THE QUARTZ-CRISTOBALITE TRANSFORMATION IN HEATED CHERT ROCK COMPOSED OF MICRO AND CRYPTO-QUARTZ BY MICRO-RAMAN AND FT-IR SPECTROSCOPY METHODS

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Abstract

The quartz-cristobalite transformation in heated natural chert (flint) rock composed of micro- and crypto-quartz was investigated in the temperature interval of 1000–1300°C by micro-Raman spectroscopy, FT-IR spectroscopy, X-ray diffraction and Scanning Electron Microscopy. A small amount of crystobalite was first observed in the chert after heating at 1000°C for 1 h and the transformation was almost completed after heating at 1300°C for 24 h. On the other hand, cristobalite was not detected in well-crystallized pure quartz after heating under the same conditions. The transformation occurs as a solid state nucleation and crystal growth of cristobalite replacing quartz at high-temperatures. The chert rock is naturally rich in crystal defects and boundaries which serve as nucleation sites and enable an earlier quartz-cristobalite transformation.

Keywords: cristobalite, crystal growth, FT-IR spectroscopy, nucleation, quartz, Raman spectroscopy, thermal transformation

Introduction

Pure quartz is readily transformed into cristobalite only at temperatures between 1470 and 1710°C [1]. However, in natural silica minerals this transformation has been observed at a lower temperature interval of 1100–1600°C [2]. There is a controversy about whether the quartz-cristobalite transformation is a direct process or necessitates the presence of an intermediate amorphous or liquid phase. Chaklader [3], Chaklader and Roberts [4] suggested that quartz goes through an amorphous transitional phase before transforming to cristobalite. On the other hand, Kuellmer and Poe [5] found no pronounced amorphous phase below 1550°C and showed that the transformation occurred through highly frag-

mented quartz with a high-temperature dislocation content. Stoch *et al.* [6–8] found that in natural quartz the presence of Al^{3+}, Na^+, K^+, Li^+ and Ce^{2+} impurities as isomorphous substitutions influence the rate of transformation into cristo-balite, the amorphous transition and the melting of quartz. Chaklader [9] found that smaller percentages of Al_2O_3 catalyze the transformation of quartz and the formation of cristobalite considerably.

In a previous publication Shoval *et al.* [10] showed by XRD that a small amount of cristobalite was formed in chert after heating at 1000°C for 1 h, and that increased amounts appeared at higher temperatures or longer heating times. In the present paper the nature of this transformation is investigated by vibra-tional Raman and IR spectroscopy.

Experimental

Samples

Samples of a local chert (collected from the Campainian Mishash Formation, Israel) were used. The dominant components of this chert are micro- and crypto-quartz [11]. A transparent rock-crystal (well-crystallized quartz collected from pegmatite of the Elat massive) was used for comparison. The samples were heated in an electric kiln at 1000, 1100, 1200 and 1300°C for 1 h and for 24 h. The measurements were obtained at room temperature.

Methods

– X-ray powder diffractograms were obtained with a Philips PW-1820/00 diffractometer (1720 based) using CuK_α radiation 35 kV–40 mA, and a curved graphite monochromator. For measuring the XRD crystallinity indexes of quartz, a step size of 0.020 2θ and a time-per-step of 10 s were used.

– Raman spectra were recorded with an XY Dilor multichannel micro-Raman spectrometer equipped with an Olympus optical microscope, a 3-stage monochromator and a CCD multichannel detector (EG&G). The green (514.5 nm) line of a Spectra Physics 2016 Argon ion laser at 500 mW was used as an exciting source. The spectra were recorded with a 50× objective and were obtained from accumulations lasting 360 s. Frequencies were calibrated with external (silicon line at 521 cm^{-1}) and internal (Argon plasma lines) standards.

– IR spectra were recorded using a Nicolet FT-IR spectrometer and 'Omnic' software. Disks containing 1 mg of the sample in 150 mg of KBr were employed. 'Galactic' software was used for peak fitting of the Raman and IR spectra. A mixed Gaussian+Lorentzian band shape was used for the fitting. The proportion between Gaussian and Lorentzian function was selected by the 'Galactic' software for best fitting.

– Scanning Electron Micrographs were obtained with a Hitachi S-800 micro-scope. The samples were broken or chipped and the freshly fractured surfaces were gold coated.

Results

X-ray diffraction

X-ray diffractograms of heated chert and well-crystallized pure quartz sam-ples are presented in Fig. 1. A small amount of cristobalite is first observed in the chert after heating at 1000°C for 1 h, and the transformation is almost completed after heating at 1300°C for 24 h, whereas only quartz is found in the unheated sample. On the other hand, cristobalite is not detected in well-crystallized pure
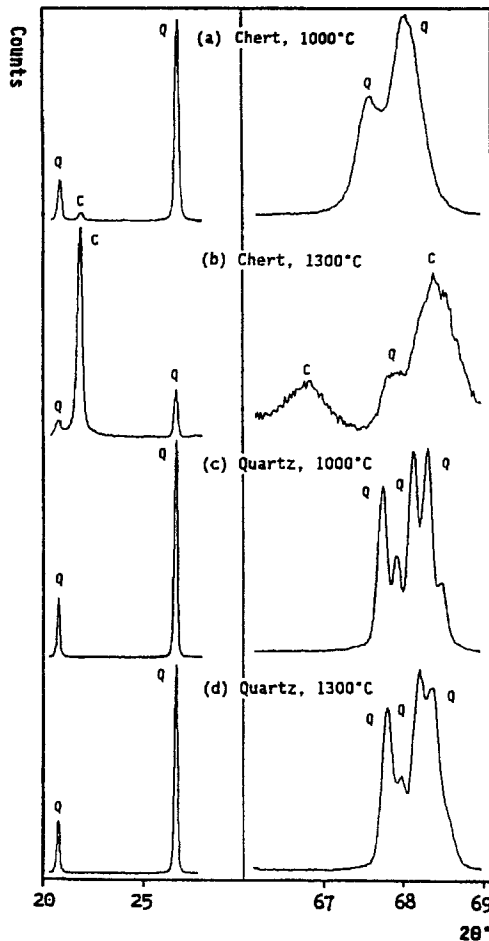

Fig. 1 X-ray diffractograms of the chert samples after heating for 1 h at 1000°C (a) and for 24 h at 1300°C (b); Well-crystallized pure quartz samples after heating for 1 h at

quartz after heating under the same conditions. The relative cristobalite to quartz height-ratios in the diffractograms of the heated chert samples, calculated by dividing the maximal intensities of the cristobalite and quartz main peaks at d=4.05 and 3.34, respectively, are listed in Table 1. The amounts of cristobalite increase with higher temperatures or longer heating times.

The XRD crystallinity indexes of the quartz in the heated chert samples, using Murata and Norman's [12] method, are summarized in Table 2. The chert

Table 1 Relative cristobalite to quartz height-ratios (in %) according to XRD, IR and micro-Raman spectroscopy after heating the chert samples for 1 h and for 24 h at 1000–1300°C. The Table demonstrates, for each sample, the Raman results measured from the spectra with the highest and lowest cristobalite signals

Heating temperature	Relative cristobalite to quartz height-ratios			
	XRD*	IR**	Raman***	
			High-content	Low-content
1000°C/1 h	2	3	0	0
1100°C/1 h	9	18	8	2
1200°C/1 h	32	76	19	7
1300°C/1 h	187	234	169	39
1000°C/24 h	6	11	22	0
1100°C/24 h	11	28	30	3
1200°C/24 h	230	219	363	42
1300°C/24 h	452	348	378	50

The relative ratios were calculated by dividing the maximal intensities of the cristobalite and quartz:
*main XRD peaks at d=4.05 and 3.34, respectively;
**IR bands at 620 and 694 cm^{-1}, respectively;
***main Raman bands at 411 and 465 cm^{-1}, respectively.

Table 2 XRD crystallinity indexes of the quartz (Murata and Norman method, [12]) after heating the chert samples for 1 h and for 24 h at 1000–1300°C, compared to well-crystallized pure quartz samples heated for 1 h at 1000°C and for 24 h at 1300°C

Temperature	XRD crystallinity index	Temperature	XRD crystallinity index
Chert samples			
1000°C/1 h	2.0	1000°C/24 h	2.5
1100°C/1 h	1.3	1100°C/24 h	1.7
1200°C/1 h	1.1	1200°C/24 h	0.6
1300°C/1 h	0.8	1300°C/24 h	>0
Quartz samples			
1000°C/1 h	10.0	1300°C/24 h	7.6

samples show very low crystallinity indexes, and above 1000°C the indexes decrease with an increase in the temperature or the heating time. Only a shallow splitting to two broad peaks (d=1.385 and 1.337) appears in the range 67–69 2θ after heating at 1000°C (Fig. 1). On the other hand, the pure quartz has a maximum crystallinity index at 1000°C, which remains high after heating at 1300°C for 24 h. A deep splitting to five sharp peaks (d=1.382, 1.379, 1.375, 1.372 and 1.369) appears in the range 67.5–69 2θ after heating at 1000°C (Fig. 1).

Infrared spectroscopy

IR spectra of heated chert samples are shown in Fig. 2. Characteristic IR bands of quartz and cristobalite [13] are observed in the spectra. As the tempera-
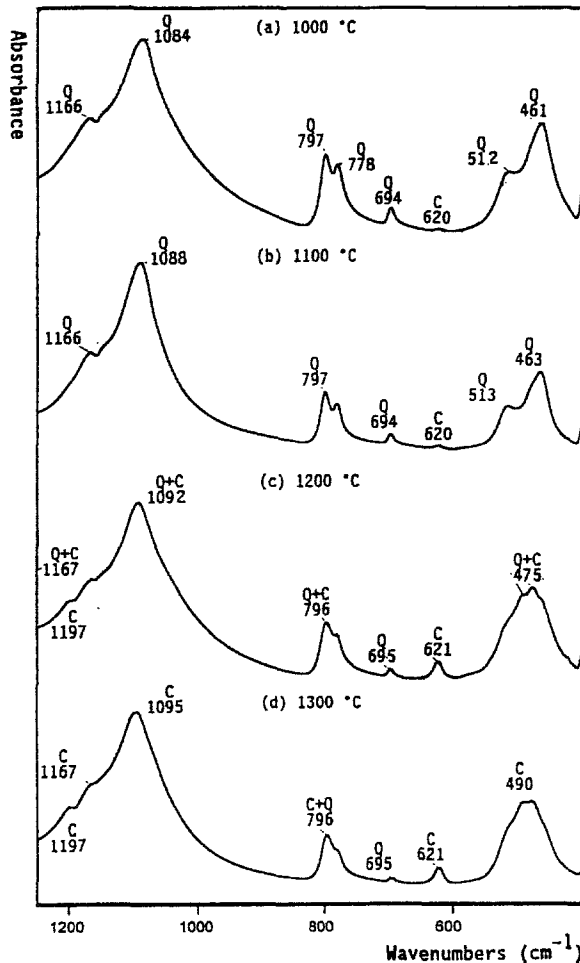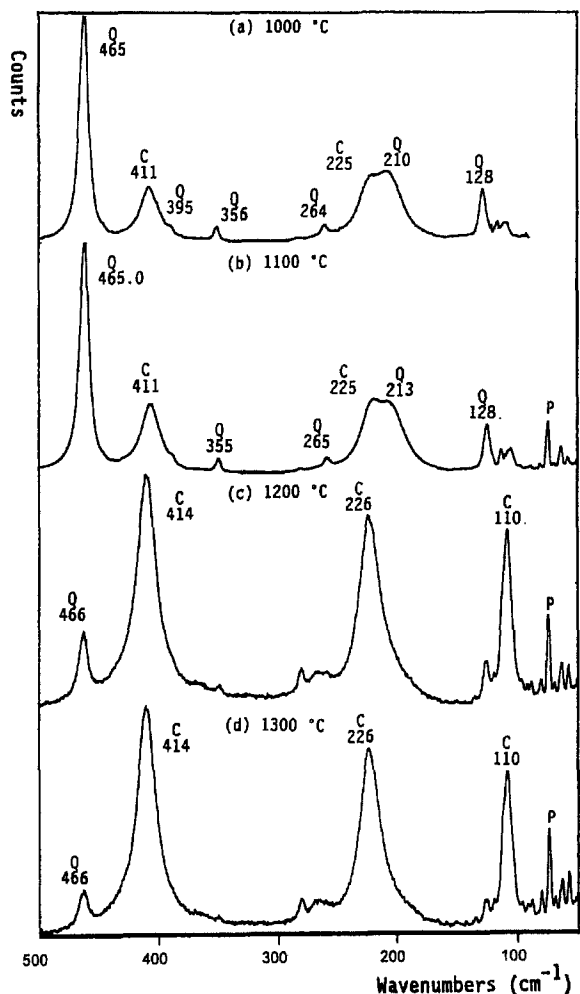

Fig. 2 IR spectra of the chert samples after heating for 24 h at 1000 (a), 1100 (b), 1200 (c) and 1300°C (d). (Q=quartz, C=cristobalite)

ture increases the quartz band at 1084 cm^{-1} shifts to the main band of cristobalite at 1095 cm^{-1}. Other quartz bands at 1166, 694 and 512 cm^{-1} become weaker and the cristobalite band at 620 cm^{-1} becomes stronger with an increase in temperature or heating time. Since the strong cristobalite and quartz bands overlap in the spectra, relative height-ratios were measured by dividing the maximal intensities of the bands at 620 and 694 cm^{-1}, respectively (Table 1). Peak fitting data of these bands are listed in Table 3. No pronounced changes were observed in the location or width of these bands with an increase in the temperature. The Lorentzian component of the cristobalite band at 620 cm^{-1} decreases at high-temperatures.

Fig. 3 Micro-Raman spectra of the chert samples after heating for 24 h at 1000 (a), 1100 (b), 1200 (c) and 1300°C (d). (Q=quartz, C=cristobalite, P=plasma lines). For each sample only the spectra with the highest cristobalite signal is represented

Table 3 Peak fitting data of some IR and Raman bands of quartz and cristobalite in the spectra of the chert samples after heating for 1 h and for 24 h at 1000–1300°C. A mixed Gaussian+Lorentzian band shape is used for the fitting

| Heating temperature	Quartz				Cristobalite			
	IR band at 694 cm^{-1}		Raman band at 465 cm^{-1}		IR band at 620 cm^{-1}		Raman band at 411 cm^{-1}	
	Width/cm^{-1}	Lorz./%	Width/cm^{-1}	Lorz./%	Width/cm^{-1}	Lorz./%	Width/cm^{-1}	Lorz./%
1000°C/1 h	10.5	100.0	8.7	84.9				
1100°C/1 h	10.7	100.0	9.5	81.9	14.4	100.0	15.7	100.00
1200°C/1 h	11.5	100.0	8.8	75.0	14.7	100.0	17.8	100.00
1300°C/1 h	9.7	100.0	8.7	32.9	16.8	51.6	19.6	100.00
1000°C/24 h	11.1	100.0	9.3	80.6	13.9	100.0	17.9	100.00
1100°C/24 h	10.3	100.0	9.3	81.9	17.0	100.0	15.0	100.00
1200°C/24 h	9.9	100.0	8.3	60.0	16.6	65.3	19.3	100.00
1300°C/24 h	9.1	100.0	8.5	8.1	16.7	68.1	20.6	100.00

Micro-Raman spectroscopy

Raman spectra of heated chert samples are shown in Fig. 3. Characteristic Raman bands of Quartz [14, 15] and cristobalite [16, 17] are observed in the spectra. The measurements with the micro-Raman equipment were carried out with a definite laser spot size of 2 micrometers. By examining several points in the same sample different amounts of cristobalite were observed, indicating nonhomogeneous distribution. Figure 3 shows, for each sample, only the spectrum with the highest cristobalite signal.

Relative cristobalite to quartz height-ratios were calculated by dividing the maximal intensities of the cristobalite and quartz bands at 411 and 465 cm^{-1}, respectively (Table 1). The Table gives, for each sample, the results measured from the Raman spectra with the highest and lowest cristobalite signals. After heating for 1 h, the maximum cristobalite amounts detected by micro-Raman spectroscopy were smaller than those observed by IR spectroscopy; however, after 24 h of heating the opposite is true. Peak fitting data of the quartz and cristobalite bands at 465 and 411 cm^{-1}, respectively are summarized in Table 3. No pronounced changes are observed in the location or width of the quartz band with an increase in the temperature. The Lorentzian component of the quartz band at 465 cm^{-1}, at high-temperatures. Small shifts toward higher frequencies and slight increases in the width of the cristobalite band at 411 cm^{-1} appear at high-temperatures.

Scanning electron microscopy

Scanning Electron Micrographs of fractured surfaces of the chert sample heated at 1300°C for 24 h are shown in Fig. 4. The micrographs show highly fragmented quartz and micro-fractures in the sample. Cementing material is not observed between the quartz fragments or within the micro-fractures.

a   b
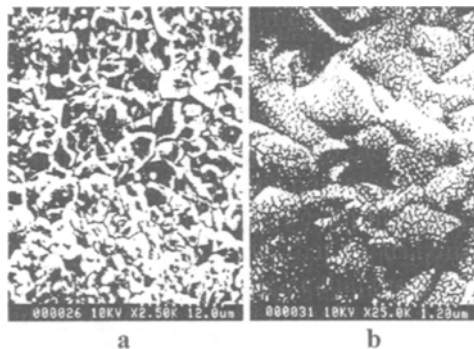
Fig. 4 Scanning Electron Micrographs of fracture surfaces of the chert sample heated at 1300°C for 24 h, showing highly fragmented quartz (a) and micro-fractures which separated areas of about 0.1 micrometer (b)

Discussion

According to the results, an earlier quartz-cristobalite transformation takes place when heating natural chert samples. Cristobalite and quartz are present in the chert samples in the temperature interval of 1000–1300°C. On the other hand, cristobalite was not found after heating well-crystallized pure quartz under the same conditions. The transformation is a slow process. The relative amount of cristobalite increases with an increase in the temperature or the heating time of the chert (Table 1).

A solid state transformation

Kuellmer and Poe [5] found no pronounced amorphous phase in quartz samples heated to less than 1550°C. Similarly, amorphous or glass phases were not observed in the chert samples heated up to 1300°C:

– A rise of the baseline in the diffractograms, which is indicative of amorphous material, is not observed.
– Characteristic IR bands of amorphous silica or glasses [18] are not observed (Fig. 2), even in the peak fitting and first derivative curves.
– Characteristic Raman bands of fused quartz, amorphous silica or glasses [1, 19–21] are not observed (Fig. 3).
– The similar location and width values of the quartz Raman band at 465 cm^{-1} (Table 3), indicate that no drastic changes occurred in the remaining quartz before transformation to cristobalite.
– The absence of cementing material between the quartz fragments or within the micro-fractures, as seen in the Scanning Electron Micrographs (Fig. 4), indicates that partial melting has not occurred.

These observations are evidence that the quartz-cristobalite transformation in the chert samples takes place in the solid state. However, the decrease in the XRD crystallinity indexes of the quartz above 1000°C (Table 2), indicates that crystal defects were formed due to the high-temperature.

Nucleation and crystal growth in a solid medium

The micro-Raman apparatus probes small areas in the sample and, by studying several points in the same sample, a nonhomogeneous distribution of the cristobalite was observed (Table 1). This result indicates that crystals of cristobalite are distributed in the solid medium of the quartz. After heating for 1 h, most of the cristobalite crystallites are too small for Raman detection and consequently its maximum amounts are smaller than these detected by IR spectroscopy (Table 1). The lower size limit detectable by micro-Raman spectroscopy is open to some dispute, but it seems that particles as small as 3 nm can produce a

distinct Raman spectrum [22]. It appears that the cristobalite crystallites are in the nucleation stage after 1 h of heating. The Raman detection of the cristobalite is increased after heating the samples for 24 h, indicating crystal growth. At this stage, the crystal size is limited to the areas between the micro-fractures observed in Scanning Electron Micrographs (Fig. 4).

The slow rate of cristobalite formation and its irreversibility upon cooling also suggest that the polymorphic transformation takes place by nucleation and crystal growth at elevated temperatures. Nucleation and crystal growth in solid state conditions are well known in high-temperature metamorphic minerals [23]. Non-direct polymorphic transformations by nucleation and crystal growth were reported for sillimanite, the high-temperature polymorph of Al_2SiO_5 [24]. Our results show that a similar process takes place in the quartz-cristobalite transformation.

Kuellmer and Poe [5] showed that the quartz-cristobalite transformation occurs through highly-fragmented quartz with a high-temperature dislocation content and suggested that when sufficient fractures are formed, the quartz converted directly to a disordered cristobalite. According to our results, the formation of defects in the quartz structure is essential for inducing the nucleation of the cristobalite. Crystal defects and boundaries or impurities may be nucleation sties [24]. The crystallinity index of the heated pure quartz remains high after heating at 1300°C for 24 h (Table 2, Fig. 1), and an elevated temperature is needed to form sufficient defects in its structure to induce the nucleation of cristobalite. Therefore, pronounced transformation of pure quartz occurs only above 1470°C [1]. The chert rock which is composed of micro- and crypto-quartz with very low crystallinity (Table 2, Fig. 1), is naturally rich in crystal defects and boundaries which serve as nucleation sites. Therefore, the quartz-cristobalite transformation in the chert starts significantly earlier after heating at 1000°C for 1 h, and is almost complete after heating at 1300°C for 24 h.

Conclusions

The quartz-cristobalite transformation occurs as a solid state nucleation and crystal growth of cristobalite replacing quartz at high-temperatures. The presence of defects in the quartz structure is essential for inducing the nucleation of the cristobalite. In a single and pure quartz crystal an elevated temperature is needed to form sufficient defects in the structure, and pronounced transformation occurs only above 1470°C. Chert rock, which is composed of micro- and crypto-quartz with very low crystallinity, is naturally rich in crystal defects and boundaries, which serve as nucleation sites and enable an earlier quartz-cristobalite transformation upon heating.

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