

YOUNG'S MODULUS OF ILLITE-BASED CERAMICS AROUND THE $\beta \leftrightarrow \alpha$ QUARTZ TRANSITION

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Abstract: In this contribution, results of dynamical thermomechanical analysis for illite-based samples are presented. The samples were prepared from illitic clay (36 wt.% illite, 10.5 wt.% kaolinite, 5 wt.% chlorite, 25 wt.% quartz and 23.5 wt.% of other minerals). The investigations were focused on Young's modulus (YM) measured during heating up to 900 °C, 1000 °C and 1100 °C and cooling from these temperatures around $\alpha \leftrightarrow \beta$ quartz transition temperature (573 °C). It was found: 1) The influence of $\alpha \rightarrow \beta$ quartz transition on YM is negligible. 2) The higher firing temperature, the higher final value of YM. This is linked with sintering and creation of the glassy phase, which are more intensive at higher temperatures. 3) Sharp minima are observed during cooling in YM around $\beta \rightarrow \alpha$ quartz transition. Here a partial recovery of the structure occurs as the result of the thermal stresses reversal. 4) Beginning from this, YM lowers its values up to room temperature. 5) S-shape curves of YM were obtained on the fired samples in which steep increase was observed around $\alpha \rightarrow \beta$ transition of quartz. It is caused by closing the circumferential cracks around the quartz grains. 6) S shape curves were also obtained during cooling around $\beta \rightarrow \alpha$ transition of quartz. This decrease of YM is caused by the opening the cracks around the quartz grains. This event begins with some delay, consequently, a hysteresis occurs.

Key words: kaolinite, illite, quartz ceramics, Young's modulus

1 Introduction

Quartz (SiO_2) is the most abundant mineral in Earth's crust due to its high stability at normal conditions which is predetermined by a bond energy of Si – O, 368 kJ/mol [1]. Around the temperature of 573 °C, however, quartz goes through a reversible modification transition which is connected with $\sim 0.7\%$ volume expansion when heated or cooled [2]. While low-temperature α -quartz expands up to 573 °C, high-temperature β -quartz slightly contracts its volume above this temperature, Fig. 1. The density of α -quartz is $\rho(20\text{ °C}) = 2.65\text{ g/cm}^3$ and the density of β -quartz is $\rho(580\text{ °C}) = 2.53\text{ g/cm}^3$ [2]. Other physical properties of quartz also show anomalous behavior around this $\alpha \leftrightarrow \beta$ transition. For example, Young's modulus and Poisson's ratio pass through the sharp V-shape minimum in their temperature relationships, Fig. 2 and Fig. 3. Poisson's ratio obtains negative value in this minimum [4, 8]. Thermal capacity changes its values by steep step [2]. The $\alpha \leftrightarrow \beta$ transition of quartz takes place in a narrow temperature interval around 573 °C and enthalpy of this transition is $\sim 4.5\text{ kJ/mol}$ [9].

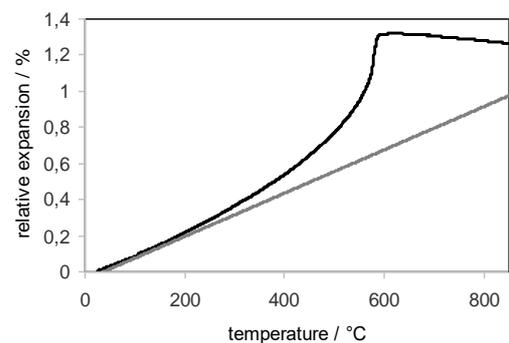


Fig. 1: Thermodilatometric curve of polycrystalline quartz (black line) and simplified course of potash glass (gray line) [3]. Quartz was measured in authors' laboratory

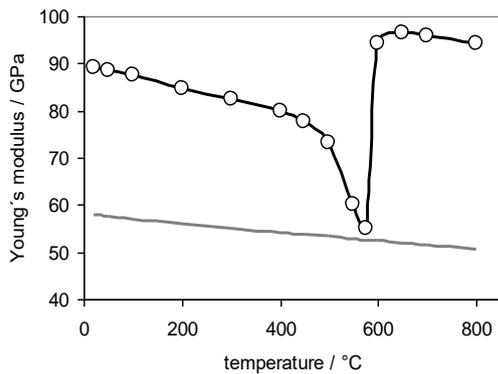


Fig. 2: Young's modulus of quartz (points after [4, 5]) and simplified course for Young's modulus of glass[6] (gray line)

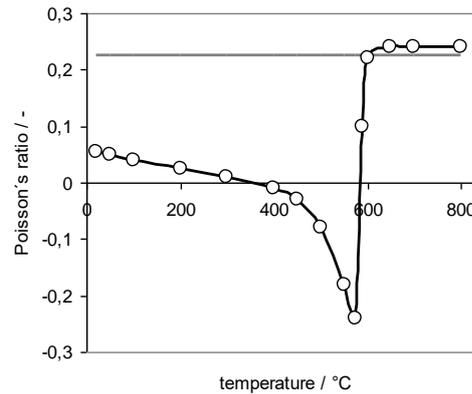


Fig. 3: Poisson's ratio of quartz (points after [4, 5]) and simplified course for Poisson's ratio of glass[7] (gray line)

Quartz is always found in natural raw materials (kaolin, illite, feldspar) for the production of traditional ceramics. Quartz is also often added to ceramic mixture to ensure dimensional stability. Contrary to it, quartz is undesirable in electroporcelain for very-high-voltage insulators, therefore, it is substituted by alumina [10, 11]. The technology of ceramics is based on the firing of ceramic bodies at temperatures 800 – 1100 °C for building ceramics and 1200 – 1400 °C for porcelains. As the result of such a thermal treatment, ceramic body becomes rigid and reaches sufficient mechanical strength and other valuable properties. From a microstructural point of view, the most significant change that occurs in the ceramic body is a decrease of its porosity. This takes place during the solid state sintering (at temperatures < 800 – 900 °C) and during the liquid phase sintering (at temperatures > 900 °C) [1, 12]. The firing conditions are not sufficient for melting the quartz grains (the melting temperature of quartz is ~1670 °C), consequently, the quartz grains surrounded with glassy matrix and new formed minerals (spinel, mullite) are very often found in traditional ceramics. In addition to that, circumferential microcracks are visible around the quartz grains. A source of these microcracks is their intimate contact with other phases in connection with their different coefficients of linear thermal expansion (CLTE). When the temperature is falling down, the stress relief can result into a crack formation. This is especially pronounced for quartz which CLTE significantly changes with the temperature at $\beta \rightarrow \alpha$ transition while CLTE of other phases changes very slowly [10, 11].

The cracking influences mechanical properties of ceramics in large extent. These properties are well characterized with Young's modulus (YM) [13]. According to the Griffith's theory, YM is directly proportional to the mechanical strength of material [14]. This also follows directly from Hooke's law [15]. In spite of the known importance of quartz in traditional ceramics, the cracking around quartz grains was not often studied directly during firing. The conclusions were done from the observation of pictures obtained by the light or electron microscopy (SEM). It has been believed that circumferential cracks around the quartz grains in glassy matrix are created during the cooling, when quartz grains shrink rapidly during $\beta \rightarrow \alpha$ transition, see for example [10, 11]. This explanation is quite reasonable and straightforward.

Perhaps one of the first investigations of YM during firing was described in [16], where authors found V-shape minimum in the relationship between YM and temperature when the porcelain sample was cooled from 1250 °C. Very similar behavior was later found for porcelain tiles [17], illite-based ceramics [18] and ceramics with high content of

crystalite [5]. More information about cracking was obtained by the help of the acoustic emission observed during the firing of porcelain samples. It was found that cracks begin to form during the cooling stage of the firing below the glass-transition temperature [19].

In [17], a V-shape minimum of YM during the cooling of ceramic tiles was attributed to the properties of quartz. A simple mixture law was used to calculate theoretical curve of YM of tiles in which YM of quartz and glassy phase (similar to Fig. 2) were used. On pre-cracked (fired) samples a hysteresis in YM values was observed. This was explained by the help of the broken connections between quartz and glassy phase which were recovered (thermal cycles up to 700 °C) due to present viscous flow. Then, during the cooling, the values of YM after $\beta \rightarrow \alpha$ transition of quartz were higher than during the heating. Original values of YM were reached afterwards the sample was cooled down to ~200 °C. Consequently, the cracks were not created during the $\beta \rightarrow \alpha$ quartz transition but during the further cooling.

YM, which is sensitive to a presence of pores and cracks, is very suitable quantity for experimental study of the crack formation in ceramic bodies. Naturally, YM must be measured during firing by the help of the sonic resonant method [20] or impulse excitation technique [21] which both of them are more preferable than ultrasonic methods. Notable progress brought a combination of the acoustic emission and YM, both measured during firing [18, 22, 23].

In this contribution, experimental results of YM obtained on illite-based ceramic samples are given and described. Special attention is paid to its development during the cooling stage around the $\beta \rightarrow \alpha$ quartz transition.

2 Experimental observations and discussion

In this contribution, some results obtained on illite-based samples are presented. Illite is a common part of the clay-based ceramic mixtures apart from the high-strength electroporcelain ones. The samples were prepared from illitic clay (36 wt.% illite, 10.5 wt.% kaolinite, 5 wt.% chlorite, 25 wt.% quartz, 11 wt.% feldspar, 3.8 wt.% carbonates, 3 wt.% hematite and 5.7 wt.% of other minerals) from a deposit Arumetsa, Estonia. The clay was mixed with distilled water to get a plastic mass, from which cylindrical samples were extruded. The dried samples were subjected to a linear heating 5 °C/min up to 900 °C, 1000 °C and 1100 °C (samples marked as FT900, FT1000 and FT1100) and then to a linear cooling with the same rate. No isothermal delay was applied. A dynamical thermomechanical analysis (DTMA), i.e. measurement of YM during heating and cooling was performed.

The results of the measurement of YM are shown in Fig. 4. A course of YM for heating has typical parts that reflect the removing of physically bound water (20 °C – 250 °C) and two steps of sintering: solid state sintering (above 700 °C) and liquid phase sintering (above 900 °C). Dehydroxylation of illite influences YM in very small extent. We could expect some increase of YM as a result of the volume expansion of the quartz grains during their $\alpha \rightarrow \beta$ transition as consequence of the decrease of porosity. But no significant

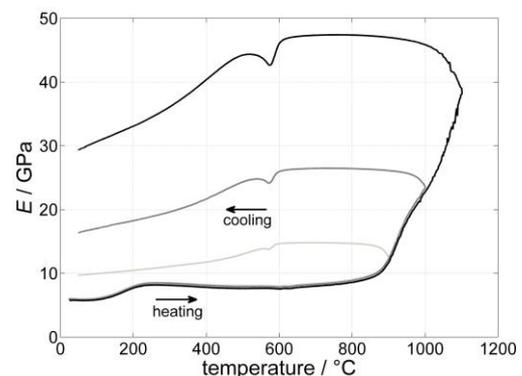


Fig. 4: Young's modulus of illitic samples during heating up to 900 °C (light gray), 1000 °C (gray) and 1100 °C (black) and during cooling from these temperatures

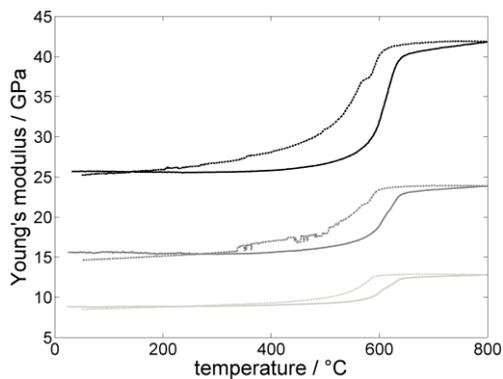


Fig. 5: Young's modulus of fired illitic samples up to 900 °C (light gray), 1000 °C (gray) and 1100 °C (black) during heating (lower lines) and during cooling from 800 °C (upper lines)

stresses reversal [22]. Below ~ 500 °C, acoustic emission signals, which belong to new microcrack creation, appear with less intensity down to room temperature. This low-temperature microcracking was also confirmed by the YM measurement showing a considerable decay of YM during a significant part of the cooling. Microcracking is possible due to the release of internal residual stress that is always present when thermal and elastic mismatch takes place in multiphase brittle material [24, 25]. Typical V-shape minima are visible on the curves in Fig. 4. The higher was the firing temperature (i.e. more glassy phase is present in the sample), the more noticeable minimum was registered.

The presence of the quartz grains in fired ceramics also influences its thermo-elastic behavior. It was observed in kaolin-based ceramics [26]. The samples used for DTMA, which was described above, were repeatedly measured. The results are pictured in Fig. 5 in which typical curves of the S-shape are visible. A steep increase in YM can be noted in the range 500 °C – 650 °C. The $\alpha \rightarrow \beta$ transition of quartz, which takes place at 573 °C, is within this interval. Most quartz grains have circumferential cracks around them at the room temperature, Fig. 6. Since quartz grains increase their volume by ~ 0.7 % during the $\alpha \rightarrow \beta$ transition, a compressive strength emerges on the surrounding glassy phase and many circumferential cracks disappear. During the cooling, these events occur in reversal order and consequently, the circumferential cracks are open. This begins with some delay, therefore a hysteresis is observed.

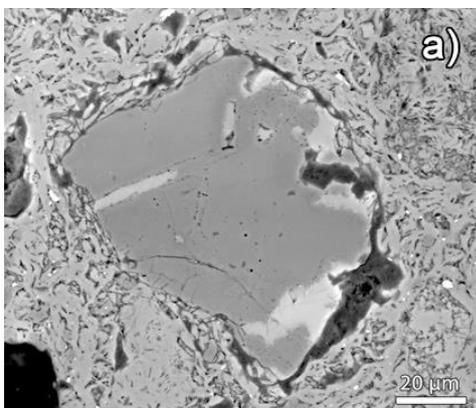


Fig. 6: SEM picture of illite-based ceramics with quartz grain and circumferential crack around it. Taken from [23]

influence of the quartz presence, as visible in Fig. 4, may be due to a small part of quartz in the clay.

Completely different picture is observed in the cooling stage of the firing, Fig. 4. As follows from [18, 19, 22, 23], the cracking begins almost immediately after reaching the glass transition temperature (~ 750 °C) as acoustic emission and YM showed. Surprisingly, at the temperature of the $\beta \rightarrow \alpha$ transition of quartz grains, cracking is temporarily interrupted and a partial recovery of the structure occurs as the result of the thermal

A healing effect of the expansion of the quartz grains during their $\alpha \rightarrow \beta$ transition leads to a steep increase in YM values: 62 % for FT900, 53 % for FT1000 and 61 % for FT1100 from initial values of YM(20 °C): 8 GPa for FT900, 15 GPa for FT1000 and 26 GPa for FT1100. This increase of the initial values is caused by a more perfect sintering at higher temperatures.

Small shoulders are visible in cooling curves for the samples FT1000 and FT1100 and very small shoulder is also visible for FT900. These shoulders are located around

573 °C. Their origin is hardly caused by the sharp V-minimum for YM of quartz, because from a mixture rule follows that these shoulders should be present also in the curves for heating. These shoulders, similarly as V-minima in the curves for cooling in Fig. 4, are linked with transitional healing of YM due to a rapid relax of the tensile stress and stress reversal acting on the glassy matrix [22].

3 Conclusions

In this contribution, results of dynamical thermomechanical analysis for illite-based samples are presented. The samples were prepared from illitic clay (36 wt.% illite) from a deposit Arumetsa, Estonia. The investigations were focused on Young's modulus (YM) measured during heating up to 900 °C, 1000 °C and 1100 °C and cooling around $\alpha \leftrightarrow \beta$ quartz transition temperature (573 °C). It was found for originally unfired samples:

- The influence of $\alpha \rightarrow \beta$ quartz transition on YM during the heating is negligible.
- The higher firing temperature, the higher final value of YM. This is linked with sintering and creation of the glassy phase, which are more intensive at higher temperatures.
- Sharp minima are observed during cooling in YM around $\beta \rightarrow \alpha$ quartz transition. Here a partial recovery of the structure occurs as the result of the thermal stresses reversal. Beginning from this, YM lowers its values up to room temperature.

It was found for fired samples:

- S-shape curves of YM were obtained in which steep increase was observed around $\alpha \rightarrow \beta$ transition of quartz. It is caused by closing the circumference cracks around the quartz grains.
- S-shape curves were also obtained during cooling around $\beta \rightarrow \alpha$ transition of quartz. This decrease of YM is caused by the opening the cracks around the quartz grains. This event begins with some delay, consequently, a hysteresis occurs.

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