

Witold ŻABIŃSKI *

THE HYDROXYL-STRETCHING REGION OF THE VESUVIANITE INFRA-RED SPECTRUM

UKD 549.619.1:543.422.4

Abstract. Five distinct absorption bands on vesuvianite spectra have been recorded in the OH-stretching region — at 3670, 3640, 3570, 3530 and ca. 3170 cm^{-1} . They correspond to vibrations of OH groups linked to different di- and trivalent cations.

Vesuvianite (idocrase) is a fairly common silicate mineral occurring principally in metamorphic rocks. General features of its structure have already been described by Warren and Modell (1931), who pointed out its remarkable similarity with that of garnet (grossular). However, much remains to be done about some details of crystal structure of vesuvianite and its physical properties. Even its chemical formula still remains an object of discussion (Ito, Arem 1970). It seems reasonable to expect, that the examination of infra-red absorption spectra of this interesting mineral will provide additional data necessary for understanding of its crystal chemistry and structure. In this paper the OH-stretching region of the vesuvianite spectrum is discussed.

The ideal formula of vesuvianite is usually expressed as: $\text{Ca}_{10}(\text{Mg}, \text{Fe})_2 \text{Al}_4 [\text{Si}_2\text{O}_7]_2 [\text{SiO}_4]_5 (\text{OH}, \text{F})_4$ (Deer et al. 1962). In its crystal lattice the presence of independent SiO_4 and Si_2O_7 groups was found. Both Al and (Mg, Fe) are octahedrally co-ordinated, while Ca is 8-co-ordinated by oxygen. In this paper the positions occupied normally by Al will be designated as X, those by (Mg, Fe) — as Y, and by Ca — as Z. As can be assumed on the basis of Warren and Modell's paper (1931), the OH groups are linked essentially to $(\text{Mg}^{2+}, \text{Fe}^{2+})$ ions (site X), and only to a lesser degree to Al^{3+} (site Y) and Ca^{2+} (site Z) the positions of which are probably more distant. However, a wide range replacement of divalent $(\text{Mg}^{2+}, \text{Fe}^{2+})$ by trivalent $(\text{Al}^{3+}, \text{Fe}^{3+})$ ions can take place. The best evidence for this has been given by the successful synthesis of Mg- and Fe-free vesuvianite in which Al replaces these elements completely

* Academy of Mining and Metallurgy, Institute of Mineralogy and Mineral Deposits, Cracow.

(Rapp, Smith 1958). In some less common varieties of vesuvianite considerable quantities of other elements have been found (Ti, Mn, Be etc.). This, however, is not the case in the here examined samples.

The infra-red spectra of vesuvianites differing in chemical composition (iron content) were recorded with an UR-10 (Zeiss) spectrometer using hexachlorobutadiene mull. Their chemical differences were manifested in variation of colour. The content of Fe^{2+} , Fe^{3+} and some other elements was checked by routine chemical methods.

Five distinct absorption bands, differing in relative intensities, are visible on the spectra. They correspond to wave numbers 3670, 3640, 3570, 3530 and ca. 3170 cm^{-1} . The 3570 and 3530 cm^{-1} bands are evidently due to vibrations of the hydroxyl groups linked to Fe^{2+} and Fe^{3+} ions, respectively: they do not appear on the spectrum of a white variety of vesuvianite from Piz Longhin, showing the smallest iron content. The 3530 cm^{-1} band appears distinctly on the spectra of green vesuvianites, displaying the highest $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio, while the 3570 cm^{-1} band is characteristic for the brown specimens, relatively rich in divalent iron.

The assignment of 3670 and 3640 cm^{-1} frequencies is less certain. These bands appearing distinctly among others on the spectrum of white vesuvianite, low in iron, are undoubtedly related to OH groups coordinated with Mg^{2+} ions as well as Al^{3+} ions occupying Mg positions (site X). It seems probable, that the higher wave number 3670 cm^{-1} corresponds to vibrations of hydroxyls linked essentially to Mg^{2+} while the lower one at 3640 cm^{-1} to these of OH-groups associated with Al^{3+} . Some evidence for these assumptions arises from taking into account the close relationship of vesuvianite and garnet structure:

1. The infra-red spectrum of a hydroandradite from the Totalp serpentine complex, low in Al and relatively rich in Fe^{3+} and Mg, shows in the $3500\text{--}3700\text{ cm}^{-1}$ region two absorption bands: a major one 3525 cm^{-1} and a minor one at 3660 cm^{-1} , no remarkable absorption at between $3600\text{--}3640$ being detected (Peters 1965).

2. The wave number of the main absorption band in hydrogrossular's spectrum is ca. 3625 cm^{-1} (W. Żabiński 1966). In the spectra of hydrogrossulars containing dispersed vesuvianite phase a distinct intensity increase of the above mentioned band has been recorded. It is to be expected, that such a vesuvianite which was exsolved from Ca-Al-hydrogarnet will be low in Mg and Fe.

Special attention should be paid to a weak absorption band near 3170 cm^{-1} . It appears most distinctly on the spectra of green, Fe^{3+} rich vesuvianites. Such a low frequency band certainly arises from OH groups engaged in very short OH...O bonds. It is worthy of notice, that in contradistinction to sheet and chain silicates, whose OH stretching frequencies occur in the $3700\text{--}3500\text{ cm}^{-1}$ region, in the case of orthosilicates containing isolated SiO_4 and Si_2O_7 groups lower frequencies are often met (zoisite 3165 cm^{-1} , clinozoisite 3340 cm^{-1} , epidote 3370 cm^{-1} , chloritoid 3450 and 2980 cm^{-1}). It seems most likely, that the close-packed structures of such silicates, manifested in their higher densities as compared with those of sheet and chain silicates, lead to shortening of

some OH...O distances and thus to lowering of corresponding OH frequencies. Unfortunately, in the case of vesuvianite the exact values of interatomic O—O distances have until now not been determined by X-ray method*, what makes more precise assignment of 3170 cm^{-1} absorption band difficult.

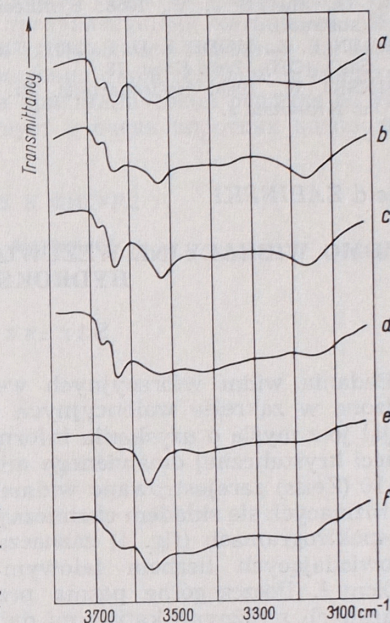


Fig. 1. Infra-red spectra of vesuvianites from

a — Cziklowa, Rumania (yellow, 0.44% FeO, 2.31% Fe_2O_3), b — Hindubagh, Pakistan (green, 0.36% FeO, 4.69% Fe_2O_3), c — Transvaal (green, 0.22% FeO, 2.96% Fe_2O_3), d — Piz Longhin, Switzerland (white, 0.35% FeO, 1.41% Fe_2O_3), e — Monzoni, Italy (brown, 1.78% FeO, 3.12% Fe_2O_3), f — Canzoccoli, Italy (brown, 0.87% FeO, 3.49% Fe_2O_3)

Conclusions. The examination of infra-red spectra of vesuvianites in OH-stretching region gives evidence for the assumption, that their OH-groups are linked to both divalent (Mg^{2+} , Fe^{2+}) and trivalent ions (Al^{3+} , Fe^{3+}). It seems probable, that some OH...O distances are very short. It should be clearly stated that the above presented interpretation of the vesuvianite OH-stretching region is simplified by taking into account the influence on the O—H stretching frequency of the closest cation only and disregarding the force field exerted by more distant ions. Moreover, the author believes that using a spectrometer of higher resolving power (grating spectrometer) more absorption frequencies in the investigated region could be detected.

Acknowledgement. The author wishes to thank Doc. Dr J. Kubisz for critically reading the manuscript and offering valuable suggestions.

* The refinement of vesuvianite structure has recently been announced by Arem (Ito, Arem 1970).

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Witold ŻABIŃSKI

WIDMO WIBRACYJNE WEZUVIANU W ZAKRESIE DRGAŃ GRUP HYDROKSYLOWYCH

Streszczenie

Badania widm wibracyjnych wezuwianu nie były dotychczas prowadzone w zakresie walencyjnych drgań grup hydroksylowych. Autor podjął je z myślą o uzyskaniu informacji o sposobie związania tych grup w sieci krystalicznej omawianego minerału. Za pomocą spektrofotometru UR-10 (Zeiss) zarejestrowano widma wibracyjne kilku okazów wezuwianu, różniących się składem chemicznym (głównie zawartością Fe^{2+} i Fe^{3+}). Na spektrogramach (fig. 1) zaznacza się wyraźnie pięć pasm absorpcji, odpowiadających liczbom falowym 3670, 3640, 3570, 3530 i około 3170 cm^{-1} . Poszczególne pasma przypisać można drganiom grup OH związanych z różnymi kationami dwu- i trójwartościowymi (Mg^{2+} , Al^{3+} , Fe^{2+} , Fe^{3+}). Na szczególną uwagę zasługuje widoczne na niektórych spektrogramach maksimum absorpcji około 3170 cm^{-1} , które zdaje się świadczyć o tym, że w sieci krystalicznej wezuwianu część protonów grup OH uczestniczy w bardzo krótkich wiązaniach wodorowych.

OBJASNIENIE FIGURY

Fig. 1. Widma absorpcyjne wezuwianów w podczerwieni

Витольд ЖАБИНСКИ

ВИБРАЦИОННЫЙ СПЕКТР ВЕЗУВИАНА В ОБЛАСТИ КОЛЕБАНИЙ ГИДРОКСИЛЬНЫХ ГРУПП

Резюме

Исследование вибрационных спектров везувиана в области валентных колебаний гидроксильных групп до сих пор не приводилось. Автор предпринял такие исследования с целью получения данных относительно

способа связи этих групп в кристаллической решетке рассматриваемого минерала. С помощью спектрофотометра УР-10 (Цейсс) были зарегистрированы вибрационные спектры нескольких образцов везувиана, отличающихся химическим составом (главным образом по содержанию Fe^{2+} и Fe^{3+}). На спектрограммах (фиг. 1) отчетливо проявляется пять полос поглощения, соответствующих волновым числам 3670, 3640, 3570, 3530 и около 3170 cm^{-1} . Отдельные полосы можно увязать с колебаниями групп OH, связанных с разными двух- и трехвалентными катионами (Mg^{2+} , Al^{3+} , Fe^{2+} , Fe^{3+}). Особого внимания заслуживает заметный на некоторых спектрограммах максимум поглощения около 3170 cm^{-1} , свидетельствующий, как кажется, о том, что в кристаллической решетке везувиана часть протонов групп OH участвует в очень коротких водородных связях.

ОБЪЯСНЕНИЕ К ФИГУРЕ

Фиг. 1. Инфракрасные спектры поглощения везувианов