



Elastic anomalies in tridymite- and cristobalite-based silica materials

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Abstract

Cristobalite and tridymite are the main SiO₂ 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.

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1. Introduction

Silica (SiO₂) 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% SiO₂. The rest is < 3% CaO and a small amount of undesired impurities (approximately 1% Fe₂O₃ and TiO₂ and less than 0.4% Al₂O₃). 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/cm³ for low-tridymite and 2.32 g/cm³ for low-cristobalite [10], the total porosities of the two samples for which results are shown here (sample dimensions 160 × 20 × 10 mm³), 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

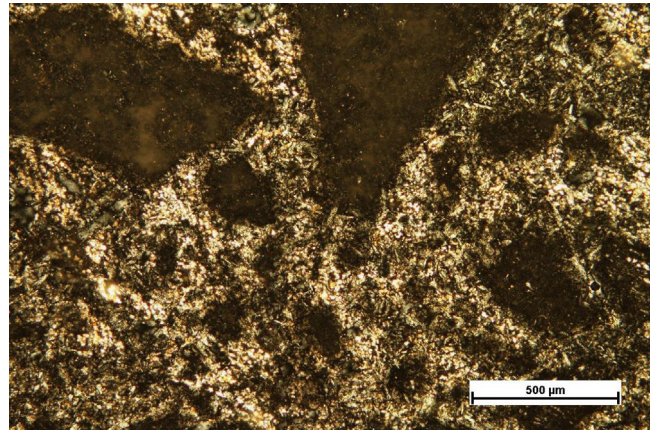


Fig. 1. Microstructure of silica brick material in transmitted polarized light under crossed Nichols (polarization microscope); the large dark islands regions are cristobalite, which is optically almost isotropic (tetragonal with only a slight deviation from cubic symmetry), while the matrix is tridymite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

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.

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

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