

# FT-IR studies of zeolites from different structural groups

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## Introduction

Natural zeolites are a group of hydrated tecto-aluminosilicates with a specific and highly differentiated structure containing voids filled with ions and water molecules having a high freedom of movement.

Primary building unit (PBU) of zeolites are tetrahedra linked by oxygen bridges and forming the so-called secondary building units (SBU), which are used for organize all of zeolites structures to the seven major groups in the currently used nomenclature (Fig. 1) [1]. These units combine with each other form a loose structure characterized by the presence of channels and chambers in different shapes (but the specific dimensions), which determine the types of framework types marked with a three-letter code [2]. Division because of the SBU is fairly conventional, because in the structure may have more than one type of SBU. Classification of zeolites based on SBU, although widely used, it is not perfect.

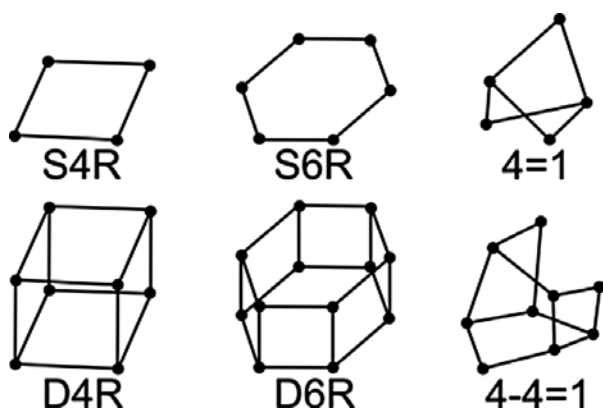


Fig. 1. Secondary building units (SBU) occurring in the zeolites structures [3]

In this paper the spectrum of zeolites belonging to six major structural groups with reference to the characteristic elements of their structure are discussed. It was shown that there is a relationship between the type of SBU and the vibrational spectrum. Assignment of bands was made on the basis of previous works [4, 5], in which, based on *ab initio* calculations, visualization of vibration obtained for the structural units composed of single and double 4- and 6-membered rings terminated by protons and various ions had been analyzed. Identification of these bands provides information related to the construction of the aluminosilicate framework of zeolite.

## Experimental

Infrared spectra of minerals were measured on a Bruker Vertex 70V spectrometer. Spectra were collected in the mid (4000–400  $\text{cm}^{-1}$ ) and far (4000–400  $\text{cm}^{-1}$ ) infrared region after 256 scans at 2  $\text{cm}^{-1}$  resolution. Samples were prepared using the standard KBr or polyethylene (Merck) pellets method.

The name of natural zeolites used in this study, their typical formulae, IUPAC code, the kind of SBU and the number of ring members created by alumino- and silicoxygen tetrahedra dominating a given structure are listed in Table I. X-ray diffraction was applied to identify the phases present in the samples [6].

Table I

List of used zeolites

| Mineral name   | Typical formula  | IUPAC code | SBU group | Rings          |
|----------------|--|------------|-----------|----------------|
| Analcime       | $\text{Na}_{16}[\text{Al}_{16}\text{Si}_{32}\text{O}_{96}] \cdot 16\text{H}_2\text{O}$                             | ANA        | S4R       | 4, 6, 8        |
| Phillipsite    | $\text{K}_2(\text{Ca}_{0.5}\text{Na})[\text{Al}_6\text{Si}_{10}\text{O}_{32}] \cdot 12\text{H}_2\text{O}$          | PHI        | S4R       | 4, 8           |
| Harmotome      | $\text{Ba}(\text{Ca}_{0.5}\text{Na})[\text{Al}_5\text{Si}_{11}\text{O}_{32}] \cdot 12\text{H}_2\text{O}$           | PHI        | S4R       | 4, 8           |
| Gismondite     | $\text{Ca}_4[\text{Al}_8\text{Si}_8\text{O}_{32}] \cdot 16\text{H}_2\text{O}$                                      | GIS        | S4R       | 4, 8           |
| Laumontite     | $\text{Ca}_4[\text{Al}_8\text{Si}_6\text{O}_{48}] \cdot 16\text{H}_2\text{O}$                                      | LAU        | S4R       | 4, 6, 10       |
| Zeolite A      | $\text{Na}_{12}[\text{Al}_{24}\text{Si}_{24}\text{O}_{48}] \cdot 27\text{H}_2\text{O}$                             | LTA        | D4R       | 4, 6, 8        |
| Cancrinite     | $\text{Na}_6\text{Ca}[\text{CO}_3(\text{AlSiO}_4)_6] \cdot 2\text{H}_2\text{O}$                                    | CAN        | S6R       | 4, 6, 12       |
| Levyne         | $\text{NaCa}_{2.5}[\text{Al}_6\text{Si}_{12}\text{O}_{36}] \cdot 18\text{H}_2\text{O}$                             | LEV        | S6R       | 4, 6, 8        |
| Offretite      | $\text{KCaMg}[\text{Al}_5\text{Si}_{13}\text{O}_{36}] \cdot 15\text{H}_2\text{O}$                                  | OFF        | S6R       | 4, 6, 8, 12    |
| Chabasite      | $\text{Ca}_2[\text{Al}_4\text{Si}_8\text{O}_{24}] \cdot 12\text{H}_2\text{O}$                                      | CHA        | D6R       | 4, 6, 8        |
| Faujasite      | $\text{Na}_{20}\text{Ca}_{12}\text{Mg}_8[\text{Al}_{60}\text{Si}_{132}\text{O}_{384}] \cdot 235\text{H}_2\text{O}$ | FAU        | D6R       | 4, 6, 12       |
| Gmelinite      | $\text{Na}_8[\text{Al}_8\text{Si}_{16}\text{O}_{48}] \cdot 22\text{H}_2\text{O}$                                   | GME        | D6R       | 4, 6, 8, 12    |
| Edingtonite    | $\text{Ba}_2[\text{Al}_4\text{Si}_6\text{O}_{20}] \cdot 8\text{H}_2\text{O}$                                       | EDI        | 4=1       | 4, 8           |
| Thomsonite     | $\text{Na}_4\text{Ca}_8[\text{Al}_{20}\text{Si}_{20}\text{O}_{80}] \cdot 24\text{H}_2\text{O}$                     | THO        | 4=1       | 4, 8           |
| Skolecite      | $\text{Ca}_8[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}] \cdot 24\text{H}_2\text{O}$                                | NAT        | 4=1       | 4, 8           |
| Natrolite      | $\text{Na}_{16}[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}] \cdot 16\text{H}_2\text{O}$                             | NAT        | 4=1       | 4, 8           |
| Brewsterite    | $\text{Sr}_2[\text{Al}_4\text{Si}_{12}\text{O}_{32}] \cdot 10\text{H}_2\text{O}$                                   | BRE        | 4-4=1     | 4, 5, 6, 8     |
| Stilbite       | $\text{NaCa}_4[\text{Al}_9\text{Si}_{27}\text{O}_{72}] \cdot 30\text{H}_2\text{O}$                                 | STI        | 4-4=1     | 4, 5, 6, 8, 10 |
| Heulandite     | $(\text{K}, \text{Na})\text{Ca}_4[\text{Al}_9\text{Si}_{27}\text{O}_{72}] \cdot 24\text{H}_2\text{O}$              | HEU        | 4-4=1     | 4, 5, 8, 10    |
| Clinoptilolite | $(\text{K}_2, \text{Na}_2, \text{Ca})_3[\text{Al}_6\text{Si}_{30}\text{O}_{72}] \cdot 20\text{H}_2\text{O}$        | HEU        | 4-4=1     | 4, 5, 8, 10    |

## Results and discussion

The IR spectra for six out of seven main zeolites structural groups are presented in Figures 2–7. The bands associated with vibrations of typical SBU are indicated schematically in Figures.

In the IR-spectra of zeolites belonging to the S4R group (Fig. 2) the bands in the range 720–780  $\text{cm}^{-1}$  are repeated. This band should be assigned to the 4-membered ring vibrations. Because these rings contain the lowest number of members of all rings occurring in the zeolite structure, therefore the bands due to these rings occur at relatively high wave numbers in the pseudolattice band range [7].

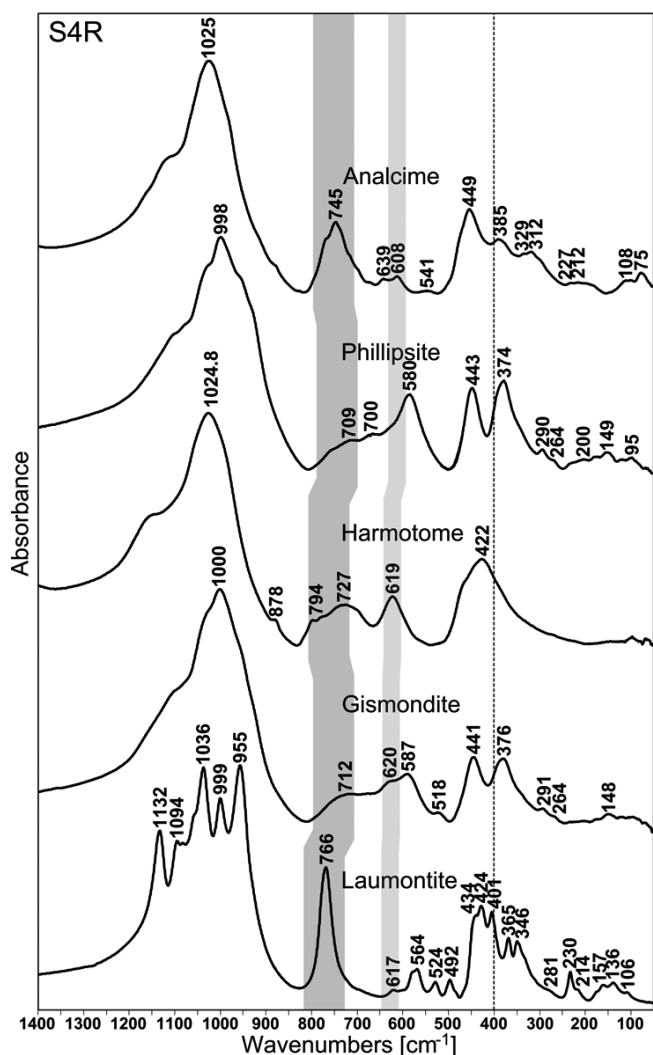


Fig. 2. IR spectra of S4R zeolites group

However, 4-membered rings are not the only ones that exist in the structures of minerals belonging to this group. In the analcime deformed 6-membered rings are also observed, which should affect the form of spectra, i.e. should cause the appearance of bands from both units. The situation is different in the structures of other zeolites from this group, i.e. phillipsite and harmotome (PHI), in which double 8-membered rings are formed by combining S4R units. In the case of next zeolite – gismondite (GIS) – is similarly. He also has a structure built with 4-membered rings, which combine to form 8-membered. Therefore, the second range of vibrations, i.e. 610–620 cm<sup>-1</sup>, due to a lower frequency [7], can be considered as characteristic for the vibrations of 6-membered rings. Such rings are present in analcime and pollucite but are not present in other structures, what means the assignment of this range to the 4- and 6-membered rings vibration. In the pseudolattice range, bands of lower wave numbers are present only in the spectra of gismondite (518 cm<sup>-1</sup>) and laumontite (524 and 492 cm<sup>-1</sup>). Their connection with the vibration of 8-membered rings can not be excluded, but these vibrations should not give the characteristic bands in the spectra [8].

The structure of the last zeolite of this group – laumontite – is clearly different. There are 4-, 6- and 10-membered rings. Additionally, the 4- and 6-membered rings occur in several conformations. Different form of the rings causes scatter of bonds length and angles. In the laumontite spectra, the number of bands is higher in comparison with the spectra of other zeolites.

Representative of the next group is the synthetic zeolite A (LTA). Its structure is built exclusively from D4R units, i.e. two bounded 4-membered rings. But except 4-membered, the 6-membered rings can be recognized.

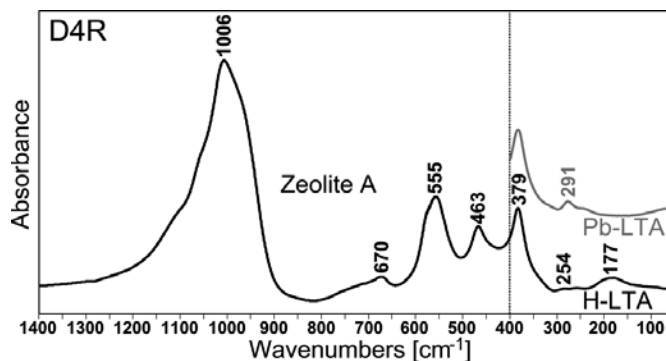


Fig. 3. IR spectra of LTA – D4R zeolites group

In the Figure 3 the experimental spectrum of LTA is presented. Based on the interpretation of the theoretical D4R units spectra [9] – vibrations of the following bands can be assigned:

- 1006 cm<sup>-1</sup> – asymmetric stretching vibrations of bridge bonds –  $\nu_{as}$  Si-O(Si) and  $\nu_{as}$  Si-O(Al)
- 726 cm<sup>-1</sup> – symmetric stretching vibrations of bridge bonds –  $\nu_s$  Si-O-Si
- 670 cm<sup>-1</sup> – symmetric stretching vibrations of bridge bonds –  $\nu_s$  Si-O-Al
- 555 cm<sup>-1</sup> – (complex band) symmetric stretching vibrations of bridge bonds –  $\nu_s$  Si-O-Si and bending vibrations –  $\delta$  O-Si-O
- 468 cm<sup>-1</sup> – bending vibrations –  $\delta$  O-Si-O, occurring in “antiphase”
- 377 cm<sup>-1</sup> – bending vibrations –  $\delta$  O-Si-O and  $\delta$  O-Al-O.

The bands at about 555 cm<sup>-1</sup> corresponds to symmetric stretching vibrations of

4-membered rings in the LTA structure [9]. Its complex envelope indicates that it is a superposition of several component bands. Calculated spectra indicate the presence of two types of 4-membered rings [9], but the connection of this band to the vibration of 6-membered rings can not be excluded. The bands located at the lowest wave numbers, i.e. at about 466 and 377 cm<sup>-1</sup>, correspond to the characteristic bending vibrations carried out in the 4-membered rings. Band appearing in the FIR region, at about 270 cm<sup>-1</sup>, is also considered to be associated with characteristic ring vibrations, and caused by presence of Na–O vibrations.

Ion exchange results in a change of location and intensity of the bands associated with ring vibrations [10, 11]. The biggest changes concern the position of the bands lying at the lowest frequencies (Fig. 3). These vibrations change the location of terminal cations in units during the vibration. Comparison of the model units spectra terminated by Na<sup>+</sup> and K<sup>+</sup> cations leads to similar conclusions [11]. The differences observed in the spectra can be attributed to differences in atomic mass and ionic radius of exchangeable cations.

Single 6-membered rings are the basic structural units in the case of another group (S6R). Vibrations of these rings should result in the bands shifting towards lower wavenumbers with respect to bands due to 4-membered rings. Infrared spectra of zeolites in this group are shown in Figure 4.

Spectra of levyne (LEV) and offretite (OFF) are similar to the spectra of zeolites from the S4R group (e.g. harmotome). This is because, in addition to 6-membered, 4- and 8-membered rings occur in the structure of zeolites from this group, like that is in the most of zeolites structures from the first group. In addition, double 6-membered rings (D6R) formed in both zeolites structures. So their spectra should contain a band located in similar areas as in the spectra of the next group (Fig. 5). Therefore, the assignment of the bands to one type of structural units is difficult. Division of zeolites due to the SBU is conventional and boundaries between the structures are difficult to determine. It is understood that based on the spectrum, SBU can not be expressly identified.

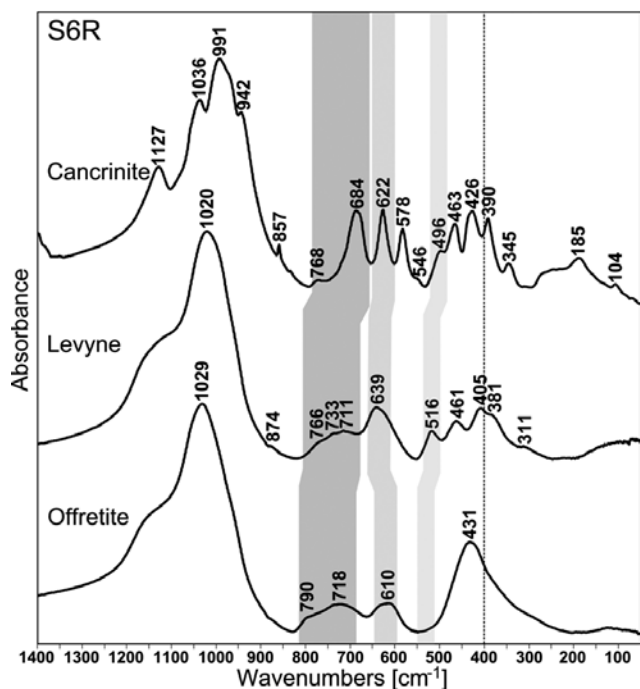


Fig. 4. IR spectra of S6R zeolites group

In the IR spectra of cancrinite, levyne and offretite (Fig. 4) in the pseudolattice range occur in at least three groups of bands. The first consists of bands at about 768 and 684 cm<sup>-1</sup> in the spectrum of cancrinite, at about 766 and 733 cm<sup>-1</sup> in the spectrum of levyne, and about 790 and 718 cm<sup>-1</sup> in the spectrum of offretite. They can be assigned to the vibrations of 4-membered rings. Fairly intense bands occur at slightly lower wave numbers, i.e. at about 622, 639 and 610 cm<sup>-1</sup> respectively. Their complex shape indicates the presence of several constituent bands. They can be assigned to the vibrations of both 4- and 6-membered rings.

In these structures, there are both single and double 6-membered rings. Based on a comparison of the spectra of another group may be assumed, that the bands associated with vibrations of the double rings occur at slightly higher wave numbers.

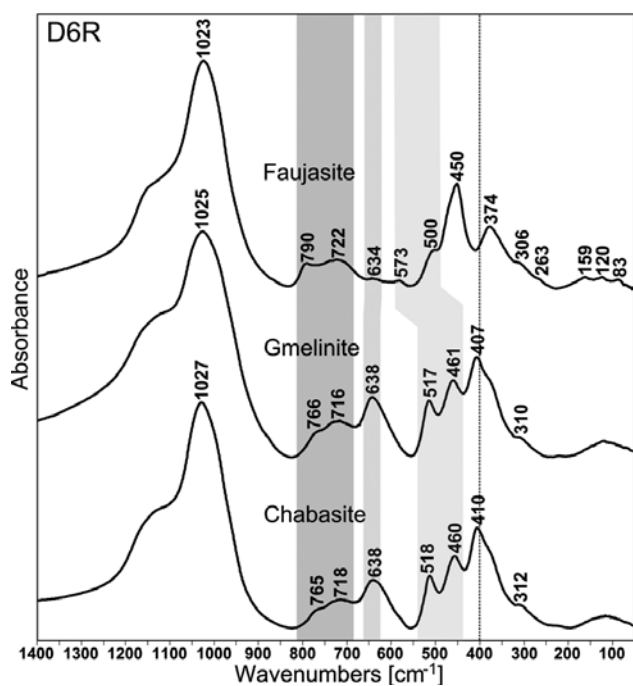


Fig. 5. IR spectra of D6R zeolites group

The third group of the bands occurs in the range of 520-410 cm<sup>-1</sup>. The connection of these bands with the bending vibrations of O-Si(Al)-O is obvious, but the band at about 496 cm<sup>-1</sup> in the spectrum of cancrinite and at about 516 cm<sup>-1</sup> in the spectrum of levyne should

be associated with ring vibrations. In the case of levyne, they could be connected with vibrations of 8-membered rings, but this is not possible in the case of cancrinite. It is more probable, that they are associated with 6-membered rings, which are significantly deformed in these structures. The lack of such bands in the spectrum of the offretite is associated with the lack of unit's deformation in their structure. It should be noted that a different form of the cancrinite spectrum is caused by the presence of bands due to the carbonate groups occurring in their structure (bands at about 857 cm<sup>-1</sup>).

All the structures of zeolites from D6R group contain double 6-membered rings and single 4-membered rings. Additionally, faujasite includes single 6- and 12-membered rings, chabasite – 8-membered, and gmelinite – 8- and 12-membered. Because the structure of zeolites from this group have – in the medium-range order – many common elements with the structures of levyne and offretite, bands assigned to characteristic vibrations of S6R group can be related to the spectra of D6R group.

Bands in the range 720–790 cm<sup>-1</sup> are associated with symmetric stretching vibration of 4-membered rings. The bands at about 635 cm<sup>-1</sup>, which are repeated in all spectra, are composed – as in the spectra of levyne and offretite – of several components bands and can be associated with different types of 6-membered rings vibrations [12]. The bands at about 574 and 502 cm<sup>-1</sup> in the spectrum of faujasite (FAU) and at about 520 and 460 cm<sup>-1</sup> in the spectrum of gmelinite (GME) and chabasite (CHA) can also be assigned to the 6-membered rings vibration of the D6R units, or alternatively to the vibration of rings with a higher number of members.

Spectrum of gmelinite and chabazite are almost identical. This is due to very similar structures of both zeolites, which differ mainly in the kind of non-tetrahedral cation (gmelinit is “sodium chabazite”). Strong similarity between the spectra of zeolites from this group and spectra of levyne and offretite from the S6R group makes that, based on oscillation enabled they would be combined into a common group. It can be concluded that vibration of D6R units can be quite clearly identified in the IR spectra.

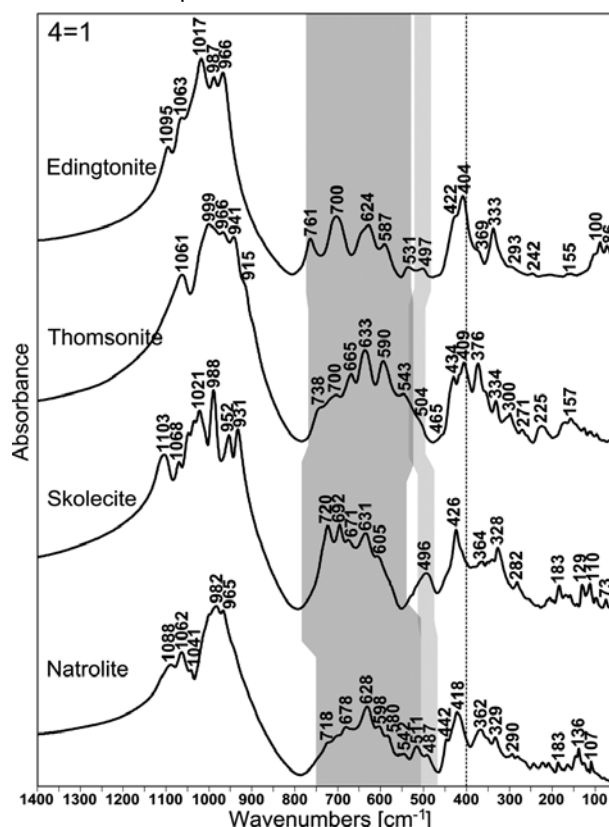


Fig. 6. IR spectra of 4=1 zeolites group

Zeolites belong to the 4=1 (T<sub>5</sub>O<sub>10</sub>) group are also known as fibrous zeolites [13] and form the most characteristic group among all discussed.

SBU units form chains, which create a spatial structure. Only because of the 4=1 units building, several types of 4-membered rings can be distinguished. Additionally, 8-membered rings are formed by combining of chains. IR spectra are very similar and are a good tool for the identification of 4=1 zeolites group, because have the same structure.

Presence of a 4=1 complex causes the appearance of the whole series of bands in the range of pseudolattice bands in the IR spectra (Fig. 6). They located in the range of 500–760  $\text{cm}^{-1}$ . The occurrence of the large number of bands should be associated with many types of 4-membered rings, which have different geometry. The bands appearing at lower wave numbers, i.e. in the range 500–490  $\text{cm}^{-1}$ , can be assigned to the vibrations of 8-membered rings.

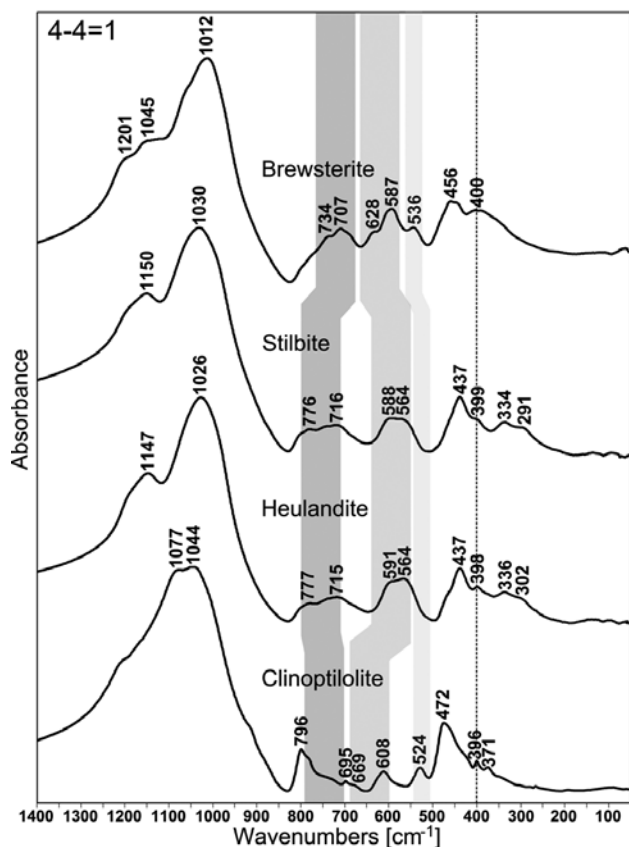


Fig. 7. IR spectra of 4–4=1 zeolites group

The 4–4=1 ( $T_{10}O_{20}$ ) complex shows the most complicated SBU structure among all zeolites. In this complex, both the 4-membered rings as well as 5-membered rings occur. Additionally, 8-membered rings are formed in all the structures. 6-membered rings occur in the structure of brewsterite (BRE), and 10-membered in the structure of heulandites (HEU), clinoptilolite (HEU) and stilbite (STI) (Tab. 1).

In the Figure 7, the IR spectra of zeolites belonging to the 4–4=1 group are shown. The bands in the range of 790–690  $\text{cm}^{-1}$  and 540–510  $\text{cm}^{-1}$  probably are connected with stretching and bending vibrations of 4-membered rings respectively. In the spectrum of brewsterite, complex band at about 587  $\text{cm}^{-1}$  can be assigned to the 6-membered rings vibrations. The bands repeated in the same range of wave numbers should be present in all spectra, because 5-membered rings are present in the structure of all zeolites from this group. Based on comparison with the calculated spectra of 4–4=1 units [11] can be assumed that the bands corresponding to the characteristic vibrations of 5-membered rings are present in the range 590–675  $\text{cm}^{-1}$ .

### Conclusions

The ring bands in the IR-spectra, which are typical for medium-range order, are present in the pseudolattice range, i.e. 400–800  $\text{cm}^{-1}$ . Bands associated with typical lattice vibrations (including the vibrations of non-tetrahedral cations like Me–O type) can be distinguished in the far infrared range (below 400  $\text{cm}^{-1}$ ). It was found that kind of

exchangeable cation have an influence on positions of bands associated with this type vibrations. It was observed that the increase in number of ring members changes the position of the pseudolattice bands towards lower wave numbers. It was also shown that identification bands in the spectra of zeolite, associated with normal vibrations of SBU units allows to its classification to appropriate structural group.

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Translation into English by the Author

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