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## INFRARED SPECTRA OF SILICA POLYMORPHS

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**Abstract.** A completement of spectra of silica polymorphs obtained both using the classical and interferometric methods in medium and far infrared range is presented.

## INTRODUCTION

Vibrational spectroscopy is useful for the phase-analysis of  $\text{SiO}_2$  polymorphs, subject to the condition of possessing reliable reference spectra of well defined samples. The purpose of this publication is a completement of spectra of silica polymorphs (with the exception of high-temperature quartz, hydrothermal  $P2_1/a$  coesite and keatite). Both the classical method (UR-10 — Zeiss) and the fourier transform method (FTS-14 — Digilab) are represented here. The fourier transform method enables obtaining of spectra in the infrared range, which are due to the low-energetic lattice vibrations of the crystals. This constitutes a supplementary method to the diffractional ones. The infrared spectra of coesite, a high-pressure form of silica, are presented here for the first time (tab. 1).

## SILICA POLYMORPHS WITH 6-MEMBERED RINGS ONLY

### Cristobalite

#### 1. Low-temperature cristobalite (LCr).

Tetragonal symmetry, space group  $P4_12_1$  or enantiomorphic  $P4_32_1$ ,  $Z=4$ . Oval ring deformation. Stacking sequence: ABC... (Peacor 1973, O'Keeffe 1976).

#### 2. High-temperature cristobalite (HCr).

Pseudocubic symmetry, space group  $Fd\bar{3}m$ ,  $Z=8$ , tetragonal domains with lower, tetragonal symmetry  $\bar{I}42d$ . Ditrigonal ring deformation. Stacking sequence: ABC... (Peacor 1973, Wright and Leadbetter 1975, O'Keeffe 1976).

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Table 1

Bands positions and assignments of silica polymorphs

Rings		SiO <sub>2</sub> polymorph		Approxim. bands assignment	
type	deformation	bending O—Si—O 400—550 cm <sup>-1</sup>	deformation Si—O—Si 600—800 cm <sup>-1</sup>	deformation Si—O—Si 600—800 cm <sup>-1</sup>	stretching Si—O 900—1250 cm <sup>-1</sup>
6-membered	ideal hexagonal	TRIDYMITE hexagonal (alpha) I	480	—	1108
6-membered	distorted hexagonal	orthorhombic (beta) I	480	783	1108
6-membered	ditrigonal and oval in ratio 2:1	orthorhombic (beta) II	480, 514 sh, 541 sh	670, 690, 783	1170 sh, 1108
6-membered	ditrigonal and oval in ratio 2:1	monoclinic (gamma)	480, 514, 541, 564, 580	648, 670, 690, 783	1170, 1108
6-membered	oval only	triclinic (low tempera- ture)	480, 514, 541, 564, 574, 586	650, 682, 698, 733, 792, 820	1175, 1108, 1145, 1165, 1197, 1220, 1245
6-membered	ditrigonal	CRISTOBALITE high-temperature (HCr)	475	785	1105, 1170 sh
6-membered	oval	low-temperature (LCr)	483	622, 795	1100, 1170 sh, 1200
6—8 mem- bered		QUARTZ low-temperature (Q)	462, 513	695, 780—800	1090, 1173
4—6—8—9 membered		COESITE high-pressure	422, 438, 464, 492, 513	565, 600, 621, 640, 680, 730, 792	898, 942, 1037, 1094, 1155, 1225

## MEDIUM RANGE INFRARED SPECTRA

Low-temperature cristobalite (LCr), obtained by a prolonged heating of a quartzite rock (Fig. 1).

Spectrophotometer UR-10 (Zeiss). Range 400—1600 cm<sup>-1</sup>. Transmission scale. Sample as a compact in KBr.

Absorption bands: 483, 622, 795, 1100, 1170 (shoulder) and 1200 cm<sup>-1</sup>.  
Identification bands: 622 and 1200 cm<sup>-1</sup>.

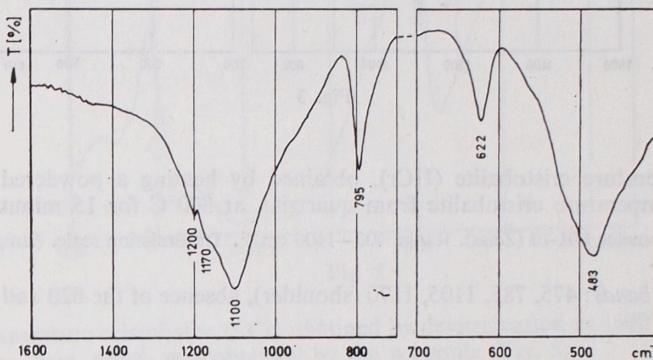


Fig. 1

Low-temperature cristobalite (LCr), obtained by devitrification at 1500°C for 4 hours of silica glass, which was obtained by the gelroute (Fig. 2) (Görlich et al. 1975). Fourier transform spectrometer FTS-14 Digilab. Range: 400—1400 cm<sup>-1</sup>. Sample in KBr. Absorbance scale.

Absorption bands: 490, 620, 795, 1095, 1160 (shoulder) and 1200 cm<sup>-1</sup>.  
Identification bands: 620 and 1200 cm<sup>-1</sup>.

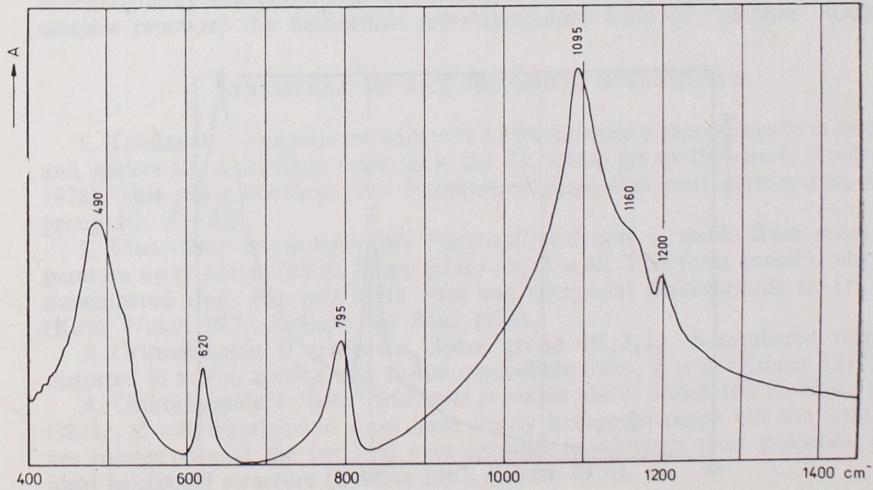


Fig. 2

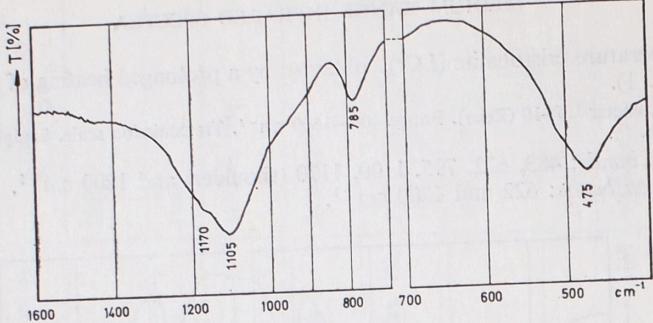


Fig. 3

High-temperature cristobalite (HCr), obtained by heating a powdered sample of the low-temperature cristobalite from quartzite, at 300°C for 15 minutes (Fig. 3). Spectrophotometer UR-10 (Zeiss). Range 400–1600 cm<sup>-1</sup>. Transmission scale. Sample as a compact in KBr.

*Absorption bands:* 475, 785, 1105, 1170 (shoulder), absence of the 620 and 1200 cm<sup>-1</sup> bands.

#### FAR-INFRARED RANGE SPECTRA

Low-temperature cristobalite (LCr) obtained by a prolonged heating of a quartzite rock (Fig. 4).

Fourier transform spectrometer FTS-14 Digilab. Range 100–400 cm<sup>-1</sup>. Sample as a compact in polyethylene. Absorbance scale.

*Identification bands:* 145, 275 (shoulder), 298 and 387 cm<sup>-1</sup>.

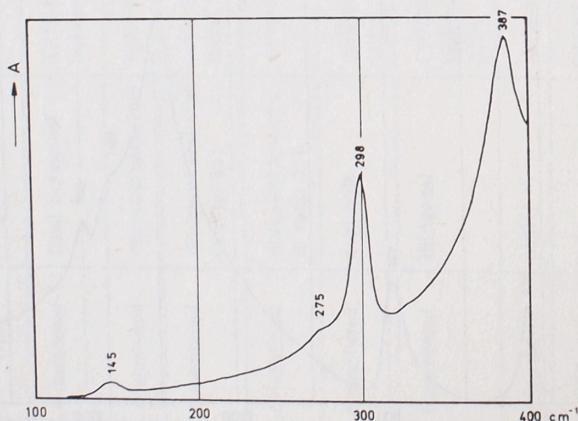


Fig. 4

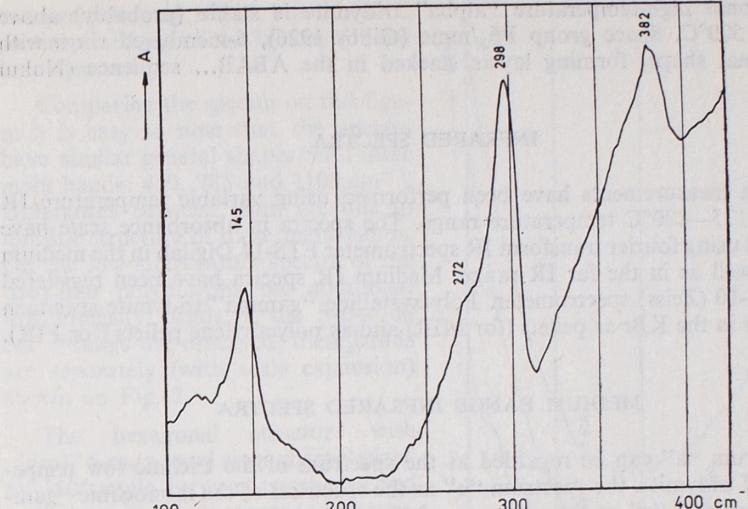


Fig. 5

Low-temperature cristobalite (LCr) obtained by devitrification at 1500°C for 4 hours of a silica glass, which was obtained by the gel-route (Fig. 5). Fourier transform spectrometer FTS-14 Digilab. Range: 100–400 cm<sup>-1</sup>. Sample in polyethylene. Absorbance scale.

*Identification bands:* 145, 272 (shoulder), 298, 382 cm<sup>-1</sup>.

#### Tridymite

Tridymite is a very rare mineral but it is known from numerous sources: terrestrial rocks, lunar rocks, meteorites and refractory silica bricks. In presented work the IR spectra for synthetic samples of tridymite are recorded. For sample identification the following investigations were made: chemical analysis of contaminations, X-ray diffractography and DTA. Due to these data it was established that the examined samples represent the monoclinic low-temperature form of "gamma" tridymite.

#### STRUCTURE OF THE TRIDYMITE POLYMORPHS

1. Triclinic low-temperature tridymite stable at lower temperatures than synthetic and meteoritic monoclinic form with the Cc space group (Konnert, Appelmann 1978). This phase contains only 6-membered rings with oval deformation. Space group F1, Z = 320.

2. Monoclinic low-temperature "gamma" tridymite is stable from room temperature up to about 110°C. Space group Cc, Z = 48. This form contains also only 6-membered rings but with both oval and ditrigonal deformations in 1:2 ratio (Kato, Nukui 1976, Dollase and Baur 1976).

3. Orthorhombic II tridymite. Space group P<sub>2</sub>1<sub>2</sub>1<sub>2</sub>1, 6-membered rings are distorted in a very similar way to the monoclinic form, Z = 24 (Kihara 1977).

4. Orthorhombic I "beta" tridymite is stable above about 160°C. Space group C<sub>222</sub><sub>1</sub>, Z = 8, 6-membered rings have nearly hexagonal shape but the tetrahedra are rotated around the two-fold axes (parallel to  $a_0$ ) from their positions in an ideal hexagonal structure (Dollase 1967, Kihara 1978).

5. Hexagonal high-temperature "alpha" tridymite is stable (probably) above 420 or even 500°C. Space group P6<sub>3</sub>/mmc (Gibbs 1926), 6-membered rings with ideal hexagonal shape, forming layers stacked in the ABAB... sequence (Nukui et al. 1978).

#### INFRARED SPECTRA

IR spectra measurements have been performed using variable temperature IR cell in the -175—480°C temperature range. The spectra in absorbance scale have been recorded using Fourier transform IR spectrometer FTS-14 Digilab in the medium IR range as well as in the far IR range. Medium IR spectra have been registered also with UR-10 (Zeiss) spectrometer. Polycrystalline "gamma" tridymite specimen were prepared in the KBr as pellets (for MIR) and as polyethylene pellets (for FIR).

#### MEDIUM RANGE INFRARED SPECTRA

The spectrum "a" can be regarded as the spectrum of the triclinic low temperature form of tridymite, the spectrum "b" as the spectrum of the monoclinic "gamma" form, spectrum "c" as the spectrum of the orthorhombic II form, "d" as the spectrum of the orthorhombic I "beta" one. Because of temperature limitations of our variable temperature IR cell the spectrum of the hexagonal form is

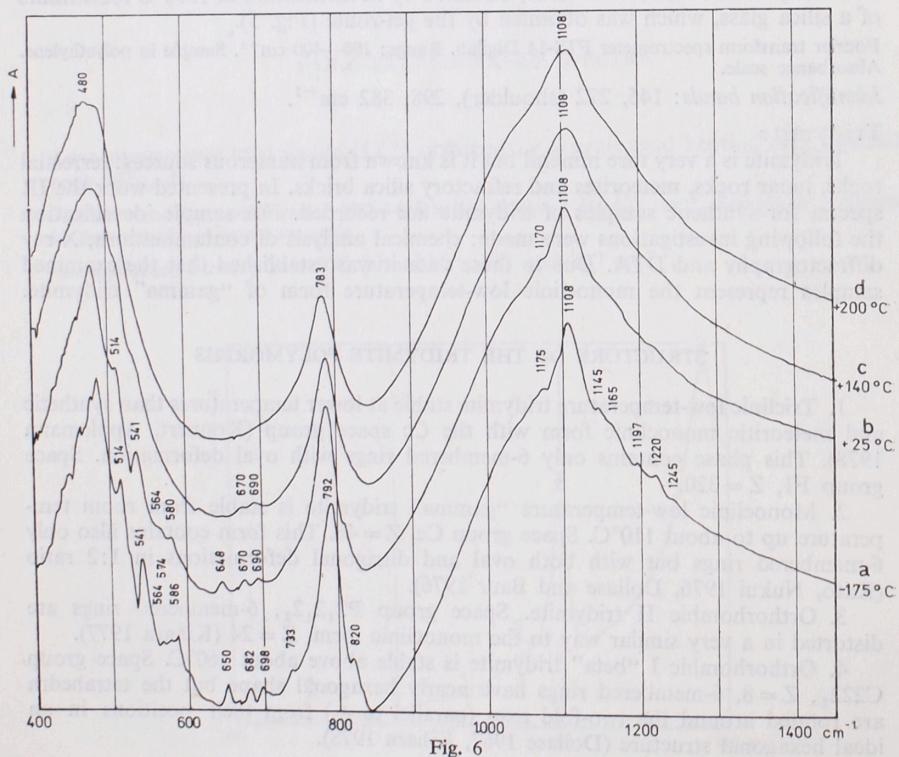


Fig. 6

not presented on Fig. 6, but at 480°C partial vanishing of the 783 cm⁻¹ band was observed.

Comparing the spectra on this figure it is easy to note that the spectra have similar general shapes with three main bands: 480, 783 and 1108 cm⁻¹. Differences between them are due to the fine structure of these main bands. On the low-temperature spectra of the tridymite polymorphs the additional low intensity bands in the 540—700 cm⁻¹ range are observed; these bands are separately (with scale expansion) shown on Fig. 7.

The hexagonal structure with "ideal" 6-membered rings characterized by 180° angle between tetrahedra and very short Si—O distances is in accordance with two bands only in IR spectrum (group-theory analysis). During polymorphic transition the symmetry of the tridymite forms is decreasing and unit cell dimensions increase. These facts effecting the Si—O—Si angle changes as well as Si—O distances cause differences which are observed as a complexity of the IR spectra.

The spectra of the same tridymite specimen were also measured on UR-10 (Zeiss) spectrophotometer in transmission scale. In this case different tridymite polymorphs can be recognized, too, but not so easily as in the FT-IR measurements (Fig. 8).

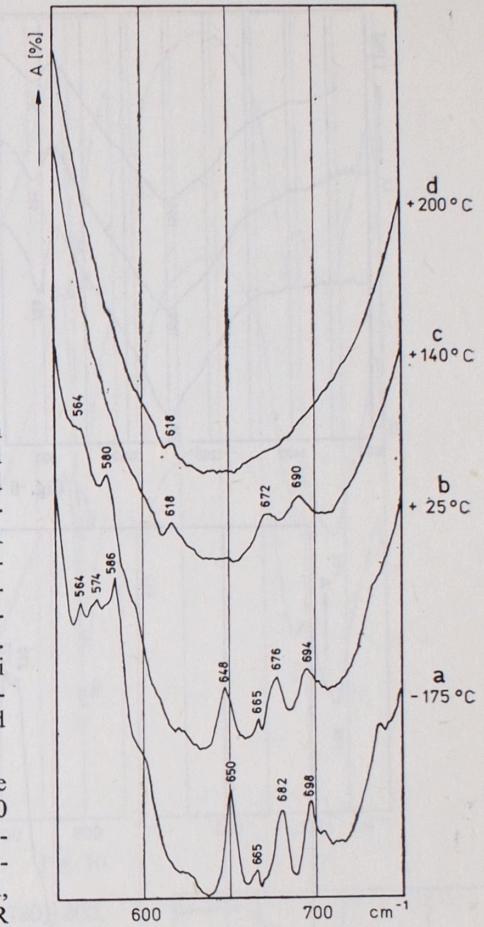


Fig. 7

#### FAR INFRARED RANGE SPECTRA

These spectra were registered at low and room temperatures only, because polyethylene technique was applied. In the room temperature far IR spectra of the monoclinic "gamma" tridymite are characterized by low intensity bands which are due to the lattice vibrations. Some of these bands split when temperature is decreasing what is in accordance with unit cell symmetry conversion from Cc to F1 space group and an increase of unit cell dimension (Fig. 9).

#### SILICA POLYMORPHS WITH 8- AND 6-MEMBERED RINGS

##### Quartz

Low-temperature quartz (Q). Trigonal symmetry, space group P3<sub>2</sub>1 or enantiomorphic P3<sub>1</sub>21, Z = 3. (Le Page, Donnay 1976, Donnay, Le Page 1978).

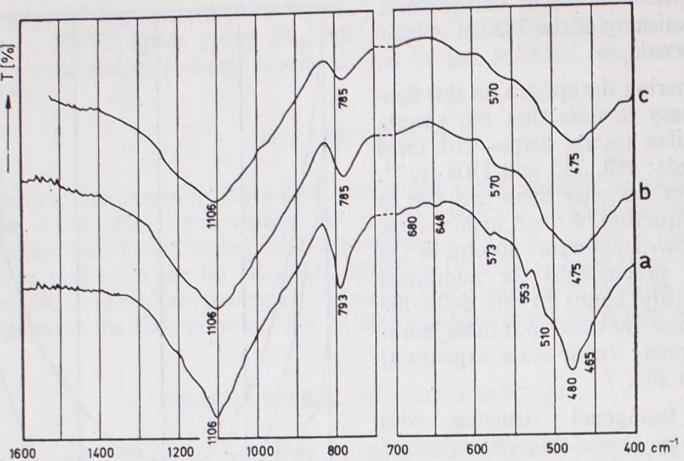


Fig. 8

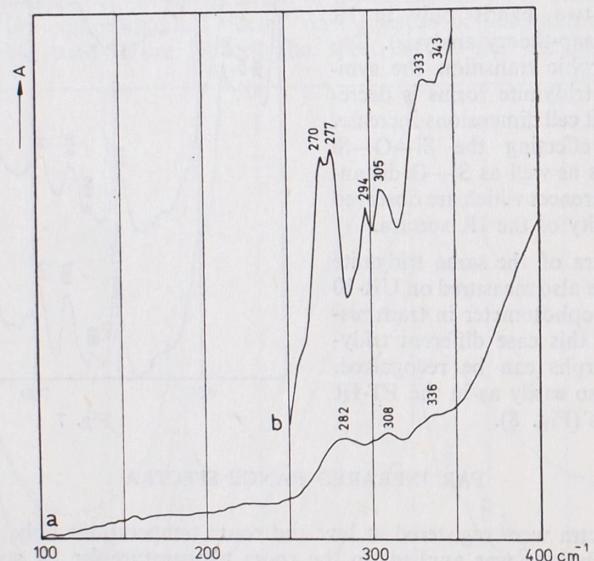


Fig. 9

#### MEDIUM RANGE INFRARED SPECTRA

Low-temperature quartz (Q), natural rock crystals (Fig. 10):

- a) Brasilian quartz ("Watanabe"),
- b) Madagascan quartz,
- c) Angolian quartz.

Spectrometer UR-10 (Zeiss). Range: 400—1600 cm<sup>-1</sup>. Transmission scale. Sample in KBr.

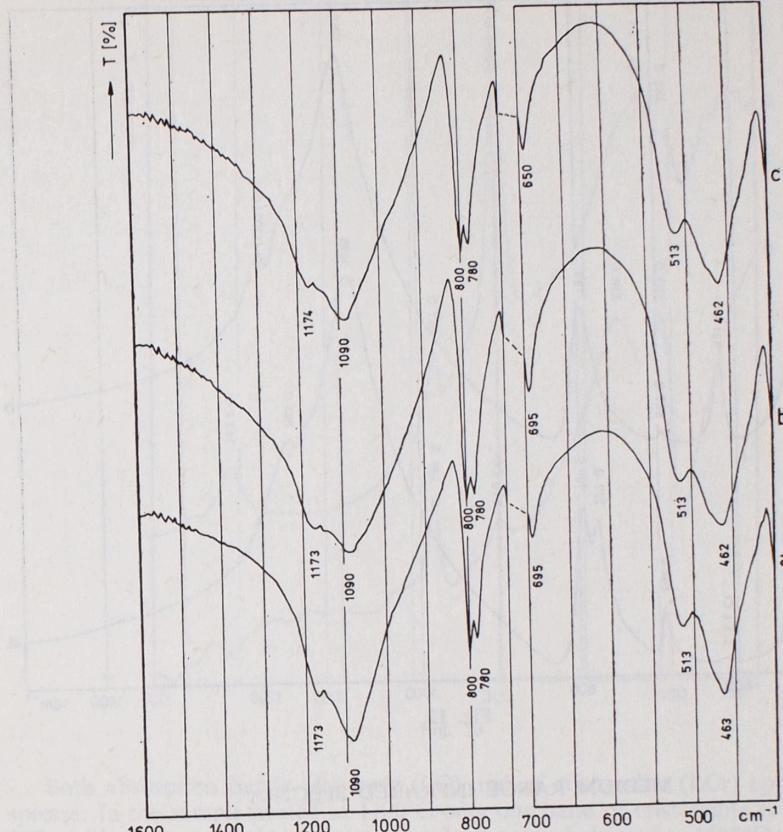


Fig. 10

Absorption bands: 462, 513, 695, 780, 800, 1090 and 1173 cm<sup>-1</sup>.

Identification bands: 513, 695, 780, 800 and 1173 cm<sup>-1</sup>.

#### FAR-INFRARED RANGE SPECTRA

Low-temperature quartz (Q) (brasilian "Watanabe" rock crystal) (Fig. 11).

Fourier transform spectrometer FTS-14 Digilab. Range: 100—400 cm<sup>-1</sup>. Sample in polyethylene. Transmission scale.

Identification bands: 265, 373, 397 cm<sup>-1</sup>.

High-temperature transformation quartz ("Watanabe")-cristobalite. Measured at room temperature.

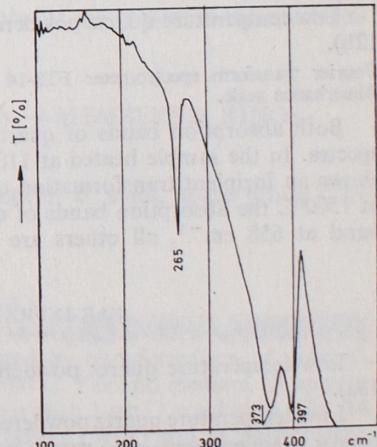


Fig. 11

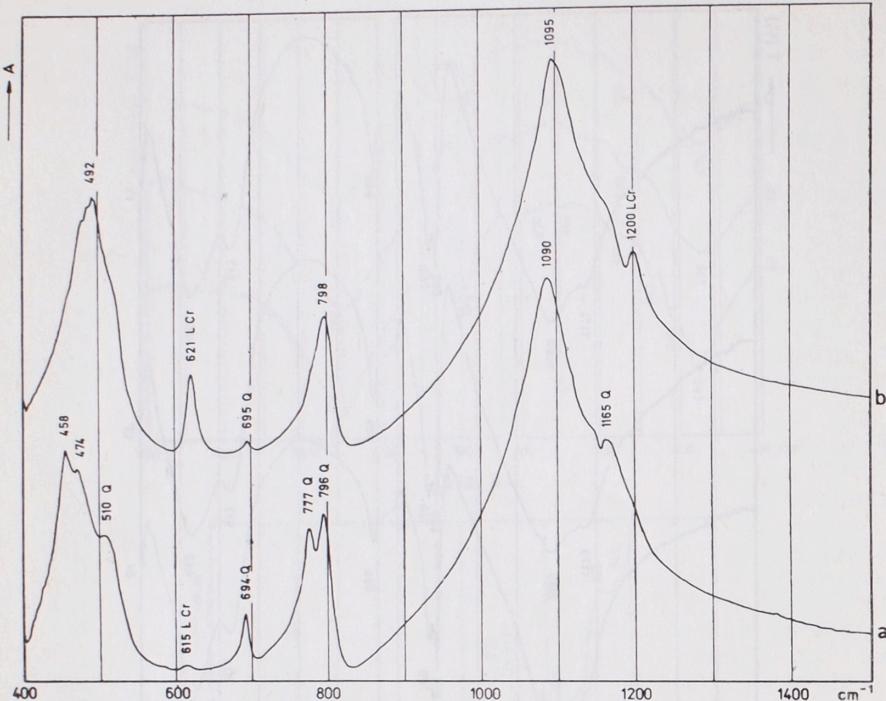


Fig. 12

#### MEDIUM RANGE INFRARED SPECTRA

Low-temperature quartz powdered sample heated at 1100°C for 90 hours (Fig. 12a).

Low-temperature quartz powdered sample heated at 1500°C for 4 hours (Fig. 12b).

Fourier transform spectrometer FTS-14 Digilab. Range: 400—1500  $\text{cm}^{-1}$ . Sample in KBr. Absorbance scale.

Both absorption bands of quartz (LQ) and of cristobalite (LCr) appear in the spectra. In the sample heated at 1100°C only a weak absorption band at 615  $\text{cm}^{-1}$  shows an incipient transformation of quartz into cristobalite. In the sample heated at 1500°C the absorption bands of quartz disappear, with an exception of the weak band at 658  $\text{cm}^{-1}$ , all others are characteristic for low-cristobalite (see Fig. 2).

#### FAR-INFRARED RANGE SPECTRA

Low-temperature quartz powdered sample heated at 1100°C for 90 hours (Fig. 13a).

Low-temperature quartz powdered sample heated at 1500°C for 4 hours (Fig. 13b). Fourier transform spectrometer FTS-14 Digilab. Range: 100—400  $\text{cm}^{-1}$ . Sample in polyethylene. Absorbance scale.

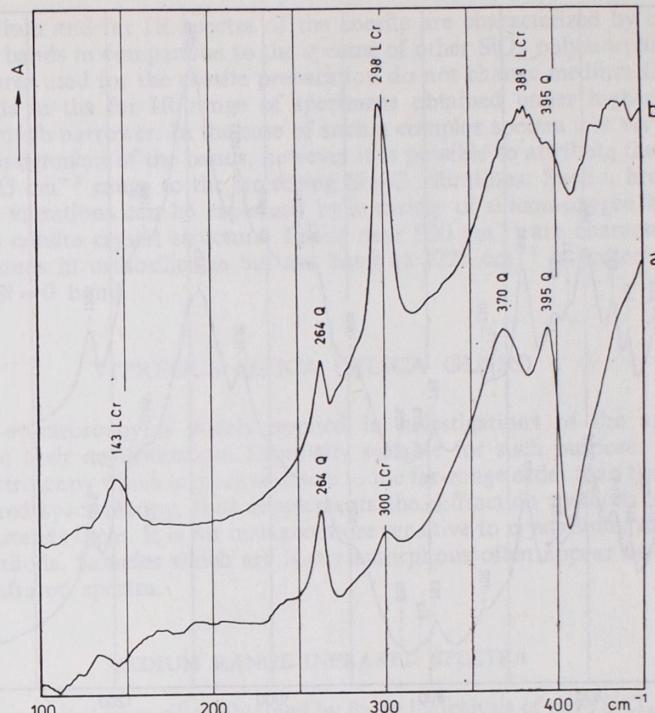


Fig. 13

Both absorption bands of quartz (LQ) and of cristobalite (LCr) appear in the spectra. In the sample heated at 1100°C only one band of cristobalite is present, at 300  $\text{cm}^{-1}$ , all the other belong to quartz. In the sample heated at 1500°C the absorption bands characteristic of quartz disappear ( $370 \text{ cm}^{-1}$ ) or are considerably weaker ( $296, 395 \text{ cm}^{-1}$ ), all bands characteristic for cristobalite are present in the spectrum. v. b. (see Fig. 5).

#### SILICA POLYMORPHS WITH 4—6—8—9-MEMBERED RINGS

##### Coesite

Coesite is a monoclinic, high-pressure polymorph of silica, space group C2/c (Araki, Zoltai 1969, Megaw 1970).

#### INFRARED SPECTRA

The synthetic sample of coesite was synthesized by transformation of polycrystalline quartz under 50 and 60 Kb pressure at 1300°C. Far and medium IR spectra were recorded using FTS-14 Digilab spectrometer with 1  $\text{cm}^{-1}$  resolution (Fig. 14 and 15). Samples were prepared in the KBr as pellets (MIR) and in polyethylene pellets (FIR). Absorbance scale.

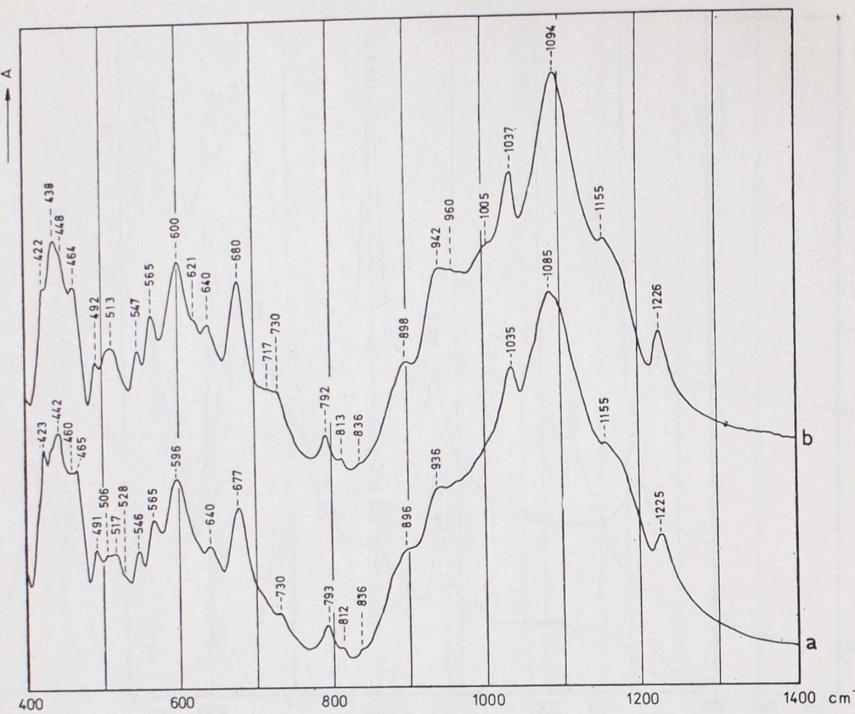


Fig. 14

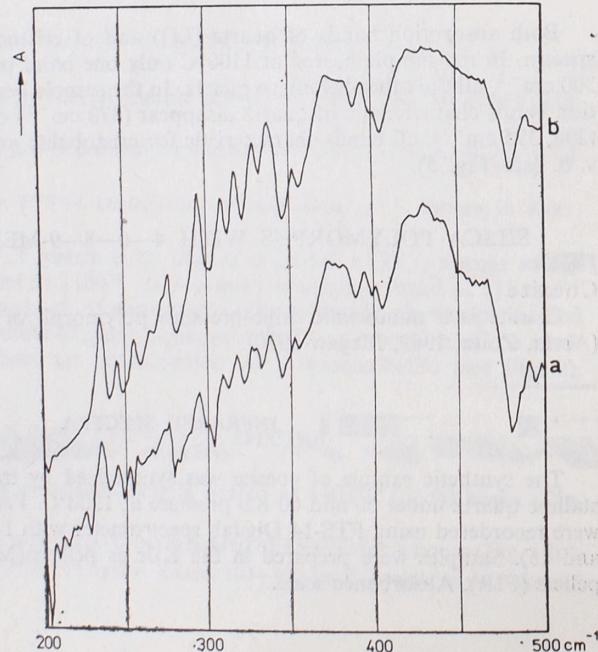


Fig. 15

Both medium and far IR spectra of the coesite are characterized by numerous and complex bands in comparison to the spectra of other  $\text{SiO}_2$  polymorphs. The different pressures used for the coesite preparation do not change medium IR spectra but the bands in the far IR range of specimens obtained under higher pressure (60 Kb) are much narrower. In the case of such a complex spectra it is very difficult to make an assignment of the bands, however it is possible to attribute the bands in the  $896\text{--}1225\text{ cm}^{-1}$  range to the stretching Si—O vibrations. Such a broad range of stretching vibrations can be explained by a variety of silicon-oxygen bond character in the coesite crystal structure. Bands near  $900\text{ cm}^{-1}$  are characteristic for the Si—O bonds in orthosilicates but the band at  $1225\text{ cm}^{-1}$  is present in  $\text{Si}_2\text{O}_2$  oxide with Si = O bond.

#### VITREOUS SILICA (SILICA GLASS)

Infrared spectroscopy is widely applied in investigations of the amorphous solids and of their devitrification. Especially suitable for such purposes is the far-infrared spectroscopy which is more sensitive to the far-range order than the medium-range infrared spectroscopy, thus supplements the diffraction methods and sometimes even extends them. It is for instance more sensitive to crystallinity than the diffraction methods. Samples which are X-ray amorphous often appear as crystalline in the far infrared spectra.

#### MEDIUM RANGE INFRARED SPECTRA

Silica glass melted from silica obtained by flame hydrolysis of pure  $\text{SiCl}_4$  (Fig. 16). Fourier transform spectrometer FTS-14 Digilab. Range:  $400\text{--}1600\text{ cm}^{-1}$ . Sample in KBr. Absorbance scale.

*Absorption bands: 475, 815, 1100,  $\text{cm}^{-1}$ .*

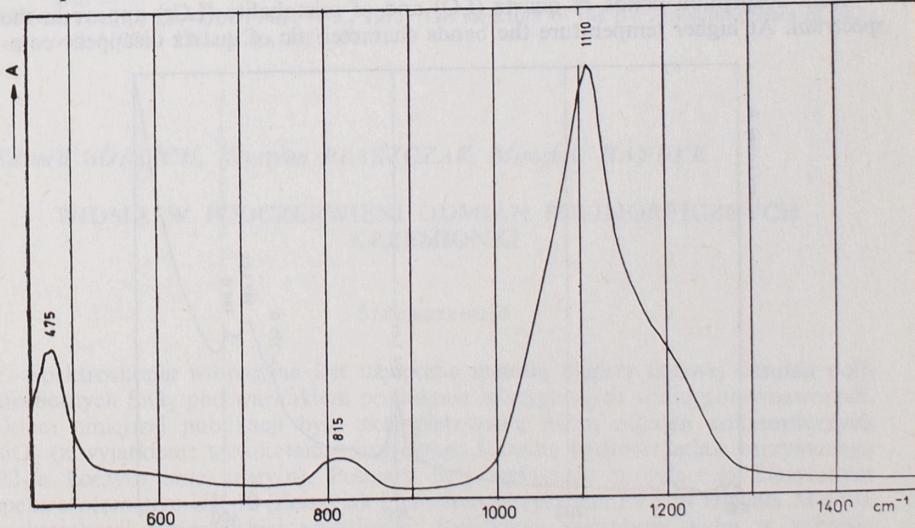


Fig. 16

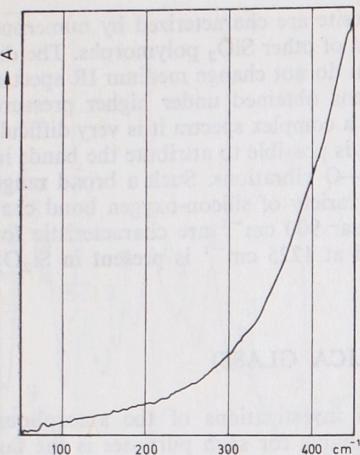


Fig. 17

This spectrum is similar to the spectra of the high-temperature six-membered ring polymorphs of silica, especially to that of high-temperature cristobalite, as the band in the range of about  $800\text{ cm}^{-1}$  tends to disappear in the spectra of tridymite above  $500^\circ\text{C}$  (see Fig. 6).

#### FAR — INFRARED RANGE SPECTRA

Silica glass melted from silica obtained by flame hydrolysis of pure  $\text{SiCl}_4$  (Fig. 17).

Fourier transform spectrometer FTS-14 Digilab. Range:  $100\text{--}400\text{ cm}^{-1}$ . Sample in polyethylene. Absorbance scale.

Lack of the absorption bands indicates fully amorphous character of the sample.

#### DEVITRIFICATION OF THE SILICA GLASS

Silica glass obtained by the gel-route. Devitrification at  $1100^\circ\text{C}$  for 90 hours (Fig. 18).

#### FAR—INFRARED RANGE SPECTRUM

Fourier transform spectrometer FTS-14 Digilab. Range:  $100\text{--}400\text{ cm}^{-1}$ . Sample in polyethylene; absorbance scale.

Both absorption bands of quartz (LQ) and of cristobalite (LCr) appear in the spectrum. At higher temperature the bands characteristic of quartz disappear com-

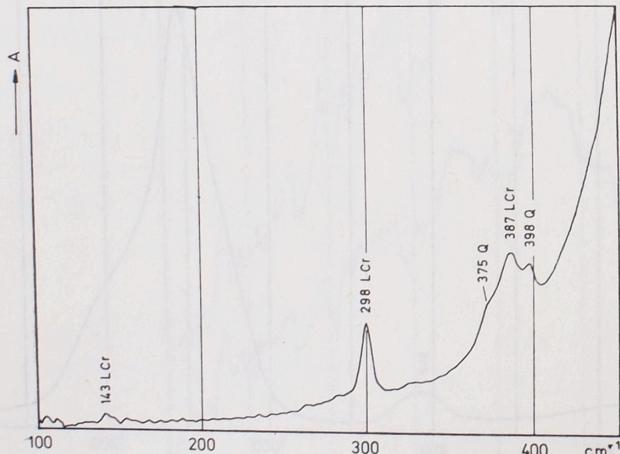


Fig. 18

pletely and only those characteristic for cristobalite remain at  $1500^\circ\text{C}$  (Fig. 5). It is thus possible to obtain quartz phase by devitrification of silica glass at temperature somewhat lower than  $1100^\circ\text{C}$ .

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WIDMA W PODCZERWIENI ODMIAN POLIMORFICZNYCH KRZEMIONKI

#### Streszczenie

Spektroskopia vibracyjna jest użyteczną metodą analizy fazowej odmian polimorficznych  $\text{SiO}_2$  pod warunkiem posiadania wiarygodnych widm porównawczych. Celem niniejszej publikacji było skompletowanie widm odmian polimorficznych  $\text{SiO}_2$  (z wyjątkiem: wysokotemperaturowego kwarcu, hydrotermalnie otrzymanego  $\text{P}_2\text{I}/\text{a}$  koezytu oraz keatytu). Pomiary były wykonane zarówno na klasycznym spektrofotometrze UR-10 (Zeiss) jak i interferometrycznym FTS-14 Digilab. Metoda spektroskopii furierowskiej umożliwiła dodatkowo rejestrację widm w zakresie niskoenergetycznych drgań sieci krystalicznej. Metoda spektroskopii vibracyjnej

okazuje się suplementarna w stosunku do metod dyfrakcyjnych. Widma w podczerwieni koezytu, formy wysokociśnieniowej krzemionki, są przedstawione w tej pracy po raz pierwszy.

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## ИК-СПЕКТРЫ ПОЛИМОРФНЫХ РАЗНОВИДНОСТЕЙ КРЕМНЕЗЕМА

### Резюме

Вибрационная спектроскопия является полезным методом фазового анализа полиморфных модификаций  $\text{SiO}_2$ , при условии, если располагаем достоверными сравнительными спектрами. Целью настоящей работы было комплектование спектров полиморфных разновидностей  $\text{SiO}_2$  (за исключением: высокотемпературного кварца, гидротермально полученного  $\text{P}_2\text{I}/\text{a}$  коэсита, а также кеатита). Представленные в работе измерения проведены как на классическом спектрофотометре UR-10 (Zeiss), так и на интерферометрическом FTS-14 Digilab. Метод фурье-спектроскопии создал возможность добавочной записи спектров в области низкоэнергетических колебаний кристаллической решетки. Метод вибрационной спектроскопии оказывается дополнительным для дифракционных методов. ИК-спектры коэсита — формы кремнезема высоких давлений — в этой работе представляются впервые.

ИК-спектры полиморфных разновидностей кремнезема

### Abstract

Vibrationsspektroskopie ist ein nützliches Phasenanalysemittel für polymorphe Modifikationen von  $\text{SiO}_2$ , falls wir zuverlässige vergleichende Spektren zur Verfügung haben. Ziel der vorliegenden Arbeit war die Erweiterung des Spektralbestandes der polymorphen Varietäten von  $\text{SiO}_2$  (ausgenommen: Quarz, hydrothermal erzeugter  $\text{P}_2\text{I}/\text{a}$ -Koesit und Kiatit). Die im Bericht vorgelegten Messungen wurden sowohl mit dem klassischen Spektrophotometer UR-10 (Zeiss) als auch mit dem Interferenzspektrometer FTS-14 Digilab durchgeführt. Der Fourier-Spektralanalyse wurde die Möglichkeit einer zusätzlichen Aufzeichnung von Spektren in der Gegend niedrigenergetischer Schwingungen der kristallinen Rautenstruktur eingeräumt. Der Vibrationsspektralanalyse wird als Ergänzung zu den diffraktionsmethodischen Mitteln dient. Die IR-Spektren des Koesits — Form des Kremnitzes unter hohem Druck — werden hier erstmals vorgestellt.