Laser ablation condensation of polymorphic ZrO$_2$ nanoparticles: Effects of laser parameters, residual stress, and kinetic phase change

Meng-Hsiu Tsai
Institute of Materials Science and Engineering, National Sun Yat-sen University, Kaohsiung 80424, Taiwan, Republic of China

Shuei-Yuan Chen$^{a)}$
Department of Mechanical Engineering, I-Shou University, Kaohsiung 84008, Taiwan, Republic of China

Roa-Pu (Claire) Shen
Department of Chemical Engineering, University of California, Los Angeles, California 90095–1592

Pouyan Shen
Institute of Materials Science and Engineering, National Sun Yat-sen University, Kaohsiung 80424, Taiwan, Republic of China

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Nd-YAG laser ablation on a Zr target under optimum oxygen flow rate and a very high-temperature route was used to fabricate fluorite-type related ZrO$_2$ nanoparticles, which are of monoclinic ($m$) and tetragonal ($t$) symmetries when the laser power density was below ca. $1 \times 10^7$ W/cm$^2$, but $t$ plus cubic ($c$) symmetry when above this threshold. Electron diffraction indicated that the dense $c$ and $t$ phases with specific size and residual stress were allowed to relax and/or kinetically phase change into lower-energy state as constrained by the intersections of the internal energy versus the cell volume plot of the two polymorphs. The $m$-ZrO$_2$ can be rationalized as a derivative of the coarsened/coalesced nanoparticles with defects vulnerable to martensitic $t$-$m$ transformation.


I. INTRODUCTION

At atmospheric pressure, zirconia (ZrO$_2$) crystallizes from melt (near 2800 K) as cubic ($c$) fluorite-type structure (space group of $Fm\bar{3}m$).$^1$ The $c$ phase becomes tetragonal ($t$) symmetry (space group of $P4_{2/1}nmc$) (Refs. 2 and 3) near 2640 K and then changes in a martensitic manner into monoclinic ($m$) symmetry ($P2_1/c$) below 1440 K.$^4$–$^6$ The equilibrium $t$-$m$ phase boundary was believed to follow a negative $dT/dP$ slope up to 1.5 GPa.$^7$ The $c/t$ phase boundary is also expected to be negative since the $c$-fluorite structure is more closely packed than the $t$ form.$^7$ Here we used a Nd-YAG (yttrium aluminum garnet) laser ablation on a Zr target under specific laser parameters and optimum oxygen flow rate to fabricate fluorite-type related ZrO$_2$ nanocondensates with various sizes, densities, and residual stresses that account for the specific route of relaxation and kinetics phase change analogous to dense titania.$^8$–$^{10}$

Nd-YAG laser pulse irradiation on oxygen-purged Ti target was originally used by us to reach high-energy state under oxygen background gas so that $\alpha$-PbO$_2$-type TiO$_2$ (Ref. 8) and fluorite-type related TiO$_2$ particles were produced.$^9$ The combined effects of laser energy, oxygen flow rate, and phase transformation on the size/shape formation of TiO$_2$ particles were also reported.$^{10}$ This synthesis route of dense TiO$_2$ polymorphs sheds light on their possible condensation around stars in addition to terrestrial occurrences as a response to static high pressure in crustal rocks attending subduction into the earth’s interior$^{11}$ and natural dynamic events in shocked gneisses from the Ries crater in Germany.$^{12}$

As for the fabrication of ZrO$_2$ condensates via this route, our preliminary study indicated that $t$-ZrO$_2$ nanocondensates with considerable residual stress can be synthesized by pulsed Nd-YAG laser ablation.$^{13}$ The $t$-ZrO$_2$ nanoparticles with a residual stress up to about 5 GPa tended to form deformation twins/faults upon local electron dosage, however, the $t$-ZrO$_2$ nanoparticles formed at an order of magnitude higher power have a residual stress above 6 GPa and tended to transform into a metastable $c$ phase vulnerable to amorphization.$^{13}$ The relaxation/transformation of the self-constrained $t$-ZrO$_2$ nanoparticles was accounted for by a lowering of internal energy under the influence of resolved shear stress and local electron heating,$^{13}$ in addition to the size effect proved experimentally for a number of semiconducting/ceramic materials.$^{14}$–$^{21}$

The motivation of this further research on the evaporation-condensation of ZrO$_2$ polymorphs by Nd-YAG laser ablation is threefolds. First, we study the effect of laser energy density on the condensation of specific $c$, $t$, and $m$ phases of ZrO$_2$. Second, we characterize the defect formation as a result of the coalescence of ZrO$_2$ nanoparticles, analogous to the imperfect oriented attachment of sol-gel derived titania nanocrystallites under hydrothermal conditions$^{22}$ or laser ablation condensation.$^{10}$ Third, we calculate the internal energy of the $c$ and $t$ polymorphs at specific size, cell volume, and temperature based on the known heat capacity and thermodynamic parameters in the Murnaghan equation of state$^{23}$ (EOS) so that the critical cell volume of kinetic phase change can be approached.

$^{a)}$Author to whom correspondence should be addressed; electronic mail: steven@isu.edu.tw
II. EXPERIMENT

The Zr target with negligible impurities (99.2% pure) was subject to energetic Nd-YAG laser (1064 nm in wavelength and beam mode of TEM00) pulse irradiation. The target purity is satisfactory in producing ZrO2 condensates without detectable impurities. All the laser parameters, i.e., pulse duration, frequency, beam size, and energy per pulse, and the resultant phase assemblages of ZrO2, are compiled in Table I. For the so-called free run mode, the pulse time duration was 2.4 ms at 30 Hz or 240 μs at 10 Hz, having the laser beam focused, respectively, to spot sizes of 0.146 and 0.03 mm² on the Zr target fixed inside the ablation chamber. Alternatively a Q-switch mode, with 16 ns pulse duration and a power density as high as 1.5 × 10¹² W/cm², was used to fabricate the ZrO2 condensates. For both modes, oxygen (99.999% purity) was supplied near a fixed flow rate of 99.999% purity and running at 8.6, 2.8, 3.6, and 4.4 W/cm² as a representative power density above 2.8 × 10⁷ W/cm². TEM images further revealed the microstructures, i.e., size, shape, defects, and coalescence, of the ZrO₂ phases fabricated under low and high power density regimes as addressed in turn.

The t+m ZrO₂ condensates produced under a relatively low power density (4.3 × 10⁵ W/cm² as a representative) were found to assemble as nanoparticle chain aggregates (NCA) or in a close-packed manner [Fig. 1(a)]. The ring SAED pattern [Fig. 1(b)] indicated that the m and t [as indicated by (110) diffraction] phases were in random orientation. The EDX spectrum [Fig. 1(c)] of a representative particle showed strong Zr and O peaks and negligible impurities. The lattice image [Fig. 2(a)] of a representative t-ZrO₂ nanoparticle ca 30 nm in size from this sample showed well-developed {111}, {110}, and (001) faces and {112} facet. The two-dimensional Fourier transform [Fig. 2(b)] and reconstructed image [Fig. 2(c)] showed dislocations with a half plane parallel to {111} and {001}. The m-ZrO₂ nanoparticles in the representative sample prepared by laser ablation condensation at 8.6 × 10⁸ W/cm² are about 20 nm in size [Fig. 3(a)] with characteristic (001) spot as indicated by the two-dimensional Fourier transform in [110] zone axis [Fig. 3(b)]. The m-ZrO₂ nanoparticles were invariably twinned with a rather high density of dislocations as shown in the reconstructed image [Fig. 3(c)]. The m-ZrO₂ condensates were presumably derived from the coarsened/coalesced nanoparticles with defects vulnerable to martensitic t→m transformation.

The c+t ZrO₂ condensates produced under a relatively high power density (3.6 × 10⁷ W/cm² as a representative) were also assembled as NCA or in a close-packed manner [Fig. 4(a)]. The ring SAED pattern [Fig. 4(b)] indicated that the c and t [as indicated by (112) diffraction] phases were in random orientation. Minor c-ZrO₂ with all the diffractions nearly superimposed with those of the t phase could survive rapid cooling under the oxygen background gas. The particles range from 2 to 24 nm in size nearly in normal distribution with a mean size of 10 nm as shown by a histogram with curve fitting in Fig. 4(c). Figure 5(a) showed the lattice image of a representative c-ZrO₂ nanoparticle ca. 15 nm in size, which was produced at 710 mJ/pulse under the Q-switching mode for a very high power density of 1.5

| TABLE I. Laser ablation parameters and resultant phase assemblages of ZrO₂. Free run at ms pulsed duration (FR) and running at Q-switched mode and ns pulsed duration (QS). |
|-----------------|--------|--------|--------|--------|--------|--------|--------|
| 1               | Running mode (FR/QS) | FR     | FR     | FR     | FR     | FR     | QS     |
| 2               | Pulse energy (mJ/pulse) | 500    | 1000   | 200    | 260    | 320    | 710    |
| 3               | Pulse duration (ms)    | 2.4    | 2.4    | 0.24   | 0.24   | 0.24   | 16     |
| 4               | Beam size (μm²)        | 0.146  | 0.146  | 0.03   | 0.03   | 0.03   | 0.03   |
| 5               | Fluence (J/cm²)        | 342    | 684    | 667    | 867    | 1067   | 2367   |
| 6               | Frequency (Hz)         | 30     | 30     | 10     | 10     | 10     | 10     |
| 7               | Power density (W/cm²)  | 0.43×10⁷ | 0.86×10⁷ | 2.8×10⁷ | 3.6×10⁷ | 4.4×10⁷ | 1.5×10⁸ |
| 8               | Zirconia phases        | t+m    | t+m    | t+c    | t+c    | t+c    | t+c    |

III. RESULTS

Electron diffraction characterization indicated that the ZrO₂ condensates are t+m phases for laser power densities between (4.3 and 8.6) × 10⁷ W/cm² but c+t phases for a laser power density above 2.8 × 10⁹ W/cm². TEM images further revealed the microstructures, i.e., size, shape, defects, and coalescence, of the ZrO₂ phases fabricated under low and high power density regimes as addressed in turn.

Copper grids overlaid with a carbon-coated collodion film and fixed in position by a plastic holder at a distance from 2.5 to 10 mm from the target were used to collect the condensates. The composition and crystal structures of the ZrO₂ polymorphs in the condensates were characterized by analytical electron microscopy (AEM) (JEOL 3010 instrument at 300 or 200 keV for a less electron-irradiation effect) with selected area electron diffraction (SAED), and point-count energy dispersive x-ray (EDX) analysis at a beam size of 10 or 15 nm. Bright field images (BFIs) taken by transmission electron microscopy (TEM) were used to study the general morphology and agglomeration of the condensed zirconia particles. Lattice imaging coupled with two-dimensional Fourier transform and inverse transform were used to analyze the crystal structure of nanosize particles and their phase transformation upon electron irradiation. The zirconia phases were indexed according to the distorted version of the c-fluorite-type parent cell. The d spacings measured from SAED patterns were used for least-squares refinement of the lattice parameters. The residual stresses of the ZrO₂ condensates were estimated from the Murnaghan EOS (Ref. 23) and the cell volume.
This particle is cubo-octahedral in shape and full of edge dislocations with half planes parallel to $\{111\}$ and $\{100\}$ as indicated by the Fourier transform [Fig. 5(b)] and the reconstructed image [Fig. 5(c)].
Regardless of laser ablation conditions and crystal structures, the zirconia particles tend to form necking at sharp contact and adjust shape/orientation for a better match at the interface more or less with dislocations. Figure 6 shows two such \( c \)-ZrO\(_2\) nanoparticles, ca. 5 and 10 nm in size produced at \( 2.8 \times 10^7 \) W/cm\(^2\), in coalescence over exact \( \{11\bar{1}\} \) face to form a single domain in \( [011] \) zone axis. The Fourier transform Fig. 6(b) and reconstructed image Fig. 6(c) showed edge dislocations at the interface but not the interior of the particles, indicating dislocation generation by such a coalescence process. The \( t \)-ZrO\(_2\) nanoparticles in the same sample were also coalesced to form dislocations as indicated by the three impinged over \( \sim \{11\bar{1}\} \) vicinal surface to form a single crystal Fig. 7(a). The two-dimensional Fourier transform Fig. 7(b) and reconstructed image Fig. 7(c) showed that the interplanar angle between \( \{11\bar{1}\} \) and 202 is ca. 89°, indicating a considerable tetragonality of the lattice. From Figs. 6 and 7, we conclude that the \( c \) and \( t \) nanoparticles tended to coalesce over \( \{11\bar{1}\} \), i.e., the most stable low-index surface for both \( t \) and \( c \) phases, to form a single faceted crystal more or less with dislocations at the interface.

**IV. DISCUSSION**

**A. Condensation of dioxides with fluoritelike rather than cotunnite-type structure**

The present laser ablation, involving thermal/residual stress as high as 10 GPa (cf. Sec. IV B), did not cause the formation of cotunnite-type (\( Pnma \) with Zr in ninefold coordination) ZrO\(_2\) which equilibrates with \( c \) and/or \( t \) phase.
above 10 GPa at about 1000 °C.7 (Using basically the same laser ablation/condensation process under similar oxygen flow rate, thermal/residual stress as high as 10 GPa was reached in our previous synthesis of dense TiO2 polymorphs with baddeleyite/fluorite-type related structures.9) A much higher temperature in the present laser ablation, in particular, when under the Q-switch mode for a power density as high as 1.5×1012 W/cm2, may account for the formation of c-ZrO2. Under such a high temperature regime, the cotunnite-type structure and the controversial orthorhombic phase, reported to occur in the pressure range from 7 to 11 GPa and temperature range of 450–800 °C,7 cannot occur. In this connection, it is of interest to note that a very high temperature is also essential to the formation of the fluorite-type rather than cotunnite-type structure for other di-oxides such as TiO2.26–28

As for the derivative of c-ZrO2, the equilibrium c/t phase boundary follows a negative dT/dP slope between 2640 K at zero pressure and 1213 K at 9.5 GPa as shown in the tentative phase diagram.7 Phase change kinetics, however, needs to be considered for the present c- and t-ZrO2 condensates with varied residual stress and size that affect the energetics as addressed below.

**B. Residual stress of the c- and t-ZrO2 condensates**

The least-squares refinement of the d spacings indicated that the present c- and t-ZrO2 condensates have a smaller cell volume (cf. Table II for the representative samples) than ambient values, 0.1320 nm3 (a=0.509 nm) and 0.1376 nm3 (a =b=0.512 nm and c=0.525 nm), respectively,29 indicating a significant residual compressive stress. The Birch-Murnaghan EOS (Ref. 30) was used to estimate the residual stress of the two polymorphs. The undoped ZrO2 with c symmetry and an isothermal bulk modulus (B0) of 194 GPa was obtained by extrapolating the elastic constant data to 0 mol % Y2O3 (Ref. 31) [i.e., C11=417 GPa, C12=82 GPa, and C44=47 GPa, B0=(C11+2C12)/3=194 GPa]. The first pressure derivative B′0 was assumed to be 8.9, the same as the Ca-doped fully stabilized zirconia with c symmetry.32 As for the t phase, Bt0=172 GPa and B′t0=8.5 were used as for undoped tetragonal nanocrystalline zirconia.33 The residual stress turned out to be 1.4 GPa for the c phase synthesized at a laser power density of 4.4×107 W/cm2, whereas 6.1, 5.3, and 5.1 GPa for the t phase produced at 4.4×107, 8.6×106, and 4.3×106 W/cm2, respectively, given the cell parameters compiled in Table II.

The residual stress is expected to affect significantly the phase change kinetics of the ZrO2 condensates at specific temperature and size. In the present laser ablation process, the temperature due to radiant heating by pulse irradiation was estimated to be up to 940 °C (1213 K) based on the fact that close-packed condensates being assembled from NCA. The residual stresses of the c/t-ZrO2 condensates and their intersection of the isothermal internal energy versus cell volume curves, as constructed in Secs. IV C and IV D for bulk and nanosized particles, respectively, shed light on the transformation/relaxation route of the condensates in Sec. IV E.

**C. Energy-cell volume curves for bulk c- and t-ZrO2 at room and high temperatures**

The internal energy of a bulk phase at a specific temperature is given by

\[
U = TS - \int PdV + \mu N, \tag{1}
\]

where U, S, and \( \mu \) are the internal energy, entropy, and chemical potential, respectively. In general, the entropy change upon the isothermal phase transition of ionic and covalent solids, e.g., semiconductors, is small.34 The chemical potential also changes little for a polymorphic transition. Assuming that the entropy and chemical potential contributions are negligible, Eq. (1) can be reduced and combined with the Murnaghan23 EOS as

**TABLE II. Cell parameters and residual stress of c- and t-ZrO2 condensates prepared under specified laser power density.**

<table>
<thead>
<tr>
<th>Power density (W/cm²)</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>V (nm³)</th>
<th>c/a</th>
<th>Residual stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3×10⁶</td>
<td>0.507±0.003</td>
<td>0.521±0.003</td>
<td>0.1340</td>
<td>1.027</td>
<td>5.1</td>
</tr>
<tr>
<td>8.6×10⁶</td>
<td>0.507±0.003</td>
<td>0.521±0.002</td>
<td>0.1339</td>
<td>1.027</td>
<td>5.3</td>
</tr>
<tr>
<td>4.4×10⁷</td>
<td>0.509±0.002</td>
<td>0.515±0.002</td>
<td>0.1334</td>
<td>1.012</td>
<td>6.1</td>
</tr>
<tr>
<td>4.4×10⁷</td>
<td>0.508±0.008</td>
<td>NA</td>
<td>0.1311</td>
<td>NA</td>
<td>1.4*</td>
</tr>
</tbody>
</table>

*For c-ZrO2.
energy curves of the c and t polymorphs at 1213 K were calculated as depicted in Fig. 8. The curve intersection, i.e., $V_{cr}$, turned out to be $12.58 \times 10^{-29}$ m$^3$. The corresponding $P_T$ is 9.6 GPa based on the Murnagahan EOS of c-ZrO$_2$. The $P_T$ was used to double check $V_{cr}$ using the Murnagahan EOS of the t phase, which agrees within 3.6% with the reading from Fig. 8. The kinetics phase boundary at 9.6 GPa and 940 °C differs slightly from the equilibrium phase boundary (9.5 GPa at 940 °C) proposed by Liu and Bassett. It should be noted that the phases produced by laser ablation condensation are the result of a dynamic nonequilibrium condition. The dense t-ZrO$_2$ condensates were likely formed from the c phase above a critical size during the rapid cooling across the kinetics (or dynamic) t/c phase boundary with a negative $dT/dP$ slope as for the equilibrium phase boundary.

**D. Energy-cell volume curves for nanosized c- and t-ZrO$_2$ at high temperature**

Tolbert and Alivisatos and Tolbert et al. found that the smaller the crystallite, the higher is the polymorphic transformation pressure for Si, CdS, and CdSe nanocrystals. A miniature-size inhibited phase change was also found for ZnO, PbS, and ZnS (Ref. 19) nanocrystals. On the other hand, a smaller size was found to decrease the transition pressure for γ- to α-Fe$_2$O$_3$ transformations, and rutile to α-PbO$_2$-type TiO$_2$ transition. In any case, the change in transition pressure upon miniature size can be estimated by the surface energy difference between the phases at specific size. For this purpose, a surface energy term was added to Eq. (3) in the following equations:

$$U_c = \int C_p \,dT - \int \{B_a/B'_a\cdot [(V/V)_{B_a'} - 1]\} \,dV + \gamma_c A,$$

$$U_t = \int C_p \,dT - \int \{B_a/B'_a\cdot [(V/V)_{B_a'} - 1]\} \,dV + \gamma_t A,$$

where $\gamma_c$ and $\gamma_t$ denote the surface energy of the nanosized c and t phases, respectively. Since (111) plane is the predominant plane of the two condensates, as commonly accepted for fluorite-type oxides, $\gamma_c(111) = 1193$ mJ/m$^2$ and $\gamma_t(111) = 1315$ mJ/m$^2$ after Ref. 25 and other parameters mentioned in the previous section were used for the internal energy calculation at 1213 K. The internal energy curves of c- and t-ZrO$_2$ (Fig. 9) thus constructed for the observed 18, 6, and 2 nm sized particles turned out to intersect at (12.64, 12.77, and 13.03) $\times 10^{-29}$ m$^3$, respectively. The corresponding $P_T$ are 8.5 GPa (3.7% deviation), 6.2 GPa (3.4% deviation), and 2.3 GPa (4.0% deviation) for 18, 6, and 2 nm particles, respectively, using the relevant EOS and $V_{cr}$ double-check as mentioned. The $c/t$ equilibrium transformation pressure also decreases with the decrease of particle size as indicated by the slope defined by the common tangent of the internal energy curves. The common tangent was determined by the MATLAB program based on the minimized difference of the slope and Y-axis intercept of the two curves (not shown). The kinetics phase boundary based on $P_T$ for the nanosized ZrO$_2$ was depicted along with the predicted equilibrium phase boundaries in Fig. 10.

**FIG. 8. Internal energy vs cell volume curves for the bulk c- and t-ZrO$_2$ having the intersection at (12.56 and 12.58) $\times 10^{-29}$ m$^3$ for room temperature and 940 °C, respectively.**

$$U = -\int PdV = -\int \{B_a/B_a'[V/V_{B_a'} - 1]\} \,dV,$$

where $P$ and $V$ have their usual meanings, $B_a$ and $B_a'$ are, respectively, the isothermal bulk modulus and its first pressure derivative, and the subscript denotes zero pressure. The $B_a$ and $B_a'$ values were mentioned before and the zero pressure cell volumes $V_a$ at room temperature are 0.1320 nm$^3$ ($a=0.509$ nm) and 0.1376 nm$^3$ ($a=b=0.512$ nm and $c=0.525$ nm) for c- and t-ZrO$_2$, respectively. The isothermal energy-volume curves for the two polymorphs were thus constructed in Fig. 8. The intersection of the two curves (i.e., critical cell volume denoted as $V_{cr}$) turned out to be 12.56 $\times 10^{-29}$ m$^3$. The corresponding phase transition pressure (denoted as $P_T$) is 12.1 GPa based on the Murnaghan EOS of c-ZrO$_2$. The $P_T$ was used to double check $V_{cr}$ using the Murnaghan EOS of the t phase. The $V_a$ turned out to be 13.02 $\times 10^{-29}$ m$^3$, which agrees within 3.6% [i.e., (13.02 $\times 10^{-29}$ m$^3$ - 12.56 $\times 10^{-29}$ m$^3$)/12.56 $\times 10^{-29}$ m$^3$] with the intersection reading from Fig. 8. The internal energy of a phase at elevated temperature is given by

$$U = \int C_p \,dT - \int \{B_a/B_a'[V/V_{B_a'} - 1]\} \,dV,$$

where $C_p$ is heat capacity. By integrating the equation $C_p$ (cal mol$^{-1}$ K$^{-1}$)=16.64 + 1.80 $\times 10^{-3}$ T$^{-1}$ - 3.36 $\times 10^{-7}$ T$^{-2}$ after Ref. 35, the internal energy contribution of $C_p$ from 300 to 1213 K was calculated to be $4.4 \times 10^{-19}$ J per unit cell for both the c- and t-ZrO$_2$. The $B_a$ of the c phase at 1213 K was estimated to be 160.2 GPa by extrapolating the elastic constant from 973 K (cf. Table IV of Ref. 31). The $B_a$ of the t phase at 1213 K is 142.1 GPa assuming that the $B_a$ difference between c and t phases is independent of temperature. Suppose $B_a'$ is also independent of temperature, the ent
The crosshatched area in Fig. 10 represents the temperature and residual stress range possible for the \( c' \) phase above a critical size during rapid cooling across the \( t'/c' \) phase boundary with a negative \( dT/dP \) slope (Fig. 10). This phase boundary would shift to lower temperatures and pressures for nanoparticles. In this regard, the \( t' - ZrO_2 \) particle of 18 nm in size was found by static compression to partially transform at room temperature into the \( c' \) structure at 8 GPa, and complete transformation occurred near 30 GPa. Besides, the dense (below \( V_{c'} \)) \( t'-ZrO_2 \) condensates were found to transform rapidly into the \( c' \) phase during TEM observations. These experimental results are in fair agreement with the linearly extrapolated kinetics \( c'/t' \) phase boundary for the 18 nm sized particle, e.g., 15 GPa at room temperature (Fig. 10).

V. CONCLUDING REMARKS

Aside from the kinetic problems, Nd-YAG laser ablation on the Zr target under relatively high power density and oxygen background gas has been shown to cause the formation of \( c' - t' - ZrO_2 \) via a very high temperature and pressure route that bypassed the phase stability field of the coctunite structure. The dense \( c' \) and \( t' \) phases with specific size, lattice parameters, and residual stress were allowed to relax and/or kinetically phase change into lower-energy state as constrained by the intersections of their internal energy versus cell volume plots. Further study is required to see if such a high-energy synthesis and relaxation/transformation route of fluorite-type dioxides can be extended to other compositions.

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