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THERMAL DECOMPOSITION OF VESUVIANITE

W. Żabiński[1], *I. Wacławska*[1] *and C. Paluszkiewicz*[2]

[1]Academy of Mining and Metallurgy, Mickiewicza 30, 30–059 Cracow
[2]Jagiellonian University, Regional Laboratory, Ingardena 3, 30–060 Cracow, Poland

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Abstract

The thermal decomposition of vesuvianite was studied by means of thermal, FTIR and X-ray methods. It was found that two structural forms of vesuvianite, a high-temperature (disordered) and a low-temperature (ordered) one, differ distinctly in the mechanism of their decomposition (dehydroxylation). Dehydroxylation of low vesuvianites begins at lower temperatures (ca. 900°C), and the strong endothermic peak with maximum at ca. 1020°C is usually followed by an exothermic peak. Dehydroxylation of high vesuvianites begins at ca. 1000°C, and the DTA curve usually displays two endothermic peaks not followed by an exothermic effect. The crystallization products of vesuvianite are grossular, gehlenite and anorthite. Vesuvianite melts in the temperature range 1100–1200°C.

Keywords: dehydroxylation, structure rebuilding, thermal decomposition, vesuvianite (high, low)

Introduction

Vesuvianite is an ortho-pyrosilicate with a very complicated structure. Its chemical formula is $Ca_{19}(Al,Fe)_{10}(Mg,Fe)_3[Si_2O_7]_4[SiO_4]_{10}(O,OH,F)_{10}$ [1] approximately, which has been discussed and improved [2]. This formula does not include minor elements occurring in vesuvianites, e.g. Ti, Mn, B, Be, REE and others. In the essentially tetragonal vesuvianite structure garnet (grossular, $Ca_3Al_2[SiO_4]_3$-like fragments alternate with partly-filled cation polyhedra lying along 4-fold axes [3]. The cations have at their disposal several non-equivalent sites with different symmetries: 8-coordinated sites (square antiprisms) occupied by calcium, 6-coordinated sites (octahedra) occupied by aluminium, magnesium and iron, 5-coordinated sites (square pyramid) occupied mainly by iron, and 4-coordinated sites (tetrahedra) occupied exclusively by silicon. Two oxygen atoms, denoted O(10) and O(11), are believed to be present in hydroxy groups [4].

The most particular feature of the vesuvianite structure consists of partially filled B (5-coordinated) and C (8-coordinated) sites lying on the 4-fold axes.

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The arrangement of cations in these partially filled sites is the basis of the discrimination of low- (ordered) and high-symmetry (disordered) vesuvianites. The former, occurring in rodingite-like rocks, are formed at relatively low temperature (< 300°C), and are called low vesuvianites, whilst vesuvianites formed in metamorphic calc-silicate rocks at higher temperatures (400–800°C) [3] are named high vesuvianites.

Table 1 List of samples and some thermal data of their dehydroxylation

Specimen, locality	Colour	Weight loss/ Temperature range/°C	wt%	Apparent E_a/ kJ mol^{-1}	Asymmetry index* of DTA peak
		HIGH VESUVIANITES			
Zulova, Czech	brown	1000–1100	2.28	885.0	1.418
Monzoni, Italy	brown	990–1100	3.22	962.4	2.197
Telemark, Norway	blue	1080–1150	1.60	990.6	1.732
		LOW VESUVIANITES			
Transvaal, S. Africa	green	860–1050	2.38	204.5	3.285
Hindubagh, Pakistan	green	820–1090	2.09	184.9	3.348

*Calculated as a ratio of peak area before and after reaching its maximum temperature

Several thermal curves of vesuvianite have been published, but only the investigation by Peters [5] deserves notice. In that study, 3 vesuvianite samples were examined by means of DTA, TG and X-ray powder methods. It was established that the decomposition (dehydroxylation) of vesuvianite, and its recrystallization into grossular, melilite (gehlenite $Ca_2[Al_2SiO_7]$) and an anorthite-like ($Ca[Al_2Si_2O_8]$) phase, take place in two steps, followed by melting of the sample above 1100°C. However, since that time, knowledge relating to the structure and crystal chemistry of vesuvianite has increased considerably and the application of IR spectroscopy, not used by Peters, permits a better insight into the mechanism of thermal decomposition and further transformation of the vesuvianite crystal lattice.

Experimental

Material

Four of the investigated vesuvianite samples came from the mineralogical collection of the Academy of Mining and Metallurgy in Cracow, while one, labelled Vapenna u Zulove, was from the Moravian Museum in Brno (Czech Republic); in this paper, the latter is briefly referred to as Zulova. Two of the above-mentioned samples (Transvaal and Hindubagh) are low vesuvianites occurring in rodingite-like rocks, whereas the other three (Zulova, Monzoni and Telemark) come from calc-silicate metamorphic rocks and are therefore high vesuvianites. This assignment is reasonable, because vesuvianites from Hindubagh and Telemark were also investigated by Allen and Burnham [3], who discriminated the two above-mentioned structural groups of these minerals.

The monomineral character of the samples was checked by X-ray powder and optical methods, and the absence of appreciable amounts of elements not shown in the above vesuvianite formula was demonstrated by means of emission spectroscopy.

Methods

Changes occurring in the vesuvianite samples during heating were studied by using Fourier transform infrared (FTIR) and X-ray methods. For each sample, DTA, TG and DTG curves were first recorded in order to choose appropriate temperatures for taking samples for further IR and X-ray studies. In the following runs, heating was stopped at the established temperatures and the samples were investigated after they had been cooled to room temperature. All vesuvianite samples were studied by IR spectroscopy, and for one high and one low vesuvianite (from Zulowa and Transvaal, respectively), X-ray powder patterns were also taken.

FTIR spectra were recorded with a Digilab FTS-60v spectrometer. Samples were prepared as KBr discs in a proportion of 1 mg sample to 300 mg KBr. The spectra were searched automatically by computer for the maxima and the positions of the peaks.

X-ray powder patterns were obtained with a DRON-3 (USSR) diffractometer, using Ni-filtered CuK$_\alpha$ radiation.

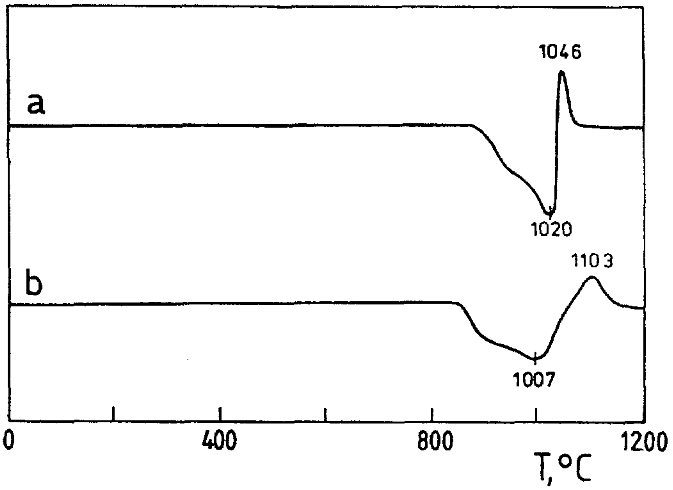

Fig. 1 DTA curves of low vesuvianites; a – Transvaal, b – Hindubagh

Results

The DTA curves of the low (ordered) vesuvianites (Fig. 1) exhibited an endothermic peak with maximum at 1007°C (Hindubagh) or 1020°C (Transvaal), the reaction (dehydroxylation) beginning below 900°C. A DTA curve with similar shape was previously recorded under the same experimental conditions for an evidently low vesuvianite from Glinica (Lower Silesia), occurring in the serpentinite massif, with peak maximum at 1021°C [6]. This peak was followed by an exothermic peak, at 1045°C (Transvaal) or 1103°C (Hindubagh).

The X-ray pattern recorded after the Transvaal sample had been heated to 980°C (Fig. 2), i.e. after a weak inflection on the low-temperature slope of the endothermic peak, showed no visible changes relative to that of the non-heated

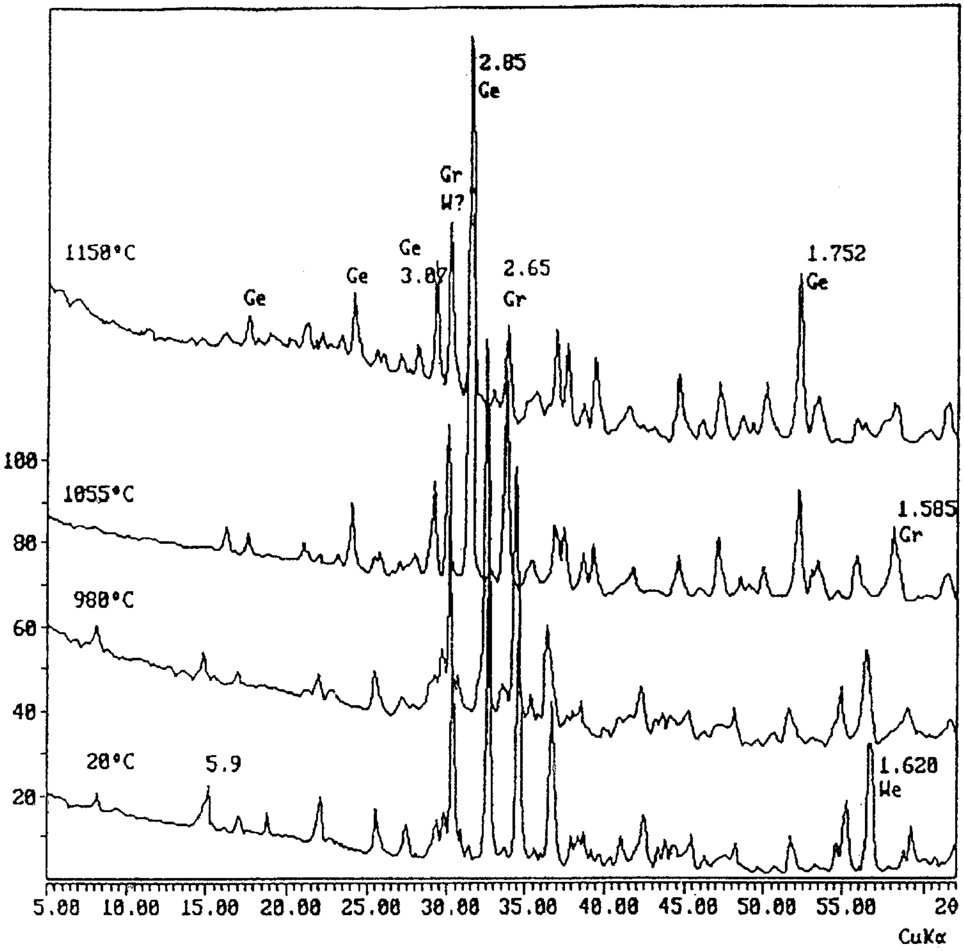

Fig. 2 X-ray powder pattern of low vesuvianite from Transvaal, Ge – gehlenite, Gr – grossular, W – wollastonite, We – vesuvianite

sample. On the other hand, after the sample had been heated to 1055°C, i.e. above the maximum of the exothermic peak, the vesuvianite reflections disappeared and were replaced by those of grossular and gehlenite. At a still higher temperature, the ratio gehlenite/grossular increased. The possible formation of other crystalline phases (e.g. clinoenstatite) is difficult to establish because of the coincidence of reflections.

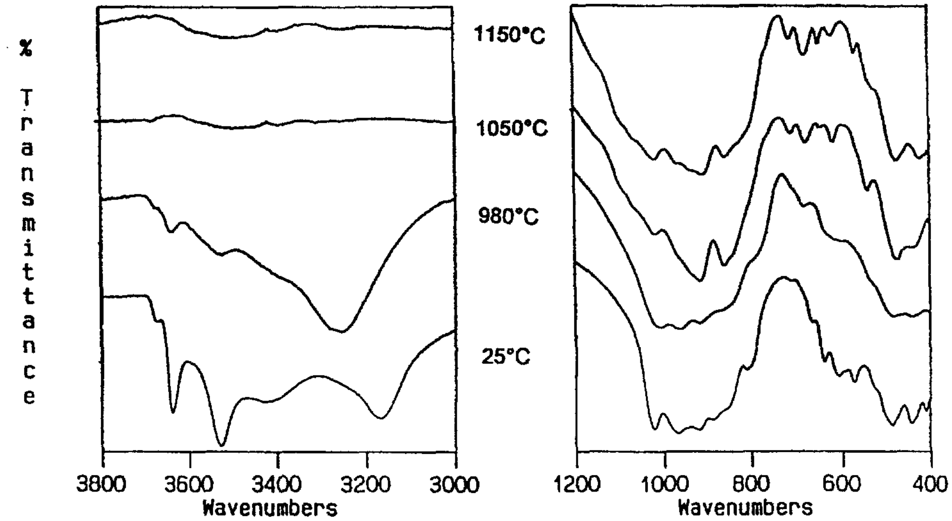

Fig. 3 FTIR spectra of low vesuvianite from Transvaal. In the spectral region 3800–3000 cm^{-1}, the transmittance scale is enlarged 5 times

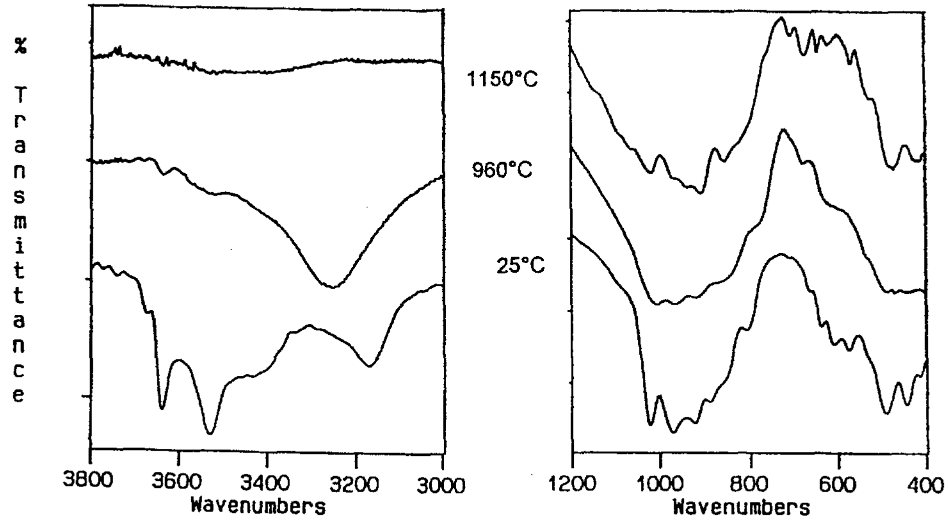

Fig. 4 FTIR spectra of low vesuvianite from Hindubagh. In the spectral region 3800–3000 cm^{-1}, the transmittance scale is enlarged 5 times

In the OH-stretching region of the IR spectra of non-heated samples from Transvaal and Hindubagh (Figs 3 and 4), the positions of the absorption bands, and especially those at 3170 and 3520 cm^{-1}, were typical of low (ordered) vesuvianites [7]. After heating to 980°C there was a distinct shift of the 3170 cm^{-1} band towards higher wavenumbers (ca. 3250 cm^{-1}). The positions of the bands at wavenumbers higher than 3500 cm^{-1} did not change, but their intensities were diminished considerably. In the IR spectra of the samples heated to 1050°C or higher temperatures, OH bands were not visible.

In the region 400–1200 cm^{-1}, the spectra of the samples heated to 960°C were rather similar to those of the non-heated ones, a distinct change being observed after heating to 1050°C (Transvaal). The most intense bands in the region 800–1050 cm^{-1} could be ascribed to grossular and gehlenite [8].

The DTA curves of high (disordered) vesuvianites (Fig. 5) showed two endothermic peaks in the narrow temperature range above 1000°C, the reaction

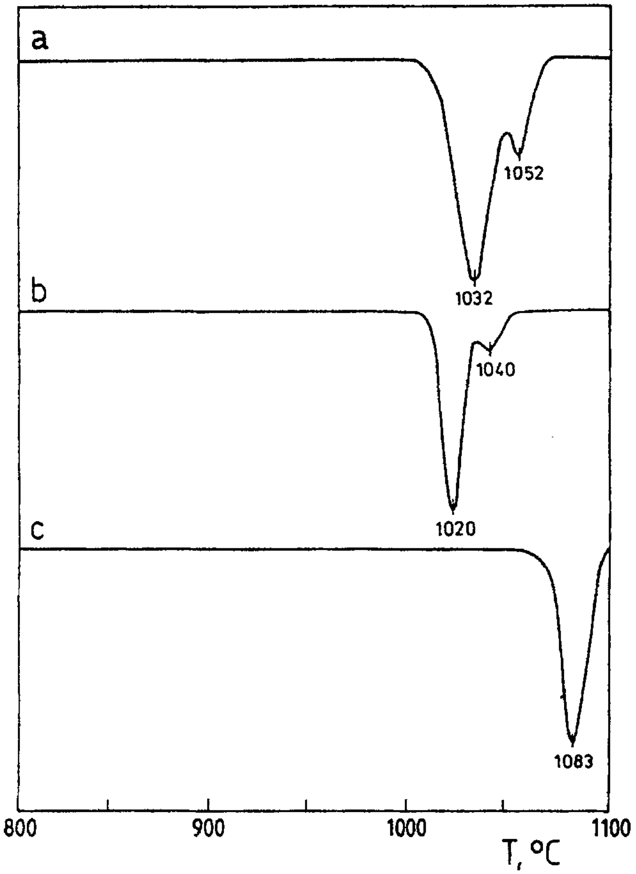

Fig. 5 DTA curves of high vesuvianites a – Zulova, b – Monzoni, c – Telemark

beginning at ca. 1000°C. The different shape of the DTA curve of the Telemark sample may be connected with its specific chemistry (Cu content). The abovementioned endothermic peaks (1020 and 1040°C for the Monzoni, 1032 and 1052°C for the Zulova, and 1083°C for the Telemark sample) were not followed by an exothermic effect. The differences in the presented DTA curves of low and high vesuvianites seem to be distinct. Vesuvianite melts in the temperature range 1100–1200°C.

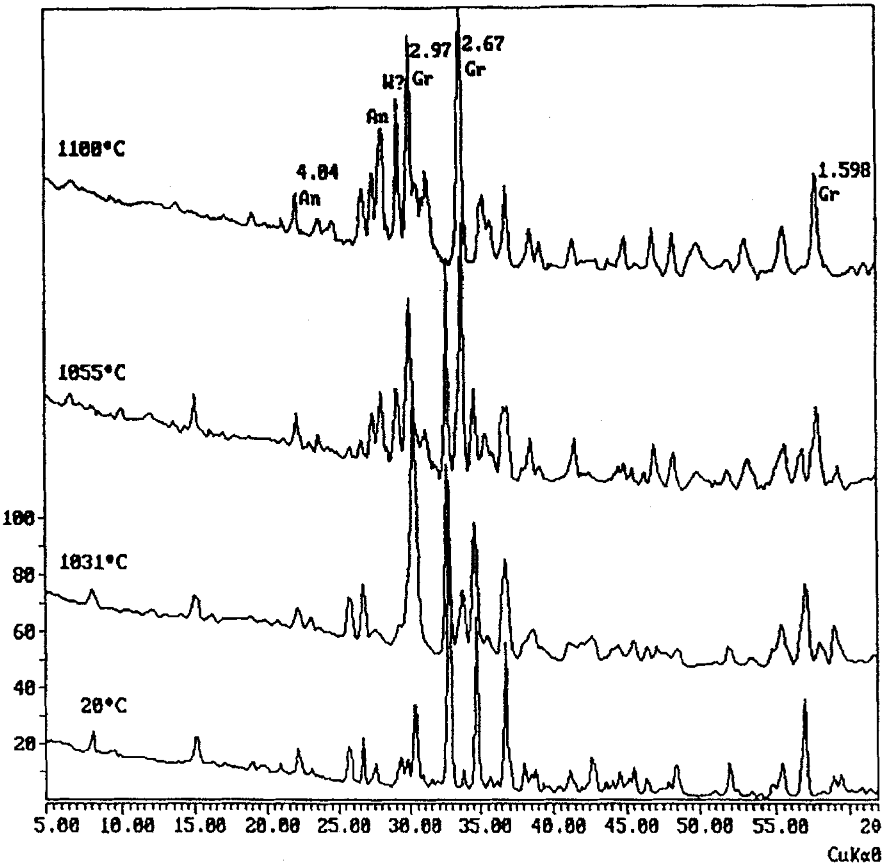

Fig. 6 X-ray powder pattern of high vesuvianite from Zulova, Gr – grossular, An – anorthite, W – wollastonite

The X-ray powder pattern of the sample from Zulova (Fig. 6), after it had been heated to 1031°C (the maximum of the first endothermic peak), revealed that the vesuvianite structure was essentially preserved, but some weak grossular reflections appeared. After heating to the temperature of the maximum of the second endothermic peak (1955°C), the intensities of the grossular reflections were considerably increased and faint reflections of other crystalline phases, most probably anorthite and gehlenite, appeared. At higher temperatures, the vesuvianite reflections completely disappeared and grossular became the predominant product of recrystallization, accompanied by smaller amounts of the above-mentioned subordinate phases.

In contrast with the ordered vesuvianites, in the IR spectra of the disordered ones (Figs 7–9) only a small shift of the ca. 3200 cm^{-1} band was observed,

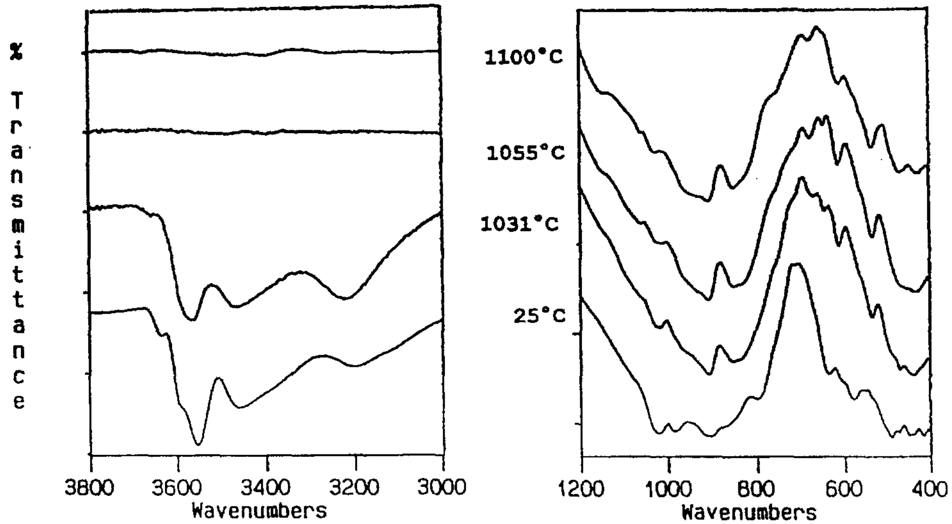

Fig. 7 FTIR spectra of high vesuvianite from Zulova. In the spectral region 3800–3000 cm^{-1}, the transmittance scale is enlarged 5 times

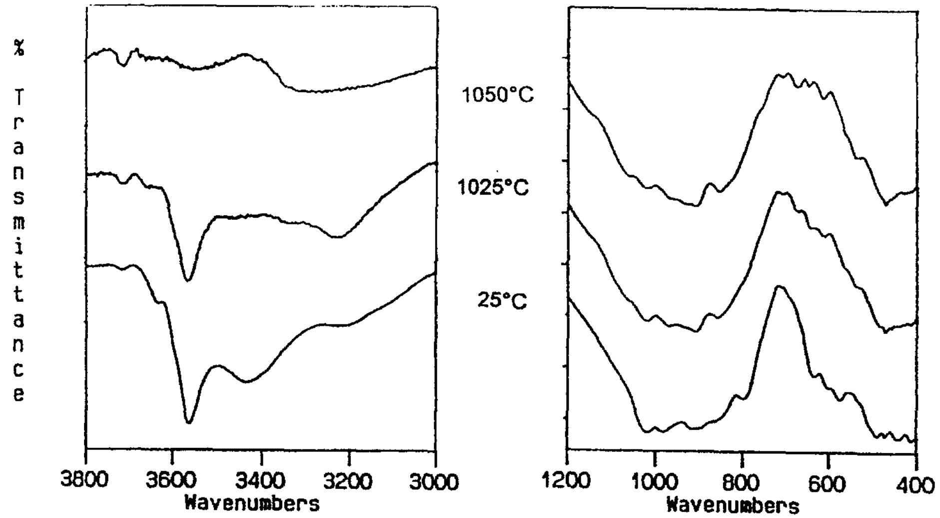

Fig. 8 FTIR spectra of high vesuvianite from Monzoni. In the spectral region 3800–3000 cm^{-1}, the transmittance scale is enlarged 5 times

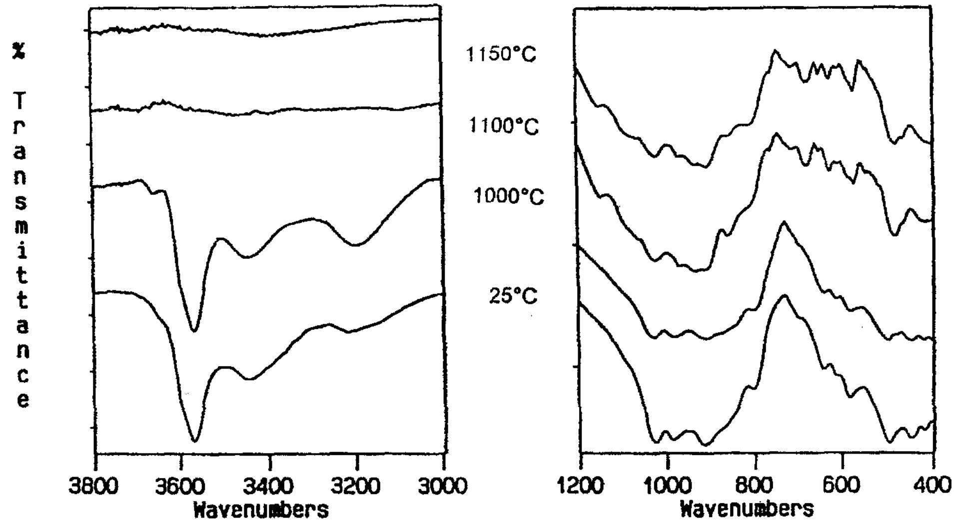

Fig. 9 FTIR spectra of high vesuvianite from Telemark. In the spectral region 3800–3000 cm^{-1}, the transmittance scale is enlarged 5 times

whereas for the vesuvianites from Monzoni and Zulova its intensity was considerably increased. The positions of the bands at ca. 3200 and 3560 cm^{-1} were typical of high (disordered) vesuvianite [7]. The latter did not shift after heating of the sample to above 1000°C, but its intensity diminished (Zulova).

In the region 400–1200 cm^{-1}, the situation was similar to that for ordered vesuvianites. It is noteworthy, however, that a weak band at 1160 cm^{-1} was clearly visible in the spectra of the Zulova and Telemark vesuvianites that had been heated to 1100°C, which could be assigned to the presence of anorthite [8].

Discussion

In spite of the fact that the interpretation of the vesuvianite IR spectrum is far from being completed [7], some conclusions concerning the mechanism of thermal decomposition of this mineral can be established.

First of all, we cannot agree with the opinion [5] that the first endothermic peak in the DTA curve of vesuvianite is due to dehydroxylation of outer parts of its grains, disturbed during grinding of the samples, whereas the second peak is connected with dehydroxylation of the remaining parts of the grains. In our study, all the investigated samples were prepared and all the DTA curves were recorded in the same way, and the observed differences in the shapes of the DTA curves can evidently be related to the structural modifications of vesuvianite.

As already mentioned, dehydroxylation of low (ordered) vesuvianites begins at lower temperature (ca. 900°C) than in the case of high (disordered) ones (ca.

1000°C). The differences in temperature and shape of the endothermal peaks in the DTA curves of vesuvianites are due to the different kinetics of their dehydroxylation. This is manifested in different values of the apparent activation energy E_a (Table 1) calculated according to the method of Arnold [9]. The values of E_a are considerably higher for high vesuvianites than for low ones. It seems, therefore, that ordering of the vesuvianite structure somehow facilitates the formation of H_2O molecules from hydroxy groups, and their diffusion towards the boundaries of domains and finally to grain boundaries. It should be emphasized that the parameter E_a was calculated on the basis of TG and DTA curves recorded under conditions of dynamic heating. Its value is therefore different from that characteristic of the equilibrium state and should be referred to specific measurements conditions. Nevertheless, it seems that for comparison purposes this parameter is useful.

X-ray investigations revealed that the first stage of dehydroxylation does not result in a noticeable change of the vesuvianite structure. The general shape of the IR absorption spectrum in the wavenumber range 400–1200 cm^{-1} is also preserved. Ont he other hand, at least in the case of low vesuvianites, a distinct change in the H-bond length is manifested in the OH region [[7]. This results in a broadening and shift of the 3170 cm^{-1} absorption band towards higher wavenumbers. According to Nakamoto *et al.* [10], the absorption at 3200 cm^{-1} corresponds to a H-bond length of ca. 2.77 Å, and the above-mentioned shift of this band indicates an appreciable elongation of the H-bonds. Int he vesuvianite structure, the distance 2.77 Å could correspond to the $O_{10}H...O_{10}$ bond, stretching along the 4-fold axis [3], but almost the same distance is observed between the oxygen atoms of the $O_{11}H...O_7$ bond [4], O_{11} belonging in common to AlFe and A octahedra in the 'garnetic' part of the vesuvianite crystal lattice. In any case, this shift and broadening are evidently due to a certain disordering of the vesuvianite structure, most probably involving the arrangement of atoms along the 4-fold axes [7]. After the first stage of dehydroxylation, the positions of the 3520 and 3630 cm^{-1} bands are not shifted, but their intensities are considerably diminished or they even disappear. The assignment of the vesuvianite OH stretching bands however, is yet not completed and required further studies.

The second stage of dehyroxylation results in the complete disappearance of vesuvianite X-ray reflections (Transvaal) or their distinct weakening, relating to newly-formed crystal phases (Zulova). The FTIR spectra no longer show OH bands and in the region 400–1200 cm^{-1} their shape is evidently changed. It is worthy to note that the recrystallization of low vesuvianites is manifested in the DTA curve by a weak but distinct exothermic peak, which does not appear for high vesuvianites. The main products of recrystallization in agreement with [5], are gehlenite, grossular and anorthite. A small admixture of quartz (a few wt.%) in the Zulova vesuvianite was probably the reason for its preferred recrystallization into grossular, while in the case of the Transvaal sample the main product of recrystallization was gehlenite, which contains less silica than grossular.

The thermal decomposition of vesuvianite is certainly an example of a topotactic reaction, since a close relationship exists between the crystal structures of vesuvianite (precursor) and grossular (one of the main products) [11]). It is also noteworthy that the main decomposition products of an ortho-pyrosilicate (vesuvianite) are orthosilicate (grossular) and pyrosilicate (gehlenite). The state of ordering of the vesuvianite structure must influence the ability of its chemical components to undergo redistribution, preceding the crystallization of new products. In the first stage of dehydroxylation, this is manifested in a lengthening of the H-bonds in low (ordered) vesuvianites. The above-mentioned facts could explain the observed phenomenon that the completion of dehydroxylation of vesuvianites connected with their recrystallization takes place at lower temperature for ordered structures than for disordered ones. Nevertheless, for a more detailed explanation of the mechanism of thermal decomposition of vesuvianite, further investigations are necessary.

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References

1 W. A. Deer, R. A. Howie and J. Zussman, Rock-forming minerals. Orthosilicates. Longmans, London 1982.
2 L. A. Groat, F. C. Hawthorne and T. S. Ercit, Canadian Miner., 30 (1992) 19.
3 F. M. Allen and Ch. W. Burnham, Canadian Miner., 30 (1992) 1.
4 A. Yoshiasa and T. Matsumoto, Miner. Journal, 13 (1986) 1.
5 T. Peters, Schweiz. Min. Petr. Mitt., 41 (1961) 325.
6 B. Przybyłowska, Geologia, 17 (1991) 87.
7 C. Paluszkiewicz and W. Żabiński, 6th Austrian Hungarian Intern. Conference on Vibrational Spectroscopy, April 6–8, 1994, Univ. of Veszprém, Hungary, Abstract P37.
8 H. Moenke, Mineralspektren, Berlin, 1962.
9 M. Arnold, G. E. Veress, J. Paulik and F. Paulik, J. Thermal Anal., 17 (1979) 507.
10 K. Nakamoto, M. Margoshes and R. E. Rundle, J. Amer. Cer. Soc., 77 (1955) 6480.
11 L. Stoch, J. Thermal Anal., 40 (1993) 107.