Colossal negative thermal expansion in reduced layered ruthenate

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Large negative thermal expansion (NTE) has been discovered during the last decade in materials of various kinds, particularly materials associated with a magnetic, ferroelectric or charge-transfer phase transition. Such NTE materials have attracted considerable attention for use as thermal-expansion compensators. Here, we report the discovery of giant NTE for reduced layered ruthenate. The total volume change related to NTE reaches 6.7% in dilatometry, a value twice as large as the largest volume change reported to date. We observed a giant negative coefficient of linear thermal expansion $\alpha = -115 \times 10^{-6} \degree K^{-1}$ over 200 K interval below 345 K. This dilatometric NTE is too large to be attributable to the crystallographic unit-cell volume variation with temperature. The highly anisotropic thermal expansion of the crystal grains might underlie giant bulk NTE via microstructural effects consuming open spaces in the sintered body on heating.

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Rapid advances in modern technology require industrial materials that can adapt to severe conditions. One means of adaptation is controlled thermal expansion. Although thermal expansion is typically a $10^{-5}$ to $10^{-6}$ change in length, even such a minute change fatally degrades the performance of devices and instruments in many fields of industry. Consequently, negative thermal expansion (NTE) materials have been attracting great attention because NTE materials can be used to tune the overall thermal expansion of materials. Remarkable development in the field of NTE materials was provoked by the discovery of large, isotropic NTE over a wide range of temperatures $T$ in $\text{ZrW}_2\text{O}_8$ (ref. 6). This NTE originates from a characteristic crystal structure called a flexible network. This class of NTE materials reaches an extremely large NTE of $\alpha = -34 \times 10^{-6} \text{K}^{-1}$ in $\text{Cd}(\text{CN})_2$ (ref. 7), where $\alpha$ is the coefficient of linear thermal expansion.

In recent years, new materials in this category, such as ScF$_3$ (ref. 8), have been identified. Another avenue towards discovery of giant NTE is the utilization of a phase transition accompanied by large volume contraction on heating. The effectiveness of this approach was recognized widely by the giant NTE of the antiperovskite manganese nitrides $\text{Mn}_3\text{AN}$, where $A$ represents a metal or semiconducting element, which use volume change caused by a magnetic transition (that is, magnetovolume effects). The giant NTE of $\text{Mn}_3\text{AN}$ strongly influenced subsequent NTE research, leading to the discovery of many phase-transition-type NTE materials such as $\text{La(Fe, Si, Co)}_{12}$ (ref. 10) and $\text{MnCo}_{0.98}\text{Cr}_{0.02}\text{Ge}$ (ref. 11), which use magnetovolume effects, $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ (ref. 12) and $\text{Bi}_{0.95}\text{La}_{0.05}\text{NiO}_3$ (ref. 13), which use intermetallic charge transfer, and $0.4\text{PbTiO}_3-0.6\text{BiFeO}_3$ (ref. 14), which uses a ferroelectric transition.

One promising mother compound for NTE materials is layered ruthenate $\text{Ca}_2\text{RuO}_4$ (refs 15–22). It undergoes a metal–insulator (MI) transition, which is apparently accompanied by volume expansion. Using dilatometry, we discovered giant NTE of large total volume change $\Delta V/V = 6.7\%$ and $\alpha = -115 \times 10^{-6} \text{K}^{-1}$ ($\Delta T$ of $\sim 210 \text{K}$) in reduced $\text{Ca}_2\text{RuO}_4$ (Supplementary Fig. 1). This gigantic volumetric NTE is too large to be attributable to the unit-cell volume NTE estimated by X-ray diffraction (XRD) study. We discuss microstructural effects that enhance the bulk NTE of sintered samples.

Results

Thermal-expansion properties. First, the present NTE of $\text{Ca}_2\text{RuO}_4$ is compared with NTE that are presently known. Figure 1 shows linear thermal expansion $\Delta L/L$ of $\text{Ca}_2\text{RuO}_4$ and $\text{Ca}_2\text{Ru}_{1-x}\text{M}_x\text{O}_4$ ($M$: Mn, Fe and Cu) in this study. The vertical (cylindrical), $z$ and horizontal, $r$ expansions of the $\text{Ca}_2\text{RuO}_4$ sintered pellets are identical. Therefore, it is isotropic and volumetric NTE (inset of Fig. 1, see ‘Methods’ section for conditions of linear thermal-expansion measurements). Parameters related to NTE for recently discovered giant NTE materials are presented in Table 1. The largest $\Delta V/V$ related to NTE reported until now is $3.2\%$ for $\text{MnCo}_{0.99}\text{Cr}_{0.02}\text{Ge}$ (ref. 11). Data of $\Delta L/L$ for this alloy are presented for comparison in Fig. 1. Data for $\text{Pu}^{23}$ and $\text{YMn}_2$ (ref. 24) are also included in Table 1 for comparison. These reference materials exhibit large volume contraction on heating at the phase transition, but they exhibit abrupt volume changes. Therefore, these materials are not categorized as NTE materials. Extreme volume contraction on heating of $\text{Pu}$ is $5.4\%$ in successive $\delta \rightarrow \delta' \rightarrow \varepsilon$ phase transitions55. $\Delta V/V$ reaches $6.7\%$ at most for the present $\text{Ca}_2\text{RuO}_4$. Such a large total volume change is the typical characteristic crystal structure called a flexible network. This class of NTE materials reaches an extremely large NTE of $\alpha = -34 \times 10^{-6} \text{K}^{-1}$ in $\text{Cd}(\text{CN})_2$ (ref. 7), where $\alpha$ is the coefficient of linear thermal expansion.

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Din Reference temperature: 500 K. The hysteresis loop was observed for #1 and #2. The abrupt jump to the Mott metal-to-insulator transition, which coincides with the oxidizing procedure, but is fully recovered by the re-reducing (inset). The giant negative thermal expansion (NTE) of #1 is suppressed to the lower temperature. In that case, the total volume change might become greater than the present estimate of 2.8% (/afii9797 L/L (10–3 ) Ca2RuO3.74 10–20). The abrupt jump in $\rho(T)$ at 345 K for #1 corresponds to the Mott metal-to-insulator transition, which coincides with the onset of NTE.

Effects of oxygen deficiency. We can examine the differences between the present materials showing giant NTE and previous materials. Figure 2 shows linear thermal expansion $\Delta L/L$ of reduced (#1), oxidized (#2), and re-reduced (#3) Ca$_2$RuO$_4$ in the present experiments (see ‘Methods’ section for sample preparation conditions). The giant NTE of the reduced sample is suppressed dramatically by high-pressure oxidizing procedures. When this oxidized sample is reduced again, the giant NTE is recovered. The results presented above imply that differences in oxygen contents produce a striking difference in thermal-expansion properties. Evaluations of the oxygen contents by thermogravimetric analysis are $y = -0.26(1), 0.03(1)$ and $-0.31(1)$, respectively, for the reduced, oxidized and re-reduced samples in the notation of Ca$_2$RuO$_{4+y}$. Reports of an earlier study described that $y$ fell within the range of $-0.01(1)$ to $+0.07(1)^{15}$. The present reduced ruthenates are regarded as having larger amounts of oxygen deficiency than the previous ones. Hereinafter, we use Ca$_{2-y}$Ru$_{1.9}$O$_{4+y}$ notation as the present materials. The $y$ values are presented in Table 2.

High-temperature L to low-temperature S phase transition. The giant NTE of Ca$_2$RuO$_{3.74}$ seems to be triggered by the transition from the high-T metallic L phase to the low-T insulating S phase. The inset of Fig. 2 presents the temperature dependence of resistivity $\rho(T)$ for the reduced and oxidized Ca$_2$RuO$_{4+y}$. The resistivity of the reduced sample indicates that the system undergoes the MI transition at $T_{MI} = 345$ K. The onset of NTE is almost identical to this MI transition. In contrast, resistivity of the oxidized sample shows no abrupt change that can be interpreted as prolonged high-T L phase down to lower temperatures. Corresponding to this MI transition, the anomaly appears in the magnetic susceptibility $\chi(T)$ (Supplementary Fig. 2). $\chi(T)$ is hysteretic ($\sim 10$ K). It therefore supports the first-order nature of this phase transition. Such hysteretic behaviour is confirmed also in the linear thermal expansion. The hysteresis loop was observed in dilatometry measurements (inset of Fig. 2). The onset of NTE is 340 and 355 K on cooling and warming processes, respectively. This loop behaviour is partly attributable to the first-order phase transition. The loop behaviour is reproducible through several successive measurements.

Table 1 | Parameters related to negative thermal expansion for recently discovered giant negative-thermal-expansion materials.

| Material | $\Delta L/L$ (%) | $T_{NTE}$ (K) | $\Delta T$ (K) | $z (10^{-6} \text{K}^{-1})$ | Structure | Method | Reference |
|----------|-----------------|----------------|----------------|---------------------|-----------|---------|-----------|
| ZrW$_2$O$_6$ | 1.2 | $<-425$ | 425 | $-9$ | Cubic | D/N | 6 |
| Cd(CN)$_2$ | 2.1 | 170–375 | 205 | $-34$ | Cubic | X | 7 |
| Mn$_3$(Ga$_{0.3}$Ge$_{0.7}$)$_2$O$_8$ | 0.5 | 197–319 | 122 | $-18$ | Cubic | D | 9 |
| LaFe$_{1.05}$Co$_{0.5}$Si$_{1.5}$ | 1.1 | 240–350 | 110 | $-26$ | Cubic | D | 10 |
| MnCo$_{0.98}$Ge | 3.2 | 122–332 | 210 | $-52$ | Orthorhombic | D | 11 |
| SrCu$_2$Fe$_2$O$_{12}$ | 0.4 | 180–250 | 70 | $-20$ | Cubic | X | 12 |
| Bi$_{0.95}$La$_{0.05}$NiO$_3$ | 2.0 | 320–380 | 60 | $-82$ | Triclinic | D | 13 |
| 0.4PbTiO$_3$·0.6BiFeO$_3$ | 2.7 | 298–923 | 625 | $-13$ | Tetragonal | X | 14 |
| Pu | 5.4 | 337–480 | — | — | Cubic/Tetragonal | D | 23 |
| YMn$_2$ | 4.7 | 75 | — | — | Cubic | X | 24 |

Parameters of materials with phase transition accompanied by large volume contraction on heating, not broadened, are also listed for comparison.

*For NTE region or lower temperature, larger-volume phase.
†D, dilatometry; N, neutron diffraction; X, X-ray diffraction.
‡Successive transitions.
§In warming process.

Figure 2 | Linear thermal expansion $\Delta L/L$ of Ca$_2$RuO$_{4+y}$. The data were collected on a warming process using a laser-interference dilatometer. Reference temperature: 500 K. The hysteresis loop was observed in $\Delta L/L$ measurements using a thermomechanical analyzer for #1 (inset). The giant negative thermal expansion (NTE) of #1 is suppressed by the oxidizing procedure, but is fully recovered by the re-reducing procedure. Inset shows temperature dependence of resistivity $\rho(T)$ for #1 and #2. The abrupt jump in $\rho(T)$ at 345 K for #1 corresponds to the Mott metal-to-insulator transition, which coincides with the onset of NTE.

for Ca$_{3-y}$Ru$_{0.9y}$Cu$_{0.1}$O$_4$ (Cu0.10). Particularly, the Fe-doped ruthenate exhibits T-linear expansion in almost the entire range of T below 500 K, which is favourable for practical applications. Thermal expansion exhibits almost T-linear behaviour, even near the lowest temperature (95 K) used for the present dilatometry measurements. Therefore, NTE apparently continues down to the lower temperature. In that case, the total volume change $\Delta V/V$ might become greater than the present estimate of 2.8% ($T = 95–500$ K).

Structural characterization of Ca$_{2-y}$Ru$_{1.9}$O$_{4+y}$. Giant NTE can be considered in terms of its crystal structure. The XRD profiles were refined using Le Bail method by RIETAN-FP$^{25}$ (Supplementary Figs 3 and 4). The structural parameters such as...
Table 2 | Crystallographic parameters of layered ruthenates obtained from Le Bail analysis of the X-ray diffraction data at 295 K.

|                | Ca2RuO4 – y | Ca2RuO4 – y | Ca2RuO4 – y | Mn0.10 | Fe0.08 | Cu0.10 |
|----------------|-------------|-------------|-------------|---------|--------|--------|
|                | Reduced     | Oxidized    | Re-reduced  | Reduced | Reduced| Reduced|
| a (Å)          | 5.4102 (3)  | 5.3295 (3)  | 5.4015 (2)  | 5.3813 (3) | 5.4156 (2) | 5.4193 (2) |
| b (Å)          | 5.4926 (4)  | 5.3089 (3)  | 5.4790 (3)  | 5.3973 (3) | 5.4481 (3) | 5.4860 (4) |
| c (Å)          | 11.9951 (3) | 12.4505 (6) | 11.9438 (4) | 12.0926 (7) | 12.0012 (4) | 11.9717 (5) |
| b/a            | 1.0152 (2)  | 0.9961 (2)  | 1.0143 (2)  | 1.0030 (2) | 1.0060 (2) | 1.0123 (2) |
| c/a            | 2.2090 (2)  | 2.3361 (3)  | 2.2112 (2)  | 2.2472 (4) | 2.2160 (2) | 2.2291 (2) |
| v (Å³)         | 355.14 (6)  | 352.27 (6)  | 353.47 (5)  | 351.22 (7) | 354.09 (5) | 355.92 (6) |

Figure 3 | Temperature dependence of the lattice parameters.
(a) Ca2RuO3.74, (b) Ca2RuO4.03 and (c) Ca2Ru0.92Fe0.08O3.82. These values are estimated based on Le Bail analysis of the XRD data. For Ca2RuO3.74, the c axis decreases abruptly below TMI = 345 K. The S phase is characterized by highly anisotropic thermal expansion. The a and b axes increase, although the c axis decreases concomitantly with decreasing temperature. The present results confirmed that the negative thermal expansion appears in the S phase.

Figure 4 | Volumetric thermal expansion of Ca2Ru1 – xMxO4 – y.
(a) Ca2RuO3.74, (b) Ca2RuO4.03 and (c) Ca2Ru0.92Fe0.08O3.82. Results estimated from crystallographic (ΔV/V) measurements are compared with the dilatometry (3ΔL/L) results. Reference temperature: 500 K. The discrepancy is conspicuous when the dilatometric negative thermal expansion becomes large.
difference between the $a$ axis and $b$ axis parameters is significantly large compared with the standard deviations of the present analysis. These features indicate that, despite discontinuous change in lattice parameters, the space group is not changed across the transition. Because the difference between the $a$ axis and $b$ axis parameters is small, some ambiguity persists as to whether $a > b$ or $a < b$ for the L phase in the present analysis. Following a detailed neutron diffraction study$^{17}$, we assumed the former.

Temperature-dependent XRD measurements provide additional information related to the mechanism behind the NTE. The S phase in which the giant NTE appears for Ca$_2$RuO$_{3.74}$ is characterized by highly anisotropic thermal expansion of lattice parameters: The $a$ and $b$ axes become longer although the $c$ axis becomes shorter concomitantly with decreasing $T$. For Ca$_2$RuO$_{3.74}$, the $b$ axis expands by 5.0% and the $c$ axis contracts by 4.2% from 340 to 100 K. Consequently, the unit-cell volume $v$ exhibits NTE behaviour. However, the dilatometric NTE of $\Delta V/V = 6.7\%$ is, surprisingly, too large to be ascribed to the unit-cell volume NTE, which is at largest 1%. For Ca$_2$Ru$_{0.92}$Fe$_{0.08}$O$_{3.82}$ (Fe0.08), which shows NTE in the entire $T$ range below 500 K, the discontinuous change in lattice parameter related to the L-to-S phase transition is not clear, presumably because of Fe-doping effects. Although the $a$ axis parameter becomes close to the $b$ axis parameter above 350 K, the $c$ axis parameter continues to increase gradually with $T$ and is still remained in 12.2140(2) Å even at 500 K. As a result, Fe0.08 is also characterized by highly anisotropic thermal expansion of lattice parameters below 500 K: the $b$ axis expands by 2.5% and the $c$ axis contracts by 3.4% from 500 to 100 K. In this $T$ range, the sintered body exhibits the NTE, though the unit-cell volume exhibits nearly zero thermal expansion. In contrast, for Ca$_2$RuO$_{3.89}$, which shows weak or no NTE, the unit-cell volume variation in $T$ is close to the result obtained using dilatometry ($3\Delta L/L$). In the prolonged L phase, the lattice parameters show no drastic $T$ dependence, contrary to Ca$_2$RuO$_{3.74}$.

### Discussion

Some materials are reported to have dilatometric NTE greater than the crystallographic unit-cell volume NTE in sintered ceramics$^1$. One well known example is $\beta$-eucryptite$^{26,27}$, which has been widely used as a practical thermal-expansion compensator. On cooling from 1,073 to 293 K, the $a$ axis in the hexagonal unit cell contracts by 0.62%, whereas the $c$ axis expands by 1.39%, which yields net unit-cell volume NTE of 0.15%. In contrast, the dilatometric NTE observed in sintered $\beta$-eucryptite reaches 1.7%, which is greater than 10 times of the crystallographic NTE (Table 3). Such a remarkable enhancement of thermal expansion has been ascribed to the characteristic microstructure of the sintered body, and particularly to spontaneous microcracking that originates from extremely anisotropic thermal expansion. Similar effects should be considered for Ca$_2$RuO$_{4+y}$ because it also exhibits extremely large anisotropic thermal expansion in the lattice parameters when the giant NTE appears.

However, the NTE of the reduced ruthenates is not accompanied by pronounced hysteresis: a characteristic of microcracking. Scanning electron microscope (SEM) observations do not confirm microcracking, but confirmed voids (Fig. 5). The preliminary measurements of specific gravity using Archimedes' method suggest that the density of the present ceramic samples is 80–90%. Compared with materials such as $\beta$-eucryptite and MgTi$_2$O$_5$ (ref. 28), for which microcracking effects have been considered, the onset temperature of the anisotropic thermal expansion is much lower (around room temperature). Therefore, cumulated inner stresses are expected to be much smaller for the reduced ruthenates. Even without generating microcracks, a porous sintered body might exhibit bulk NTE if extremely anisotropic thermal expansion of the grains produces deformation, consuming open spaces (voids) on heating. More detailed micrographic observations must be done to clarify the microstructural effects.

Here, we summarize the effects of oxygen deficiency on the NTE. Thermal-expansion properties of Ca$_2$RuO$_4$ show some scattering among results reported by different research groups. For example, Qi et al. 20 reported no NTE of the unit-cell volume $v$ in pure Ca$_2$RuO$_4$, although Braden et al. 15 reported NTE of $\Delta v/v = 1\%$. The discrepancy might be explained by differences in oxygen contents. The effects of oxygen deficiency might become remarkable for the doped ruthenates. The present Fe-doped ruthenate exhibits almost constant unit-cell volume, whereas the sample of Qi et al. 21 preserved NTE of $\Delta v/v = 0.8\%$. The SEM observation (Fig. 5) shows that the morphology changes from #1 to #2 despite heat treatment at much lower temperatures (773–823 K) than the sintering temperature (1,573–1,623 K). In addition, thermal expansion of a sintered body consisting of grains with highly anisotropic thermal expansion and voids might depend on the elastic properties of the grains. The NTE behaviour of the ruthenates is sensitive to the oxygen contents. The oxygen deficiency might affect the bulk thermal expansion via the alternation of elastic properties and morphology as well as intrinsic crystallographic parameters. Further structural analyses are expected to be useful to elucidate the roles of oxygen deficiency.

This study provides a strategy for realizing giant NTE, elaboration of sintered-body structure by combining grains having extremely anisotropic thermal expansion and moderate amount of voids. Control of thermal expansion using specific characteristics of materials, particularly in a negative $x$ region, is highly limited in an operating temperature and/or a magnitude of $x$ because of the severe constraint of available materials. To overcome these difficulties, designated structures consisting of

### Table 3 | Parameters related to negative thermal expansion for materials with highly anisotropic structural distortion.

| Material | $\Delta V/V(%)$ | $T_{NTE}(K)$ | $\Delta T(K)$ | $x (10^{-6} K^{-1})$ | Structure | Method | Reference |
|----------|----------------|-------------|--------------|-----------------|-----------|--------|----------|
| $\beta$-eucryptite | 0.15 | 293–1,073 | 780 | $-0.6$ | Tetragonal | X | 26 |
| Ca$_2$RuO$_{3.74}$ | 1.0 | 135–345 | 210 | $-7.6$ | D | This work |
| Ca$_2$Ru$_{0.92}$Fe$_{0.08}$O$_{3.82}$ | 0 | 100–500 | 400 | $-17$ | D | This work |

*For dilatometry, it is estimated using the relation of $\Delta L/L = (1/3)\Delta V/V$.  
+Averaged value when the material is anisotropic.  
+$\Delta v/v$ is the NTE region.  
+$D$ is dilatometry.  
+$X$ is X-ray diffraction.  
+$C$ is crystallographic volumetric thermal expansion is nearly zero.
two materials having different (positive) thermal expansions and voids are proposed as an artificial material showing NTE. The present result is expected to stimulate those activities as a 'natural' counterpart of the artificial structures. The capability of thermal-expansion compensation is related directly to dilatometric NTE measured in a finite size of materials, not necessarily to unit-cell volume thermal expansion, as might be apparent in the case of β-eucryptite. A high-performance thermal-expansion compensator will be realized by optimizing the microstructure of a material, such as amount of voids, microgran orientation, and binding state of grains, as well as intrinsic characteristics of materials such as anisotropic thermal expansion and elastic properties.

Methods
Sample fabrication. Sintered polycrystalline samples of Ca$_2$Ru$_{1-x}$M$_x$O$_4$ ($M = $ Mn, Fe and Cu) were prepared using solid-state reactions. Powders of CaCO$_3$, Ru$_2$O$_3$, MnO$_2$, Fe$_2$O$_3$ and CuO (purity: 99.9% or higher) weighed at appropriate molar ratios were mixed and heated in air at 1,273–1,373 K for 18 h. The obtained powder was reground, pressed into a pellet and sintered under flowing mixed gas of O$_2$ 0.02 MPa/Ar 0.08 MPa at 1,573–1,623 K for 48 h. Materials of this type are designated as 'reduced' samples. These reduced samples were heated under 0.5 MPa of O$_2$ at 773–823 K for 50 h. Materials of this type are designated as 'oxidized' samples. Then, the oxidized samples were heated under flowing mixed gas of O$_2$ 0.02 MPa/Ar 0.08 MPa at 1,573–1,623 K for 48 h. Materials of this type are designated as 'reduced' samples. We analysed the chemical compositions of the samples using energy dispersive X-ray spectroscopy (EDX, Genesis2000K; EDAX). The oxygen contents were investigated using thermogravimetric analysis (TGA, TG-DTA2020AH; Bruker Analytik GmbH). XRD was used to identify the samples as layered ruthenate Ca$_2$Ru$_2$O$_{6-2x}$O$_x$ and to analyse their crystal structure. The XRD analyses were conducted at 295 K (RINT2100; Rigaku) and at 100–500 K (D8 Advance; Bruker Analytik GmbH) with Cu K$_\alpha$ radiation. The sample surfaces were observed using a scanning electron microscope (SEM, VE-7800; Keyence). Specific gravity was measured by an Archimedes’ method (GR-200 and AD-1653; A&D).

Characterization of thermal dependence of sample properties. Linear thermal expansion $\alpha(T)/L$ along with the horizontal direction was measured using a laser-interference dilatometer (LIX-2; Ulvac) with a warming process. $\alpha(T)/L$ along with the vertical and the horizontal directions on both warming and cooling processes were measured using a thermomechanical analyzer (TMA8310; Rigaku). For sintered polycrystalline samples, $\alpha(L)/L$ is related directly to the volume ($V$) expansion in a manner of $\alpha(L)/L = (1/3)\alpha(V)/V$. Temperature-dependent resistivity $\rho(T)$ was measured using a conventional four-probe method (PPMS; Quantum Design). Temperature-dependent magnetization $M(T)$ was measured at 1 T using a superconducting quantum interference device magnetometer (MPMS; Quantum Design).

Data availability. The data that support the findings of this study are available from the corresponding author on request.

References
1. Chu, C. N., Saka, N. & Suh, N. P. Negative thermal expansion ceramics: a review. Mater. Sci. Eng. 95, 303–308 (1987).
2. Sleight, A. W. Compounds that contract on heating. Inorg. Chem. 37, 2854–2860 (1998).
3. Barrera, G. D., Bruno, J. A. O., Barron, T. H. K. & Allan, N. L. Negative thermal expansion. J. Phys.: Condens. Matter 17, R217–R252 (2005).
4. Takenaka, K. Negative thermal expansion materials: technological key for control of thermal expansion. Sci. Technol. Adv. Mater. 13, 103801 (2012).
5. Chui, J., Hu, L., Deng, J. X. & Xing, X. R. Negative thermal expansion in functional materials: controllable thermal expansion by chemical modifications. Chem. Soc. Rev. 44, 3522–3567 (2015).
6. Mary, T. A., Evans, J. S. O., Vogt, T. & Sleight, A. W. Negative thermal expansion from 0.3 to 1050 Kelvin in Zr$_2$W$_3$O$_{12}$. Science 272, 90–92 (1996).
7. Phillips, A. E., Goodwin, A. L., Halder, G. J., Southon, P. D. & Kepert, C. J. Nanoporosity and exceptional negative thermal expansion in single-network cadmium cyanide. Angew. Chem. Int. Ed. 47, 1396–1399 (2008).
8. Attfield, J. P. A fresh twist on shrinking materials. Nature 480, 465–466 (2011).
9. Takenaka, K. & Takagi, H. Giant negative thermal expansion in Ge-doped antiperovskite manganese nitrates. Appl. Phys. Lett. 87, 261902 (2005).
10. Hoth, G. Friday, R. J. et al. Giant negative thermal expansion in NaTaO$_4$-type La(Fe, Si, Co)$_3$ compounds. J. Am. Chem. Soc. 135, 11469–11472 (2013).
11. Zhao, Y. Y. et al. Giant negative thermal expansion in bonded MnCoGe-based compounds with Ni-In-type hexagonal structure. J. Am. Chem. Soc. 137, 1746–1749 (2015).
12. Yamada, I. et al. Giant negative thermal expansion in the iron perovskite SrCu$_2$FeO$_4$. Angew. Chem. Int. Ed. 50, 6579–6582 (2011).
13. Azuma, M. et al. Colossal negative thermal expansion in BiNiO$_3$ induced by intermetallic charge transfer. Nat. Commun. 2, 347 (2011).
14. Chen, J., Xing, X. R., Liu, G. R., Li, J. H. & Liu, Y. T. Structure and negative thermal expansion in the PbTiO$_3$–BiFeO$_3$ system. Appl. Phys. Lett. 89, 101914 (2006).
15. Rhen, M., Andre, G., Nakatsuji, S. & Maeno, Y. Crystal and magnetic structure of Ca$_2$RuO$_4$: Magnetoelastic coupling and the metal–insulator transition. Phys. Rev. B 58, 847–861 (1998).
16. Alexander, C. S. et al. Destruction of the Mott insulating state of Ca$_2$RuO$_4$ by a structural transition. Phys. Rev. B 60, R8422–R8425 (1999).
17. Friedt, O. et al. Structural and magnetic aspects of the metal–insulator transition in Ca$_2$$_{1-x}$Sr$_x$RuO$_4$. Phys. Rev. B 63, 174432 (2001).
18. Steffens, P. et al. High pressure diffraction studies on Ca$_2$RuO$_4$. Phys. Rev. B 72, 094104 (2005).
19. Zegkinoglou, I. et al. Orbital order transition in Ca$_2$RuO$_4$ observed with resonant X-ray diffraction. Phys. Rev. Lett. 95, 136401 (2005).
20. Qi, T. F. et al. Negative volume orbital expansion and magnetic orders in Ca$_2$Ru$_{1-x}$Cr$_x$O$_4$ (0 < x < 0.13). Phys. Rev. Lett. 105, 177203 (2010).
21. Qi, T. F., Korneta, O. B., Parkin, S., Hu, J. P. & Cao, G. Magnetic and orbital orders coupled to negative thermal expansion in Mott insulators Ca$_2$M$_{1-x}$Cr$_x$O$_4$ (M = Mn and Fe). Phys. Rev. B 85, 165143 (2012).
22. Okazaki, R. et al. Disorder effect for an orbital order in Ca$_2$RuO$_4$ revealed by infrared imaging spectroscopy. J. Phys. Soc. Jpn 83, 084701 (2014).
23. Jette, E. R. Some physical properties of plutonium metal. J. Chem. Phys. 23, 365–368 (1955).
24. Nakamura, H. et al. Effect of chemical pressure on the magnetism of Y$_2$M$_x$Ni$_{2-x}$Mn$_2$; Y$_1$La$_x$Ni$_{2-x}$Mn$_2$. J. Phys. F: Met. Phys. 19, 981–991 (1988).
25. Izumi, F. & Ikeda, T. A Rietveld-analysis program RIETAN-98 and its applications to zeolites. Mater. Sci. Forum 321–324, 198–205 (2000).
26. Gillery, F. H. & Bush, E. A. Thermal contraction of β-eucryptite (Li$_2$O, Al$_2$O$_3$, 2SiO$_2$) by X-ray and dilatometer methods. J. Am. Ceram. Soc. 42, 175–177 (1959).
27. Benavente, R., Salvador, M. D., Martinez-Amesti, A., Fernandez, A. & Borrell, A. Effect of sintering technology in β-eucryptite ceramics: Influence on fatigue life and effect of microcracks. Mater. Sci. Eng. A 651, 668–674 (2016).
28. Kuszyk, J. A. & Bradt, R. C. Influence of grain size effects of thermal expansion anisotropy in MgTi$_2$O$_5$. J. Am. Ceram. Soc. 56, 420–423 (1973).
29. Sigmund, O. & Torquato, S. Composites with external thermal expansion coefficients 3203–3205 (1973).
30. Takezawa, A., Kobashi, M. & Kitamura, M. Porous composite with negative thermal expansion obtained by photopolymer additive manufacturing. APL Mater. 3, 076103 (2015).

Acknowledgements
We are grateful to R. Kazui and N. Inoue for their help with experiments. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas.
Author contributions
K.T. proposed and organized the project and wrote the manuscript. Y.O. provided advice on the conditions necessary to fabricate high-quality samples and conducted chemical analyses and magnetization measurements of the samples. T.S. fabricated the samples and performed structural analysis as well as dilatometry and transport measurements. N.K. provided advice on the structural analysis. Y.S. conducted temperature-dependent X-ray diffraction and specific gravity measurements. All authors discussed the results and worked 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.

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How to cite this article: Takenaka, K. et al. Colossal negative thermal expansion in reduced layered ruthenate. Nat. Commun. 8, 14102 doi: 10.1038/ncomms14102 (2017).

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