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DETERMINATION OF THE CRYSTALLINITY
OF CHALCEDONIES

Abstract. Quartz and chalcedony samples from Poland and other countries were subjected to investigations. The crystallinity indices of low-temperature quartz, determined by X-ray diffraction and IR spectroscopic methods were discussed. CI index proposed by Murata and Norman was assumed as reliable. It was found that the spectroscopic index K of Plusnina failed to arrange the samples studied according to the degree of order.

INTRODUCTION

Chalcedony has a special position among silica varieties. Structurally it is a low-temperature quartz, differing from the latter in the form of occurrence and to some extent, in physical properties, such as hardness and refractive indices. In thin section chalcedony displays spherulitic, fan-shaped and radial forms, or fine-grained, scaly aggregates. Frondel (1978) is of the opinion that a single chalcedony crystal is a whisker elongated along the X axis and contains a screw dislocation parallel to this axis. The length of the Burgers vector is 20—300 µm. Barsanov et al. (1979) maintain that chalcedony is an intergrowth of blocks 100—400 nm in size, which grow on one another with certain angular deviation.

Over the last few years most studies have focussed on the structural perfection of chalcedony and quartz. This term, commonly referred to as crystallinity, is understood to mean primarily long-range order, with points defects considered as being less important. Long-range order means that translational symmetry is preserved at every point of the crystalline structure. The existence of rotational symmetry alone, on the other hand, implies short-range order.

CRYSTALLINITY INDICES OF LOW-TEMPERATURE QUARTZ

Several indices determined from X-ray diffractometry, infrared spectroscopy and differential thermal analysis have been proposed to-date to determine the crystallinity of quartz varieties.

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Plusnina (1978, 1979) assumed that the difference in intensity of the *111*, *102* and *111* reflections, noticed earlier by Jakovleva et al. (1975), can be utilized for the determination of the degree of crystallinity of chalcedonies. She proposed the intensity ratio of reflections from the (*102*) planes (d = 2.28 Å) and (*111*) planes (d = 2.24 Å), i.e. $\frac{I_{102}}{I_{111}}$, as an X-ray measure of crystallinity of quartz. It was assumed that the lower the ratio, the more crystalline was the given variety (Plusnina 1978, 1979; Barsanov et al. 1979).

In 1976 Murata and Norman suggested the following X-ray crystallinity index:

$$CI = 10 \cdot F \cdot \frac{a}{b} \qquad (1)$$

The quantities a and b in equation (1) are measured from X-ray diffraction patterns in the way shown in Fig. 1. The quantity b is the total height of the $\lambda\alpha_1$ peak from the (*212*) plane, measured from the background level, while a is partial height of the same peak measured from the level of the $\lambda\alpha_2$ component of diffraction from the same plane. F is an instrumental factor chosen in such a way that the CI index will be 10 for quartz showing the highest degree of crystalline perfection.
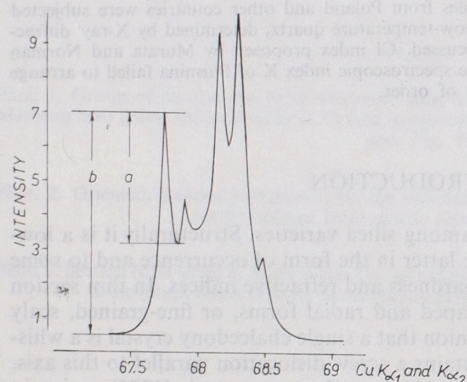

Fig. 1. X-ray index of crystallinity *CI* for quartz after Murata and Norman (1976)

The *CI* index of Murata and Norman estimates the crystallinity of a quartz variety as the ability to separate X-ray diffraction on the (*212*) plane for the two components, $\lambda\alpha_1$ and $\lambda\alpha_2$, of the radiation used.

Infrared spectroscopy was used for the determination of crystalline perfection of low-temperature quartz varieties by Plusnina (1978, 1979), who noticed that the 800—780 cm⁻¹ doublet changes its appearance from quartz to opal — chalcedony. The 780 cm⁻¹ band becomes less and less distinct, and a new band appears at 565——555 cm⁻¹, arising from Si—O—Si units typical of tridymite. Plusnina suggested that the spectroscopic crystallinity index be determined from the following equation:

$$K = 10 \cdot f \cdot \frac{a}{b} \qquad (2)$$

The quantities a and b from equation (2) are measured from infrared spectra in the way shown in Fig. 2. The quantity b is the total height of the 780 cm⁻¹ band, measured from the background level, whereas the quantity a is partial height of the same band measured from the level of its separation (so-called deep) from the doublet.
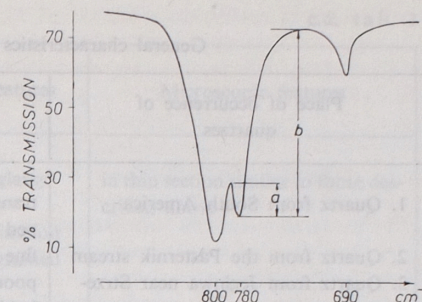

Fig. 2. Crystallinity index *K* from IR-spectroscopy after Plusnina (1979)

The instrumental factor is selected as in X-ray method. Moreover, Plusnina found a correlation between the spectroscopic crystallinity index and the X-ray index $\frac{I_{102}}{I_{111}}$.

In earlier papers it was suggested that the intensity ratios of the 800 to 695 cm⁻¹ bands be taken as a measure of crystallinity (Nemecz et al., 1962 fide Hlavay 1978). Badia et al. (1975), on the other hand, made use of the intensity ratios of 400 and 378 cm⁻¹ bands.

Differential thermal analysis of different quartz varieties has shown that the breadth of endothermic peak (about 573°C) is variable, and its maximum temperature shifts depending on the crystallinity of quartz variety (Smykatz-Kloss 1970, 1972). It has been found that cryptocrystalline quartz varieties display a broad, diffuse minimum instead of the sharp peak with considerable hysteresis.

MATERIALS

The studies of crystalline perfection of different forms of silica were carried out on 12 quartz samples from Poland and other countries, 9 chalcedony samples from Szklary and 7 chalcedonies from Lubiechowa (Sudetes). Their general macroscopic and partial microscopic characteristics are presented in Table 1.

RESULTS

Crystallinity indices for the samples studied were determined with X-ray diffraction and infrared spectroscopic methods.

The X-ray crystallinity index of Murata and Norman (1976) was adopted. The $\frac{I_{102}}{I_{111}}$ ratio was rejected as a measure of crystallinity because it was noticed that its value changed in response to the change in orientation of powdered sample. Moreover, this index failed to arrange the set of samples according to the macroscopically discernible differences in crystallinity. Thus, many (but not all) quartzes and chalcedonies of the agate type would have to be classified as having the highest degree of crystallinity, chalcedonies and several quartzes as medium-crystalline, whereas chalcedonies with tridymite groupings and some chalcedonies of the agate type — as having the lowest degree of perfection. It is evident, therefore, that this index has no ordering value.

X-ray diffraction patterns were recorded with a Geigerflex Rigaku diffractometer, using Ni-filtered CuK$_\alpha$ radiation at U = 30 kV and I = 20 mA. The instrument settings

Table 1

General characteristics of investigated samples

Place of occurrence of quartzes	Macroscopic features
1. Quartz from South America	transparent crystals a few cm in size, with well-developed faces and pronounced transverse striation
2. Quartz from the Pasternik stream	fine crystals referred to as "Marmarossa diamonds"
3. Quartz from Jegłowa near Strzegom	poorly transparent crystal with markedly elongate habit
4. Quartz from Karpniki near Jelenia Góra	nearly transparent crystal a few cm in size
5. Quartz from Brazil	fragment of poorly transparent crystal, a few cm in size
6. Quartz from Młoty near Bystrzyca Kłodzka	medium-grained milky quatrz
7. Goiana quartz — Brazil	fragment of poorly transparent crystal, a few cm in size
8. Quartz from Lubiechowa near Świerzawa	transparent crystals a few mm in size
9. Quartz from Rudno near Krzeszowice	transparent crystals a few mm in size
10. Quartz from the Rhodopes — Bulgaria	fairly transparent crystals a few mm in size
11. Synthetic quartz manufactured in Experimental Department of Inst. of Electronic Materials Technology in Warsaw	fragment of transparent monocrystal
12. Quartz from Harz — GDR	automorphic crystals a few mm in size, with poorly defined faces of vertical prism

Place of occurrence of chalcedonies	Macroscopic features	Microscopic features
Chalcedonies from Szklary near Ząbkowice Śląskie:		
1. Dark honey-yellow chalcedony	semivitreous, uniformly coloured	"salt-and-pepper" groundmass, scales up to 6 μm in size, averaging 1—2 μm, separated by short-fibrous chalcedony of fibre length 2—7 μm, on which grow quartz grains 5—20 μm in size
2. Vitreous chalcedony (chrysoprase)	intensely green, with glassy lustre	"salt-and-pepper" groundmass with grains up to 1 μm and less; groundmass contains spherulites 3—6 μm in size and rosette-like quartz aggregates 7—20 μm, sometimes up to 25 μm in size

Place of occurrence of chalcedonies	Macroscopic features	Microscopic features
3. New chalcedony	colourless, with glassy lustre	in thin section similar to those described above
4. Laminated chalcedony	open-work combination of white sugary-grained forms	
5. White sugary-grained chalcedony	compact, very fine-grained, resembling sugar	
6. Blue sugary-grained chalcedony	bluish sugary-grained variety	groundmass made up of fine scales 1—5 μm in size, containing rosette-like quartz grains 10—20 μm in size; the bulk of groundmass is weakly birefringent, resembling tridymite
7. White chalcedony	similar to white sugary-grained variety	
8. Chrysoprase	green-coloured sugary-grained chalcedony	similar to white and blue sugary-grained varieties
9. Translucent chalcedony	colourless, translucent, with glassy lustre	
Chalcedonies from vacuoles in "amygdaloids" from Lubiechowa near Świerzawa:		
1. flint druse	multicoloured, spotted	feathery forms 5—15 μm, fibrous up to 35 μm in size. "Salt-and-pepper" groundmass of grain-size up to 2 μm, also containing quartz grains 5—12 μm, sporadically up to 30 μm in size
2. chalcedony druse	agate a few cm in size, grey and pale-blue in colour	long (60—220 μm) and short (10—50 μm) fibres adjoin less common fine-grained and finescaly forms up to 7 μm in size
3. Lubiechowa IV	matt, blue-grey agate	
4. Blue chalcedony	intensely blue, with semivitreous lustre	fine-scaly forms 1—3 μm in size
5. Lubiechowa II	similar to blue chalcedony	in thin section similar to blue chalcedony
6. White chalcedony	white reniform bodies, sometimes with subtle, banded arrangement of white hues	scaly forms 15—35 μm in size, less common thin fibres 5 μm in length
7. Pink chalcedony	matt variety occurring in association with calcite	

Table 2

X-ray crystallinity index

Sample	CI
1. Quartz from South America	9.9
2. Quartz from the Pasternik stream	9.9
3. Quartz from Jegłowa near Strzegom	9.9
4. Quartz from Karpniki near Jelenia Góra	8.5
5. Quartz from Brazil	8.5
6. Quartz from Młoty near Bystrzyca Kłodzka	8.2
7. Goiana quartz — Brazil	8.1
8. Quartz from Lubiechowa near Świerzawa	7.8
9. Quartz from Harz — GDR	7.8
10. Dark honey-yellow chalcedony from Szklary	7.8
11. Quartz from Rudno near Krzeszowice	7.1
12. Quartz from the Rhodopes — Bulgaria	7.1
13. Synthetic quartz — Warsaw	7.1
14. Vitreous chalcedony (chrysoprase) — Szklary	5.7
15. New chalcedony — Szklary	5.7
16. Flint druse — Lubiechowa	5.2
17. Laminated chalcedony — Szklary	4.5
18. White sugary-grained chalcedony — Szklary	4.3
19. Pink chalcedony — Lubiechowa	4.3
20. White chalcedony — Lubiechowa	2.8
21. Blue sugary-grained chalcedony — Szklary	1.8 Tr
22. Chalcedony druse — Lubiechowa	2.8
23. Lubiechowa IV	2.4
24. Lubiechowa II	1.4
25. Blue chalcedony — Lubiechowa	1.4
26. White chalcedony — Szklary	1.4 Tr
27. Chrysoprase — Szklary	<1.0 Tr
28. Translucent chalcedony — Szklary	<1.0 Tr

Index Tr denotes the presence of groupings of the tridymite type

in the 2θ angle range of 67—69° were: sensitivity 400 cps, time constant 5 sec., scanning speed 1/4°/min., chart speed 5 mm/min. For each powdered sample orientation was changed five times. The arithmetic mean of five measurements was taken as the quantity $\frac{a}{b}$ for equation (1). Since the highest obtained value of $\frac{a}{b}$ av. was 0.7, the selected instrumental factor F was 1.42.

X-ray crystallinity index for the samples studied is given in Table 2.

The macro- and microscopic differences between the samples are reflected in the value of crystallinity indices. For quartzes CI indices are not less than 7.0. Chalcedonies containing a great number of quartz grains have indices from 7.8 to 5.2. Scaly forms show low, and long-fibrous forms still lower crystallinity. Chalcedonies containing tridymite groupings exhibit the lowest degree of order.

Owing to several reorientations of the powdered sample it was found that the $\frac{a}{b}$ ratio, i.e. CI index value, did not virtually depend on the orientation of crystallites

in the sample. It was noticed, however, that the relative intensities of three lines: $\lambda\alpha_1$ from (212), $\lambda\alpha_1$ from (203), and $\lambda\alpha_1$ from (301) changed for different orientations of the sample. The change in intensity was the more pronounced, the better ordered was the sample. In fact, the better the long-range order, the greater is the variability of the number of crystallites with the (hkl) planes parallel to the surface of a flat sample, that is, the greater is the variability of the relative intensities of reflections. However interesting this inference, it can hardly be used for suggesting a new X-ray crystallinity index.

On the basis of the above considerations it can be stated that the X-ray crystallinity index CI of Murata and Norman is reliable.

During the present studies, special emphasis was laid on the determination of the spectroscopic crystallinity index K. This index seems to be most questionable because, contrary to Plusnina's suggestion (1978), no correlation was noted between

Table 3

Spectroscopic crystallinity index

Sample	K	CI
1. Pink chalcedony — Lubiechowa	9.8	4.3
2. White chalcedony — Lubiechowa	8.2	2.8
3. Flint druse — Lubiechowa	6.5	5.2
4. Chalcedony druse — Lubiechowa	5.8	2.8
5. Blue chalcedony — Lubiechowa	5.8	1.4
6. Quartz from Brazil	5.3	8.5
7. Quartz from Karpniki near Jelenia Góra	5.0	8.5
8. Vitreous chalcedony (chrysoprase) — Szklary	4.6	5.7
9. Quartz from South America	4.3	9.9
10. Dark honey-yellow chalcedony — Szklary	4.3	7.8
11. New chalcedony — Szklary	4.1	5.7
12. Lubiechowa IV	4.1	4.1
13. Quartz from Lubiechowa	3.9	7.8
14. Quartz from Harz — GDR	3.9	7.8
15. Quartz from Młoty near Bystrzyca Kłodzka	3.5	8.1
16. Quartz from the Pasternik stream	3.4	9.9
17. Quartz from Rudno near Krzeszowice	3.4	7.1
18. Quartz from the Rhodopes — Bulgaria	3.4	7.1
19. Synthetic quartz — Warsaw	3.4	7.1
20. Goiana quartz — Brazil	3.2	8.1
21. White sugary-grained chalcedony — Szklary	3.2	4.3
22. White chalcedony — Szklary	3.1 Tr	1.4 Tr
23. Quartz from Jegłowa near Strzegom	2.9	9.9
24. Laminated chalcedony — Szklary	2.6	4.5
25. Lubiechowa II	2.4	1.4
26. Blue sugary-grained chalcedony — Szklary	1.9 Tr	2.8 Tr
27. Translucent chalcedony — Szklary	1.4 Tr	<1.0 Tr
28. Chrysoprase — Szklary	0.9 Tr	<1.0 Tr

Index Tr denotes the presence of groupings of the tridymite type

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the X-ray and spectroscopic indices. Infrared spectra for the samples studied were obtained with Beckman 4220, C. Zeiss-Jena UR-20 and Specord 71 IR spectrometers, using 1 : 400 KBr discs. Several measurements were made for each sample. Crystallinity indices were determined by the method of Plusnina from spectra recorded with a Beckman 4220 spectrometer. The highest obtained value of $\frac{a}{b}$ av. was 0.4, so the instrumental factor F was taken as 2.42.

The values of the index K are listed in Table 3, along with X-ray crystallinity indices determined for the same samples. A comparison of these indices shows that samples with the same or similar values of CI index often have quite different spectroscopic indices. It appears, therefore, that there is no simple or direct correlation between them.
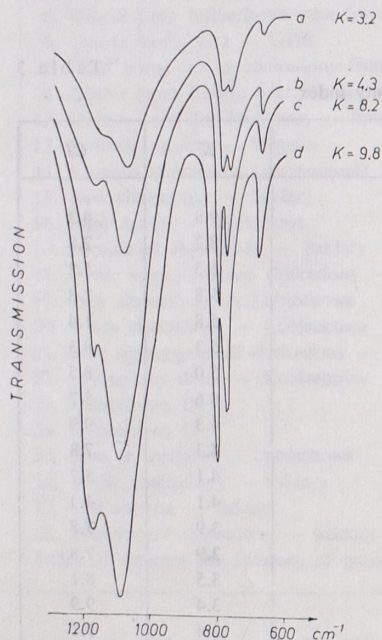

Fig. 3. IR-spectra of certain samples

a — Goiana quartz, b — South America quartz, c — white chalcedony, Lubiechowa, d — rose chalcedony, Lubiechowa

The author accounts for this lack of agreement in the following way: It should be remembered that the 800—780 cm^{-1} doublet lies in the region of short- to medium-range order. Infrared spectroscopy provides information on short- and medium-range order only (up to 20 Å), that is below the range comprised by X-ray diffractometry. In consequence, the poorly ordered pink chalcedony from Lubiechowa, most fine-grained of the samples studied, appeared to have the highest spectroscopic crystallinity index ($CI = 4.3$). The absorption bands of this sample are narrow, showing the highest level of absorption. This is because the sample is characterized by medium-range order. The spectrum of the Lubiechowa pink chalcedony is compared with other spectra in Fig. 3. In conclusion, it can be stated that there is no correlation between the X-ray and spectroscopic crystallinity indices because such correlation is not possible. The two methods, and therefore the two indices, determine crystallinity for different, not fully coinciding areas in the structure of quartz.

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Infrared spectra were also recorded for samples in the form of Nujol mulls and evaporated suspensions in isoamyl alcohol. For each sample five measurements were made, changing the orientation of the sample on the KBr carrier plate. It has been found that for samples prepared in this way, the intensity of the component bands of the 800—780 cm^{-1} doublet becomes reversed compared with the spectra of KBr disks (Fig. 4). This observation was confirmed by investigations repeated several times on different spectrometers. The samples were prepared in such a way that the absorption level at 1300 cm^{-1} would be constant for successive samples.
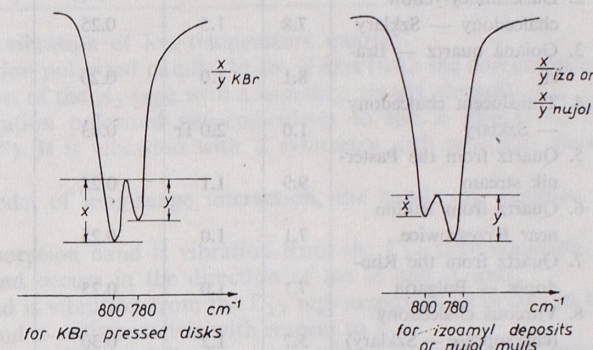

Fig. 4. Reversibility of intensity of quartz doublet bands for samples prepared in form of sediment in izoamyl alcohol or nujol mull

The author suggests that the following equations be taken as a measure of reversibility of the intensity of bands in the 800—780 cm^{-1} doublet:

$$r_{iso} = \frac{\frac{x}{y} KBr}{\frac{x}{y}_{Isol}} ; \qquad r_{nujol} = \frac{\frac{x}{y} KBr}{\frac{x}{y}_{nuJol}} \qquad (3)$$

where: x — intensity of the 800 cm^{-1} band, measured to the level of separation of the doublet components,
y — intensity of the 780 cm^{-1} band, measured to the same level (see Fig. 4).
$\frac{x}{y_{KBr}}$ is the value of $\frac{x}{y}$ determined for KBr disks, $\frac{x}{y_{iso}}$ — for evaporated suspensions in isoamyl alcohol, $\frac{x}{y_{nujol}}$ — for Nujol mulls.

The arithmetic mean of five measurements was taken as the value of $\frac{x}{y_{Iso}}$ or $\frac{x}{y_{nuJol}}$. It is worth noting that several samples, especially quartzes and chalcedonies with tridymite groupings, showed significant variation in the values of r_{iso} and r_{nujol}, evidently dependent on the actual orientation of grains on the KBr carrier plate. Table 4 gives the determined values of the index r, together with the crystallinity indices CI and K from Tables 1 and 2.

An attempt was made to explain the intensity reversal of the component bands of the quartz doublet, basing on the studies of Kleinman and Spitzer (1961), Spitzer and Kleinman (1962), Scott and Porto (1967), and Elcombe (1967). These studies determine the frequency of quartz vibrations, adopting the model of short-range and long-range interaction.

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Table 4

Intensity reversal of the doublet components in different media with respect to KBr

Sample	CI	$\dfrac{x}{y_{KBr}}$	$\dfrac{x}{y_{iso}}$	r_{iso}	$\dfrac{x}{y_{nuJol}}$	r_{nuJol}
1. Quartz from South America	9.9	1.0	0.14—0.17	7.1—5.8	0.3	3.3
2. Dark honey-yellow chalcedony — Szklary	7.8	1.5	0.25	6.0	0.3	5.0
3. Goiana quartz — Brazil	8.1	1.0	0.20	5.0	0.45	2.2
4. Translucent chalcedony — Szklary	1.0	2.0 Tr	0.43	4.6	0.47	4.2
5. Quartz from the Pasternik stream	9.9	1.1	0.25	4.4	0.87	1.4
6. Quartz from Rudno near Krzeszowice	7.1	1.0	0.25	4.0	0.44	2.3
7. Quartz from the Rhodopes — Bulgaria	7.1	1.0	0.25	4.0	0.38	2.6
8. Vitreous chalcedony (chrysoprase — Szklary)	5.7	1.2	0.30	4.0	0.5	2.4
9. Quartz from Karpniki near Jelenia Góra	8.5	1.4	0.37	3.8	0.5	2.0
10. Quartz from Młoty near Bystrzyca Kłodzka	8.2	1.4	0.36	3.8	0.43	3.0
11. New chalcedony — Szklary	5.7	1.1	0.30	3.7	0.5	2.5
12. Laminated chalcedony	4.5	0.9	0.25	3.6	0.35	2.5
13. Synthetic quartz — Warsaw	7.1	1.0	0.28	3.5	0.31	3.0
14. White sugary-grained chalcedony — Szklary	4.3	1.4	0.4	3.5	0.47	3.6
15. Quartz from Jegłowa near Strzegom	9.9	1.1	0.33	3.4	0.33	3.4
16. Quartz from Lubiechowa	7.8	1.0	0.30	3.3	0.39	2.5
17. Quartz from Harz — GDR	7.8	1.0	0.31	3.2	0.50	2.0
18. Quartz from Brazil	8.5	1.5	0.5	3.0	0.85	1.8
19. Blue sugary-grained chalcedony — Szklary	2.8	1.7 Tr	0.6	2.8	0.74	2.5
20. White chalcedony — Szklary	1.4	2.0 Tr	0.76	2.6	1.0	2.0
21. Chrysoprase — Szklary	1.0	2.5 Tr	1.0	2.5	1.0	2.5
22. Flint druse — Lubiechowa	5.2	1.5	0.65	2.4	0.65	2.1
23. Lubiechowa IV	2.4	1.6	0.83	2.0	1.1	1.8
24. Chalcedony druse — Lubiechowa	2.8	1.2	0.67	1.8	0.67	1.7
25. Blue chalcedony — Lubiechowa	1.4	1.7	1.0	1.7	1.1	1.5
26. Lubiechowa II	1.4	0.9	0.6	1.6	0.7	1.4
27. White chalcedony — Lubiechowa	2.8	1.7	1.22	1.4	1.3	1.3
28. Pink chalcedony — Lubiechowa	4.3	1.6	1.6	1.0	1.6	1.0

Table 4 (c.d.)

Si—O—Si stretching vibration of low-temperature quartz:

— 778 cm^{-1} is vibration polarized parallel to the Z axis (with the corresponding radius "e"). It is vibration of the A_2 type with a non-zero matrix element M_z;

— 797 cm^{-1} is vibration polarized perpendicularly to the Z axis (with the corresponding radius "o"). It is vibration with E symmetry with non-zero matrix elements $M_x = M_y$.

According to the model of long-range interaction, the bands are assigned as follows:

— the 778 cm^{-1} absorption band is vibration from the Γ_{3T} representation. It is doubly degenerated and occurs in the direction of the Z and X axis;

— the 797 cm^{-1} band is vibration from the Γ_{2T} representation. It occurs in the direction of the X axis and is antisymmetric with respect to it.

Samples to be subjected to X-ray diffraction and infrared spectroscopic investigations are ground to a grain-size of 1—2 μm. For highly crystalline samples this size is at least equal to the range of order. This means that the ground grains have the clearly defined position of crystallographic axes. Simultaneously, grinding disrupts bonds. The broken bonds are located at the grain boundaries, so that the grains can interact as weak dipoles. The most advantageous situation from the viewpoint of energy involved will be when the directions of strongest bonds are concordant. For low-temperature quartz the strongest bond is in the direction of the Z axis, but bonds in the direction of the X axis are equally strong. If such grains are immersed in liquid, e.g. in nujol or isoamyl alcohol, this medium helps the molecule dipoles interact and orientate themselves with respect to one another. These grains will arrange themselves on the surface of KBr plate in such a way that the directions of their Z axes, or the directions close to these axes, will be concordant, i.e. parallel to the plate surface. Diagrams of such idealized situations are presented in Figs. 5 and 6. Non-polarized radiation was used.

The oriented position of grains with respect to the incidence directions of infrared radiation results in that the recorded intensity of vibration occurring along the X_1, X_2 or X_3 axis (Γ_{2T} or $M_x = M_y$), i.e. vibration of a frequency of 797 cm^{-1} occurring in the direction of radiation propagation $\vec{k}$, is less than the intensity of the 778 cm^{-1} band. This change in the intensity of bands may be referred to as partial polarization by orientation. This phenomenon is undoubtedly caused by the dipole-dipole interaction. A comparison of r_{iso} and r_{nujol} values shows that the intensity reversal of the doublet component bands depends on the dielectric constant of a liquid and on the strength of dipole moments of its molecules. This statement is borne out by the higher r_{iso} than r_{nujol} value (see Table 4).

The oriented arrangement of grains on the plate surface was demonstrated experimentally. The KBr plate with sediment was inclined in the beam path (Fig. 7).
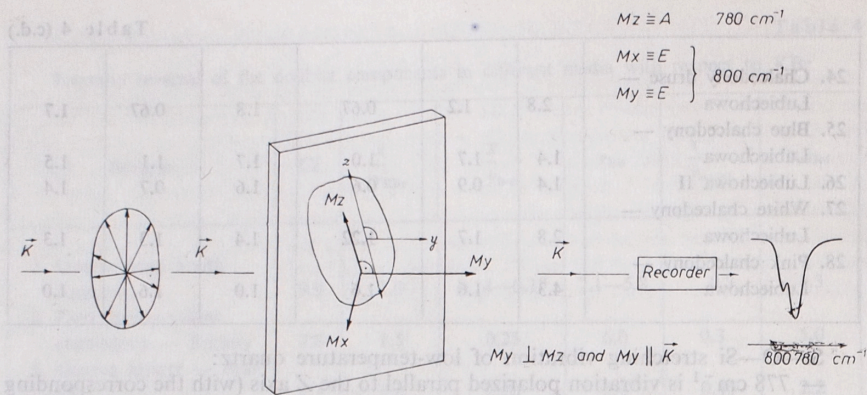
$$Mz \equiv A \qquad 780\ cm^{-1}$$
$$\left.\begin{array}{l} Mx \equiv E \\ My \equiv E \end{array}\right\} \quad 800\ cm^{-1}$$

$$My \perp Mz \text{ and } My \parallel \vec{K}$$

$$800\ 780\ cm^{-1}$$

Fig. 5. Oriented arrange of quartz grains in sediment or mull on KBr window (short — range interaction model)

$$Mz \equiv \Gamma_{3T} \qquad 780\ cm^{-1}$$
$$Mx_1 = Mx_2 = Mx_3 \equiv \Gamma_{3T} \quad 800\ cm^{-1}$$

$$Mx_2 \perp Mz \text{ and } Mx_2 \parallel \vec{K}$$

$$800\ 780\ cm^{-1}$$
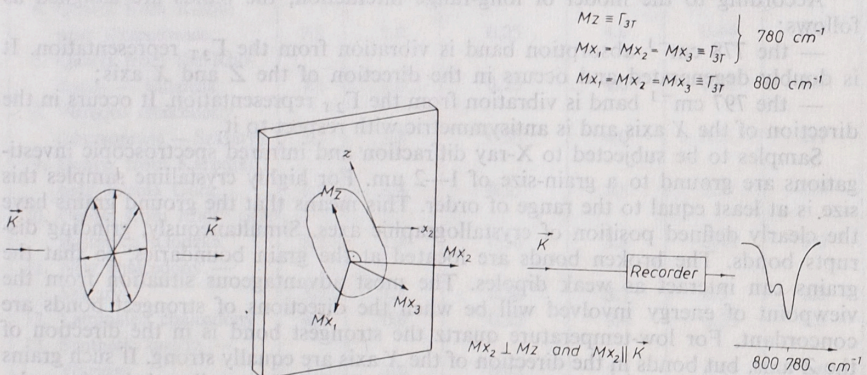
Fig. 6. Oriented arrange of quartz grains in sediment or mull on KBr window (long — range interaction model)

$$My \perp Mz \text{ but } My \nparallel \vec{K}$$
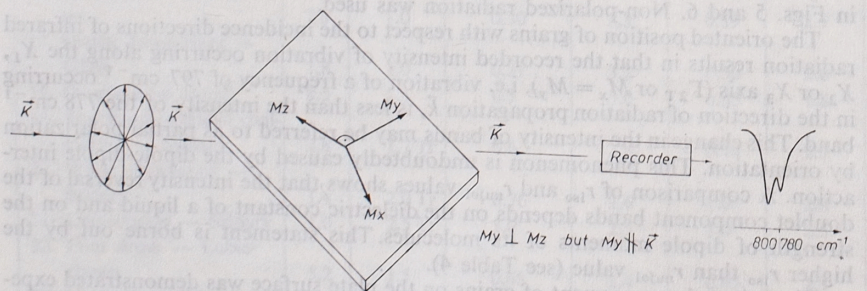
$$800\ 780\ cm^{-1}$$

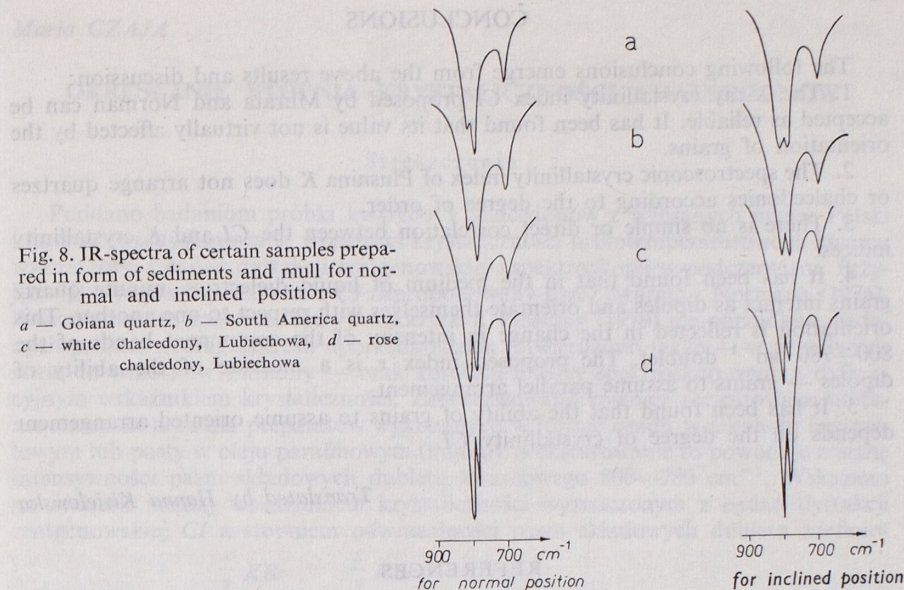Fig. 7. Inclined position of KBr window with sediment or mull

Fig. 8. IR-spectra of certain samples prepared in form of sediments and mull for normal and inclined positions

a — Goiana quartz, b — South America quartz, c — white chalcedony, Lubiechowa, d — rose chalcedony, Lubiechowa

for normal position

for inclined position

It was noted that the 797 cm⁻¹ band became more and more intense. From a comparison of Figs. 5 and 7 or 6 and 7 it appears that for the inclined plate, vibrations which were previously parallel to the direction of radiation propagation are no longer parallel, and therefore can be recorded. In a *KBr* disc the oriented arrangement of quartz grains does not exist. This fact was also checked by mounting the disc in an inclined position in the beam path. Figure 8 shows spectra obtained for selected samples at their perpendicular and inclined positions.

RELATIONSHIP BETWEEN THE INDEX OF BAND INTENSITY REVERSAL r AND X-RAY CRYSTALLINITY INDEX CI

Table 4 shows that samples which have a high X-ray crystallinity index are also characterized by a high reversibility index. In apparent disagreement with this conclusion are samples containing tridymite groupings, i.e. those having low *CI* (samples 4, 19, 20, 21). It should be remembered, however, that Si—O—Si groupings of the tridymite type display a single band at 800 cm⁻¹ in the frequency range in question. This band "adds up" to the 797 cm⁻¹ band from the quartz doublet, whereby its intensity falsely increases. In fact, the $\frac{c}{a}$ *KBr* ratio is for these samples the highest. For that reason the quotient *r* is, as it were, falsely high. Worth noting are also the two last samples in Table 4. Pink chalcedony from Lubiechowa does not show any orientation in the medium of isoamyl alcohol or nujol, whereas white chalcedony exhibits slight orientation. The crystallites of pink chalcedony are small, usually less than 0.5 μm in size. Therefore, in a grain obtained by grinding (1—2 μm) a few randomly oriented crystallites may be present. A single grain is then a very weak dipole or no dipole at all. There is, therefore, no reason for mutual orientation of grains (pink chalcedony), or it is very slight (white chalcedony).

CONCLUSIONS

The following conclusions emerge from the above results and discussion:

1. The X-ray crystallinity index *CI* proposed by Murata and Norman can be accepted as reliable. It has been found that its value is not virtually affected by the orientation of grains.

2. The spectroscopic crystallinity index of Plusnina *K* does not arrange quartzes or chalcedonies according to the degree of order.

3. There is no simple or direct correlation between the *CI* and *K* crystallinity indices.

4. It has been found that in the medium of liquid dielectrics, minute quartz grains interact as dipoles and orientate themselves with respect to one another. This orientation is reflected in the change in intensity of the component bands of the $800\text{—}780 \text{ cm}^{-1}$ doublet. The proposed index *r* is a measure of the ability of dipoles — grains to assume parallel arrangement.

5. It has been found that the ability of grains to assume oriented arrangement depends on the degree of crystallinity *CI*.

Translated by Hanna Kisielewska

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Maria CZAJA

OKREŚLANIE STOPNIA KRYSTALICZNOŚCI CHALCEDONÓW

Streszczenie

Poddano badaniom próbki kwarców i chalcedonów z wybranych miejsc Polski i świata. Przedyskutowano wskaźniki krystaliczności niskotemperaturowego kwarcu wyznaczone z badań dyfrakcji rentgenowskiej i spektroskopii w podczerwieni. Przyjęto jako poprawny wskaźnik *CI* zaproponowany przez Muratę i Normana (1976). Stwierdzono, że spektroskopowy wskaźnik *K* Plusniny (1979) nie porządkuje badanych próbek według zakresu uporządkowania. Stwierdzono także — w przeciwieństwie do wniosków Plusniny — brak korelacji między spektroskopowym a dyfrakcyjnym wskaźnikiem krystaliczności. Zaobserwowano również zorientowane ułożenie ziaren kwarcu dla preparatów wykonanych w formie osadu w alkoholu izoamylowym lub pasty w oleju parafinowym (nujolu). Stexturowanie to powoduje zmianę intensywności pasm składowych dubletu kwarcowego $800\text{—}780 \text{ cm}^{-1}$. Wskazano na związek między wskaźnikiem krystaliczności wyznaczonym z badań dyfrakcji rentgenowskiej *CI* a stopniem odwracalności pasm składowych dubletu zdefinio-

wanym jako $r_{izo} = \dfrac{\frac{x}{y} KBr}{\frac{x}{y_{izo}}}$ lub $\dfrac{\frac{x}{y} KBr}{\frac{x}{y_{nujol}}} = r_{nujol}.$

OBJAŚNIENIA FIGUR

Fig. 1. Rentgenowski wskaźnik krystaliczności *CI* według Muraty i Normana (1976)

Fig. 2. Spektroskopowy wskaźnik krystaliczności *K* według Plusniny (1979)

Fig. 3. Spektrogramy wybranych próbek
  a — kwarc, Goiana, *b* — kwarc, Ameryka Południowa, *c* — chalcedon biały, Lubiechowa, *d* — chalcedon różowy, Lubiechowa

Fig. 4. Odwracanie intensywności pasm składowych dubletu kwarcowego dla próbek w postaci osadu w alkoholu izoamylowym lub pasty w oleju parafinowym (nujolu)

Fig. 5. Zorientowane ułożenie ziaren w osadzie lub paście na okienku z KBr (model oddziaływania bliskiego zasięgu)

Fig. 6. Zorientowane ułożenie ziaren w osadzie lub paście na okienku z KBr (model oddziaływania dalekiego zasięgu)

Fig. 7. Pochylone ustawienie okienka KBr z naniesionym osadem lub pastą

Fig. 8. Spektrogramy wybranych próbek wykonane metodą osadzania w alkoholu izoamylowym dla normalnego i pochylonego ustawienia okienka w torze wiązki
  a — kwarc, Goiana, *b* — kwarc, Ameryka Południowa, *c* — chalcedon biały, Lubiechowa, *d* — chalcedon różowy, Lubiechowa

Марья ЧАЯ

ОПРЕДЕЛЕНИЕ СТЕПЕНИ КРИСТАЛЛИЧНОСТИ МИНЕРАЛОВ

Резюме

Подверглись исследованиям образцы кварцев и халцедонов из некоторых мест Польши и мира. Были обсуждены показатели кристалличности низкотемпературного кварца, определенные на основании рентгеновской дифракции и ИК-спектроскопии. Как верный принято показатель *Cl*, предложенный Муратой и Норманом (1976). Констатировано, что спектроскопический показатель *К* Плюснины (1979) не приводит в порядок изучаемые образцы по степени упорядоченности. Констатировано также, — в противоположность выводам Плюснины — отсутствие корреляции между спектральным и дифракционным показателями кристалличности. Наблюдалось также ориентированное размещение кварцевых зерен для препаратов, сделанных в виде осадка в изоамиловом алкоголе или пасты в парафиновом масле (nujol). Такое сложение вызывает изменение интенсивностей составных полос кварцевого дублета 800— —780 см$^{-1}$. Указано на связь между показателем кристалличности, установленным на основании рентгеновской дифракции *CI* и степенью обратимости составных полос дублета, определенного как $r_{izo} = \dfrac{\dfrac{x}{y} \text{KBr}}{\dfrac{x}{y}_{izo}}$ или $\dfrac{\dfrac{x}{y} \text{KBr}}{\dfrac{x}{y}_{nujol}} = r_{nujol}$

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Рентгеновский показатель кристалличности *CI*, по Мурату и Норману (1976)
Фиг. 2. Спектроскопический показатель кристалличности *К*, по Плюснине (1979)
Фиг. 3. Спектрограммы избранных образцов
а — кварц, Гоиана, *b* — кварц, Южная Америка, *с* — белый халцедон, Любехова, *d* — розовый халцедон, Любехова
Фиг. 4. Реверсия интенсивности составных полос кварцевого дублета для образцов в виде осадка в изоамиловом алкоголе или пасты в парафиновом масле (nujol)
Фиг. 5. Ориентированное размещение зерен в осадке или в пасте на окошке с КВг (модель близкого воздействия)
Фиг. 6. Ориентированное расположение зерен в осадке или в пасте на окошке с КВг (модель далекого воздействия)
Фиг. 7. Наклонная установка окна КВг с нанесенным осадком или пастой
Фиг. 8. Спектрограммы избранных образцов, полученных методом осаждения в изоамиловом алкоголе для нормального или наклонного положения окна в траектории пучка
а — кварц, Гоиана, *b* — кварц, Южная Америка, *с* — белый халцедон, Любехова, *d* — розовый халцедон, Любехова