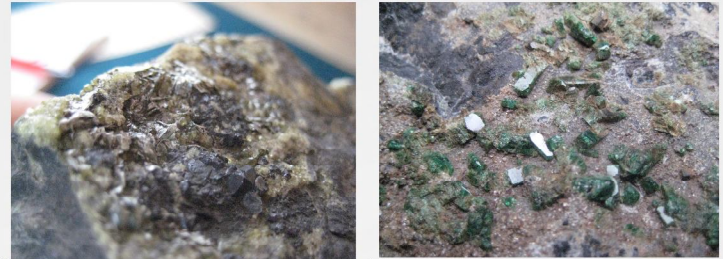


Fig. 3. (a) sample of vesuvianite from Kharmankulskiy mine (b) sample of vesuvianite from Monetnaya Dacha

Along the rods (structure channels) are occupied by the X4a, X4b, Y1a, Y1b, OH10a and OH10b sites. Different occupancies of the Y1a, Y1b sites (75 and 25 %, respectively) results in dominant orientation of chains of the intra-channel sites along the c axis, which favors formation of ordered domains and reduction of symmetry from P4/nnc to P4/n. The crystal studied can be conditionally characterized as consisting up to 75% of parallelly oriented domains with the P4/n symmetry for sample from Monetnaya Dacha (fig.4) [8].

For sample of vesuvianite from Kharmankulskiy mine different occupancies of the Y1a, Y1b sites (8 and 92%, respectively) results in dominant orientation of chains of the intra-channel sites along the c axis (fig.5). And for this sample we can see big differences of bond length in fivefold coordinated Y' position.

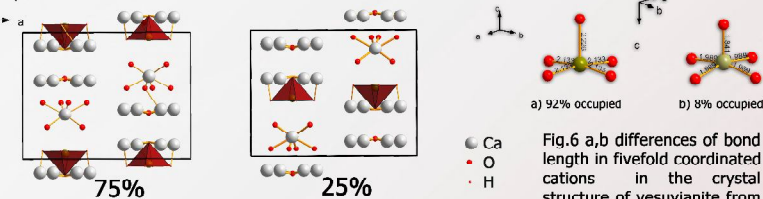


Fig.4 Ration of the ordered domains in the crystal structure of vesuvianite from Monetnaya Dacha

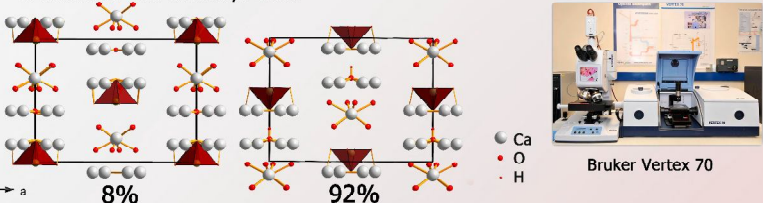


Fig.5 Ration of the ordered domains in the polar crystal structure of vesuvianite from Kharmankulskiy mines

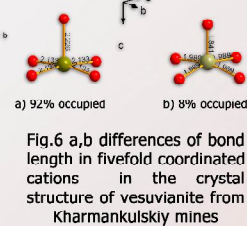
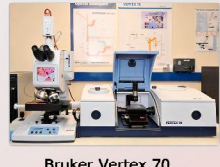


Fig.6 a,b differences of bond length in fivefold coordinated cations in the crystal structure of vesuvianite from Kharmankulskiy mines



Bruker Vertex 70

Infrared spectra

Infrared spectrum of vesuvianite was collected using Bruker Vertex 70 IR spectrometer at room temperature. Interpretation of the IR spectrum obtained was done on the basis of methodology developed by Kurazhkovskaya et al. [7]. In the IR spectrum, two absorption bands at 438 and 476 cm⁻¹ belong to the v₂ symmetric deformation vibrations of the Si-O bonds. The bands at 563, 607 and 632 cm⁻¹ correspond to the v₄ asymmetric deformation vibrations of the same bonds. The bands 800, 881, 918, 964 and 1016 cm⁻¹ may be attributed to asymmetric stretching vibrations of the Si-O and Si-O-Si bonds. The bands in the range 1610-3637 cm⁻¹ correspond to regions of the hydroxyl vibrations. In terms of the group-theoretic analysis for the space group P4nc lowering of the symmetry of the tetrahedron to C₂ results in the appearance of three bands in the 620-570 cm⁻¹ region [7]. Therefore, IR data correspond to the 'low' P4nc vesuvianite, which is in good agreement with the results of structure refinement. For sample from Monetnaya Dacha we have some differences: only two bonds of v₄ asymmetric deformation vibrations 605 and 572 cm⁻¹ and shift of vibrations in the hydroxyl region and this data in good agreement with the model of IR-absorption for P4/n vesuvianite.

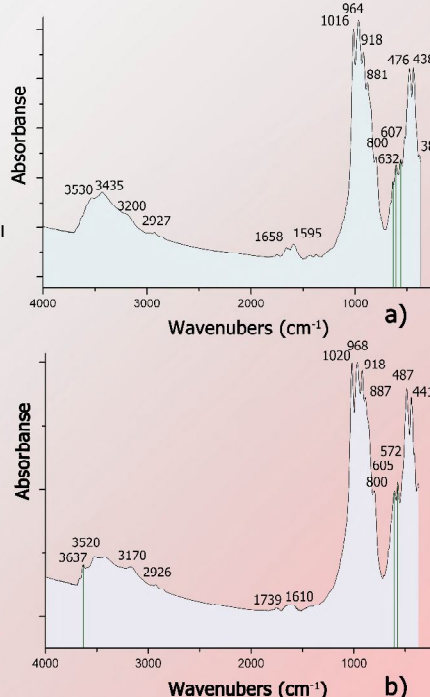


Fig.7 (a) Absorbance IR-spectra for Kharmankulskiy sample (b) absorbance IR-spectra for Monetnaya Dacha sample

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