External stimulation-controllable heat-storage ceramics

Hiroko Tokoro1,2,3, Marie Yoshikiyo1, Kenta Imoto1, Asuka Namai1, Tomomichi Nasu1, Kosuke Nakagawa1, Noriaki Ozaki1, Fumiyoshi Hakoe1, Kenji Tanaka1, Kouji Chiba4, Rie Makiura5,6, Kosmas Prassides7 & Shin-ichi Ohkoshi1,2

Commonly available heat-storage materials cannot usually store the energy for a prolonged period. If a solid material could conserve the accumulated thermal energy, then its heat-storage application potential is considerably widened. Here we report a phase transition material that can conserve the latent heat energy in a wide temperature range, $T < 530 \text{ K}$ and release the heat energy on the application of pressure. This material is stripe-type lambda-trititanium pentoxide, $\lambda$-Ti$_3$O$_5$, which exhibits a solid-solid phase transition to beta-trititanium pentoxide, $\beta$-Ti$_3$O$_5$. The pressure for conversion is extremely small, only 600 bar (60 MPa) at ambient temperature, and the accumulated heat energy is surprisingly large (230 kJ L$^{-1}$). Conversely, the pressure-produced beta-trititanium pentoxide transforms to lambda-trititanium pentoxide by heat, light or electric current. That is, the present system exhibits pressure-and-heat, pressure-and-light and pressure-and-current reversible phase transitions. The material may be useful for heat storage, as well as in sensor and switching memory device applications.
Phase transition phenomena, such as metal-insulator, ferroelectric ferromagnetic, and spin transitions, are attractive issues in the fields of physics, chemistry and materials science. Phase transitions are controlled not only by temperature change but also by other external stimuli such as pressure, light-irradiation or electric current flow. For example, for pressure-induced phase transitions, pressure-induced metal-semiconductor transition in a molybdenum disulphide$^1$, pressure-induced superconductor transition in a fulleride$^2$ and pressure-induced ferroelectric–antiferroelectric transition in a perovskite system$^3$ have been reported. For light-induced phase transitions, light-induced crystalline-amorphous transitions in chalcogenides$^4,5$, light-induced metal-semiconductor transition in a trititanium pentoxide$^6$ and insulator-metal transition in perovskite manganites$^7,8$, light-induced spin-crossover transitions in metal complexes$^9-12$ and light-induced charge-transfer transition in organic molecules$^{13,14}$ and metal complexes$^{15}$ have been reported. Furthermore, for current-induced phase transitions$^{16-18}$, current-induced insulator-metal transition in organic compound and current-induced magnetic-domain-wall switching in gallium manganese arsenide have been reported.

In recent years, heat-storage materials have been attracting attention from the viewpoint of energy saving. Development of high-performance heat-storage materials is important for the effective use of waste heat from blast furnaces in factories. Phase transition materials are considered to be useful as latent heat-storage materials. These are divided into solid–liquid and solid–solid phase transition types. In the former, the phase transition at the melting point (m.p.) is used for the heat storage. For example, water (320 kJ L$^{-1}$ at m.p. = 0 °C), paraffin (140 kJ L$^{-1}$ at m.p. = 64 °C)$^{19}$ and polyethylene glycol (165 kJ L$^{-1}$ at m.p. = 20 °C)$^{20}$ are known. In these cases, there are concerns of liquid spill from the system and mixing (or reaction) with the surrounding media. From this angle, a solid–solid phase transition material is stiff and its form is maintained without support, while at the same time it has chemical stability against the surrounding media. Well-known solid–solid phase transition materials for heat-storage usage include copolymers (for example, hyperbranched polyurethane: 150 kJ L$^{-1}$ at 67 °C)$^{21}$, organic compounds (for example, neopentylglycol: 165 kJ L$^{-1}$ at 48 °C and pentaerythritol: 360 kJ L$^{-1}$ at 188 °C)$^{22,23}$ and organometallic compounds (for example, bis(n-hexadecylammonium) tetrachlorozincate: 120 kJ L$^{-1}$ at 103 °C and bis(n-decamethylnonium) tetrachlorocuprate: 60 kJ L$^{-1}$ at 34 °C)$^{24,25}$. In general, such phase change heat-storage materials cannot store the energy for a prolonged period below the phase transition temperature. If a solid material could conserve the accumulated thermal energy and release it only on demand, then its heat-storage application potential is considerably widened. From this angle, our work focused on a phase transition where the latent heat of thermal phase transition could be stored.

In this paper, we report a heat-storage material composed of lambda-trititanium pentoxide. The solid–solid phase transition of this material can be controlled by heat, pressure application, light-irradiation and current flow. This heat-storage material can conserve a high accumulation of energy and release it by the application of a remarkably small external pressure.

**Results**

**Material and morphology.** The sample of the titanium oxide, a new series of lambda-trititanium pentoxide ($\lambda$-Ti$_3$O$_5$), was produced by sintering rutile-TiO$_2$ particles in a hydrogen atmosphere (see Methods). Elemental analysis using inductively coupled plasma mass spectrometry confirms that the formula of the material is Ti$_3$O$_5$. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the obtained sample show a coral-like morphology with particle size of $\sim$4 × 1 μm (Supplementary Fig. 1), composed of aggregates of rectangular-shaped nanorods, of which the majority are $\sim$200 × 30 nm dimensions (hereafter called ‘stripe-type-\(\lambda\)-Ti$_3$O$_5$’, Fig. 1a). The high-resolution TEM (HRTEM) image is shown in Fig. 1b. The Fourier transform analysis of the HRTEM image showed that the growth direction of the nanorods is along the crystallographic $b$ axis. The atomic level image from HRTEM corresponds to the visualized electron density distribution map on the $bc$ plane calculated by the maximum entropy method (MEM; Fig. 1c), described later.

**Pressure-induced phase transition.** X-ray powder diffraction (XRPD) measurements were performed to investigate the pressure ($P$) dependence of the crystal structure of the stripe-type-\(\lambda\)-Ti$_3$O$_5$. The XRPD pattern at 300 K under atmospheric pressure ($P = 0.1$ MPa) is shown in Fig. 1d and Supplementary Fig. 2. Rietveld analysis indicates that this sample is composed of 80.0(2)% \(\lambda\)-Ti$_3$O$_5$ and 20.0(2)% $\beta$-Ti$_3$O$_5$. \(\lambda\)-Ti$_3$O$_5$ adopts a monoclinic crystal structure (space group C2/m) with lattice parameters of $a = 9.83119(19)$ Å, $b = 3.78798(7)$ Å, $c = 9.97039(19)$ Å and $\beta = 91.2909(7)$, and a unit cell volume, $V = 371.207(12)$ Å$^3$. \(\lambda\)-Ti$_3$O$_5$ has three symmetry-inequivalent Ti sites, Ti(1), Ti(2) and Ti(3), and five-symmetry-inequivalent O sites, O(1) to O(5). All the Ti sites form a six-coordinate structure. In the previous investigation$^9$ of the same polymorph prepared from anatase-TiO$_2$ nanoparticles, we observed some indications of a pressure effect. In the present research, the sample was pressed at various external pressures with a pellet press, and XRPD patterns were measured for the pellets after pressure release. With increasing $P$, the intensity of the XRDP peaks of \(\lambda\)-Ti$_3$O$_5$ decreased and those of $\beta$-Ti$_3$O$_5$ increased (Fig. 1d and Supplementary Fig. 3). The pressure where the fraction of \(\lambda\)-Ti$_3$O$_5$ becomes 50% ($\lambda$-$\beta$-Ti$_3$O$_5$) is $\sim$60 MPa as shown in Fig. 1e. The crystal structure of $\beta$-Ti$_3$O$_5$ is monoclinic (space group C2/m; $a = 9.75252(18)$ Å, $b = 3.80034(6)$ Å, $c = 9.44413(19)$ Å, $\beta = 91.5322(10)$ and $V = 349.902(11)$ Å$^3$) (Supplementary Fig. 4). After pressurizing the sample and releasing the pressure at room temperature, heating the sample causes $\beta$-Ti$_3$O$_5$ to revert back to \(\lambda\)-Ti$_3$O$_5$ at 470 K (Fig. 1d,f and Supplementary Fig. 5a). Above 530 K, \(\lambda\)-Ti$_3$O$_5$ further transforms to $\alpha$-Ti$_3$O$_5$. On the other hand, in the cooling process from 620 to 300 K, $\alpha$-Ti$_3$O$_5$ returns to \(\lambda\)-Ti$_3$O$_5$ (Supplementary Fig. 5b). This \(\lambda\)-Ti$_3$O$_5$ is very stable in the wide temperature range of $0 < T < 530$ K. Furthermore, when external pressure was applied to this recovered \(\lambda\)-Ti$_3$O$_5$ sample, \(\lambda\)-Ti$_3$O$_5$ exhibited again the phase transition to $\beta$-Ti$_3$O$_5$ (Supplementary Figs 6 and 7).

The visualized electron density distributions of \(\lambda\)-Ti$_3$O$_5$ and $\beta$-Ti$_3$O$_5$ obtained using MEM from the XRPD patterns, are shown in Fig. 2a. The MEM image of \(\lambda\)-Ti$_3$O$_5$ shows that the electron density is spread between both Ti and O atoms, while in $\beta$-Ti$_3$O$_5$, the electron density is localized around each atom. This result indicates the electron delocalized character of \(\lambda\)-Ti$_3$O$_5$ and localized character of $\beta$-Ti$_3$O$_5$, which are consistent with the fact that \(\lambda\)-Ti$_3$O$_5$ is a metallic conductor and $\beta$-Ti$_3$O$_5$ is a semiconductor. In addition, the visualized electron density distribution of \(\lambda\)-Ti$_3$O$_5$ in the $bc$ plane well reproduces the HRTEM image, as mentioned in Figs 1b and c.

**First-principles calculation of phonon mode.** To elucidate the pressure-induced phase transition, first-principles phonon mode calculations were conducted. Figure 2b shows the phonon density of states (DOS) based on the lattice vibrations for \(\lambda\)-Ti$_3$O$_5$ and $\beta$-Ti$_3$O$_5$.
Ti₃O₅. The phonon dispersion and phonon frequencies at the Brillouin zone centre, Γ point, for each of the phonon dispersions are listed in Supplementary Fig. 8. Comparison of the two crystal structures shows that the coordination geometry of Ti(3) is different between λ-Ti₃O₅ and β-Ti₃O₅: Ti(3) is connected to O(5) in λ-Ti₃O₅, while it bonds to O(4) in β-Ti₃O₅. Therefore, in the pressure-induced phase transition from λ-Ti₃O₅ to β-Ti₃O₅, the Ti(3)–O(5) bond is considered to break, and the Ti(3)–O(4) bond to form. The corresponding phonon modes of λ-Ti₃O₅ lie at 248.6, 318.5 and 445.8 cm⁻¹. For example, the B₁u phonon mode at 445.8 cm⁻¹, Ti(3) vibrates significantly toward O(4) and moves further away from O(5) (Fig. 2c (upper) and Supplementary Movie 1). On the contrary, in the course of the thermal phase transition (that is, heat-storage process) from β-Ti₃O₅ to λ-Ti₃O₅, the Ti(3)–O(4) bond is broken and the Ti(3)–O(5) bond is generated. The corresponding phonon modes now lie at 226.7 and 339.3 cm⁻¹. For example, visualization of the B₁u phonon mode at 226.7 cm⁻¹ shows that Ti(3) significantly vibrates towards O(5) (Fig. 2c (lower) and Supplementary Movie 2).

Accumulated heat energy and pressure-released energy. To investigate the heat-storage process from pressure-produced β-Ti₃O₅ to λ-Ti₃O₅ and the amount of accumulated thermal
energy in the system, heat capacity measurements were performed. First, we investigated the heat capacity of the pressure-produced $\beta$-$\text{Ti}_3\text{O}_5$. In the temperature region from 5 to 300 K, specific heat was measured by the relaxation technique using the physical properties measurement system (Fig. 5a), and above 300 K, specific heat accompanying the thermal phase transition from pressure-produced $\beta$-$\text{Ti}_3\text{O}_5$ to $\lambda$-$\text{Ti}_3\text{O}_5$ was measured by differential scanning calorimetry (DSC, Fig. 5b). By combining the results from the physical properties measurement system and DSC measurements and integrating with temperature, the experimental enthalpy ($H$) curves of $\lambda$-$\text{Ti}_3\text{O}_5$ and $\beta$-$\text{Ti}_3\text{O}_5$ versus temperature were obtained up to 600 K (Fig. 5c; see Methods). The transition enthalpy ($\Delta H$) associated with the first-order phase transition from $\beta$-$\text{Ti}_3\text{O}_5$ to $\lambda$-$\text{Ti}_3\text{O}_5$ was $230 \pm 20 \text{kJ L}^{-1}$ ($12 \pm 1 \text{kJ mol}^{-1}$). In the temperature decreasing process of the DSC measurement, there was no peak, indicating that the accumulated heat energy of the phase transition from $\beta$-$\text{Ti}_3\text{O}_5$ to $\lambda$-$\text{Ti}_3\text{O}_5$ was conserved in the system.

Next the released energy of the pressure-induced phase transition from stripe-type-$\lambda$-$\text{Ti}_3\text{O}_5$ to $\beta$-$\text{Ti}_3\text{O}_5$ was measured using a high-pressure micro-DSC measurement system at room temperature. After applying pressure, heat energy of $240 \pm 40 \text{kJ L}^{-1}$ was released, which almost corresponds to the heat accumulated energy (Fig. 5d). Therefore, this material conserves the heat energy of the phase transition from pressure-produced $\beta$-$\text{Ti}_3\text{O}_5$ to $\lambda$-$\text{Ti}_3\text{O}_5$ and releases the accumulated heat energy by applying low pressure through the pressure-induced phase transition from $\lambda$-$\text{Ti}_3\text{O}_5$ to $\beta$-$\text{Ti}_3\text{O}_5$ (Supplementary Movie 3).

**Thermal conductivity and sensible heat-storage performance.** Bricks and concrete are useful as sensible heat-storage materials after,26–28 since they release thermal energy slowly. Thermal conductivity measurements were performed for the stripe-type-$\lambda$-$\text{Ti}_3\text{O}_5$ and pressure-produced $\beta$-$\text{Ti}_3\text{O}_5$. The thermal conductivities were $0.20 \pm 0.02 \text{W m}^{-1}\text{K}^{-1}$ and $0.41 \pm 0.02 \text{W m}^{-1}\text{K}^{-1}$ for $\lambda$-$\text{Ti}_3\text{O}_5$ and $\beta$-$\text{Ti}_3\text{O}_5$, respectively, which are similar to the values of bricks (for example, $0.16 \text{W m}^{-1}\text{K}^{-1}$)26 and concrete (for example, $0.57 \text{W m}^{-1}\text{K}^{-1}$)28.

**Current-induced and light-induced phase transitions.** Electric current was flowed to the pressure-produced $\beta$-$\text{Ti}_3\text{O}_5$ sample at 298 K. By flowing a current of $0.4 \text{A mm}^{-2}$, the colour of the sample changed from brown to dark blue (Fig. 4a). The XRPD patterns before and after flowing the current indicate that $\beta$-$\text{Ti}_3\text{O}_5$ is transformed into $\lambda$-$\text{Ti}_3\text{O}_5$ (Fig. 4b and Supplementary Movie 4). The electric current dependence on the conversion from the pressure-produced $\beta$-$\text{Ti}_3\text{O}_5$ to $\lambda$-$\text{Ti}_3\text{O}_5$ shows that the threshold current value of the current-induced phase transition is $0.2 \text{A mm}^{-2}$ (Supplementary Fig. 9). The origin of this current-induced phase transition is regarded as breaking of charge ordering or (and) Joule heat.16–18 The mechanism by breaking of charge ordering is considered as follows: $\beta$-$\text{Ti}_3\text{O}_5$ is a charge-localized state whose charge is localized on Ti$^{3+}$ (3) with empty orbital on Ti$^{4+}$ (2). In contrast, $\lambda$-$\text{Ti}_3\text{O}_5$ is a charge-delocalized state whose charge is delocalized on Ti(2) and Ti(3). By flowing electric current to $\beta$-$\text{Ti}_3\text{O}_5$, the localized charge on Ti(3) is forcedly moved to the empty orbital on Ti(2), resulting in a transition to metallic $\lambda$-$\text{Ti}_3\text{O}_5$.

Light irradiation experiment was also conducted on a pressure-produced $\beta$-$\text{Ti}_3\text{O}_5$. The reverse phase transition from $\beta$-$\text{Ti}_3\text{O}_5$ to $\lambda$-$\text{Ti}_3\text{O}_5$ was observed by irradiation of 410-nm laser light (Supplementary Fig. 10 and Supplementary Movie 5).
Discussion

The generation of stripe-type-$\beta$-Ti$_3$O$_5$ originates from the change in the Gibbs free energy ($G$) of the material compared with the bulk or single crystal Ti$_3$O$_5$. This change in the $G$ value is considered to be due to the interface (and/or surface) energy of the nanoscale domain. It is noted that there is no oxygen vacancy, which was confirmed by electron spin resonance. To understand why the stripe-type-$\lambda$-Ti$_3$O$_5$ undergoes a pressure-induced phase transition to $\beta$-Ti$_3$O$_5$, we considered the thermodynamics of the present phase transition phenomena using the mean-field model, developed by Slichter and Drickamer.

In this model, $G$ is described by $\Delta H$, the transition entropy ($\Delta S$) and the interaction parameter between $\lambda$-Ti$_3$O$_5$ and $\beta$-Ti$_3$O$_5$ phases. The calculation shows that at atmospheric pressure ($P = 0.1 \text{MPa}$), the sample exists as $\lambda$-Ti$_3$O$_5$ (Supplementary Movie 6). This is because $\lambda$-Ti$_3$O$_5$ is synthesized by sintering at a high temperature, and it remains as $\lambda$-Ti$_3$O$_5$ with decreasing temperature due to the energy barrier between $\lambda$-Ti$_3$O$_5$ and $\beta$-Ti$_3$O$_5$ as shown in the $G$ versus fraction ($x$) of $\lambda$-Ti$_3$O$_5$ curves (Fig. 5a (i)). On the contrary, on applying external pressure, the $G$ versus $x$ curves change; for example, the energy barrier disappears $<400 \text{K}$ when $P$ is $60 \text{MPa}$, and hence, $\lambda$-Ti$_3$O$_5$ transforms into $\beta$-Ti$_3$O$_5$ on applying pressure (Fig. 5a (ii)). The $x$ versus temperature curves of $P = 0.1 \text{MPa}$ and $P = 60 \text{MPa}$ are shown in Fig. 5b. As shown in Fig. 5c, $x$ versus pressure plots indicate the threshold of the pressure-induced phase transition. The origin of the pressure-induced phase transition is the PAV term of $\Delta H (= \Delta U + \Delta V)$, where $\Delta U$ and $\Delta V$ are the changes of internal energy and volume, respectively. At such a low pressure, the pressure-induced change on $\Delta U$ is very small and negligible. In fact, the phonon mode calculation under external pressure shows that the pressure-induced change of $\Delta U$ is $\sim 1 \times 10^{-3} \text{kJ mol}^{-1}$ at $60 \text{MPa}$, which is two orders smaller compared with $\Delta PAV = 0.19 \text{kJ mol}^{-1}$. The pressure-induced change on $\Delta S$ is also very small and cannot contribute to the pressure-induced phase transition in the present system (see Methods, Supplementary Fig. 11 and Supplementary Tables 1, 2). It is noted that the observed $x$ versus $P$ plots of Fig. 1e is somewhat gradual. This is explained by the presence of a distribution in the transition pressure of the Slichter and Drickamer model, which may be due to the crystal size distribution. We have simulated this gradual pressure-induced phase transition with a distribution of transition pressures (Supplementary Fig. 12).

In summary, we report the first metal-oxide capable of conserving the accumulated heat energy of a phase transition. Stripe-type-$\lambda$-Ti$_3$O$_5$ can store a large heat energy of $230 \text{kJ L}^{-1}$, and this energy can be released by applying external pressure only when demand. The magnitude of the required pressure is extremely small, $\sim 60 \text{MPa}$. This value is remarkably smaller than the typical pressures observed in the pressure-induced phase transition to $\beta$-Ti$_3$O$_5$.
transitions in metal oxide materials\cite{30-35} and metallic compounds\cite{36-41}, for example, the pressure-induced phase transition from rutile-TiO$_2$ to baddeleyite-type TiO$_2$ at 1.043 K occurs at 20,000 MPa (\approx 20 GPa)$^{39}$. From the viewpoint of the energy balance of the thermodynamic cycle, pressure of 60 MPa corresponds to \textasciitilde10 kJ L$^{-1}$, which is \textasciitilde5\% of the pressure-releasing heat energy. Pressure of \textasciitilde60 MPa can be realized even by the water pressure of a high-pressure washing machine, and hence, \textit{\lambda}-Ti$_3$O$_5$ has the potential to be employed as pressure-sensitive sheets or reusable portable heating pads. In addition, since \textit{\lambda}-Ti$_3$O$_5$ is a metallic conductor and \textit{\beta}-Ti$_3$O$_5$ is a semiconductor, it has possibilities as a pressure-sensitive conductivity sensor or pressure-sensitive optical sensor. Furthermore, because \textit{\lambda}-Ti$_3$O$_5$ is composed of common elements (titanium and oxygen), it is safe and environmentally friendly. \textit{\lambda}-Ti$_3$O$_5$ could be useful for heat-retaining systems for residential use and may realize more efficient uses of industrial waste heat generated from furnaces (Supplementary Fig. 13)$^{42,43}$. In addition, light-induced and current-induced phase transitions from pressure-produced \textit{\beta}-Ti$_3$O$_5$ to \textit{\lambda}-Ti$_3$O$_5$ are also observed, that is, stripe-type \textit{\lambda}-Ti$_3$O$_5$ shows reversible pressure-and-light-induced phase transition and reversible pressure-and-current-induced phase transition. These effects are also attractive phenomena from the viewpoint of advanced electronic devices.

**Methods**

**Material.** A new series of \textit{\lambda}-Ti$_3$O$_5$ nanocrystallites was produced by sintering rutile-TiO$_2$ particles in a hydrogen atmosphere (flow rates of 0.7 dm$^3$ min$^{-1}$) at 1,117 $^\circ$C for 2 h, followed by a slow cooling process of \textasciitilde9 h from the sintering temperature to room temperature (Supplementary Fig. 14). Elemental analysis using inductively coupled plasma mass spectrometry confirms that the formula is Ti$_{5.00(1)}$O$_{8.00(1)}$ (Calc.: Ti, 64.2\%; Found: Ti, 64.2\%). The experimentally obtained density is 4.000 \pm 0.048 g cm$^{-3}$, which is consistent with the theoretical value of 4.000 g cm$^{-3}$ from the crystal structure of \textit{\lambda}-Ti$_3$O$_5$ as determined by XRPD measurements. SEM and TEM images of the obtained sample show a coral-like morphology with particle size of \textasciitilde4 \times 1 \mu m, composed of rectangular-shaped nanorods, of which the majority are \textasciitilde200 \times 30 nm dimensions (Supplementary Fig. 1a). The Fourier transform analysis of the HRTEM image showed that the growth direction of the nanorods is along the crystallographic \textit{b} axis. This new series of \textit{\lambda}-Ti$_3$O$_5$ have larger crystal size than the previous series, which were prepared from anatase-TiO$_2$ (ref. 6; Supplementary Fig. 1b).

**XRPD measurements.** XRPD measurements were performed with a Rigaku Ultima IV diffractometer with Cu $K_\alpha$ radiation ($\lambda$ = 1.5418 A). The temperature-dependent XRPD measurements were undertaken using a high-temperature chamber with atmosphere control (RIGAKU-OAT003S) under N$_2$ flow. The RIETAN-FP computer programme was used for the Rietveld analyses, while Dysmonia was used for the MEM analyses. The refined crystal structures and charge densities were visualized by the computer programme VESTA. Although both \textit{\lambda}-Ti$_3$O$_5^6$ and its high-temperature phase$^{44,45}$ can be considered as candidates of the present material with C2/m crystal structure, we assigned the present material to \textit{\lambda}-Ti$_3$O$_5$ because it is obtained by a very slow cooling process taking of \textasciitilde9 h from the sintering temperature to room temperature, and it is thermally stable.

**Heat capacity measurements.** To investigate the temperature dependence of the lattice specific heat, \textit{C}(T), in the temperature range of 5–300 K, we carried out curve fitting of the observed plots with the equation based on the two-Debye model$^{36}$ expressed by \textit{C}(T) = $\sum^N_{\nu = 1}9R\nu(T/\theta_\nu)^2/\theta_\nu^4 \times e^{\nu T}/(e^{\nu T} - 1)$, where \nu is the angular frequency, $\theta$ is the reduced Planck constant, \nu is phonon frequency and $\theta_\nu$ is Boltzmann constant, with the fit parameters of $\nu_1 = 3.2(1)$, $\nu_2 = 5.6(1)$, $\theta_1 = 4.1(1) \times 10^2$ K and $\theta_2 = 9.3(1) \times 10^2$ K for \textit{\lambda}-Ti$_3$O$_5$, and $\nu_1 = 2.7(1)$, $\nu_2 = 5.8(1)$, $\theta_1 = 4.3(1) \times 10^2$ K and $\theta_2 = 9.2(2) \times 10^2$ K for \textit{\beta}-Ti$_3$O$_5$. We then developed the temperature dependence curve of the specific heat in the temperature range of 5–600 K using both the fitted curve and the anomalous specific heat associated with the first-order phase transition from \textit{\beta}-Ti$_3$O$_5$ to \textit{\lambda}-Ti$_3$O$_5$ obtained from the DSC measurement.

**Released heat energy on pressure application.** Released heat energy on pressure application was measured with a high-pressure DSC measurement system (mDSC VII, SETARAM Instrumentation) at 300 K. Pressure application of 40 MPa was achieved by instant injection of N$_2$ gas into the sample cell.

**Thermal conductivity measurements.** The specific heat and thermal diffusivity of \textit{\lambda}-Ti$_3$O$_5$ and \textit{\beta}-Ti$_3$O$_5$ pellet samples were measured with a DSC measurement system (DSC200F3 Maia (NETZSCH), NSST Co., Ltd.) and Light Flash Apparatus (LFA447NanoFlash, NSST Co., Ltd.), respectively.

**First-principles phonon mode calculations.** First-principles calculations based on the density functional theory were carried out for \textit{\lambda}-Ti$_3$O$_5$ and \textit{\beta}-Ti$_3$O$_5$ using the VASP (Vienna \textit{ab initio} simulation package) code. The wavefunctions based on plane waves and potentials of the core orbitals were represented by the projector-augmented wave of Blöchl, and the exchange-correlation term was evaluated by the generalized gradient approximation by Perdew, Burke, and Ernzerhof. The crystal structures of \textit{\lambda}-Ti$_3$O$_5$ and \textit{\beta}-Ti$_3$O$_5$ obtained from the XRPD measurements were used for computed models as the initial structures. The lattice parameters and atomic positions were optimized under no pressure and 1000 MPa with an energy

**Figure 5 | Mechanism of the pressure-induced phase transition based on a thermodynamic model.** (a) Gibbs free energy ($G$) versus \textit{\lambda}-Ti$_3$O$_5$ fraction ($x$) for every 10 K between 250 K to 500 K calculated using the Slichter-Drickamer mean-field model at $P = 0.1$ MPa (i) and 60 MPa (ii). Blue and red circles indicate \textit{\lambda}-Ti$_3$O$_5$ and \textit{\beta}-Ti$_3$O$_5$, respectively. \textit{\lambda}-Ti$_3$O$_5$ undergoes a pressure-induced phase transition to \textit{\beta}-Ti$_3$O$_5$ because the energy barrier (shown by brown shadows) disappears by the application of external pressure above \textasciitilde60 MPa as shown in the insets (see Supplementary Movie 6). (b) Calculated $x$ versus temperature curves at $P = 0.1$ MPa (blue) and 60 MPa (red). (c) Calculated $x$ versus pressure curve at 300 K indicating a threshold pressure of \textasciitilde60 MPa.
cutoff of 300 eV and 3 × 7 × 3 k-mesh until satisfying 10−5 eV pm−1 force tolerance. Supercells (1 × 3 × 1) of the optimized structures were used to calculate the thermodynamic functions of β-2TiO3 and β′-2TiO3, which were calculated by the direct method implemented in Phonon code with 2 pm displacements using the optimized structures.

Thermodynamic analysis. In the Slichter and Drickamer mean-field model, the Gibbs free energy of the system is described as $G = x(\Delta H) + x(1-x) + T[x(\ln x + (1-x)\ln(1-x)) - x(\Delta S)] + G_0$, where $x$ is the ratio of the charge-delocalized unit of Ti(3)3+: Ti(3)3+: Ti(3)3+, corresponding to $\lambda$-Ti3O5 and $\gamma$- Ti3O5 phases; $G_0$ is Gibbs free energy of $\beta$-2TiO3 set as the origin of the energies, and $R$ is the gas constant. The observed phase transition was considered to be a metal-semiconductor phase transition between charge-delocalized Ti(3)3+: Ti(2)3+: Ti(2)3+: Ti(2)3+: Ti(2)3+: Ti(3)3+ and charge-localized Ti(3)3+: Ti(2)3+: Ti(2)3+: Ti(2)3+: Ti(2)3+: Ti(3)3+ systems, which were regarded as $\lambda$-2TiO3 and $\gamma$-2TiO3, respectively. The values of $\Delta H = 11.5 \text{kJ mol}^{-1}$ and $\Delta S = 25.2 \text{kJ mol}^{-1}$, and a suitable value of $\gamma = \gamma_2 + \gamma_2 T$, where $\gamma_2 = 14 \text{kJ mol}^{-1}$ and $\gamma_2 = 10.8 \times 10^{-5} \text{K}^{-1} \text{mol}^{-1}$ to be consistent with the observation results, were used. When the external pressure is applied to the sample, $\Delta H$ is perturbed by the pressure-induced change on the $\Delta S$. Thus, when the external pressure is applied to the sample, the change on $\Delta S$ was evaluated by the first-principles phonon mode calculations is negligibly small, for example, $1 \times 10^{-3} \text{kJ mol}^{-1}$ at $P = 60 \text{MPa}$, the change on $\Delta S$ evaluated by the first-principles phonon mode calculations is negligibly small, for example, $1 \times 10^{-3} \text{kJ mol}^{-1}$ at $P = 60 \text{MPa}$. Thus, $\Delta H$ is controlled by the $\Delta S$ term in the present system. The pressure-induced change on $\Delta S$ is also very small, for example, $\Delta S/\Delta P_x = 10^{-10}$ K−1 mol−1 at $P = 60 \text{MPa}$, from the results of first-principles phonon mode calculations.

Current-induced phase transition study. Stainless electrodes are attached to $\beta$-2TiO3 pellet by Ag paste with an adhesion area of 5 mm2 and electric current of 2 A was flowed ($0.4 \text{A mm}^{-2}$). Stainless electrodes are attached to $\beta$-2TiO3 pellet by Ag paste with a suitable value of $\gamma = \gamma_2 + \gamma_2 T$, where $\gamma_2 = 14 \text{kJ mol}^{-1}$ and $\gamma_2 = 10.8 \times 10^{-5} \text{K}^{-1} \text{mol}^{-1}$ at $P = 60 \text{MPa}$, the change on $\Delta S$ evaluated by the first-principles phonon mode calculations is negligibly small, for example, $1 \times 10^{-3} \text{kJ mol}^{-1}$ at $P = 60 \text{MPa}$. Thus, $\Delta H$ is controlled by the $\Delta S$ term in the present system. The pressure-induced change on $\Delta S$ is also very small, for example, $\Delta S/\Delta P_x = 10^{-10}$ K−1 mol−1 at $P = 60 \text{MPa}$, from the results of first-principles phonon mode calculations.

References
1. Nayak, A. P. et al. Pressure-induced semimetal to metallic transition in multilayered molybdenum disulfide. Nat. Commun. 5, 3731 (2014).
2. Takabayashi, Y. et al. The disorder-free non-BCS superconductor Cs2Cu2CO3 emerges from an antiferromagnetic insulator parent state. Science 323, 1585–1590 (2009).
3. Avdeev, M. et al. Pressure-induced ferroelectric to antiferroelectric phase transition in Pb0.99(Zr0.95Ti0.05)0.98Nb0.02O3. Phys. Rev. B 73, 064105/1–14 (2006).
4. Kolobov, A. V. et al. Understanding the phase-change mechanism of rewritable optical media. Nat. Mater. 3, 703–708 (2004).
5. Wuttig, M. & Yamada, N. Phase-change materials for rewritable data storage. Energ. Convers. Manage. 45, 2142–2150 (2004).
6. Medvedev, S. et al. Electronic and magnetic phase diagram of $\beta$-Fe2O3 with superconductivity at 36.7 K under pressure. Nat. Mater. 8, 630–633 (2009).
7. Tolbert, S. H. & Alivisatos, A. P. Size dependence of a first-order solid-liquid phase transition: the wurtzite to rock salt transformation in CdSe nanocrystals. Science 265, 373–376 (1994).
8. Hanfland, M., Syassen, K., Christensen, N. E. & Novikov, D. L. New high-pressure phases of lithium. Nature 408, 174–178 (2000).
9. McMahon, M. I., Nelmes, R. I., Allan, D. R., Belmonte, S. A. & Boqvistararakis, T. Observation of a simple-cubic phase of GaAs with a 16-atom basis. Phys. Rev. Lett. 80, 5564–5567 (1998).
10. Mijuce, A., Rubio, A., Muñoz, A. & Needs, R. J. High-pressure phases of group-IV, III-V, and II-VI compounds. Rev. Mod. Phys. 75, 863–912 (2003).
11. Nelmes, R. I. & McMahon, M. I. Identity of InSb-II and InSb-III. Phys. Rev. Lett. 77, 663–666 (1996).
12. Crabtree, G. W. & Lewis, N. S. Solar energy conversion. Phys. Today 60, 37–42 (2007).
13. Cartledge, E. Saving for a rainy day. Science 334, 922–924 (2011).
14. Grey, I. E., Li, C. & Madden, J. C. Phase equilibria and structural studies on the solid solution. J. Solid State Chem. 113, 62–73 (1994).
15. Onoda, M. Phase transitions of TiO2. J. Solid State Chem. 136, 67–73 (1998).
16. Tomita, D. G., Ramakrishnan, S., Nieuwenhuys, G. J. & Mydosh, J. A. The magnetic susceptibility, specific heat and dielectric constant of hexagonal YMnO3, LuMnO3 and SmCoO3. J. Phys.: Condens. Matter 13, 4543–4552 (2001).

Acknowledgements
We are grateful to Mr. Y. Kagegawa, Mr. H. Tsunakawa and Mr. S. Ohtsuka (The University of Tokyo) for collecting the TEM and SEM images and we also recognize the Cryogenic Research Center and the Center for Nano Lithography and Analysis, The University of Tokyo, which are supported by METX. We are grateful to Mr. R. Uemura (Nippon Steel and Sumikin Technology Co., Ltd.) for the thermal conductivity measurement and Mr T. Tomura and Mr Y. Okada (NIRIKISO Co., Ltd.) for the knowledge of the pressure experiment. The present research was supported in part by the CREST project of JST, the Grant-in-Aid for Young Scientists (A), (B), Research Activity Start-up and the NEXT program from JSPS, the VPI Research Center Initiative for Atoms, Molecules and Materials, SCP for Promoting Science and Technology and APAX from MEXT, Izumi Foundation and Kurata Foundation. M.Y. and N.O. are grateful to JSPS Research Foundation. M.Y. is grateful to APS and T.N. is grateful to MERIT from METX.

Authors contribution
S.O. designed and coordinated this study, contributed to all the measurements and calculations and wrote the paper. H.T. conducted the temperature-dependent XRPD
measurements, heat capacity measurements and thermodynamic calculations. M.Y. analysed the first-principles phonon mode calculation results and partially wrote the paper. K.I. carried out the Rietveld analyses of the XRPD patterns and heat capacity data analyses. A.N. conducted the Rietveld analyses and prepared the figures. T.N. carried out the pressure- and temperature-dependent XRPD measurements. K.N. carried out the elemental analyses and background research. N.O. carried out the DSC measurements and MEM analyses. F.H. obtained the TEM and SEM images. K.T. contributed to the synthesis and Rietveld analyses. K.C. carried out the first-principles phonon mode calculations. R.M. and K.P. contributed to the interpretation of the results and to the writing of the paper. All the authors commented on the manuscript.

Additional information
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

How to cite this article: H Tokoro et al. External stimulation-controllable heat storage ceramics. Nat. Commun. 6:7037 doi: 10.1038/ncomms8037 (2015).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/