Transient structure determination of resonantly vibrating quartz by short-pulse X-ray diffraction under alternating electric field

Quartz is the most common mineral on earth and is widely used as an oscillator to generate a stable clock signal for watches and other electric circuits because of its piezoelectricity and stable mechanical vibration. The piezoelectricity of quartz (SiO_2) has typically been explained by ionic displacements of Si^{4+} and O^{2-} relative to each other under a mechanical stress and/or an electric field [1]. However, the ionic displacements of Si^{4+} and O^{2-} are strongly restricted by covalent Si–O bonds and are too small to be detected by usual X-ray diffraction experiments. The small atomic displacements induced by an electric field should be enhanced by applying an alternating electric field with the resonant frequency. In order to detect the small atomic displacements induced by an electric field, we determined the transient crystal structure of a resonantly vibrating quartz crystal under an alternating electric field by time-resolved X-ray diffraction at SPring-8 **BL02B1** [2].

A commercial AT-cut quartz oscillator with a resonant frequency of 30 MHz was used in the experiment. AT-cut crystals, which are most commonly used for oscillators because of their high frequency stability over a wide temperature range, show a thickness-shear vibration under an alternating electric field. Transient X-ray diffraction patterns during the resonant vibration were measured by using short-pulse X-rays with a pulse width of 50 ps radiated from SPring-8. The sample was repeatedly irradiated with short-pulse X-rays with a fixed frequency of 26.1 kHz by applying a high-speed X-ray pulse chopper. To synchronize the resonant vibration of the quartz oscillator with the repetitive short-pulse X-rays, a hybrid alternating electric field consisting of 1000 cycles of a sine wave with the resonant frequency (1000 cycles × 1/30 MHz = 33 μs) and repetitions at 26.1 kHz (38 μs/period) was used to drive the resonant thickness-shear vibration. Momentary X-ray diffraction patterns (X-ray wavelength: 0.41 Å) diffracted within 50 ps in a period around the 995th cycle of the alternating electric field were repeatedly stored on a cylindrical image plate camera to improve the counting statistics during the exposure time. The transient crystal structure was investigated over one period by tuning the delay time Δt of the alternating electric field to the reference clock signal of SPring-8.

Figure 1 shows the time dependence of the lattice constant γ under the alternating electric field with an amplitude of 0.18 kV/mm, which was determined by the least-squares refinement of ~400 Bragg peak positions (d-spacing > 0.40 Å) recorded on one oscillation photograph. The γ angle substantially changes sinusoidally with a period of 33 ns = 1/30 MHz. The change in γ, $|\Delta\gamma| = |\gamma - 90°|$, reaches a maximum of 0.15° at Δt = 9 and 25 ns. $|\Delta\gamma|$ under a static electric field of 0.18 kV/mm is estimated to be ~10^{-5}° from the piezoelectric constant d_{11} = –2.31 pm/V [3]. Therefore, the lattice strain is amplified by ~10^4 times by the resonant effect.

The momentary crystal structures of the resonantly

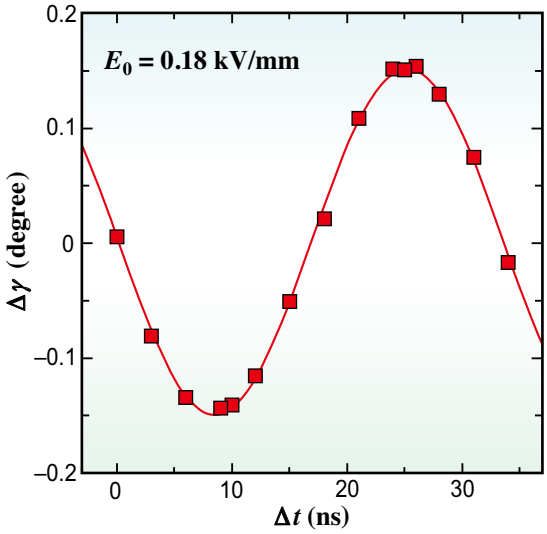

Fig. 1. Time dependence of the lattice constant γ of resonantly vibrating quartz.

vibrating quartz at Δt = 9 and 25 ns were determined by the least-squares refinement of over 3700 Bragg intensities (d-spacing > 0.35 Å). The strained quartz consisted of three crystallographically independent SiO_4 tetrahedra. The Si–O distances (~1.61 Å), O–Si–O angles, (~109°) and Si–O–Si angles (~143°) at the times Δt = 9 and 25 ns were investigated. No changes in the Si–O distances and O–Si–O angles were observed within the standard deviations (~0.2 pm and ~0.1°, respectively) during the resonant vibration. This indicates that the rigid SiO_4 tetrahedra were hardly distorted against the substantial lattice strain. However, specific Si–O–Si angles bridging the rigid SiO_4 tetrahedra changed under the lattice strain as shown in Table 1. The stained triclinic unit cell contains six independent oxygen atoms (O(1)–O(6)). The changes in the four independent Si–O–Si angles at O(1), O(4), O(5) and O(6) are comparable with the standard deviations (~0.1°). In contrast, the Si–O–Si angles at O(2) and O(3) appear to decrease and increase, respectively, from Δt = 9 to 25 ns.

The substantial deformation of the Si–O–Si angles at O(2) and O(3) can be explained by oxygen displacements induced by the electric field and the orientation relations between the Si–O–Si planes and the electric field. The shifts of electron charge from the neutral atoms, which were estimated from the electron charge densities obtained by the maximum entropy method, were +2.8(1)e (e: elementary charge) for a silicon atom and –1.4(1)e for an oxygen atom. These values are comparable with those obtained from the theoretical ionic formula [4]. When the anionic oxygen atoms are displaced by the electric field, the Si–O–Si angles are deformed. However, the oxygen is hardly displaced if the Si–O–Si plane is parallel to the electric field due to the rigid Si–O bonds. The angles between the electric field and vectors normal to the Si–O–Si planes, ϕ, at O(2) and O(3) are closer to 90° than those at other oxygen atoms as shown in Table 1 and Fig. 2.

Table 1. Si–O–Si angles at the times Δt = 9 and 25 ns, and angles between the electric field and vectors normal to the Si–O–Si planes ϕ

	Si–O–Si angle (deg.)		ϕ (deg.)
	Δt = 9 (ns)	Δt = 25 (ns)	
Si(1)–O(1)–Si(3)	143.97(11)	143.81(12)	60
Si(1)–O(2)–Si(3)	144.19(11)	143.41(12)	83
Si(2)–O(3)–Si(1)	143.37(10)	144.02(11)	83
Si(2)–O(4)–Si(1)	143.50(11)	143.82(12)	59
Si(3)–O(5)–Si(2)	143.73(16)	143.27(17)	26
Si(3)–O(6)–Si(2)	143.42(15)	143.61(17)	26

Therefore, the Si–O–Si angles at O(2) and O(3) are substantially deformed during the resonant vibration.

The easy displacements of specific anionic oxygen atoms (O(2) and O(3)) and the collateral resilient deformation of Si–O–Si angles resulted in the resonant vibration under substantial lattice strain. The resilient bending vibration of Si–O–Si angles in the AT-cut quartz oscillator revealed in this study is essential for the generation of a stable clock signal for watches and other electric circuits.

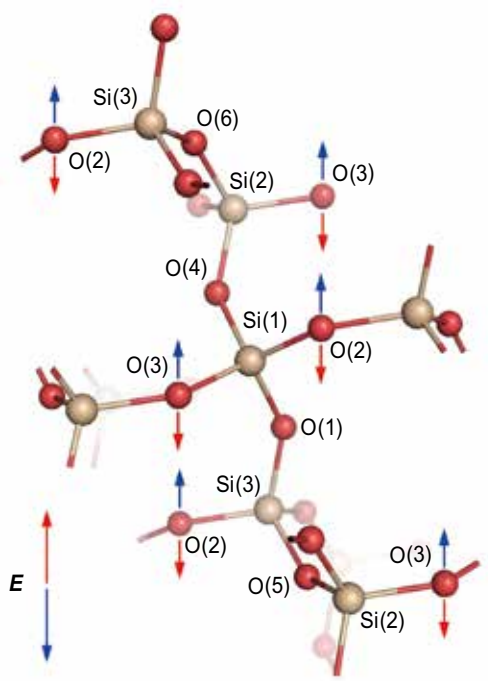

Fig. 2. Crystal structure of quartz and oxygen displacements of O(2) and O(3) induced by the electric field E.

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References

[1] A. Meissner: Z. Tech. Phys. **8** (1927) 74.
[2] *S. Aoyagi, H. Osawa, K. Sugimoto, A. Fujiwara, S. Takeda, C. Moriyoshi and Y. Kuroiwa: Appl. Phys. Lett.* ***107*** *(2015) 201905.*
[3] R. Bechmann: Phys. Rev. **110** (1958) 1060.
[4] Y.-N. Xu and W.Y. Ching: Phys. Rev. B **51** (1995) 17379.