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Elastic anomalies in tridymite- and cristobalite-based silica materials

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Abstract

Cristobalite and tridymite are the main SiO_2 phases in silica bricks, a widespread refractory product. The elastic properties of cristobalite at room temperature have been extensively studied, because it is known for auxetic behavior, i.e. negative Poisson ratios, whereas the elastic properties of tridymite are essentially unknown. Here we show that silica brick materials, consisting almost entirely of tridymite and cristobalite, exhibit remarkable anomalies in the temperature dependence of the Young modulus: in the intermediate temperature range between approximately 50 and 250 °C these materials become very compliant, with stiffness minima of around 60% of the room temperature values, with a broad transition region at the low-temperature end, a sharp transition at the high-temperature end and a precisely reproducible hysteresis during heating and cooling. Furthermore, it is shown that Young's moduli at around 800 °C can be more than three times as high as the room temperature values.

Keywords: C. Mechanical properties; D. SiO_2; E. Refractories; Elastic modulus (Young's modulus); Silica brick materials (cristobalite, tridymite)

1. Introduction

Silica (SiO_2) in the form of sand, sandstone, quartzite and rock quartz is a ubiquitous natural raw material for many branches of materials technology. While the high-pressure polymorphs coesite and stishovite are of interest in geophysics, the high-temperature (and low-pressure) polymorphs tridymite and cristobalite are the most important phases in silica bricks, a special product family that is – mainly due to its chemical resistance to certain aggressive high-temperature environments – still irreplaceable in some refractory applications such as glass-melter roof constructions and coke ovens [1,2]. A very old rule of practice says that the high-temperature equipment in which silica bricks are used should never be cooled down (even if operated batchwise). There are several reasons for that. First of all, the abrupt volume changes during cooling (which can imply a 3% volume contraction in the case of cristobalite [2]) causes microcracking that may lead to a total collapse e.g. of roof constructions. Secondly, the elastic behavior of silica bricks is rather unusual. Surprisingly, it seems that the temperature dependence of the elastic properties of these materials has not been investigated so far, although considerable efforts have been made in the last two decades to confirm and explain the auxetic behavior of cristobalite at room temperature [3–7]. Indeed, cristobalite is one of the very few solid phases whose dense isotropic polycrystalline compact materials can exhibit negative Poisson ratios. For cristobalite a computer simulation study has been published [6,7] which tried to simulate the transition from low- to high-cristobalite, but this simulation failed (by at least 500 °C!) to predict a realistic transition temperature and did not exhibit a clear increase of Young's modulus with temperature, which is characteristic e.g. for high-quartz [8] and silica glass [9]. Nevertheless, this simulation confirmed that dense isotropic polycrystalline cristobalite aggregates should be auxetic in the whole range of temperatures from room temperature to more than 1000 °C, whereas analogous quartz aggregates can become auxetic only in a very restricted temperature range around and below the low-to-high-quartz transition (419–576 °C), as can be confirmed by calculating Voigt–Reuss–Hill averages using published single crystal data [8]. The elastic properties of silica phases have been summarized in a recent review [10]. For tridymite no high-temperature values are available, neither from

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simulations nor from experiments. Experimental measurements, even at room temperature, exist only for quartz, cristobalite, and the high pressure polymorphs of silica [11,12], but not for tridymite. Thus it must be stated that the elastic properties of tridymite are essentially unknown, and even for cristobalite there are no experimental single crystal data available that would allow the calculation of the elastic constants of dense isotropic polycrystalline cristobalite compacts at elevated temperature. That means, the only true benchmark values that are reliably known so far are the room-temperature values of the elastic constants for silica glass [9] and the effective elastic constants of dense isotropic polycrystalline compacts calculated as Voigt–Reuss–Hill averages from the published single crystal data for quartz and cristobalite [3–13]. Young's moduli thus calculated are 95.6, 65.2 and 72.2 GPa for low-quartz, low-cristobalite and silica glass, respectively [10]. It is evident that the elastic moduli of low-cristobalite are significantly lower than those of low-quartz. As indicated in our review [10] the same seems to be true for tridymite. In this work we present experimental evidence for unexpected elastic anomalies in silica brick materials

2. Materials and methods

The silica brick samples investigated here are typical commercial products made in large quantities for industrial use. According to X-ray diffraction (XRD) analysis the present samples contain approximately 36% cristobalite and 64% tridymite. The residual quartz content is negligibly low ($<$ 1%) and cannot be detected via XRD. XRD shows no indication of a glass phase. Chemically the material consists of approximately 96% SiO_2. The rest is $<3\%$ CaO and a small amount of undesired impurities (approximately 1% Fe_2O_3 and TiO_2 and less than 0.4% Al_2O_3). The microstructure consists of large (millimeter-sized) cristobalite grains in a tridymite matrix, see Fig. 1.

Young's moduli at room temperature and at elevated temperatures have been measured by the impulse excitation technique according to ASTM E 1876–99 [14] in a high-temperature electrical furnace (Resonant Frequency and Damping Analyzer RFDA 23, high-temperature version 1600, IMCE, Belgium). Resonant frequencies have been measured from room temperature to 1200 °C (first heating), down to room temperature (first cooling), followed by two more complete heating and cooling cycles (second and third heating and cooling cycles). Controlled heating and cooling with a rate of 5 °C/min was used throughout, i.e. for all three cycles.

3. Results and discussion

Assuming a density of 2.26 g/cm^3 for low-tridymite and 2.32 g/cm^3 for low-cristobalite [10], the total porosities of the two samples for which results are shown here (sample dimensions $160 \times 20 \times 10$ mm^3), is 19.4% and 22.4%. For these two samples the room temperature values of Young's modulus, measured via the impulse excitation technique, were 13.0 GPa and 7.3 GPa, respectively. Even if the porosity is taken into account via the most efficient relation for porosity correction (i.e. the one yielding the highest extrapolated values for the dense materials), viz. our exponential relation [15], the extrapolated Young's moduli of these two silica brick samples would be only around 21.4 GPa and 13.0 GPa, respectively. Although the elastic constants of tridymite are not known, there is no reason to believe that tridymite would have Young's modulus very much below that of cristobalite, since the differences between these two phases are fuzzy in several respects [1]. In fact, in order to explain such low values, Young's modulus of tridymite would have to be of order 1–10 GPa, which is clearly unrealistic (a value of 58.1 GPa has been estimated for the Young modulus of tridymite in [10]). Since the grain and pore size dependence of the elastic constants is negligible unless nanocrystalline or nanoporous solids are considered [16], such low Young's modulus values can only be caused by an extremely oblate pore shape, i.e. by the presence of microcracks or crack-like defects [17]. Only the presence of microcracks, i.e. strongly oblate high-aspect-ratio “pores” with a negligible volume, can explain the large difference in the absolute values of Young's moduli for very small differences in porosity. However, all the aforementioned microstructural influences affect only the absolute Young modulus values of individual samples. These are only of secondary concern in this paper, since no attempt is made here to extract an experimental value for the Young modulus of tridymite. The main point of interest here is the temperature dependence of Young's moduli of silica brick materials. The results for the two samples are shown in Figs. 2–5.

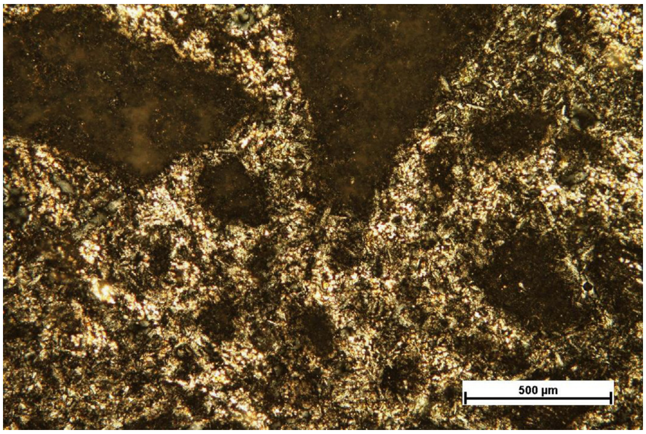

Fig. 1. Microstructure of silica brick material in transmitted polarized light under crossed Nichols (polarization microscope); the large dark islands regions are cristobalite, which is optically almost isotropic (tetragonal with only a slight deviation from cubic symmetry), while the matrix is tridymite (well known for triple or multiple twinning). Courtesy A. Kloužková (ICT Prague) and M. Černý (ASCR Prague).

It is evident that the temperature dependence of the Young modulus during the first heating is always different from the subsequent heating branches. Surprisingly, however, after the first heating to 1200 °C all subsequent cooling and heating cycles are completely reproducible. That means, the materials have an inherent thermal memory, which can be deleted by

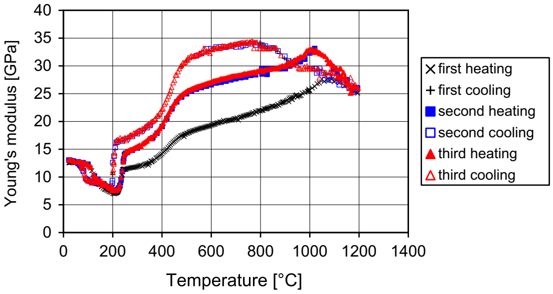

Fig. 2. Temperature dependence of Young's modulus of a silica brick material with 19.4% porosity, measured by impulse excitation (three complete heating and cooling cycles).

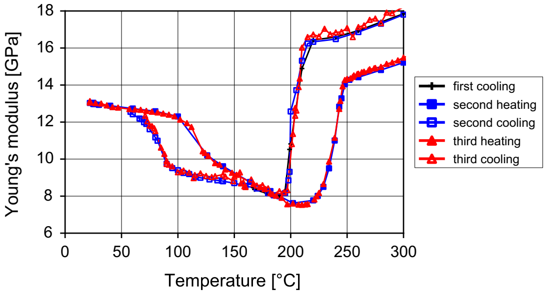

Fig. 3. Detailed view of the temperature dependence of the Young's modulus of a silica brick material with 19.4% porosity from room temperature to 300 °C (without first heating).

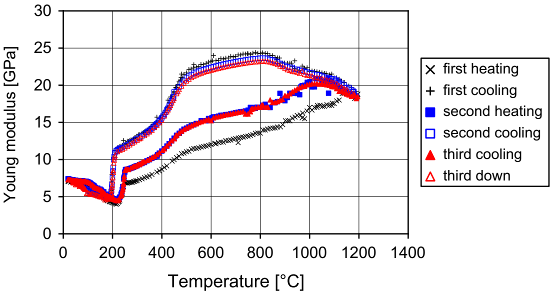

Fig. 4. Temperature dependence of the Young's modulus of a silica brick material with 22.4% porosity, measured by impulse excitation (three complete heating and cooling cycles).

heating to 1200 °C. Previous experience has shown, that heating to lower temperatures, say 800 °C or 1000 °C, is not sufficient to reset this thermal memory, so that the interpretation of the results is complicated by the memory effect, although also in this case the elastic anomalies appear at the same temperatures and the principal conclusions would be very similar as in the present case. The heating and cooling branches of the cycles are distinctly different. Most important, however, is the fact that both types of branches show very significant elastic anomalies in the low-temperature region (below 250 °C), where in a certain temperature range the material becomes very compliant. Moreover, the transition temperatures between stiff and compliant behavior exhibit a significant hysteresis between heating and cooling. In order to compare the course of the curves for both samples mutually (and to other materials) in a more quantitative manner it is useful to ignore the first heating branch and to normalize the tangent slopes with respect to the room temperature value of Young's modulus.

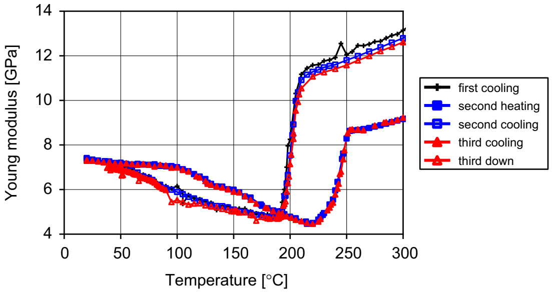

Fig. 5. Detailed view of the temperature dependence of Young's modulus of a silica brick material with 22.4% porosity from room temperature to 300 °C (without first heating).

During heating, after an initially linear decrease of the Young's modulus up to 100 °C with a normalized tangent slope of approximately $-0.0006\ \mathrm{K}^{-1}$ (for comparison: quartz has a normalized tangent slope of $-0.0002\ \mathrm{K}^{-1}$ in this range [8]), the tridymite–cristobalite-based silica materials become significantly more compliant at temperatures above 110 °C: Young's modulus decreases nonlinearly with normalized tangent slopes ranging from -0.0029 to $-0.0077\ \mathrm{K}^{-1}$ and finally go through a stiffness minimum at 210–220 °C, where Young's modulus is only about 58–61% of the initial room temperature value. During further heating, the Young's modulus steeply increases with temperature, so that within only 30–40 °C it rises by 89–92%, to values higher than the room temperature value (110–117% of the room temperature value). The corresponding normalized tangent slopes are approximately $+0.0175\ \mathrm{K}^{-1}$ (for comparison: quartz has a normalized tangent slope of $+0.1114\ \mathrm{K}^{-1}$ directly above the transition point from low-to-high-quartz in the narrow temperature range 573–575 °C [8]). At 250 °C there is a sharp discontinuity in the temperature dependence of the Young's modulus during heating.

When heating to temperatures higher than 250 °C the temperature dependence of Young's modulus first undergoes a weak increase (with an initial slope of $+0.0015$ to $+0.0020\ \mathrm{K}^{-1}$) with a steadily growing increase rate (concave increasing-rate segment of the curve) and then – after passing an inflection point – seems to level off before increasing the slope again, passing a maximum at around 1030 °C (with peak Young's moduli of about 254–284% of the room temperature values) and subsequently decreasing down to values of about 200–253% of the initial room temperature values at 1200 °C. Severely increased damping in the temperature region above 1000 °C (not shown here, but readily accessible via impulse excitation measurements) indicates that in this high-temperature region anelastic behavior comes into play, i.e. the material cannot be considered as purely elastic anymore and, of course, Hooke's law ceases to be valid at these high temperatures.

During cooling, the temperature dependence of Young's modulus is not the same as during heating. Instead of the relative sharp maximum at 1030 °C the curve exhibits a very broad plateau in the region 500–900 °C with a relatively flat maximum at around 800 °C, where maximum Young's moduli of approximately 262–344% of the room temperature values are attained. It is characteristic for the aforementioned presence of microcracks that the sample with the slightly higher porosity and thus the significantly higher amount of microcracks (which is responsible for the lower overall level of Young's modulus) exhibits a more significant relative Young's modulus increase (by up to 244% from the room temperature values, when the maximum value is considered) after heating to 1200 °C (in contrast to the other samples, for which the maximum values attained during cooling are "only" by 162% higher than the room temperature value). This can be interpreted as a crack healing effect, which further supports the hypothesis of microcracks. During further cooling the temperature dependence of the Young's modulus largely copies the heating curve, but in the temperature region above 200 °C it is shifted to higher modulus values (higher by approximately 16–41%, depending on the microstructure of the materials, at temperatures above 250 °C) and the phase transitions are shifted to lower temperatures (by approximately 35 ± 10 °C). "Hysteresis effects" of this kind (i.e. in the sense of shifts of phase transition temperatures between silica subpolymorphs) of around 30 K are well known for cristobalite [18]. The normalized tangent slopes referring to the cooling branches have similar orders of magnitude as for the heating branches (0.021–0.046 K^{-1} below 220–210 °C), but the minimum Young's modulus values are slightly higher (62–68% of the room temperature values) than on the heating branches (58–61% of the room temperature values, see above). Finally, after cooling below 40–60 °C the cooling and heating curves reunite again and the initial room temperature value of the Young's modulus is regained. In contrast to the sharp phase transition between 190 °C (phase transition end during cooling) and 250 °C (phase transition end during heating), the low-temperature phase transition between 40 °C (phase transition end during cooling) and 130 °C (phase transition end during heating) is very diffuse.

Thus, after a complete heating-cooling cycle (from room temperature up to 1200 °C and down again) the initial room temperature Young's modulus is regained, i.e. during thermal cycling the material undergoes a kind of "hysteresis loop". In other words, the elastic modulus of these materials is not a unique function of the temperature, but – due to the thermal memory of these materials – it is dependent on the thermal history. At the same time, the fact that after cooling the initial room temperature values are regained indicates that the temperature of 1200 °C, while obviously sufficient for crack healing, does not cause irreversible changes in the microstructure. This is plausible, because the temperature of 1200 °C is still far below the usual sintering temperature of silica brick materials (1400–1500 °C [2–18]). It should be evident from Figs. 2–5 that this hysteresis loop can be reproduced many times, and that the microstructure (including microcracks and crack-like defects in individual samples) affects the absolute values of Young's moduli, while the transition temperatures are generic features of the solid phases present, essentially unaffected by microstructural details. Therefore impulse excitation measurements can be considered as a highly sensitive tool for the investigation of phase transitions.

Of course, compared to other typical polycrystalline oxides (e.g. alumina, magnesia, thoria and others [19]), almost all the aforementioned features (except for the temperature dependence below 50 °C) would be considered as "anomalous". It should be emphasized, however, that although the temperature dependence of Young's moduli of silica brick materials is uncommon from several viewpoints, some of the unusual features can be plausibly explained:

1. The overall temperature dependence of the Young's modulus indicates an increase of the stiffness of the material with increasing temperature; such an increase of the elastic moduli with temperature is known also for silica glass [9] and for high-quartz [8], see [10].
2. Sudden changes in the decrease rate of Young's modulus at temperatures not much higher than 100 °C during heating and corresponding changes in the increase rate below 100 °C during cooling are obviously related to a phase transition between subpolymorphs of tridymite, because for transitions between cristobalite subpolymorphs these temperatures are definitely too low, see [10].
3. The very steep increase of Young's modulus upon heating above 210–220 °C (and the correspondingly steep decrease upon cooling) is evidently related to phase transitions between the low- and high-temperature subpolymorphs of cristobalite [2–18]; however, apart from the sharpness of the effect, it is remarkable that Young's modulus increases while the density decreases (from 2.32 g/cm^3 for low-temperature cristobalite to 2.20 g/cm^3 for high-temperature cristobalite [2–18]).
4. Hysteresis effects in the more restricted sense, i.e. shifts of the phase transition temperature (of around 30 °C), have been reported for cristobalite materials in the literature [18]; however, the finding of this work that, as a consequence of the hysteresis, Young's moduli of silica materials are really path-dependent, seems to be new and can only be explained by microcrack opening, closure and healing.
5. In contrast to the smooth change in the low-temperature end of the elastic anomaly, the high-temperature edge of the elastic anomaly is very sharp, both during heating (250 °C) and cooling (210–220 °C). This sharp edge on the right hand side of the elastic anomaly has a certain analogy in the (experimentally measured) lambda-shape of the low-to-high-quartz transition [8] and the (simulated) low-to-high-cristobalite transition [6,7]. However, in the lambda-shaped transition points (according to Landau theory classified as homogenous second-order phase transitions [1]) the low elasticity region shrinks more or less to a singularity, or is at least confined to a very narrow temperature region, while in the present case it forms a broad valley.
6. The fact that in the temperature range 50–250 °C the materials are more compliant than outside of this range, can only be explained by assuming two phase transitions; while cristobalite has only one low- and one high-temperature subpolymorph, most authors acknowledge the

existence of at least three tridymite subpolymorphs [10–18]; however, the higher Young's moduli on either side of the valley in the temperature dependence can only be explained by assuming that the "middle" (medium-temperature) tridymite has a higher density than the two other subpolymorphs; indeed, some authors [2] list density values of 2.26, 2.29 and 2.22 g/cm^3 for the low-, medium- and high-temperature subpolymorphs of tridymite, respectively.

This leads us to the most likely and plausible explanation of the elastic anomaly and also to a deeper understanding of the hysteresis effect: the volume contraction in this temperature region (transient during heating or cooling) opens up preexisting microcracks and thus makes the material more compliant. In other words, although the changes in the elastic properties clearly (and very precisely) indicate phase transitions, it is not the solid phase alone that is responsible for the large effects in the temperature dependence curves. The difference in the intrinsic elastic properties of the subpolymorphs of tridymite and cristobalite would be much too small to explain the observed effects. The key factor is that the density differences and the concomitant, more or less abrupt, volume changes during heating and cooling over phase transitions are responsible for microcrack opening or closure. Of course, it is this "indirect" enhancing effect via the microstructure of the materials that makes the impulse excitation measurements in the end a very sensitive tool for monitoring solid phase transitions. Microcrack opening, closure and healing also explains the "hysteresis effects" in a natural way. The fact that elasticity can be controlled and switched in these materials in such an effective way, may open new possibilities in materials design and possibly new fields of applications for a traditional material that has long laid aside the mainstream of current research.

4. Conclusion

It has been shown that silica brick materials, consisting almost entirely of tridymite and cristobalite, exhibit remarkable anomalies in the temperature dependence of the Young modulus: in the intermediate temperature range between approximately 50 and 250 °C these materials become very compliant, with stiffness minima of around 60% of the room temperature values, with a broad transition region at the low-temperature end, a sharp transition at the high-temperature end and a precisely reproducible "hysteresis loop" during heating and cooling. Furthermore, it has been shown that the maximum Young moduli at around 800 °C can be more than three times as high as the room temperature values. Both the elastic anomalies and the hysteresis loop have been thoroughly discussed in terms of intrinsic effects (phase transitions between subpolymorphs of critobalite and tridymite) and microstructural influences (microcrack opening, closure and healing), leading at the phenomenological level to material behavior with memory.

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