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THERMAL TRANSFORMATIONS OF SYNTHETIC PYROPHYLLITE

TERESA ZAREMBA

Silesian Technical University, Institute of Chemistry, Inorganic Technology and Electrochemistry, 44-100 Gliwice, Poland

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Abstract: Thermal transformations of synthetic pyrophyllite prepared by hydrothermal reaction of kaolinite and silica were investigated, using infrared spectroscopy, X-ray diffraction and thermal analysis. It has been found that an intermediate phase, i.e. dehydroxylate of pyrophyllite, is formed as a result of heating pyrophyllite within the range 500 to 800 °C. A dehydroxylate of pyrophyllite is generally of the same structure as pyrophyllite. Decomposition of dehydroxylate into mullite and cristobalite starts at about 1000 °C. The thermal transformations of synthetic pyrophyllite are compared with the thermal stability of natural pyrophyllite from South Africa.

Key words: synthetic pyrophyllite, natural pyrophyllite, thermal transformations, infrared spectroscopy, XRD, DTA, TG.

Introduction

Pyrophyllite $Al_2[Si_4O_{10}](OH)_2$, layer aluminium silicate of type 2:1, is a mineral characterized by high resistance to chemical agents, low electrical conductivity, low conduction of heat, very low compressibility and transmission of pressure in a nearly hydrostatic manner. Advantageous properties of pyrophyllite permit its use it in different branches of industry. It is an important ceramic raw material, especially to manufacture materials for electrical and thermal insulation. This mineral is widely used for production of containers, the so-called ceramic shields, gasketing, insulating and transmitting pressure, in which high-temperature and high-pressure syntheses are carried out (e.g. diamond synthesis from graphite). These containers are bored on machine tools from blocks or pressed powders of chemically bounded minerals (Chao & Ruoff 1970; Kirfel & Neuhaus 1971; Wisniewski et al. 1980).

There are no pyrophyllite deposits in Poland that would be suitable for industrial exploitation. Pyrophyllite from South Africa is employed in the domestic production of synthetic diamond for ceramic shields. The shields contain elements made of raw pyrophyllite and pyrophyllite calcined at 875 °C i.e. of pyrophyllite dehydroxylate.

Thermal transformations of the pyrophyllite mineral have been studied by a number of workers (Nakahira & Kato 1964; Hennicke & Niesel 1965; Bialoskórski 1970; Brindley & Wardle 1970; Sircar & Roy 1973; Schomburg 1985; Sánchez-Soto & Pérez-Rodriquez 1989a,b; Pérez-Rodriquez & Sánchez-Soto 1991; Pérez-Maqueda et al. 1993). Initially, dehydroxylation of pyrophyllite was examined from the point of view of work on preparation of mullite from layer dioctahedral silicates, and then attention was paid to the mechanism of dehydration reaction taking it as a model for such reactions in minerals having pyrophyllite-like structures i.e. some montmorillonites and micas (Heller 1962; Heller et al. 1962; Wiedmann 1969; Vedder & Wilkins 1969; Guggenheim et al. 1987). Taking into consideration a relatively simple chemical formula of pyrophyllite it was presumed that the mechanism of its dehydroxylation could be examined more easily than the mechanism of dehydroxylation in other minerals with similar structure but having a more complex composition. These investigations were also expected to give further information on the causes of differences in the thermal alterations of di- and trioctahedral silicates. In respect of these properties, pyrophyllite can be grouped within other dioctahedral silicates and so, for example with kaolinite. In this group, unlike among trioctahedral silicates, the dehydration process is characterized by occurrence of intermediate phases which appear at the end of so-called rapid dehydration. This also applies to pyrophyllite which, after being heated to 700–800 °C, yields a crystalline transmediate phase, usually called anhydride or dehydroxylate of pyrophyllite, from which mullite and cristobalite are formed at elevated temperatures.

At the Institute of Chemistry, Inorganic Technology and Electrochemistry of the Silesian Technical University studies have been undertaken on the possibility of preparing synthetic pyrophyllite by a hydrothermal reaction from aluminium hydroxide and silica mixtures, kaolinite and silica mixtures, and as a result of hydrothermal decomposition of the kaolinite itself (Starczewski & Zaremba 1986, 1987, 1988; Zaremba 1991, 1995). The best results, i.e. complete reaction of the substrates, were achieved in pyrophyllite synthesis from mixtures of kaolins and amorphous silicas.

In this study, the results of investigations on thermal transformations of synthetic pyrophyllite are presented.

Experimental

The synthetic pyrophyllite was obtained by hydrothermal reaction of kaolinite and silica. Washed kaolin from Sedlec (Czech Republic) and waste amorphous silica remaining from ferrosilicon production at the Laziska Steel Mill were used as raw materials (Starczewski & Zaremba 1987, 1988). The substrates were mixed in a ball mill for 5 hours to obtain accurate homogenization. The mixture was pressed to form briquettes of diameter 30 mm and height of 30 mm. The pressed specimens were heated in a laboratory autoclave under conditions

of temperature 400 °C, water-vapor pressure 30 MPa and time 4 days. The phase composition of the products of the hydrothermal process was studied by infrared absorption spectroscopy, X-ray diffraction and thermal analysis.

Examinations of thermal decomposition of the synthetic pyrophyllite in comparison with natural pyrophyllite from South Africa were carried out within the range of 400–1400 °C. Samples were heated in air for one hour to temperatures of 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 1000, 1100, 1200, 1300 and 1400 °C, and identified using infrared absorption spectroscopy and X-ray diffraction.

Infrared absorption spectra were recorded in the range from 400 to 4000 cm^{-1} with a Carl Zeiss infrared spectrophotometer, model UR-20, using a KBr disc technique.

X-ray powder diffraction analyses were performed in a diffractometer, model DRON-2,0, using Ni-filtered CuKα radiation.

Thermal analyses (DTA, TG) of natural and synthetic pyrophyllite samples were performed with a Derivatograph OD-102 (MOM Budapest) under the following conditions: weight of samples 600 mg; heating rate 10 deg.min^{-1}; atmosphere: air, static.

Results and discussion

Fig. 1 shows infrared absorption spectra of natural pyrophyllite from South Africa and synthetic pyrophyllite. The spectrum of the synthetic pyrophyllite shows typical assignment of natural pyrophyllite sample. The weak band at 3620 cm^{-1} in the spectrum of natural pyrophyllite result from the presence of clay minerals.

X-ray diffraction patterns of synthetic and natural pyrophyllite are shown in Fig. 2. Fig. 3 shows thermogravimetric and differential thermal analysis curves of synthetic and natural pyrophyllite.

Pyrophyllite is the main component of the synthetic material obtained. There are also small amounts of muscovite and quartz from the initial Sedlec kaolin. The relatively broadened peaks observed in the diffraction pattern of the synthetic pyrophyllite compare to natural pyrophyllite may be evidence of very fine crystals and not well ordered crystalline structure. Thermal analysis as well as X-ray tests of natural pyrophyllite from South Africa showed that it contained about 90 % of pyrophyllite mineral and the rest contained mainly clay minerals (kaolinite) and diaspore.

The DTA curve for natural pyrophyllite shows an extensive endothermic peak in the temperature range of 600–850 °C with the maximum within the range 700–720 °C, corresponding to loss of constitutional water, and a small exothermic peak at about 1100 °C, where decomposition to mullite and cristobalite takes place. The endothermic peak with the maximum at about 530 °C is related to dehydroxylation of minerals accompanying pyrophyllite (diaspore, clay minerals).

Two endothermic peaks related to dehydroxylation and exothermic peak at about 1010 °C (decomposition to mullite and cristobalite) are observed on the DTA curve of the synthetic pyrophyllite. Two endothermic peaks occur in the temperature range of 450–800 °C and the maxima are reached at about 590 and 750 °C. A weight loss in that temperature range is 4.9 %; theoretical water content in pyrophyllite $Al_2O_3.4SiO_2.H_2O$ is 5.0 %.

The IR spectrum of synthetic pyrophyllite sample heated to a temperature of 400 °C (Fig. 4) is practically analogous to that of non-heated pyrophyllite (Fig. 1). A sample heated to

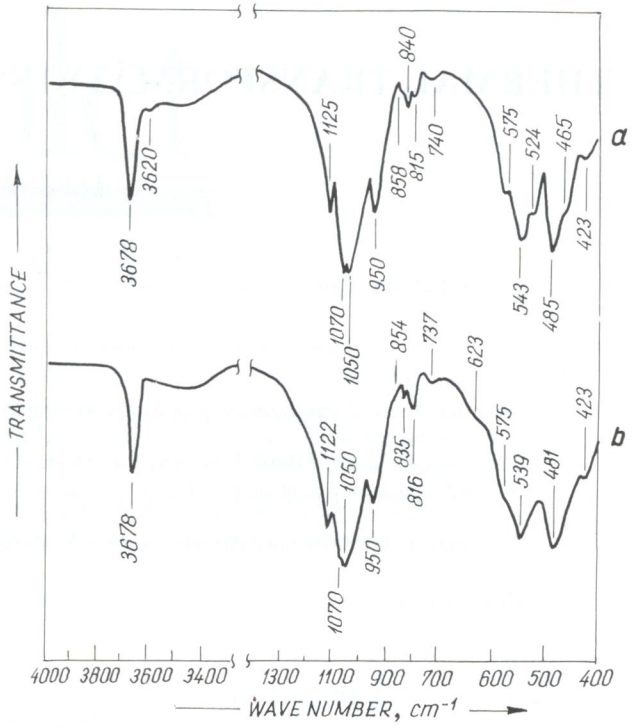

Fig. 1. IR spectra: a) natural pyrophyllite; b) synthetic pyrophyllite.

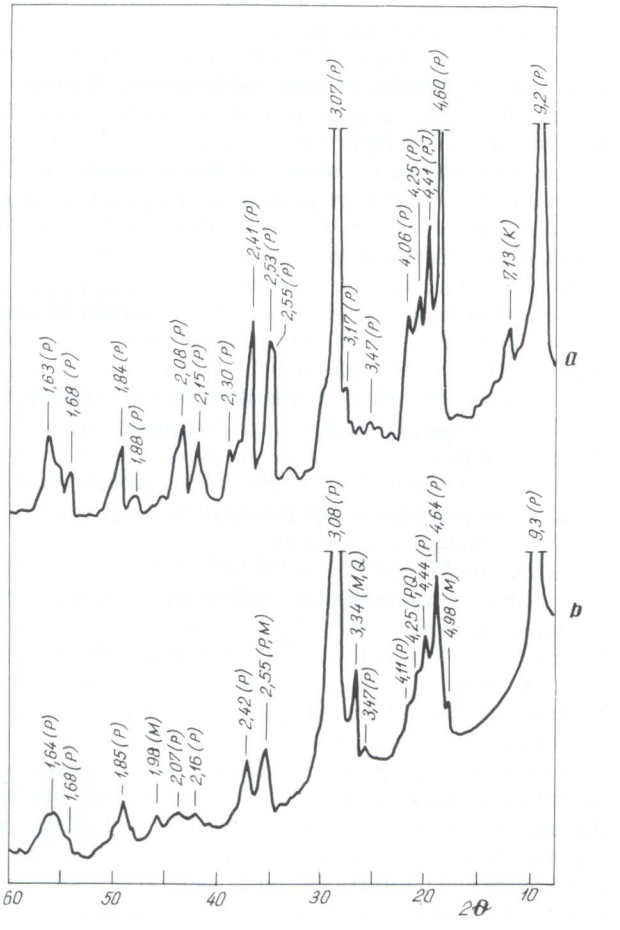

Fig. 2. X-ray diffraction patterns: a) natural pyrophyllite; b) synthetic pyrophyllite. **I** – illite, **K** – kaolinite, **M** – muscovite, **P** – pyrophyllite, **Q** – quartz.

500 °C already reveals a partial dehydroxylation; the spectrum shows a decrease in the intensity of the bands 3678, 950 and 539 cm^{-1} with coincident occurrence of a new weak band at 568 cm^{-1}. Further heating at temperatures of 550–650 °C causes further dehydroxylation. As the dehydroxylation reaction proceeds in pyrophyllite samples heated to elevated temperatures, a systematic decrease in the intensity of the band at 950 cm^{-1} due to Al-O-H bending vibrations and the band at 3678 cm^{-1} corresponding to O-H stretching vibrations, can be observed in the spectra. A systematic decrease in the intensity of the band at 539 cm^{-1} associated with Al-O/Si/ vibrations is also observed and a new band at 568 cm^{-1} occurs as a result of structural changes in the octahedral layer. Well-marked advancement of dehydroxylation reaction can be seen in the spectrum of sample heated to 700 °C. The bands due to OH vibrations and the band at 539 cm^{-1} disappeared almost completely, and at the same time a strong band occurs at 568 cm^{-1}.

The dehydroxylation of the synthetic pyrophyllite ends at 800 °C and a new phase is formed i.e. pyrophyllite dehydroxylate with specified infrared absorption bands. Within the range of 500–750 °C this phase co-exists with pyrophyllite, which is reflected in the presence of the bands assigned to vibrations of both phases e.g. bands at 539 and 568 cm^{-1} (Fig. 4).

The dehydroxylation of the natural pyrophyllite from South Africa begins at slightly elevated temperatures, i.e. in the range of 550–600 °C and ends at 850 °C (Figs. 3 and 5).

The similarity of spectra of both pyrophyllites and their dehydroxylates in the region of Si-O-Si stretching vibrations is thought to be due to the structural resemblance of the tetrahedral layer of dehydroxylate and pyrophyllite. This is confirmed by X-ray examination. In principle, diffraction patterns of synthetic and natural pyrophyllite heated to 900 °C (Fig. 6) indicate only an increase in the corresponding interplanar spacings within the structure of pyrophyllite dehydroxylate in relation to the interplanar spacings of pyrophyllite (Fig. 2). Preservation of the same type of structure with a decreased quantity of atoms in the unit cell of pyrophyllite — removing H_2O molecules during dehydroxylation — provides evidence that symmetry is reduced and stresses occur in the dehydroxylate structure.

In the 400–700 cm^{-1} region, larger changes are observed in the dehydroxylate spectra, i.e. bands are observed at higher wave numbers and it is more difficult to find equivalents of pyrophyllite bands. Apart from four bands located below 500 cm^{-1} and ascribed to bending vibrations of the tetrahedral layer, two more bands are observed, located at relatively high wave numbers. The first band at about 570 cm^{-1} corresponding to Al-O/Si/ vibrations (Bialoskórski 1971) is shifted by about 30 cm^{-1} higher than the corresponding band in pyrophyllite, which could be evidence of a shorter Al-O/Si/ bond in the dehydroxylate than in the pyrophyllite. A second band at about 655 cm^{-1} is typical of Al-O bonds that exist in aluminium spinels, and its presence in the spectrum of pyrophyllite dehydroxylate is probably a result of decreasing the coordination number of aluminium cations, and thus shortening the Al-O/Al/ bonds. The same bands were also observed for dehydroxylated montmorillonites (Tennakoon et al. 1986). At the present level of investigations, it seems that occurrence of 5-coordinated Al in pyrophyllite dehydroxylate is the most probable alternative of the cationic layer structure of dehydroxylate. To generalize, it can be noted that the dehydroxylation causes a change in the coordination geometry round the aluminium. The tetrahedral layer adapts to these changes by

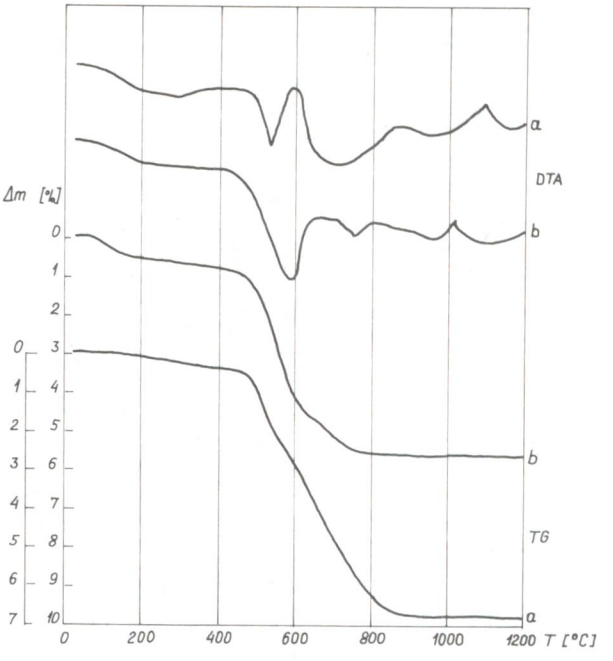

Fig. 3. Thermogravimetric and differential thermal analysis curves: **a** — natural pyrophyllite; **b** — synthetic pyrophyllite.

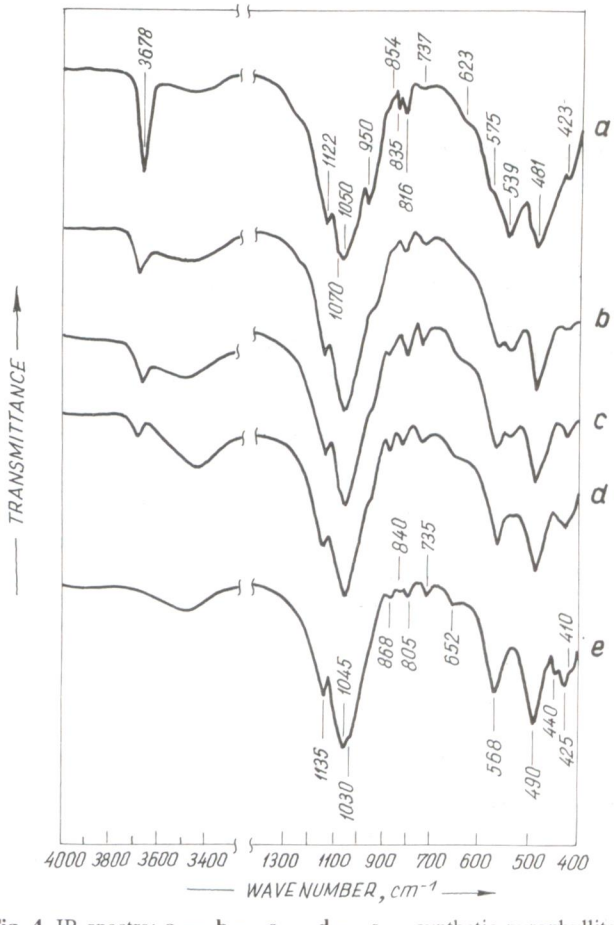

Fig. 4. IR spectra: **a** —, **b** —, **c** —, **d** —, **e** — synthetic pyrophyllite heated to 400, 500, 600, 700 and 800 °C, respectively.

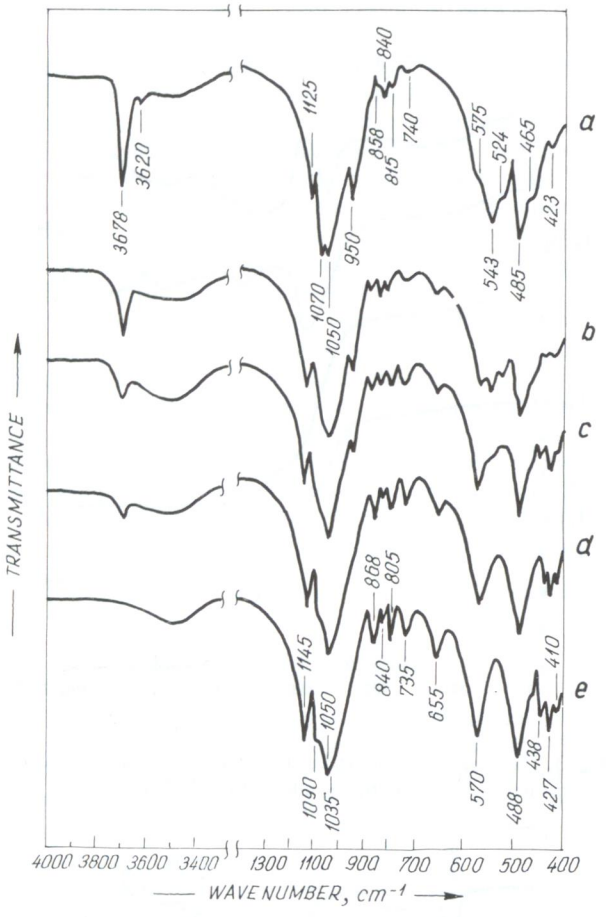

Fig. 5. IR spectra: **a** —, **b** —, **c** —, **d** —, **e** — natural pyrophyllite heated to 500, 600, 650, 700 and 800 °C, respectively.

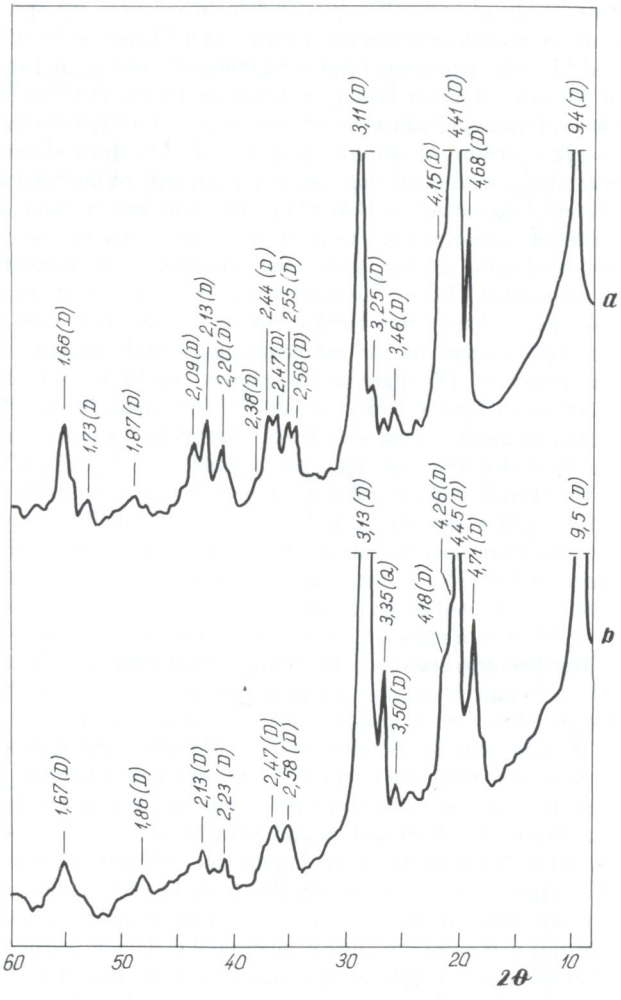

Fig. 6. X-ray diffraction patterns: **a** — natural pyrophyllite heated to 900 °C; **b** — synthetic pyrophyllite heated to 900 °C. **D** — dehydroxylate, **Q** — quartz.

small displacements possibly because of the large elasticity of the Si-O-Si bridge.

The phase that has been formed after pyrophyllite dehydroxylation is stable up to 1000 °C. Decomposition of natural pyrophyllite into mullite and cristobalite begins at 1000-1100 °C, while the decomposition of synthetic pyrophyllite dehydroxylate already begins at 1000 °C. Spectra of the synthetic and natural pyrophyllites heated at 900-1400 °C are reproduced in Figs. 7 and 8. Cristobalite is characterized by the bands at about 1100, 800, 620 and 480 cm^{-1}. A weak and broad band at 830-960 cm^{-1} reveals the presence of mullite; the mullite bands at 1176 and 1136 cm^{-1} in the spectra are screened by the strong 1100 cm^{-1} band of cristobalite.

The presence of cristobalite and mullite in the tested samples after heating at 1400 °C is also confirmed by X-ray investigations (Fig. 9).

Conclusions

1. The dehydroxylation of the synthetic pyrophyllite begins at about 500 °C and terminates at 750-800 °C with the formation of a new phase i.e. pyrophyllite dehydroxylate of specified infrared absorption bands, without any other decomposition products except H_2O vapour. Within the range of 500-700 °C this phase co-exists with pyrophyllite, which is proved by the occurrence of corresponding absorption bands in the samples spectra. Dehydroxylation of the natural pyrophyllite from South Africa begins at 550-600 °C and ends at 800-850 °C. Absence of absorption bands 950 and 3678 cm^{-1}, due to OH vibrations, in the infrared absorption spectra of both samples shows the complete dehydroxylation of synthetic and natural pyrophyllite.

2. The similarity of the spectra of both pyrophyllites and their dehydroxylates in the region of Si-O-Si stretching vibrations is thought to be due to structural resemblance of the tetrahedral layer of dehydroxylate and pyrophyllite. This is confirmed by X-ray examinations of dehydroxylate samples which, in principle, indicate only an increase in the corresponding interplanar spacings within the structure of pyrophyllite dehydroxylate in relation to the interplanar spacings of pyrophyllite.

3. In the 400-700 cm^{-1} range, for dehydroxylate spectra, bands are observed at lower wave lengths and equivalents of pyrophyllite bands are more difficult to find. The band at about 570 cm^{-1} corresponding to Al-O/Si/ vibrations is shifted by about 30 cm^{-1} higher than the corresponding band in pyrophyllite, which could be evidence of a shorter Al-O/Si/ bond in the dehydroxylate than in pyrophyllite. The band at about 655 cm^{-1} is typical for Al-O bonds that exist in aluminium spinels, and its presence in the spectrum of pyrophyllite dehy-

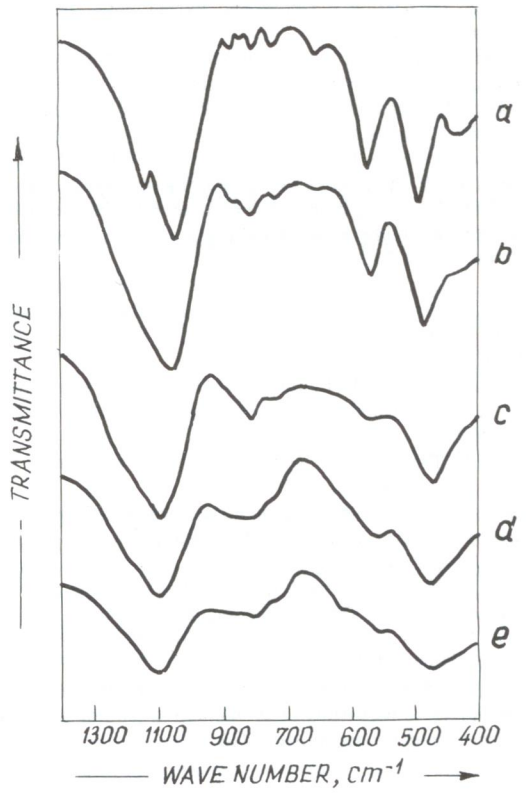

Fig. 7. IR spectra: **a** —, **b** —, **c** —, **d** —, **e** — synthetic pyrophyllite heated to 900, 1000, 1100, 1200 and 1400 °C, respectively.

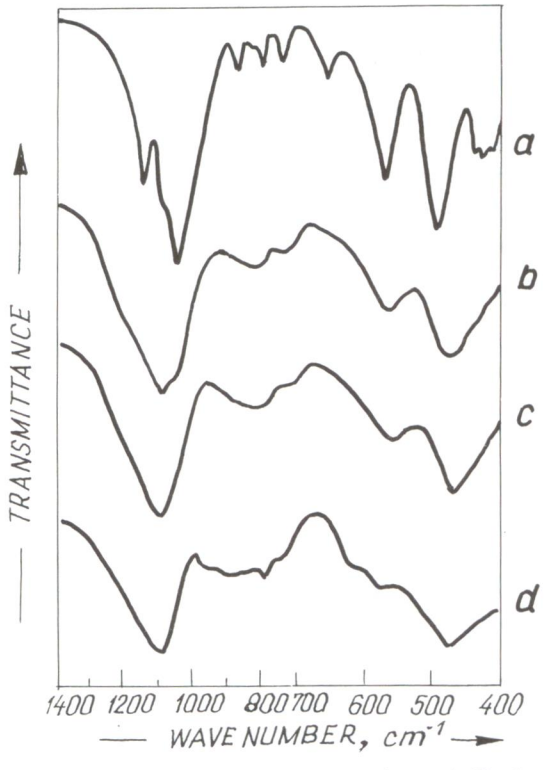

Fig. 8. IR spectra: **a** —, **b** —, **c** —, **d** — natural pyrophyllite heated to 1000, 1100, 1200 and 1400 °C, respectively.

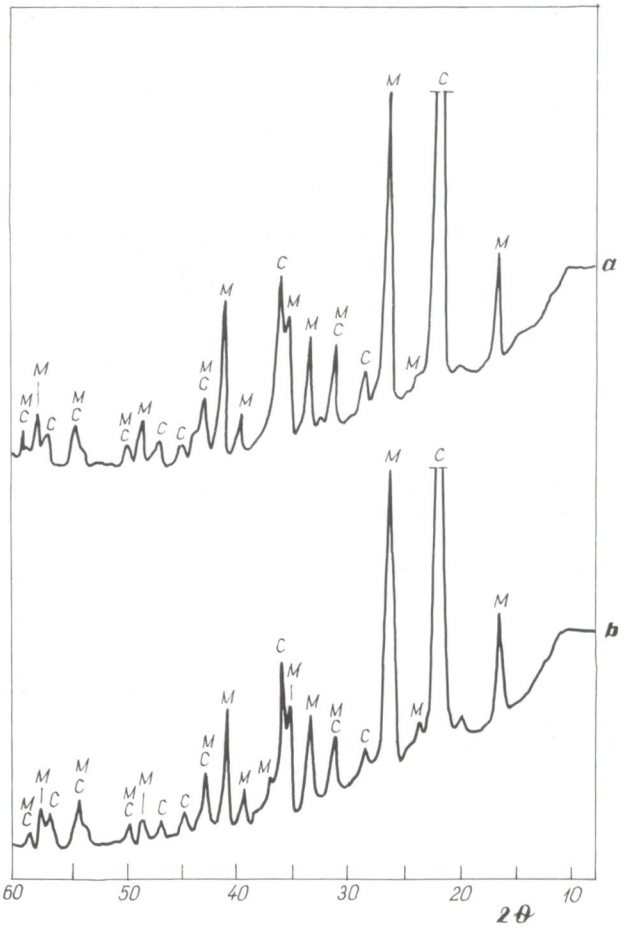

Fig. 9. X-ray diffraction patterns: **a** — natural pyrophyllite heated to 1400 °C; **b** — synthetic pyrophyllite heated to 1400 °C. **C** — cristobalite, **M** — mullite.

droxylate is probably a result of decreasing the Al^{3+} coordination number (the formation of 5-coordinated Al), and thus shortening the Al-O bonds. The dehydroxylation causes a change in the coordination geometry round the aluminium; the tetrahedral layer adapts to those changes.

4. After burning both natural and synthetic pyrophyllite at 1400 °C, a mullite-cristobalite ceramic material is formed; decomposition of synthetic pyrophyllite dehydroxylate into mullite and cristobalite begins at 1000 °C, whereas that of natural pyrophyllite dehydroxylate begins at 1000-1100 °C.

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