Terahertz-induced martensitic transformation in partially stabilized zirconia

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Abstract

Martensitic crystal structures are usually obtained by rapid thermal quenching of certain alloys, which induces stress and subsequent shear deformation. Here, we demonstrate that it is also possible to intentionally excite a suitable transverse acoustic phonon mode to induce a local shear deformation. We irradiate the surface of a partially stabilized zirconia plate with intense terahertz pulses and verify martensitic transformation from the tetragonal to the monoclinic phases by Raman spectroscopy and the observed destructive spallation of the zirconia microcrystals. We calculate the phonon modes in tetragonal zirconia and determine the effective channel that triggers the transformation. This mode can be excited via the Klemens process. Since terahertz pulses can induce a specific local shear deformation beyond thermal equilibrium, they can be used to elucidate phase transformation mechanisms with dynamical approaches. Terahertz-induced martensitic transformation is considered to be useful for material strengthening and shape memory ceramics.

Introduction

Owing to recent advances in laser technology it is now possible to access nonlinear phonon dynamics, which can be used to control physical properties of solids. For example, an intense ultrashort optical pulse can generate coherent lattice vibrations with large displacements via the impulse Raman-scattering process \(^1,2\). By using the phonon anharmonicity under photoexcitation, several methods for the control of material properties have been explored. In particular, owing to wavelength conversion techniques \(^3\), infrared-active phonons can be driven efficiently \(^4,5,6\). Such strongly driven phonons can cause the atomic rearrangement in the crystal and change the material functionality, e.g. reveal an otherwise hidden ferroelectricity in a quantum paraelectric material \(^7\). The driven phonons can also induce exotic electron phenomena in strongly correlated systems \(^8,9,10,11\). These phenomena can be enhanced by an electric-field enhancement with a sub-wavelength periodic structure of a metal \(^12\).

Here, we propose another method to control materials by phonon excitation: we consider the possibility of a martensitic transformation that is triggered by the nonlinear response of phonons under excitation with terahertz (THz) pulses. The term martensitic transformation describes a particular crystal-structure transformation that occurs via shear deformation. The obtained crystal structure is exceptionally hard and the transformation is usually induced by rapid thermal quenching of suitable alloys. This transformation has been intensively investigated in steel alloys by applying mechanical stress \(^13\) or magnetic fields \(^14\), and has been widely used for shape memory alloys \(^15\). Since softening of transverse acoustic (TA) phonons with large wavenumbers has been reported in the premartensitic phase \(^15,16\), TA phonons are considered to play an important role in the transformation. Acoustic phonons at the zone boundary are accessible via the Klemens process from the -point transverse optical (TO) phonon \(^17,18\). Note that the Klemens process has also been identified as a decay channel of coherent phonons \(^19,20\).
Thus, we expect that large-amplitude TA phonons generated from resonant TO phonon excitation via the Klemens process can cause a martensitic transformation in certain alloys. To demonstrate this, we use tetragonal zirconia (t-ZrO$_2$). To populate the TA phonon mode that triggers the martensitic transformation, we use a THz-free electron laser (THz-FEL). Recently, a high-efficiency elastic wave generation at the surface of water has been reported using this THz source$^{21,22}$, suggesting that generation of a mechanical force in t-ZrO$_2$ is possible.

Results

Verification of suitable phonon modes. Zirconia is an ionic material with a large phonon anharmonicity and it has been shown that zirconia doped with about 3 mol% Y$_2$O$_3$ consists mainly of a meta-stable tetragonal phase at room temperature$^{23,24}$. In this work, we used commercial partially stabilized zirconia ceramic plates (3.5 mol% Y$_2$O$_3$) with a high volume-fraction of t-ZrO$_2$. t-ZrO$_2$ becomes cubic (c-ZrO$_2$) at higher temperatures and can become monoclinic (m-ZrO$_2$) due to mechanical strain$^{23,24,25}$. Figure 1a shows the crystal structures of ZrO$_2$ (different projections are shown in Fig. S1 of the Supplementary Information). The skeleton of the m-ZrO$_2$ lattice exhibits a shear distortion of 9° parallel to the basal plane of the unit cell of t-ZrO$_2$.$^{23}$ Since the tetragonal to monoclinic transformation is accompanied by a volume expansion, the microcracks that are normally caused by the deformation of a polycrystalline material, are suppressed via this stress-induced transformation of t-ZrO$_2$.$^{23,24,25,26}$ Figure 1b shows the infrared reflection and Raman spectra, indicating that the t-ZrO$_2$ has phonons near 4 THz$^{27}$. This mode was excited resonantly by the THz-FEL. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) data of our sample are provided in Fig. S2 of the Supplementary Information.

Irradiation of the sample with a single THz macropulse. For this experiment, a partially stabilized zirconia ceramic plate was irradiated with a single macropulse as shown in Fig. 2a. Each photograph in Figs. 2b–2e shows a scar on the surface of the t-ZrO$_2$ plate generated by a different macropulse energy. The photograph of the whole plate is shown in Fig. S3 of the Supplementary Information. Irradiation scars were already clearly visible above macropulse energies of 2 mJ. Figure 2g shows that, when a macropulse energy of 29 mJ is used, the height of the centre of the irradiation spot lies below the initial level while the outer regions lie above. These features indicate the occurrence of melting; we interpret that the t-ZrO$_2$ was melted in the centre by thermal heating and a strong elastic wave propagated towards the outer region and the rebound of the elastic wave results in the higher region around the depressed centre area. On the other hand, at a macropulse energy of 7.5 mJ as shown in Fig. 2f, the height of the centre of the irradiation spot of t-ZrO$_2$ rises. We confirmed that this rough surface does not consist of individual small particles that can be simply removed by cleaning the surface.
In order to investigate the THz-induced crystal-structure change, we performed XRD measurements. Figure 3a shows three XRD patterns recorded at sample areas without irradiation (black curve), with weak single-shot irradiation (red curve; no melting), and with strong single-shot irradiation (blue curve; melting occurred). The photograph of the plate used in this experiment and the XRD data of the whole data range are shown in Fig. S4 of the Supplementary Information. The peaks at 30.16°, 34.60°, and 35.14° are characteristic of t-ZrO$_2$. We also can confirm two peaks at 28.16° and 31.36°, which are the same 2θ-values as those of peaks observed for m-ZrO$_2$. However, the intensity ratio of these two peaks in the spectrum of the area without irradiation is not that observed for typical m-ZrO$_2$. It has been reported that t-ZrO$_2$ sometimes has planar defects with the same structure as m-ZrO$_2$ for the crystal twinning. This is also supported by the broad linewidth of the XRD peak at 30.16° in Fig. 3a and the transmission electron microscope (TEM) image in Fig. S5a of the Supplementary Information. By the irradiation of the sample with the weak THz pulse, the XRD peak at 28.16° decreases and that at 31.36° increases. These relative intensities are consistent with bulk monoclinic zirconia, suggesting that the weak THz pulses induce a martensitic transformation to the monoclinic phase.

To selectively characterize the phase at the centre of an individual irradiation scar, we performed Raman spectroscopy using a confocal microscope. Figure 3c shows the Raman spectra obtained at the centres of irradiation scars generated by different macropulse energies. For the region without irradiation, Raman peaks characteristic of t-ZrO$_2$ appear. On the other hand, for the irradiation scar generated by a macropulse with an energy of 7.5 mJ (Fig. 3c; red curve), new Raman peaks appear at 170, 184, and 369 cm$^{-1}$. These peaks are characteristic of m-ZrO$_2$, suggesting that the phase transformation contributed to the overall height increase in Fig. 2f. Above excitation pulse energies of 20 mJ (Fig. 3c; blue curve), the Raman peaks that are characteristic of m-ZrO$_2$, are less pronounced and all Raman peaks become broad due to crystal melting.

To clarify the contribution of the phase transformation to the deformation of the zirconia surface as seen in Fig. 2f, we also investigated the irradiation scar on an 8-mol% Y$_2$O$_3$-stabilized zirconia sintered plate. It is intrinsically cubic and does not exhibit a phase transformation under pressure or exposure to high temperatures. The photographs, height profiles, and Raman spectra of irradiation scars for different macropulse energies are shown in the Extended Data Fig. 1. The Raman spectroscopy data clarifies that a phase transformation has not occurred in this sample. Innumerable peeling structures on the surface suggesting a thermal volume expansion and its rebound without melting.

**Temporal evolution of the surface roughness.** The changes in the surface condition of the irradiation spot were investigated in the time domain by detecting the intensity of a visible laser reflected from the
irradiation spot. Figure 4a shows the experimental setup. In this experiment, we reduced the macropulse width to 1 ms to improve the temporal resolution. Fifty consecutive shots of a weak macropulse (repetition rate 5 Hz) were used and we measured the temporal evolution of the change in the reflected intensity, \( \Delta I \), for each macropulse. Figure 4b shows the photographs of the three irradiation scars generated by the irradiation with fifty macropulses at three different pulse energies (0.99, 1.7, and 2.4 mJ). Note that irradiation scars appeared even below the threshold macropulse energy of 2 mJ for the single-shot excitation, implying a partial phase transformation even by low-energy macropulses. Figure 4c shows the three time profiles of the changes in \( \Delta I \) observed after the first macropulse for 0.99, 1.7, and 2.4 mJ, respectively (is the initial reflected-beam intensity). Here, \( \Delta I \) decreases sharply within the macropulse width, indicating that the THz pulse irradiation causes a rapid volume expansion. The reflected intensity decreases, because the surface roughness increases as shown in Fig. 2f. In all three curves, this reduction continues up to 10 ms after excitation. This is the time required by all modes, including high-frequency phonons, to reach thermal equilibrium. The inset plots the macropulse energy dependence of \( \Delta I \) measured at a time of 10 ms after the excitation.

These observed changes of \( \Delta I \) in the early time region were mainly reversible and they decayed within several milliseconds. We extracted the magnitude of the THz-induced irreversible change of each macropulse by measuring the \( \Delta I \) that occurs immediately before irradiation with the next macropulse about 200 ms later. Figure 4d plots the dependences of the irreversible component on the number of macropulse shots. For pulse energies larger than 2 mJ, the irreversible component is positive after the first pulse and it becomes negative in subsequent shots. For 1.7 mJ, a gradual increase of the irreversible component with the shot number can be confirmed. A plausible interpretation is that a partial phase transformation compensated the voids in the ceramic\(^{24}\).

**Irradiation with a near-infrared pulse**

Figures 5a and 5b show the irradiation scars generated by irradiation with near-infrared (NIR) pulses using excitation intensities of 10 \( \mu \)J and 200 \( \mu \)J, respectively. Clear traces of ablation due to electron heating and evaporation are observed. The black spots are characteristic of oxygen-deficient zirconia\(^{31}\). These results reproduce the results of a previous report, in which laser ablation of zirconia was investigated from the aspect of laser machining and laser pulse deposition techniques\(^ {32}\). In spite of the large bandgap energy (>5 eV)\(^{31}\), laser-induced plasma is generated via multi-photon absorption, which accelerates the desorption of oxygen atoms.

Figure 5c shows a Raman spectrum at the centre position of the irradiation scar generated by using a NIR optical pulse. Tiny Raman peaks that are characteristic of the monoclinic phase can be confirmed, which
indicates a phase transformation due to stress induced by rapid heating and/or cooling near the ablation trace. However, the comparison between the purple and red curves in Fig. 5c shows that the peak intensity of the monoclinic phase induced by the NIR optical pulse is much weaker than that induced by the THz pulse. We found that the irradiation scar generated by the NIR pulse is quite different from that generated by the THz pulse. We consider that this is a result of the selective excitation of the lowest infrared-active phonon by the THz pulse, while the NIR pulse can only populate the phonon modes via electron-phonon equilibration.

Discussion

Our experimental results suggest that the t-ZrO$_2$ surface was deformed due to the THz-induced martensitic transformation to the monoclinic phase. This transformation observed for relatively weak pulse energies is different from the thermal stress-induced martensitic transformation. It is known that zirconia undergoes a 4% volume expansion during the martensitic transformation from the tetragonal to the monoclinic phases. We consider that the THz pulse induced a uniform phase transformation, which is beyond the conventional scheme of stress-induced phase transformation toughening. This is supported by the decrease of the lattice constant after the irradiation due to compression (see the peak shift of the XRD peak at 30.16° to 31.20° in Fig. 3a). Moreover, the TEM image of the irradiated zirconia, shown in Fig. S5b of the Supplementary Information, exhibits a herringbone structure with multiple twinning on the nanometer scale, which is characteristic of the shear stress.

Below we explain why we consider that the THz-induced phase transformation is not triggered by conventional thermal expansion at the irradiation spot. The latter mechanism has also been discussed with respect to desorption/ionization of molecules during thermal spallation. In our experiment, we found traces of melting at macropulse energies above 20 mJ, suggesting that the sample temperature exceeded the melting temperature of 2977 K at the centre of the irradiation spot. Therefore, we expect that a 2-mJ macropulse leads to a temperature increase of about 270 K. If we assume that volume expansion is inhibited, we can estimate a maximum hydrostatic pressure of about 0.7 GPa by using a thermal expansion of $11 \times 10^{-6} \text{ K}^{-1}$ and a Young's modulus of 222 GPa for this temperature increase. It is known that t-ZrO$_2$ partially undergoes a phase transition from tetragonal to monoclinic phases under applied mechanical stress of above 0.69 GPa, which is comparable to our estimated value. However, partial transformation at the threshold causes a transformation toughening. Similarly, the local surface-roughness change shown in Fig. 4d serves as evidence against the assumption of no volume expansion. Therefore, the thermal pressure should be lower than the threshold of 0.69 GPa and we conclude that the THz-induced transformation is induced by another mechanism.
The contribution of TA phonons with large wavenumbers to a martensitic transformation is considered crucial for the transformation of the t-ZrO$_2$, because they are also important in metal alloys $^{16}$. The prominent difference between the t- and m-ZrO$_2$ crystal structures in Fig. 1a is the tilt of the lattice skeleton, which corresponds to the displacement described by the TA phonons at the zone boundary. Although low-frequency phonon modes at the M-point may also direct atoms from positions in the tetragonal phase to stabilized positions corresponding to the monoclinic phase $^{37}$, we consider that lattice vibrations in another coherent phonon mode may trigger shear deformation of the lattice at a primary stage of this transformation. Thus, in the following discussion, we focus on the acoustic phonons that can be generated by a conversion from excited optical phonon by the Klemens process.

Figure 6a shows the schematic of the Klemens process, which has been intensively investigated by ultrafast spectroscopy $^{19,20}$. The efficiency of this process is determined by the energy-momentum conservation law. To evaluate it, we calculated the phonon dispersion curves of t-ZrO$_2$ by using density functional perturbation theory $^{38,39}$. Figure 6b shows the calculated phonon dispersion curves along the major high-symmetry directions. The complete dispersion and the corresponding phonon density of states (pDOS) are shown in the extended Data Fig. 2, which almost reproduces the previously reported data $^{27}$. We find that the TO mode (T$_u$) at the $\Gamma$-point lies at 2.16 THz, which is lower than the value in the previous report $^{27}$. Below 6 THz, the partial pDOS of Zr is dominant, suggesting the existence of critical modes for the lattice skeleton distortion.

Figure 6c visualizes the atomic displacements due to the infrared-active TO phonon at 2.16 THz, which cannot induce share deformation. Figure 6d shows the atomic displacements due to the lowest TA phonon mode at the M-point. This mode can induce a shear deformation between individual layers because all displacement vectors lie in the x–y plane $^{37}$. However, its frequency (2.65 THz) is higher than that of the T$_u$ mode, and thus is not accessible according to the Klemens selection rule. On the other hand, the lowest-frequency TA phonons at Z-point lies at 0.81 THz, which almost satisfies the selection rule of the Klemens process. Figure 6e shows the atomic displacements induced by the lowest TA phonon mode at the Z-point. This phonon mode can also cause a tilting motion of ions that is matched to the crystal skeleton of t-ZrO$_2$. However, since the phonons at the zone boundary have relatively short wavelengths, an additional mechanism is required for the macroscopic phase transformation. Note that softening of TA phonons with large wavenumbers has been reported in premartensitic phase in metal alloys $^{15,16}$. Therefore, we consider that a similar softening of TA phonons also occurred in our demonstration.
The above discussion identified the importance of the lowest TA phonon mode at the Z-point, but the mechanisms of the martensitic transformation in zirconia are still under debate. This transformation from t- to m-ZrO$_2$ requires a translational shift of the crystal cell as well as a crystal tilt$^{40}$, indicating that the additional mechanism for the shift needs to be identified. A different pathway of the transformation via the orthorhombic phase as an intermediate phase has also been proposed$^{41}$. Our present results do not provide direct answers regarding the additional mechanism, but we believe that spectroscopic measurements regarding infrared-pulse-induced shear perturbation is a powerful tool to reveal the details of the martensitic phase transformation.

In conclusion, we have demonstrated the THz-induced martensitic transformation in a t-ZrO$_2$ sintered plate. From the height profiles and the Raman spectroscopy data of the irradiation scar generated by the THz-FEL pulse, we found that the drastic volume expansion due to the martensitic transformation causes a destructive spallation of the zirconia microcrystal. This martensitic transformation is caused by shear deformation due to an acoustic phonon that is generated from the optical phonon via the Klemens process. We calculated the phonon modes in t-ZrO$_2$ and confirmed an effective channel from the infrared-active phonon mode to the mode required for the transformation. Since the THz pulse excitation can access specific channels of the transformation (which is in contrast to the conventional martensitic transformation via thermal expansion and/or mechanical stress), it can be used to elucidate complex martensitic transformation mechanisms in various materials with dynamical approaches. The THz-induced martensitic transformation is a unique method for material strengthening and strain-control of shape memory ceramics$^{42}$.

**Methods**

**Sample characterization.** We used a commercial 3.5-mol% Y$_2$O$_3$-doped zirconia ceramic plates (MIT corporation) with dimensions of 10 10 0.5 mm and a polished surface. We characterized the samples with infrared reflection spectroscopy (Fig. 1b), Raman spectroscopy (Fig. 1b), and XRD measurements and SEM (Fig. S2 in the Supplementary Information).

**Terahertz source.** For the irradiation of the sample with THz pulses, we used a THz-FEL based on the L-band electron linear accelerator at the Research Laboratory for Quantum Beam Science, Institute of Scientific and Industrial Research, Osaka University$^{43}$. The THz-FEL generates a linearly polarised THz pulse train consisting of ca. 30–150 pulses (THz-FEL micropulses) with a micropulse interval of 37 ns. This forms the THz-FEL macropulse with a duration of 1–6 ms. The macropulse repetition rate of this system is 5 Hz. By electro-optic sampling using a synchronized Ti:sapphire laser with pulse duration of 100 fs, we evaluated a controllable micropulse duration of 2–6 ps$^{44}$. We carefully confirmed that observed phenomena are insensitive to the macropulse and micropulse widths. In the present
experiments, the peak frequency of the THz-FEL was tuned in the range from 4.2 to 5.2 THz, because the irradiation scars appeared above frequencies of 3.8 THz. As the THz-FEL characteristics depend on the optical cavity length, the sample was set at the position where the macropulse energy was the highest. We summarized the data of the THz-FEL pulses in Fig. S6 of the Supplementary Information. The THz-FEL was focused by a 50-mm gold-coated 90° off-axis parabolic mirror. Since the beam diameter was 20 mm, the spot size at the focal point was about 0.2 mm. During the irradiation experiments, the sample was moved with a constant speed (5 mm/s) along the y axis to obtain many individual scars on the surface, each generated by a single macropulse.

**Scar characterization.** The irradiation scars on the sample were characterized by using a digital microscope (Keyence, VHX6000) and a confocal microscope (OPTELICS, H1200). The structure of the samples was characterized by XRD (Rigaku, UltimaIV, CuKa). Since the X-ray irradiation spot had an extension of mm, we prepared a surface with many irradiation scars as explained above. The photograph of the sample is shown in Fig. S4a of the Supplementary Information. XRD measurements were used to characterize two types of scars: The scars that include a melted region were created by irradiating a 40-mJ single macropulse with a spot size of 0.2 mm. The scars without melted regions were created by irradiating a 40-mJ single macropulse with a spot size of 0.5 mm. We also characterized the scars by cross-sectional high-resolution transmission electron microscopy (HR-TEM: JEOL, JEM-ARM200F). In this measurement, we used the plate shown in Fig. S3 of the Supplementary Information. For the Raman spectroscopy, we used a commercial Raman spectroscopy system (Tokyo Instruments, Nanofinder30) with a 488-nm laser (COHERENT, Sapphire-488-20). In the measurement of the surface roughness change in the time domain, a 532-nm beam from a diode-pumped solid-state green laser (LSR532NL) was focused on the THz irradiation spot by a lens with a focus length of 300 mm and the reflected beam was detected by a photodiode (Thorlabs, DET10A) at a distance of 300 mm from the sample without any lens.

**Near-infrared pulse source.** For the irradiation with the NIR pulse, we used an amplified Yb: YAG laser (HighQ laser, SC-1042-1000fs Reg Amp HE) with a centre wavelength of 1.04 µm, a repetition rate of 1 kHz, an output pulse energy of 1.0 mJ, and a pulse duration of 440 fs. Also in this experiment, the sample was moved during the irradiation experiment by a motorized x–y stage.

**Calculation of the phonon dispersion curves.** The phonon dispersion of t-ZrO_2_ was derived by using density-functional perturbation theory. The calculations were performed using Quantum Espresso ver. 6.3 and applying the generalized gradient approximation by Perdew–Burke–Ernzerhof \(^{45}\) and ultra-soft pseudo potentials \(^{46}\). Convergence with respect to the \(k\)-point sampling and the energy cut-off values (\(E_w\)
= 50 Ry and $E_c = 500$ Ry for the wave function and the charge density, respectively) for the plane-wave expansion was confirmed, and a uniform $k$-point mesh of $8 \times 8 \times 8$ in the $1^{\text{st}}$ Brillouin zone was used.

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