<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Synthesis of monodisperse CeO2-ZrO2 particles exhibiting cyclic superelasticity over hundreds of cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Du, Zehui; Ye, Pengcheng; Zeng, Xiao Mei; Schuh, Christopher A.; Tamura, Nobumichi; Zhou, Xinran; Gan, Chee Lip</td>
</tr>
<tr>
<td><strong>Date</strong></td>
<td>2017</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10220/44187">http://hdl.handle.net/10220/44187</a></td>
</tr>
<tr>
<td><strong>Rights</strong></td>
<td>© 2017 The American Ceramic Society. This is the author created version of a work that has been peer reviewed and accepted for publication by Journal of the American Ceramic Society, The American Ceramic Society. It incorporates referee’s comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<a href="http://dx.doi.org/10.1111/jace.14972">http://dx.doi.org/10.1111/jace.14972</a>].</td>
</tr>
</tbody>
</table>
Synthesis of monodisperse CeO$_2$-ZrO$_2$ particles exhibiting cyclic superelasticity over hundreds of cycles

Zehui Du$^1$, Pengcheng Ye$^1$, Xiao Mei Zeng$^{1,2}$, Christopher A Schuh$^3$, Nobumichi Tamura$^4$, Xinran Zhou$^2$, Chee Lip Gan$^{1,2,*}$

Dr. Zehui Du, Pengcheng Ye, Xiao Mei Zeng, Prof. Chee Lip Gan*
1. Temasek Laboratories, Nanyang Technological University, 637553, Singapore

* Corresponding author: Chee Lip Gan, CLGan@ntu.edu.sg.

Prof. Chee Lip Gan, Xiao Mei Zeng, Xinran Zhou
2. School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore

Prof. Christopher A Schuh
3. Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Dr. Nobumichi Tamura
4. Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL), Berkeley, California, 94720, USA

Keywords: CeO$_2$-ZrO$_2$, particles, sol-gel, shape memory, superelasticity

* Corresponding author: Chee Lip Gan, CLGan@ntu.edu.sg

* Zehui Du and Pengcheng Ye contributed equally to this article
Abstract

Nano- and microscale CeO$_2$-ZrO$_2$ (CZ) shape memory ceramics are promising materials for smart micro-electro-mechanical systems (MEMS), sensing, actuation and energy damping applications, but the processing science for scalable production of such small volume ceramics has not yet been established. Herein, we report a modified sol-gel method to synthesize highly monodisperse spherical CZ particles with diameters in the range of ~0.8-3.0 µm. Synchrotron X-ray micro-diffraction (µSXRD) confirmed that most of the particles are single crystal after annealing at 1450°C. Having a monocrystalline structure and a small specimen length scale, the particles exhibit significantly enhanced shape memory and superelasticity properties with up to ~4.7% of compression being completely recoverable. Highly reproducible superelasticity through over five hundred strain cycles, with dissipated energy up to ~40 MJ/m$^3$ per cycle, is achieved in the CZ particles containing 16 mol% ceria. This cycling capability is enhanced by ten times compared with our first demonstration using micropillars (only 50 cycles in Lai et al., Science, 2013, 341, 1505). Furthermore, the effects of cycling and testing temperature (in 25-400°C) on superelasticity have been investigated.
1 Introduction

Ceria stabilized tetragonal zirconia polycrystals (xCeO$_2$-(1-x)ZrO$_2$) are an important group of shape memory ceramics with many potential applications in sensing, actuation and mechanical energy damping systems. These ceramics have been reported to exhibit shape memory effect and superelasticity in a very limited way since it was first studied in bulk materials in the 1980s: the macroscopic stress-induced transformation strain in bulk samples was reported to be very small, only ~0.5-1.0%, and could only be cycled once or perhaps a few times before intergranular cracking would compromise the specimen. In contrast, our recent work has shown that single crystal or oligocrystalline micro- or nano-pillars of ceria doped zirconia can alleviate the cracking problem, as such structures relax the martensitic-transformation-induced mismatch stresses. The micro- or nano-pillars in those works exhibited significantly enhanced superelastic cycling capabilities (up to 50 cycles) and large shape memory strains of several percent.

However, for practical engineering applications, superelastic behavior that is reproducible over hundreds or even thousands of cycles would be desirable for integration into devices or systems. Furthermore, it is important to explore other form factors that have mass production and engineering application potential, and to establish the processing science for small volume shape memory ceramics. As the key to the enhanced shape memory and superelasticiticy in zirconia ceramics appears to be fine-scale oligocrystalline or single crystal structures, a promising candidate form factor is monodisperse nano or microparticles of spherical shape. Since such particles have an intrinsically small specimen volume, they can be easily crystallized into single crystals or oligocrystals through an annealing process. Moreover, such particles can be uniformly and closely packed into bulk powder compacts, or even ordered
colloidal crystals, retaining their large free surface area and yet enabling superelastic properties through a larger volume. Monodisperse zirconia microspheres can be synthesized by a sol-gel processing method in which zirconium alkoxides are hydrolyzed and condensed in an alcoholic solvent using a small amount of water and catalyst. For example, Lerot et al. have synthesized zirconia microspheres by hydrolysis of zirconium tetra-n-propoxide in propanol, in the presence of long-chain carboxylic acids such as caproic acid as catalysts, obtaining particles with average sizes of ~0.1-2.5 µm. Yan et al. have attained particle sizes of 0.8-4.0 µm through hydrolysis of zirconium propoxide in butanol with stearic acid. Van Canfort et al. have used 2-methoxyethanol (2-MOE) and decanoic acid as the solvent and the catalyst, respectively.

Although the hydrolysis kinetics of the zirconium alkoxide as well as the resultant zirconia particle size appear strongly dependent on the concentration of water and the carboxylic acids, the interplay between these variables remains unclear. A comprehensive diagram mapping these parameters would be very useful as a guideline for the synthesis of zirconia microspheres for various fundamental studies and engineering applications. More urgently, the studies described above only address undoped zirconia microspheres produced by the sol-gel method, whereas superelasticity and shape memory behavior require substantial doping to bring the tetragonal/monoclinic martensitic transformation temperatures into a suitable range (e.g., to room temperature).

It is our goal in this work to address these challenges, by developing a modified sol-gel processing method to produce ceria-doped zirconia microspheres, and to do so with an eye towards shape memory and superelastic properties. Our approach is based on the co-hydrolysis of zirconium tetrabutoxide (Zr(oBu)₄) and cerium (IV) methoxyethoxide (CeOEM) in 2-MOE with decanoic acid as catalyst. Monodisperse CeO₂-ZrO₂ microspheres with diameters varying
over the range ~0.8-3.0 µm have been synthesized for the first time and a binary water-acid
diagram aimed at designable particle production has been established. For single-crystal particles,
we have further explored the shape memory effect and superelasticity properties at both room
temperature and elevated temperatures up to 400°C by *in-situ* nanocompression, showing highly
cyclic superelastic properties with large energy dissipation in these particles.

2 Experimental Procedure

2.1 Materials

All of the chemicals used in the experiments were analytical grade and were used without
further purification. Zirconium tetrabutoxide (80% in butanol), anhydrous 2-methoxyethanol and
decanoic acid were purchased from Sigma-Aldrich. Cerium (IV) methoxyethoxide (18-20% in
methoxyethanol) was purchased from Gulf Chemical.

2.2 Synthesis of Monodisperse Spherical CZ Particles

Our synthesis process for monodisperse CeO$_2$-ZrO$_2$ (CZ) microspheres is schematically
illustrated in Figure S1A-D. To synthesize the zirconia particles containing 16-20 mol% ceria,
Zr(oBu)$_4$ and CeOEM are first mixed in 2-MOE according to the molar ratios of Ce:Zr in the
desirable particles. The total concentration of cerium and zirconium alkoxides in 2-MOE was
kept at 0.1M. The mixture was kept stirring for one hour, after which decanoic acid was added.
After stirring for an additional hour, water was added, whereupon precipitation occurred after
about 10 seconds. In order to study the effect of water and decanoic acid concentration on the
particle size, water concentration was varied over the range ~0.40-1.5 M with acid
concentrations ~ 0.05-0.1 M.

After aging, CZ particles were extracted from the suspensions by centrifuging at 3500
rpm for 3 minutes and washing in 2-MOE. The morphology and chemical composition of the CZ
particles were analyzed by a field emission scanning electron microscope (FESEM, FEI Nova 600i Nanolab, 5-15 kV) equipped with energy-dispersive X-ray spectroscopy (EDS). The particle size was analyzed with image analysis software (ImageJ, National Institutes of Health, West Bethesda, MD).

2.3 Annealing of the CZ Particles

The as-prepared particles were firstly dispersed in 2-MOE and then dropped onto a sapphire (0001) substrate. After drying, the samples were annealed in a box furnace at 700°C for 30 mins, or 1300, 1400 or 1450 °C for 5 mins, and the ramping rate was kept at 10-20°C/min (Figure S1D). The particles were analyzed by X-ray diffraction (D8, Bruker) with Cu Kα radiation and FESEM. The crystal structure of some individual particles was also studied by synchrotron radiation scanning X-ray micro-diffraction (µSXRD) technique using a white beam on Beamline 12.3.2 at the Advanced Light Source, Berkeley, CA. The µXRD patterns were collected in 1 second at a step size of 1 µm for each frame by a DECTRIS Pilatus hybrid pixel array detector and analyzed using the XMAS (µXRD analysis software) software package.

2.4 Micro-compression tests on the CZ particles

Micro-compression tests on the CZ particles (14 mol% or 16 mol% ceria) were carried out on an in-situ nanoindenter (PI85, Hysitron) equipped with a 60° conical tip with a flat end and a diameter of 5 µm (Figure S1E). The loads applied were in the range ~500-1500 µN and the loading rate was ~50 µN/s. To perform hundreds of cycles, we separated the tests into ~40-50 segments in which 10 identical loading and unloading cycles were conducted with the specified maximum load and constant loading rate. Between the segments, a set-point 2 µN contact force was always maintained and contact with the specimen was never broken.
The CZ particles were also tested at elevated temperatures of 200°C and 400°C using an in-situ nanoindenter PI87 (Hysitron, Minneapolis, MN) equipped with 1 µm flat punch and a 400°C heating stage. The heating was controlled by a MEMs heater embedded with a thermocouple. Each test was commenced after 20 minutes from the point that the targeted temperature had been reached. The loads applied were in the range ~500-750 µN and the loading rate was ~50 µN/s. A total of five cycles were applied at each temperature, including 25, 200 and 400°C.

3 Results and discussion

3.1 Effect of acid/water ratio on the particle sizes

Figure 1 shows the CZ microspheres prepared with various molar concentrations of water and decanoic acid. Monodisperse CZ microspheres are obtained when the acid concentration is 0.065 M and the water concentration is in the range of ~0.7-1.5 M (Figure 1A-D). Figure S2A (in Supplementary Materials) shows the average particle sizes measured using ImageJ software as a function of the water concentration; these decline monotonically from ~2.0 to 0.77 µm when the water concentration is increased from 0.7 to 1.5 M. The coefficient of variation (CV%, equals to standard deviation divided by mean diameter) over this range increases only slightly from ~5% to ~9%, reflecting a tight size distribution of highly monodisperse spheres. Figure S2B reveals the effect of acid concentration on the particle sizes at constant water concentration of 1.0 M; it has little effect at lower concentrations, but leads to loss of monodispersion above about 0.075 M, where the average diameter also drops to ~0.8 µm. This significant change in the particle size distribution as a function of the acid concentration can be clearly observed in Figure 1C and Figure S3A-B.
It is possible to obtain CZ microspheres with diameters as large as 4-6 µm by reducing the water concentration to 0.5 M, as shown in Figure S3C-D, but their sizes mostly have high coefficients of variation of ~25% and they must be considered polydisperse. When the water concentration is 0.4 M or lower, no precipitation is observed and the solution cures into a transparent gel. A water-acid diagram mapping the conditions that results in monodisperse or polydisperse particles or gel can be constructed as shown in Figure 2. The average particle sizes (in micron) obtained from experiments are also marked in the map. Here we define particles with CV% of 12% or less as monodisperse, and those above this CV% range as polydisperse particles. From this map, monodisperse CZ microspheres with diameter of ~0.8-3.0 µm are achievable by using acid concentrations lower than 0.075 M and water concentrations in the range of 0.6-1.5 M. The map can serve as a reference to prepare the CZ particles with desirable sizes and size distributions.

To prepare particles containing 16 to 20 mol% ceria, the molar concentration of the cerium precursor in the solution was changed over the range 0.016 to 0.02 M. In addition to changing the doping level in the particles, we observed that the average diameter of the resultant CZ microspheres slightly increased from 1.7 to 2.0 µm with ceria addition, while the particles remained monodisperse (Figure S2C). This increase of particle size can likely be attributed to the formation of bimetallic complexes from zirconium tetrabutoxide and cerium methoxyethoxide through ligand exchanges. As bimetallic complexes have higher stability than the corresponding single metal alkoxides, hydrolysis will be slowed down, as has been evidenced in our experiments. We observed that the induction time preceding precipitation doubled from ~30 seconds to about one minute with the increase in the concentration of cerium precursor; this
supports an interpretation that the hydrolysis reaction was retarded. With fewer nuclei formed in the first burst, more matter is available for growth, resulting in larger particles.

We have used energy-dispersive X-ray spectroscopy (EDS) to semi-quantitatively measure the elementary compositions of the CZ microspheres prepared by adding cerium precursors at a 16 mol% level. As shown in Figure S2D, the actual cerium concentration incorporated in the CZ particles is very sensitive to the water level. At 0.45-0.85 M water, the incorporated cerium concentration is ~16-18 mol%, close to the initial addition level. When the water addition increased to 1.0-1.5 M, the cerium concentration increased monotonically to ~26 mol%, and the typically light yellow color of the particles became darkened.

3.2 Crystallization of the particles

The CZ microspheres prepared by the sol-gel method are amorphous, and are therefore subsequently annealed at 700-1450°C in order to obtain single crystal or oligocrystal particles for studies of their shape memory and superelastic properties. SEM images of the particles after annealing are shown in Figure 3A-D. The particles annealed at 700°C are nanocrystalline with a grain size less than 50 nm. With increasing annealing temperature from 700 to 1400°C, the grain size rises and the grain boundaries become thermally etched. At 1400°C, the particles are polycrystalline with a grain size of ~200-500 nm. The grain boundaries disappear at 1450°C, and the prominence of crystallographic faceting suggests that a single crystalline state has been achieved.

X-ray powder diffraction measurements on these annealed samples show that the crystals are in the tetragonal phase, and bear no special orientation relationship with the (0001) sapphire substrate (Figure S4). To study the sample crystallography at the particle level, synchrotron
radiation scanning X-ray micro-diffraction (µSXRD) has been carried out using a white beam. Figure 3E shows a SEM image of a typical area containing six single particles or particle clusters, labeled as #1-6. Figure 3F shows the corresponding Laue diffraction orientation map in which each color represents one crystal orientation. It reveals that each isolated particle has only one crystal orientation (e.g. #1, #2 and #3), i.e., these particles are single crystalline. Particle clusters, on the other hand, shows 2-3 crystal orientations, for example #4-6. A representative Laue diffraction pattern from particle #3 is shown in Figure 3G, and indexed as tetragonal zirconia with a specific crystal orientation (indexed spots are marked by squares). The unindexed diffraction spots are associated with the sapphire substrate (cf. Figure S5). Similar µSXRD analysis has been carried out on several other areas of the sample, generally confirming that the majority of the particles are single crystals, especially those that appear free of grain boundaries by SEM.

3.3 Shape memory and superelastic properties of the particles

The shape memory and superelastic properties of the CZ particles annealed at 1450°C have been studied by in-situ nanocompression in an SEM. Two types of single crystal particles containing 14 and 16 mol% Ce respectively have been chosen for these studies. The 16 mol% Ce stabilized zirconia has been reported to have the monoclinic→tetragonal transformation finish temperature (which is called austenite finish temperature $A_f$ in the context of shape memory materials) at about $0^\circ$C. This composition is suitable for superelasticity studies because at room temperature, they lie at a temperature above $A_f$. So applied stresses at room temperature can induce transformation to monoclinic phase which should be subsequently recovered to tetragonal phase upon unloading. The 14 mol% Ce stabilized zirconia is suitable for shape memory studies.
because it has $A_f$ at $179^\circ C$, much higher than room temperature. So the recovery of the stress-induced monoclinic phase can be triggered only by heating to over $A_f$ temperatures.

Particle #7 provides an example of superelastic properties. This particle contains 16 mol% Ce stabilized zirconia, with a diameter of 0.94 µm, and a crystal orientation close to (111) aligned with the compression axis. Figure 4A shows the load-displacement curve obtained by applying a maximum compressive load of 750 µN at a loading rate of 50 µN/s. After an initial elastic deflection, a single large displacement plateau spanning ~18 nm is observed at a load of ~620 µN. This plateau is attributable to the stress-induced martensitic transformation from tetragonal to monoclinic zirconia$^5, 15$, and corresponds to a relative particle distortion, or transformation “strain” ($\varepsilon_{a\rightarrow m}$)$^{16}$:

$$\varepsilon_{a\rightarrow m} = \frac{d_{a\rightarrow m}}{2R}$$  (1)

where $d_{a\rightarrow m}$ is the total displacement in the displacement plateau and $R$ is the radius of particle. Therefore the transformation strain of particle #7 is ~1.91%. That the 1.91% strain is a result of the transformation is supported by its perfect recovery during unloading, with another displacement plateau at 170 µN corresponding to the reverse martensitic transformation from monoclinic to tetragonal zirconia. The sample hence exhibits the essential characteristics of the superelastic effect.$^{17}$ Based on the load-displacement curves, the dissipated energy for one superelastic cycle of particle #7 is estimated to be ~25.2 MJ/m$^3$.

This superelastic deformation and shape recovery have been observed in real-time by in-situ SEM during the testing (video can be provided upon request). What is more, we have applied over five hundreds cycles of compression on this particle at the same fixed load of 750 µN, as shown in Figure S6 of the Supplementary Materials. Figure 4B-C shows the particle
before the first compression and after compression through 502 cycles; the particle is intact and shows no major change in its shape. The particle remains as tetragonal phase, as has been evidenced in our earlier work\textsuperscript{18}. A more detailed discussion on the effect of cyclic superelasticity will be made in the next section.

Particle #8 is 14 mol\% Ce stabilized zirconia and has a diameter of \(
\sim 1.64 \, \mu m\). It exhibited a very typical load-displacement curve for a shape memory material below the reversion temperature; as shown in Figure 4D, it experienced a sudden displacement plateau spanning 77 nm at \(~ 916 \, \mu N\) corresponding to the forward martensitic transformation, but it did not recover this strain upon unloading. The transformation induced strain is estimated to be \(\sim 4.7\%\) in this case. By comparing the SEM images of the particle before and after compression (Figure 4E-F), the shape change is made clear. The small features that appear to be cracks on the surface of this particle are in the Pt coating which locally delaminated from the particle in some spots after compression (note that the Pt coating is used to improve imaging of the particle). In fact, the shape change in the particle of Figure 4F can be attributed to the martensitic transformation, as confirmed by heating it through the reverse transformation; after 1 hour at 500°C, the particle shape resembles its uncompressed form (cf. Figure 4E and G).

We have tested dozens of particles of different sizes and cerium doping concentrations. In general, the particles exhibited robust shape memory or superelasticity properties depending on the cerium doping concentration, although a few did not, and merely fractured upon loading. These are most likely associated with unfavorable crystallographic orientations which favor slip or fracture before the martensitic transformation.\textsuperscript{5} The concentration of stresses between transformed and untransformed regions within a single particle due to the Hertzian contact geometry could be another reason for the failure.\textsuperscript{18} Nevertheless, the shape memory strain up to
~4.7%, highly reproducible superelasticity over five hundred cycles, and very high dissipated energy of ~25.2 MJ/m$^3$ (some particles can reach ~40 MJ/m$^3$) are all noteworthy. In particular, the cycling capacity documented here is about ten times greater than we reported in micropillars$^3$, and much higher than we found in spray dried shape memory zirconia particles that failed after about 100 cycles$^{18}$. The improvement in the superelastic cycling can be attributed to the single crystal structure of the present sol@gel particles and their uniform microstructures. With few structural flaws and a single crystal structure that gives the transformation access to free surfaces and accommodates the transformation mismatch, these particles exhibit much more robust shape memory properties.

### 3.4 Superelastic cycling of the particles

The effect of cyclic superelastic loading has been studied on particles of diameter ~0.85 µm and containing 16 mol% Ce. Figure 5A-B shows a series of load-displacement curves of a representative particle (#9) for the 1$^{\text{st}}$-412$^{\text{th}}$ cycles of compression. On the 1$^{\text{st}}$ cycle, the forward transformation occurs through two to three displacement plateaus in the loading curve. In the unloading curve, there are also a few steps in the displacement plateau associated with the reverse martensitic transformation. Over the subsequent 2-32 cycles, we observe a shakedown in the superelastic curves as the particle adopts its favored kinematic transformation pathway, and also accommodates the shape constraint of the diamond punch (note the initial unrecovered strains in these early cycles, which are eventually shaken out as the cycles become fully reversible).

From the 32$^{\text{nd}}$ to 87$^{\text{th}}$ cycles, similar displacement plateaus are found in each loading-unloading curve, with a slight training effect stabilizing the preferred configuration of monoclinic domains; after such stabilization the superelastic cycles become reasonably
superimposable, for example, the 112\textsuperscript{th} - 262\textsuperscript{th} cycles in Figure 5B. We stopped the loading of this particle after the 412\textsuperscript{th} cycle although it showed no sign of failure at that point.

One interesting observation in Figure 5A-B is that the critical load for inducing martensitic transformation decreases with continued cycling of the applied load, as summarized in Figure 5C. This decreasing tendency is more pronounced in the first 100 cycles during the shakedown period, ranging from ∼793 to ∼360 µN between the 1\textsuperscript{st} and 100\textsuperscript{th} cycle. A similar cycling shakedown effect has been reported in fine-grain Ni-Ti shape memory alloy (SMA), Cu-Zn-Al SMA microwires\textsuperscript{19} and Cu-Al-Ni micropillars\textsuperscript{20}, and can be attributed to the development of dislocation substructure which accommodates the monoclinic domains in the tetragonal zirconia matrix.\textsuperscript{21,22} As a consequence, monoclinic domains can evolve at lower stresses in the subsequent loading cycles. The critical load becomes almost constant in the 100\textsuperscript{th} -300\textsuperscript{th} cycle. Similar trends are reflected in the energy dissipated on each cycle, i.e. the area inside the superelastic loop, which is shown in Figure 5D. Nevertheless, the dissipated energy in all these cycles is very high. In the first ten cycles, it averages ∼40 MJ/m\textsuperscript{3} and slightly drops to ∼20-30 MJ/m\textsuperscript{3} in the subsequent 10\textsuperscript{th} -40\textsuperscript{th} cycles. This dissipated energy is higher than that achieved in many shape memory alloys such as Ni-Ti, Cu-Al-Mn-Ni and Ni-Ti-Nb alloys (10-20 MJ/m\textsuperscript{3}).\textsuperscript{23,24,25}

3.5 High temperature superelasticity

A series of CZ particles of diameter 0.92 µm was also tested using the \textit{in-situ} nanoindenter PI 87 (Hysitron) equipped with a MEMs heater, to explore the role of temperature on the transformation properties. The particles were compressed at three different temperatures, namely 25, 200 and 400°C, sequentially and for only five loading cycles at each temperature. Figure 6A shows the load-displacement curves at 25°C. The curves are typical superelastic loops. After 1\textsuperscript{st} cycle for the platen accommodation, the displacement becomes fully recoverable in the
subsequent 2\textsuperscript{nd}-5\textsuperscript{th} cycles, and the curves are highly repeatable. The load-displacement curves of the 2\textsuperscript{nd} cycle of compression at each of 25, 200 and 400\degree C are plotted in Figure 6B for comparison. The curves are very similar except that the critical load for initiating martensitic transformation and the area enclosed in the hysteresis loops are changed. The critical load gradually increases with testing temperature (Figure S7A), which is expected as the tetragonal phase is more stable at high temperatures and thus higher stress is required for the stress-induced martensitic transformation.\textsuperscript{26} Figure S7B reveals that the dissipated energy in each superelastic cycle decreased with increasing of testing temperatures, owing to a reduction in the transformation strain, as shown in Figure 6B, and also likely due to an accumulation of shakedown/training cycles over the course of this experiment (cf. Figure 5D). Nevertheless, these observations are the first we are aware of to show that superelasticity can be retained in CZ at elevated temperatures up to 400\degree C. It indicates that the as-developed CZ particles have the potential to be used for energy damping or actuation applications at high temperatures.

4 Conclusion

Monodisperse ceria-doped zirconia (CZ) microspheres have been produced by a modified sol-gel processing method, for which we have empirically optimized the concentrations of water, decanoic acid and cerium precursors to achieve shape memory and superelastic particles. Monodisperse CZ microspheres with diameters of 0.8-3.0 \mu m are obtained for acid concentrations lower than 0.075M and water concentrations in the range of 0.6-1.5M. The particle size rises with decreasing water addition. Larger microspheres with diameters of 4.0-6.0 \mu m can be obtained by using 0.5M water and 0.075-0.085M acid, although these conditions lead to greater polydispersity. The particle size is also increased by increasing the concentration of
cerium precursor. Upon annealing at 1450°C, we obtained mostly single crystal particles suitable for superelastic and shape memory testing.

The CZ single crystal particles exhibited excellent shape memory and superelastic properties with recoverable transformation strains up to 4.7%. At 16 mol% ceria addition, these CZ particles exhibited highly reproducible superelasticity through over 500 load cycles, with dissipated energy up to ~40 MJ/m³ per cycle in the early cycles. Superelasticity was also observed directly in-situ during microcompression, and is attributed to the reversible martensitic transformation. Upon cycling, we observe gradual accommodation of the platen geometry, as well as a shakedown in critical load and dissipated energy of the particle. At temperatures above ambient, the transformation requires higher stresses to trigger, but superelastic properties are retained to at least 400°C.

5 Supporting Information

Supporting Information (Figures S1-S7) is available from the Wiley Online Library or from the author.

6 Acknowledgments

We would like to thank Joseph Lefebvre, Ryan J. Stromberg and Ariel Leonard from Hysitron. Inc. for their kind help with high temperature in-situ indentation at Hysitron in Minnesota, USA. The Advanced Light Source (ALS) and the National Energy Research Scientific Computing Center (NERSC) are supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 at the Lawrence Berkeley National Laboratory (LBNL).
7 References


8 Caption list

**Figure 1** SEM images of CZ microspheres with different water and acid concentrations. [water]/[acid]: (A) 0.7 M/ 0.065 M; (B) 0.85 M/0.065 M; (C) 1.0 M/0.065 M; (D) 1.5 M/0.065 M. The Ce mol% is kept at 16 mol%.
Figure 2 A water-acid diagram mapping the conditions resulting in monodisperse or polydisperse particles or gel. The particle size data (in micrometer) obtained experimentally are marked in the map and ● indicates gel; ★ for polydisperse; ■ for monodisperse. Ce mol%=16%.

Figure 3 SEM images of the CZ particles after annealing at (A) 700°C for 30 mins; (B) 1300 °C for 5 mins; (C) 1400 °C for 5 mins; and (D) 1450 °C for 5 mins. (E) SEM image of a few particles on sapphire substrate; (F) the orientation map of the particles corresponding with (E); (G) white beam microdiffraction pattern of Particle #3 in (E); The particles were prepared using [water]/[acid]=0.85 M/0.065 M and with 16 mol% ceria doping.

Figure 4 Load-displacement curves of the CZ particles (A) #7, with 16% cerium doping; (D) #8, with 14% cerium doping (Ce mol% was confirmed by EDX). (B-C) are the SEM images of Particle #7 before and after compression. (D-G) SEM images of Particle 8# before and after compression and after heating. The particles were sintered on c-cut sapphire substrate at 1450 °C for 5 minutes.

Figure 5 Load-displacement curves of the CZ particle #9 during the (A) 1-42th cycles and (B) 43-412th cycles of compression; (C) the critical load and (D) the dissipated energy of the particle during different superelastic cycles.

Figure 6 Load-displacement curves of superelastic CZ particle #10 during the (A) 1-5th cycles of compression at room temperature (RT) and (B) 2nd cycle at 25 °C, 200 °C and 400 °C.
Figure 1 SEM images of CZ microspheres with different water and acid concentrations. [water]/[acid]: (A) 0.7 M/0.065 M; (B) 0.85 M/0.065 M; (C) 1.0 M/0.065 M; (D) 1.5 M/0.065 M. The Ce mol% is kept at 16 mol%.

52x36mm (300 x 300 DPI)
Figure 2 A water-acid diagram mapping the conditions resulting in monodisperse or polydisperse particles or gel. The particle size data (in micrometer) obtained experimentally are marked in the map and ● indicates gel; ★ for polydisperse; ■ for monodisperse. Ce mol%=16%.
Figure 3 SEM images of the CZ particles after annealing at (A) 700 °C for 30 mins; (B) 1300 °C for 5 mins; (C) 1400 °C for 5 mins; and (D) 1450 °C for 5 mins. (E) SEM image of a few particles on sapphire substrate; (F) the orientation map of the particles corresponding with (E); (G) white beam microdiffraction pattern of Particle #3 in (E); The particles were prepared using [water]/[acid]=0.85 M/0.065 M and with 16 mol% ceria doping.
Figure 4 Load-displacement curves of the CZ particles (A) #7, with 16% cerium doping; (D) #8, with 14% cerium doping (Ce mol% was confirmed by EDX). (B-C) are the SEM images of Particle #7 before and after compression. (D-G) SEM images of Particle #8 before and after compression and after heating. The particles were sintered on c-cut sapphire substrate at 1450 °C for 5 minutes.
Figure 5 Load-displacement curves of the CZ particle #9 during the (A) 1-42th cycles and (B) 43-412th cycles of compression; (C) the critical load and (D) the dissipated energy of the particle during different superelastic cycles.

316x242mm (300 x 300 DPI)
Figure 6 Load-displacement curves of superelastic CZ particle #10 during the (A) 1-5th cycles of compression at room temperature (RT) and (B) 2nd cycle at 25 °C, 200 °C and 400 °C;
Figure S1 Schematic illustration of the synthesis processes for the monodisperse CZ microspheres and the setup for *in-situ* compression tests.

Figure S2 (A-C) The plots of average particle diameter and coefficient of variation (CV) of the CZ particles with different concentrations of water ([acid] = 0.065 M) (A), decanoic acid ([water] = 1.0 M) (B) and cerium precursor ([water]/[acid] = 0.85 M/0.065 M) (C); (D) atomic percentage of cerium in the CZ particles after drying ([acid] = 0.065 and initial Ce addition= 16%)
Figure S3 SEM images of CZ microspheres with different water and acid concentrations. [water]/[acid]: (A) 1.0 M/0.08 M; (B) 1.0 M/0.1 M; (C) 0.5 M/0.075 M; (D) 0.5 M/0.085 M. The Ce mol% is kept at 16 mol% and the samples were dried at 80 °C before observation in the SEM.

Figure S4 XRD pattern of the CZ microspheres after annealing at 1450 °C, 5 minutes.
Figure S5 Laue diffraction pattern of the (0001) sapphire substrate
Figure S6 Load-displacement curves of the CZ particle #7 under 1-502th cycles of compression;
**Figure S7** (A) The critical load and (B) the dissipated energy of the particle #10 tested at different temperatures.