

VESUVIANITE: IR AND MÖSSBAUER SPECTROSCOPY DATA

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Vesuvianite is chemically and structurally one of the most complicated rock-forming minerals. Vesuvianite can crystallize in three space groups: *P4/nnc* (high vesuvianites), *P4/n* and *P4nc* (low vesuvianites) in dependence on string ordering in structural channels. The circumstance that the space group of vesuvianite depends on ordering of only 4 atoms in the unit cell makes it difficult to distinguish these “rod” polytypes by diffraction methods. Spectroscopic methods are more sensible to local structure and therefore we used IR and Mössbauer spectroscopy to investigate these samples.

We recorded the infrared spectra of high and low vesuvianite samples in the region of Si-O and B-O fundamental vibrations and also in the OH stretching region. It was revealed that by means of factor group analysis it is possible to predict the number of infrared active internal modes of SiO₄ ions and hydroxyl in different positions and to explain the differences of the spectra due to symmetry and composition of these varieties. Thus, IR spectra gave us the possibility to immediately differentiate between high and low vesuvianites. In addition, also the IR spectra of partly ordered vesuvianite samples were described: they have the characteristic features of both varieties in the OH stretching region.

It is considered that high vesuvianite forms at high temperature (> 400 °C) and low vesuvianite is characteristic for rocks formed at low temperatures (< 300 °C). But we have found in our collection some samples which do not obey this rule. The fact that temperature is not the only factor leading to one or another space group is of great importance from a petrological point of view.

We assigned the absorption bands in low vesuvianites spectra to MgAlOH, AlAlOH, AlTiOH, AlFe³⁺OH. These cations are ordered in the inequivalent Y(3a) and Y(3b) octahedra of the low vesuvianite structure. IR spectra of boron-bearing samples have shown that boron occurs only in triangular positions of the low vesuvianite structure and in both, triangular and tetrahedral positions of the high vesuvianite structure. A diffuse character of the IR spectra and the presence of a band at 1110 cm⁻¹ are prominent features of wiluite.

A Mössbauer spectroscopy study has been carried out with the purpose to determine the valence and structural conditions of iron atoms and also to investigate isomorphic substitutions in the vesuvianite structure. It was shown that Fe²⁺ and Fe³⁺ ions occupy both octahedral and 5-coordinated sites with a slight preference for the latter. Concerning the relative content of Fe²⁺ and Fe³⁺ ions, Mössbauer data allowed to establish two main schemes of isovalent substitutions in the investigated collection of vesuvianite samples: Mg²⁺ ⇌ Fe²⁺ and Fe³⁺ ⇌ Al³⁺. It is shown that along with isovalent schemes, two schemes of heterovalent substitutions occur: B³⁺ + Mg²⁺ ⇌ 2H⁺ + (Fe³⁺, Al³⁺) and Ti⁴⁺ + O²⁻ ⇌ (Al³⁺, Fe³⁺) + OH⁻. The case of replacement including Fe³⁺ ions is preferable for the first mechanism of heterovalent substitution, and the second scheme involves predominantly Al ions.