Tunable giant negative thermal expansion in Ti$_2$O$_3$-based polycrystalline materials

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Thermal expansion properties are investigated for Ti$_2$O$_3$-based sintered polycrystalline materials by controlling crystal lattice parameters and microstructures. Negative thermal expansion (NTE) is observed in a temperature range between room temperature and 593 K, and found to exceed $\Delta L/L = -0.7\%$ at high temperatures. Although the unit cell volume increases by approximately 0.5% as temperature is raised, the macroscopic NTE is observed in a wide temperature range between room temperature and 593 K, and found to exceed $\Delta L/L = -0.7\%$ at high temperatures. We also find that the magnitude of NTE is affected by the total amount of pore volume in sintered polycrystalline samples. This indicates that the microstructural effect plays an important role in the NTE of this material.

All polycrystalline samples were synthesized by a spark plasma sintering (SPS) process. Starting materials [Ti$_2$O$_3$: 99.9% (averaged particle size: 41 $\mu$m and 12 $\mu$m denoted as large and small particle, respectively), Ti: 99.95%, Nb$_2$O$_5$: 99.9% in purity] with a prescribed ratio were mixed and pressed into pellets, and then subject to the SPS process in an argon atmosphere under a pressure of 40 MPa for 10 min at respective temperatures. In this work, 7 samples were investigated in total. The obtained samples were checked by using a powder X-ray diffractometer (Smart Lab, Rigaku), and confirmed that main phase was of corundum-type Ti$_2$O$_3$ at ambient temperature. Cumulative pore volume was obtained by mercury intrusion porosimetry using Micromeritics AutoPore IV 9520. Table I summarizes starting materials, composition of each sample throughout this paper. High-temperature X-ray powder diffraction measurements were performed that main phase was of corundum-type Ti$_2$O$_3$ at ambient temperature. Cumulative pore volume was obtained by mercury intrusion porosimetry using Micromeritics AutoPore IV 9520. Table I summarizes starting materials, composition of each sample throughout this paper. High-temperature X-ray powder diffraction measurements were performed.
performed for 303–673 K in Ar-flow condition. Linear thermal expansion $\Delta L/L$ was measured for 303–593 K using thermo-mechanical property analysis equipment (Thermo plus EVO2 8310, Rigaku). Resistivity was measured in a helium atmosphere from 300 up to 593 K by using a commercial apparatus (ZEM-3, ADVANCE-RIKO, Inc.).

Figure 1(a) shows temperature dependence of resistivity for selected samples. The metal-insulator transition is observed around 450–500 K as a steep increase in resistivity upon cooling in samples (D) and (E), while it takes place in Nb-doped sample (G) at lower temperatures as compared with the samples (D) and (E), indicating good tunability of the transition temperature in terms of Nb-doping. Figure 1(b) shows the $T$-dependence of the linear thermal expansion $\Delta L/L$ (303 K) $\equiv (L(T) - L(303 K))/L(303 K)$ for all samples. NTE is observed in a wide temperature range between 593 K, and the magnitude $|\Delta L/L|$ exceeds 0.7% for sample (D) around 590 K. Figure 1(c) displays the coefficient of linear thermal expansion $\alpha$ derived from the slope between $\Delta L(T - 10 \text{ K})/L$ and $\Delta L(T + 10 \text{ K})/L$. Nb-doping effectively lowers the temperature region where the magnitude of $\alpha$ takes a maximum, as evident in sample (G). Oxygen deficiency leads to the increase in the temperature range of NTE, as discerned in sample (E).

To unveil microscopic mechanism of the NTE in Ti$_2$O$_3$-based polycrystalline materials, we conducted high-temperature powder X-ray diffraction analysis to deduce the temperature-dependent lattice constants. Here, to clarify how the anisotropic deformation of a unit cell contributes to the bulk NTE, we introduce an anisotropy parameter $R$ defined as $R = a/c$, following Ref. 18. Lattice constants, anisotropy parameter $R$, and unit cell volume are plotted in Figs. 2(a)–2(d) as a function of temperature for selected samples. Clearly, structural evolution associated with the destruction of Ti$^{3+}$–Ti$^{3+}$ singlet dimer is observed as elongation of $c$-axis and contraction of $a$-axis as the temperature is increased. In the Nb-doped samples (F) and (G), the temperature range of the rapid structural evolution is lowered. On the other hand, in the oxygen-deficient sample (E), the temperature range of the phase transition is shifted to higher side.

In Fig. 3, we replot the bulk volume expansion estimated from the thermo-mechanical measurements (3$\Delta L/L$) against the change in anisotropy parameter $\Delta R/R$. A linear relationship between the bulk volume expansion and the change in anisotropy parameter is obvious, indicating that the anisotropic deformation of unit cell in the polycrystalline material is responsible for the macroscopic NTE. For Nb-doped samples (F) and (G), the relationship slightly deviates from the linear one. This deviation may be caused by the existence of the certain amount of impurity phase in the Nb-doped samples.

To investigate the possible role of porous structure quantitatively, we obtained cumulative pore volume for several samples by the mercury intrusion method, and the results are presented in Fig. 4(a). For each sample, distribution of the pore radius from sub-micrometer to micrometer scale is observed as rapid change in the cumulative pore volume. By using the cumulative pore volume, we can calculate the total porosity in each sample.

### Table I

| No | Nominal composition | Starting materials | Sintering temperature [K] | $a$ [Å] | $c$ [Å] | Porosity [%] |
|----|---------------------|-------------------|--------------------------|--------|--------|-------------|
| A  | Ti$_2$O$_3$         | Ti$_2$O$_3$(L)    | 1773                     | 5.147  | 13.639 | 4.9         |
| B  | Ti$_2$O$_3$         | Ti$_2$O$_3$(L)    | 1623                     | 5.149  | 13.625 | 11.6        |
| C  | Ti$_2$O$_3$         | Ti$_2$O$_3$(S)    | 1623                     | 5.148  | 13.614 | 20.5        |
| D  | Ti$_2$O$_3$         | Ti$_2$O$_3$(S)    | 1753                     | 5.148  | 13.593 | —           |
| E  | Ti$_2$O$_3$         | Ti$_2$O$_3$(L), Ti, Nb$_2$O$_3$ | 1623 | 5.151  | 13.668 | 5.1         |
| F  | Ti$_{0.87}$Nb$_{0.13}$O$_{2.92}$ | Ti$_2$O$_3$(L), Ti, Nb$_2$O$_3$ | 1623 | 5.151  | 13.668 | 5.1         |
| G  | Ti$_{0.75}$Nb$_{0.25}$O$_{2.92}$ | Ti$_2$O$_3$(L), Ti, Nb$_2$O$_3$ | 1623 | 5.151  | 13.668 | 5.1         |
Figure 4(b) shows the relation between the total porosity and the bulk volume expansion \(3\Delta L/L\) as estimated by the thermo-mechanical measurement. As the total porosity increases, the magnitude of the NTE between 303 and 593 K is enhanced. This relationship indicates that the porous structure effectively contributes to the observed bulk NTE through the anisotropic deformation of each grain.

Table II shows the relevant parameters for reported NTE materials. In some materials, bulk NTE values as obtained by dilatometry or thermo-mechanical measurements are greater than those deduced from the crystallographic unit cell volume. For example, the bulk NTE value was enhanced over that of an unit cell in CaRuO_{4}-based sintered materials and it was ascribed to the microstructural effect arising from the polycrystalline grains with large anisotropic deformation. In comparison with other NTE materials where the microstructural effects are important, the unique feature to the Ti_{2}O_{3}-based materials in this work is that NTE is observed in bulk poly-crystals in spite of the positive thermal expansion of a unit cell. This significant difference in the thermal expansion property between bulk and a crystallographic unit cell highlights the extremely important role of the microstructural effect in this material.

The major accomplishment of the present work in comparison with the previous studies is the demonstration of the tunability of the temperature range where the NTE emerges. As shown in Figs. 1(a)–1(c), pristine Ti_{2}O_{3} of sample (D) has the largest absolute value of NTE coefficient around approximately 473 K that corresponds to the metal-insulator transition temperature, indicating that the electronic state is strongly coupled with crystal lattice in this system. Presumably, doped Nb prevents from Ti^{3+}{\text{–}}Ti^{3+} dimer formation and therefore the metal-insulator transition temperature shifts to lower temperature region, and as a result, the temperature range of NTE also shifts to a lower one due to the strong electron-lattice coupling. On the other hand, oxygen deficiency increases the phase transition temperature. Reduction in the number of hole-type carriers by the oxygen deficiencies is probably responsible for the observed shift of phase transition temperature to higher temperatures.

Another important achievement is the quantitative analysis for the effects of porous structure and anisotropic deformation of unit cell on the NTE. In the conventional NTE materials, the macroscopic NTE due to contraction of a unit cell is observed upon heating and recently the NTE effect has been found to be enhanced by the microstructural effects in strongly correlated materials, but the link between the NTE and the effects of porous structure and anisotropic deformation has remained elusive. The linear relationship between anisotropy parameter and the NTE (Fig. 3) indicates...
Table II. Parameters related to negative thermal expansion for reported materials. The values of bulk volume expansion are derived by dilatometry or thermo-mechanical property measurement. The values of unit cell volume expansion are derived by powder X-ray or neutron measurement. \( \alpha_{\text{bulk}} \) is the coefficient of linear thermal expansion derived by dilatometry or thermo-mechanical property measurement. \( \alpha_a \), \( \alpha_b \) and \( \alpha_c \) denote the crystallographic lattice thermal expansion for \( a \), \( b \) and \( c \)-axis derived by powder X-ray or neutron measurement respectively.

| Materials            | Bulk volume expansion \( \Delta V_{\text{bulk}}/V_{\text{bulk}} \) [%] | \( \alpha_{\text{bulk}} \) [ppm K\(^{-1}\)] | Unit cell volume expansion \( \Delta V/V \) [%] | Crystal structure | \( \alpha_a \) [ppm K\(^{-1}\)] | \( \alpha_b \) [ppm K\(^{-1}\)] | \( \alpha_c \) [ppm K\(^{-1}\)] | \( T_{\text{NTE}} \) [K] | References |
|----------------------|---------------------------------------------------------------|---------------------------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|--------------|-----------|
| \( \beta \)-eucryptite | -1.7\(^{a}\)                                                  | -8                              | -0.15                           | Tetragonal      | +8              | +8              | -18             | 291          | 6         |
| ZrW\(_2\)O\(_8\)     | -0.5\(^{b}\)                                                 | -9                              | -1.2                            | Cubic           | -9              | -9              | -9              | 0.3–425      | 7         |
| Bi\(_{0.15}\)La\(_{0.05}\)NiO\(_3\) | -1.8\(^{b}\)                                            | -82                             | -2.6                            | Triclinic       | —               | —               | —               | 270–400      | 11        |
| Ca\(_3\)Ru\(_2\)O\(_7\) | -6.7\(^{a}\)                                                | -115                            | -1.0                            | Orthorhombic    | -23             | -200            | +174            | 135–345      | 16        |
| Ca\(_3\)Ru\(_0.92\)Fe\(_{0.08}\)O\(_3.82\) | -2.8\(^{a}\)                                                | -28                             | 0                               | Orthorhombic    | -14             | -63             | +83             | 100–500      | 16        |
| \( \beta \)-Cu\(_{1.8}\)Zn\(_{0.2}\)V\(_2\)O\(_7\) | -2.6\(^{a}\)                                                | -14                             | -0.8\(^{3}\)                     | Orthorhombic    | -28             | +19             | -7              | 100–700      | 18        |
| Ti\(_2\)O\(_3\)       | -2.1\(^{b}\)                                                 | -28                             | +0.5                            | Hexagonal       | -18             | -18             | +55             | 300–593      | This work |

\(^{a}\) For dilatometry measurements, the values are derived by using a relation of \( \Delta V/V = 3 \Delta L/L \). \(^{b}\) For dilatometry measurements from 300 to 425 K, the values are derived by using a relation of \( \Delta V/V = 3 \Delta L/L \). \(^{c}\) From X-ray measurements from 200 to 70 K. \(^{d}\) For thermal mechanical property measurement analysis, the relation of \( \Delta V/V = 3 \Delta L/L \) is used.
that the anisotropic deformation of respective crystalline grains is relevant to the bulk NTE. Also, the magnitude of bulk NTE is found to be enhanced by increasing the porosity [Fig. 4(b)]: cumulative pore volume measurement shows that the total porosity in bulk polycrystalline material is well correlated with the NTE, indicating that microstructural effects are important for the NTE.

In summary, we have investigated the NTE for Ti2O3-based polycrystalline materials by changing lattice parameters and porous structures. The temperature range of NTE is demonstrated to be successfully tuned by controlling the phase transition temperature via chemical doping. Although the unit cell volume monotonically increases as temperature is elevated, the bulk NTE is observed in a wide temperature range between room temperature and 593 K, and exceeds $|\Delta L/L| = 0.7\%$ at high temperatures. The NTE is correlated with the anisotropic deformation of a unit cell, and the magnitude is enhanced as total pore volume in sintered polycrystalline samples is increased. These observations indicate that the microstructural effects play an important role in the NTE of this material. In view of the versatile tunability of the temperature range for NTE as well as environment-related aspects, Ti2O3-based materials possess high potential for practical applications.

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