

CHANGE OF VESUVIANITE STRUCTURAL PECULIARITY AT ISOMORPHISM

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Vesuvianite is an orto-diortosilicate with general composition $X_{19}Y_{13}Z_{18}O_{68}W_{10}$, where X – Ca and other cations filling in position with CN=8, Y – cations filling in octahedral and 5-coordination: Al, Fe, Mg, Ti etc., Z – Si in tetrahedral coordination, W – anions. The structures of vesuvianites is studied in dependence on character of cations regulation in different positions in limits of 3 space groups: $P4/nnc$ and 2 subgroups $P4nc$ (C_{4v}) and $P4/n$ (C_{4h}). It is described [1, 2] that the base of structure is 2 “garnet blocks” (GB) being parts of structure of garnet with grossular composition. Due to connection of GB the formation of diortogroups $[Si_2O_7]$ occurs. The cations composition of GB $\{Ca_{18}Al_8Si_{18}\}$ is practically constant. Cations of “vesuvianite filling” (VF) are took place in holes of formed framework. Isomorphic substitutions occur in positions of VF (table 1). Hypo-

thetical position R is suggested for vesuvianites with superfluous quantity of cations (>19).

The structural peculiarities of vesuvianites of different compositions with abundance of cations have been studied by the method of Infrared spectroscopy. Basing on cations compositions of positions VF (table 2) and character of infrared spectra (fig. 1, table 3) vesuvianites can be divided into 2 groups: 1) with Al and Fe, without Mg or with small amounts of Mg and Ni, and 2) with Mg. In first group the amount of Al exceeds the amount of Fe. The second group consists of: 1) Al and Mg with small amounts of Fe, 2) Al, Fe, Mg and 3) Fe, Mg and small amount of Al. Unit cell parameters are changed insignificantly: $a_0=15.554 - 15.578\text{\AA}$, $c_0=11.796 - 11.805\text{\AA}$.

Table 1

CN	Positions of cations							
	Garnet block (GB)				Vesuvianite filling (VF)			
8	(Ca1) ₂	(Ca2) ₈	(Ca3) ₈		(Ca4) ₁			
6				(Al1) ₈		(Al2) ₄		(R?) _{2 and >}
5							(Al3) ₁	

Table 2

N of sample	Positions of “vesuvianite filling”			
	(Ca4) ₁	(Al2) ₄	(Al3) ₁	(R?) _{2 and >}
1	Ca ₁	Al _{2.93} Fe _{1.07}	Ca _{0.66} Na _{0.34}	Fe _{2.1} Mn _{0.11}
2	Ca ₁	Al _{3.72} Fe _{0.24} Ti _{0.04}	Ca _{0.58} Na _{0.23} Mg _{0.14} Zn _{0.05}	Fe _{0.38} Mg _{2.03}
3	Ca ₁	Al _{2.16} Fe _{0.93} Ti _{0.92}	Ca _{0.92} Na _{0.39?}	Fe _{0.91} Mg _{1.88} Mn _{0.1}
4	Ca ₁	Al _{1.16} Fe _{2.05} Mg _{0.84}	Ca _{0.61} Na _{0.18} Mn _{0.1} Zn _{0.02}	Mg _{2.12}

Table 3

N of sample	Infrared bands (cm ⁻¹)							
	ν_{as} Si-O-Si	ν_3 Si-O	ν_1 Si-O	ν_s Si-O-Si	ν_4 Si-O	ν Me ^{VI} -O	ν_2 Si-O	$\Delta\nu_3$
1	1020	980,990		800	635,575	475	440	80
2	1020	970,920	890	800	605,575	485	435	50
3	1020	975,915	860	800	595,570	470	430	60
4	1020	980,920		800	595,570	470	435	60

On infrared spectrum of first sample splitting of bands of ν_3 is 80 cm⁻¹, numbers of ν_4 are higher than for next spectra. It means that Fe is Fe³⁺: size of Fe³⁺ is smaller than Mg and Fe²⁺, change of infrared bands Si-O to low frequency takes place due to penetrating of larger cations to polyhedra. Sample 2 has in main part of spectrum triplet with band of equal intensity, one of which 1020 cm⁻¹ concerns to vibrations ν_{as} -connection of Si-O-Si diortogroup. The

splitting ν_3 -vibration falls down to 50 cm⁻¹. Deformational ν_4 -vibrations change to low frequency on 30 cm⁻¹. Big decreasing of splitting of ν_3 -vibrations for magnesial samples is same to process taking place due to penetration of larger cations to 8-coordination in garnets. In this process decreasing of tetrahedral distortion with positional symmetry S_4 . Evidently in vesuvianite the decreasing of bands splitting is occurred by substitution Fe³⁺>Mg. With increasing

amounts of Fe and Ti in Al2-position (3) the intensity of ν_3 -vibrations falls down, but the splitting of bands grows up to 60 cm^{-1} . Small moving (10 cm^{-1}) of deformational bands to lower frequencies occurs increasing sizes of cations in Al2-octahedral positions. These octahedra are connected with tetrahedra of diortogroup by common top. With increasing of cations sizes in octahedra the difference of vibrations of onephase and antiphase tetrahedra of diortogroup increases. Due to this process the splitting of bands grows. The spectrum of last sample in the area of valence vibrations is intensive band ν_{as} Si-O-Si- vibrations; on this background there are bands of 980 cm^{-1} and 910 cm^{-1} . This spectrum is the same to spectrum of viluit – B-containing vesuvianite with Mg and Fe^{2+} . Evidently Fe-Mg-samples also contain Mg and Fe^{2+} .

In the results of studying of vesuvianites by the method of Infrared spectroscopy the thin structural changes have been described. These changes are connected with distortion of SiO_4 -tetrahedras at the process of isomorphic substitutions in VF-position of cations. The several types of infrared spectra depending on composition of vesuvianites have been described. The changes of spectra with conversion from vesuvianites containing Al and Fe^{3+} to vesuvianites containing Mg and Fe^{2+} have been discovered. The possible filling of these positions in studied vesuvianites is in table 3.

1. Dorokhova G.I., Kononov O.V., Zykova T.B., Silaev M.V. Genetic and structural relationship of garnet and vezuvianite. Thesis of International Conference "Spectroscopy, X-Ray diffraction and crystal chemistry of minerals", Kazan, 1997.
2. Kononov O.V., Dorokhova G.I., Silaev M.V. The principles of systematic of vezuvianites. Thesis of International Symposium of history of mineralogy and mineralogical museums, gemology, crystal chemistry and classification of minerals, St-Peterburg, 1998.

