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Structural disorder and loss of piezoelectric properties in α-quartz at high temperature

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The piezoelectric properties of α-quartz-based resonators, characterized by the mechanical quality factor, Q, are found to degrade beginning above 300 °C. This is well below the transition at 573 °C to the β phase, which in principle limits the piezoelectric response of this material. This gradual loss of piezoelectric response can be linked to the increase in structural disorder in α-quartz found in total neutron scattering measurements. Analysis of these data by reverse Monte Carlo modeling indicates that between 200 and 400 °C, the local disorder in the instantaneous structure of α-quartz becomes comparable to that of β-quartz.
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α-Quartz is the most commonly used piezoelectric material at the present time. Its performances are limited at high temperature, which has important repercussions for applications as components in microbalances, high-temperature pressure sensors, and field-test viscometers. Piezoelectric properties are limited by the α-β phase transition at 573 °C, at which the piezoelectric constant d_{11} vanishes and d_{14} remains as the only piezoelectric constant of β-quartz.[1] Structure-property relationships have been developed for α-quartz homeotypes at ambient temperature.[2–6] The piezoelectric response was found to be a function of the structural distortion of a material with respect to the β-quartz structure type. This distortion in α-quartz can be described in terms of the intertetrahedral Si–O–Si bridging angle θ and the SiO_4 tetrahedral tilt angle δ, which is the order parameter for the α-β phase transition (note[7] that for α-quartz at room temperature, $\theta = 143.6°$, $\delta = 16.4°$ and for β-quartz at 848 K, $\theta = 153.3°$, $\delta = 0°$). Up to the present, no detailed studies have been performed, which correlate the piezoelectric properties of α-quartz at high temperature to its crystal structure, in spite of the importance of such results for understanding the origin of the observed high-temperature behavior of this material.

The piezoelectric properties of an α-quartz resonator can be characterized in terms of two quantities, the mechanical quality factor, Q, which is a measure of the quality of the resonator with respect to, for example, acoustic attenuation, and the electromechanical coupling coefficient k. These two properties are defined as follows:

$$Q = 2\pi L f_r / R, \tag{1}$$

$$k = \pi/2[(f_a - f_r)/f_a]^{1/2}, \tag{2}$$

where L is the self-inductance and R is the resistance of the resonator and f_r and f_a are the frequencies of resonance and anti-resonance. The mechanical quality factor is very sensitive to structural disorder and defects in the material and characterizes the purity of the spectral signal.

The piezoelectric response of AT (athermal, i.e., −35.15° Y-rotated cut) cut, α-quartz resonators (C-MAC Frequency Products) was measured with a Hewlett–Packard 8753A network analyzer using the third harmonic signals at close to 10 MHz. High-temperature experiments were performed in a controlled temperature furnace (±0.5 °C) and the temperature measured with a thermocouple. Electrical contacts with the electrodes on the resonator and its base were made using a high-temperature, silver containing, conducting polyimide resin (Epotecny P200). The Q and k values were obtained from the average of data from three high-temperature runs on two different resonators. Reproducible values were obtained both on heating and cooling runs.

The distribution functions of the order parameter, δ, and the intertetrahedral O–O–O angles at each temperature were obtained by reverse Monte Carlo (RMC) modeling of total neutron scattering data.[8,9] Total scattering contains both the Bragg and diffuse scattering signal from the sample and is sensitive to the average structure (via interpretation of the elastic Bragg signal) and instantaneous structural correlations (via Fourier transformation of the so-called "total scattering structure factor"[10]). Here, total neutron scattering data, corrected in the usual way,[11] were obtained from quartz powder using the LAD diffractometer at ISIS at a number of temperatures between 20 and 1073 K. Three-dimensional structural models were refined using RMC modeling.[12] These models, which are $10\times10\times10$ supercells of the quartz

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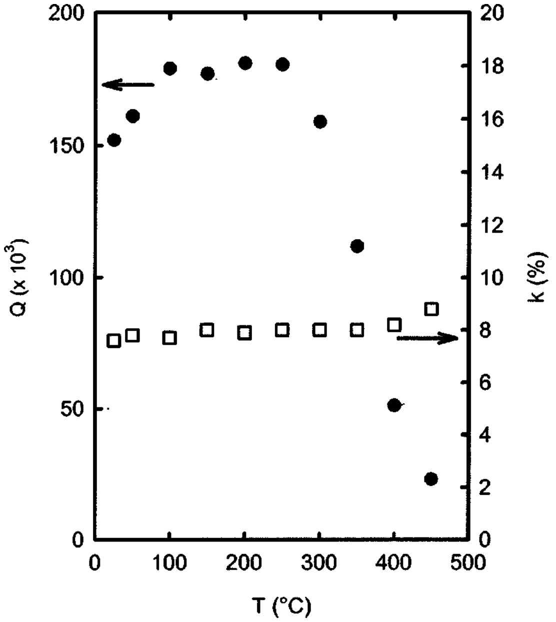

FIG. 1. Quality factor Q(●) and piezoelectric coupling constant k(☐) of AT-cut α-quartz resonators as a function of temperature.

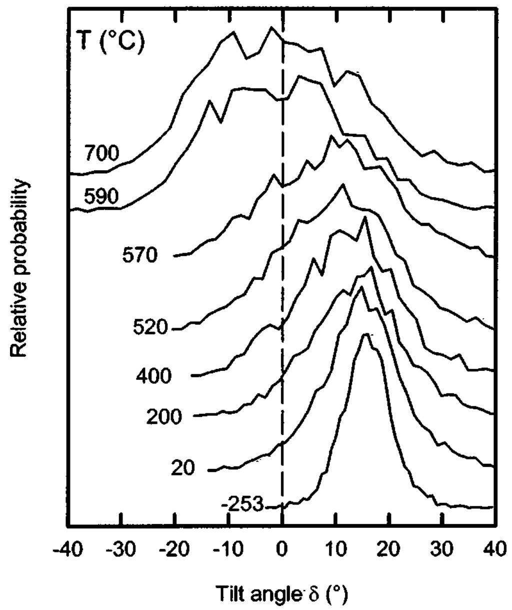

FIG. 2. Distribution functions of the tilt angle δ in quartz as a function of temperature. Note that at temperatures of 590 and 700 °C, the material is in the β-quartz form.

unit cell, are essentially a "snapshot" of the disordered structure, and are consistent with the Rietveld refined average structure, the measured pair correlation functions, and the local network topology. The distributions of δ and the intertetrahedral O–O–O angles were extracted directly from these models. The former were obtained by projecting each SiO_4 tetrahedron onto the a-b plane and calculating the angular deviation from the ideal $\delta=0$ projection. The latter were obtained by calculating the angle defined by each set of three oxygen atoms that had two O–O distances less than the first minimum in the O–O partial radial distribution functions.

Piezoelectric measurements were performed between 25 and 450 °C. The piezoelectric coupling constant k retained a constant value of close to 8% over this temperature range. The high-quality resonators studied had Q values of over 150 000. A decrease in the Q value was found to begin above 300 °C (Fig. 1) and the Q values obtained above 400 °C are characteristic of a poor resonator. It has been known for many decades[1] that the d_{11} piezoelectric constant of α-quartz begins to decrease gradually at temperatures above 200 °C. The known, time-averaged structure[7] of α-quartz does not provide an explanation for this behavior, as the order parameter δ only decreases gradually from 16.4° to 13.2°, for example, between 25 and 424 °C.

The origin of the deterioration of the piezoelectric response in α-quartz might be expected, in contrast, to arise from local instantaneous structural disorder, which can be characterized by bond length, bond angle, tilt angle (Fig. 2) and intertetrahedral O–O–O angle (Fig. 3) distributions obtained from total neutron scattering measurements. This is supported by the fact that the Q factor, which is very sensitive to structural disorder and defects, decreases rapidly above 300 °C, whereas k, which has been correlated to the static average value[2–6] of δ, remains constant. An explanation for the latter can be obtained from the tilt angle distributions, in which the average value of δ is found to decrease very slowly up to 400 °C, while the full width at half maximum of the distribution increases by 50% between 20 and 400 °C.

The effect of thermally induced disorder is particularly marked in the distributions of the intertetrahedral O–O–O angles (Fig. 3), which represent the relative orientations of interconnected tetrahedra at any instant in time. Whereas the distribution of δ angles at each temperature reflects the variation of individual tetrahedra with respect to the crystallographic axes, the intertetrahedral O–O–O angle distribution shows how neighboring tetrahedra are arranged, implicitly containing the distribution of Si–O–Si bridging angles and tetrahedral torsional angles. The O–O–O distribution is

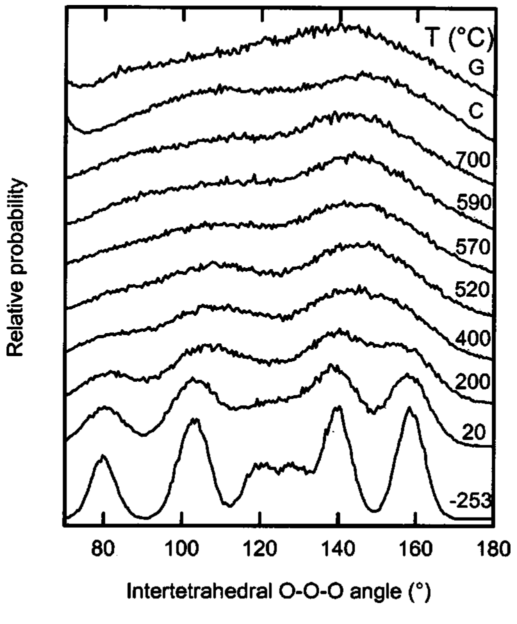

FIG. 3. Distribution functions of the intertetrahedral O–O–O angle in quartz as a function of temperature and those of β cristobalite (C) and silica glass (G). Note that temperatures of 590 and 700 °C correspond to β-quartz and *intra*tetrahedral O–O–O angles form a peak centered at $\theta=60°$ (not shown).

therefore a very good measure of the degree of instantaneous local disorder. At lower temperatures, the instantaneous structure of α-quartz is characterized by distributions about a few well-defined intertetrahedral angles. A major change occurs in the interval between 200° and 400°, at which point the distribution becomes very broad. In addition, it is relatively insensitive to further increases in temperature. No significant change is observed at the α-β phase transition. The distributions are also similar to those of other disordered silica forms such as β cristobalite[13] and even silica glass.[14] This local dynamic disorder in α-quartz at high temperature, which is comparable to that present in β-quartz, rapidly dissipates the induced dipoles and results in the observed decrease in the quality factor Q. The onset of this thermally induced disorder is also apparent from heat-capacity measurements,[15] in which a significant disorder-induced pretransitional effect beginning at around 400 °C is observed by a marked premonitory rise in C_p.

The presence of this dynamic disorder also can explain the observed ferrobielastic behavior of α-quartz at high temperature.[16] The stress threshold for twinning, corresponding to the coercive stress, decreases with temperature and exhibits a discontinuity in the decrease around 250 °C. Here again, the large distributions in the relative orientations of interconnected tetrahedra in the instantaneous structure in this temperature range can provide a mechanism for twinning induced by the ferrobielastic effect.

In summary, the present study has shown that the degradation of the piezoelectric properties of α-quartz resonators, in particular the quality factor Q, well below the α-β phase transition can be related to increased structural disorder as characterized by total neutron scattering.

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