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Liquid-feed flame spray pyrolysis (LF-FSP) for combinatorial processing of nanooxide powders along the $(ZrO_2)_{1-x}(Al_2O_3)_x$ tie-line. Phase segregation and the formation of core-shell nanoparticles

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We report here the synthesis of $(ZrO_2)_{1-x}(Al_2O_3)_x$ nanooxide powders with molar ratios that span the ZrO_2 -Al_2O₃ composition range. Liquid-feed flame spray pyrolysis (LF-FSP) of mixtures of N(CH₂CH₂O)₃Al (alumatrane) and Zr(CH₃CH₂COO)₂(OH)₂ precursors dissolved in ethanol, were aerosolized with O₂, combusted at temperatures of 1500-2000°C and rapidly quenched thereafter to provide (ZrO₂)_{1-x}(Al₂O₃)_x nanopowders of selected compositions. All powders exhibit average particle sizes (APSs) < 20 nm and corresponding surface areas of ~50 m²/g when produced at rates of 100-300 g/h. The as-processed powders were characterized in terms of phase, APS, specific surface area, composition, and morphology by BET, XRD, XRF, SEM, TEM, FT-IR, and TGA-DTA. The presence of δ -alumina and tetragonal zirconia is observed over most of the compositions studied. Furthermore, this phase segregation leads to the formation of core-shell materials. Evidence is presented suggesting the incorporation of Zr^{2+/3+} ions above the published solubility limit of ZrO₂ in δ -alumina.

Key words: core-shell nanoparticles, liquid-feed flame spray pyrolysis, $(ZrO_2)_{1-x}(Al_2O_3)_x$ nanopowders, $(ZrO_2)_{1-x}(Al_2O_3)_x$ tie-line, phase-separated nanopowders.

Introduction

Zirconia is an important material for a wide range of applications [1, 2]. Besides its traditional uses in refractory ceramics and abrasion-resistant materials, highsurface area zirconia is used in applications ranging from catalysts [3] to oxygen sensors [4], to solid oxide fuel cells (oxygen electrolyte) [5] to gate dielectrics for MOSFET [6, 8]. Zirconia has a high dielectric constant (~25), a wide energy band gap (7.8 eV), and when alloyed with ceria as the oxygen storage media in three way auto exhaust catalytic converters, TWCs, it greatly improves sinter resistance [3-7]. Doping zirconia with yttria (YSZ) or alumina (ZTA) to stablize the tetragonal phase, provides unusual toughening for a wide variety of mechanical applications. ZTA materials combine high flexural strength (~910 MPa) and hardness (~15 GPa) with good fracture toughness (~7 MPa $m^{1/2}$) [8, 9]. Unfortunately ZTA's very useful high temperature properties also contribute to difficulties in its processing to dense, defect-free composite materials [10, 11].

We have developed a new approach to high surface area, micropore free, mixed-metal oxide nanopowders using liquid-feed flame spray pyrolysis (LF-FSP). LF-FSP offers the potential to make a wide variety of single and mixed-metal oxide nanopowders in a single step [12-18]. The LF-FSP process aerosolizes metalloorganic precursors dissolved in an alcohol solvent with O_2 , combusts the aerosol within a quartz chamber at 1500-2000 °C, and then rapidly quenches the gaseous species to produce nanosize oxide "soot" with compositions identical to those in the starting metalloorganic precursors. See the experimental section below for details.

In previous studies we have used LF-FSP to make phase-pure nanopowders of single metal oxides including Al₂O₃, CeO₂, ZrO₂ and NiO [12-18]. These LF-FSP nanopowders are unaggregated and as-produced are without microporosity at surface areas of 30-50 m²/ g and average particle sizes (APSs) of 15-30 nm. We have also made binary metal oxide nanopowders along the (MO_z)_{1-x}(Al₂O₃)_x tielines were M=Ni, Ti, Co, Mg, Cu, Zn and Ce by LF-FSP [15-18]. The majority of these nanopowders are solid solutions without microporosity with SSAs of 45-70 m²/g and APSs of 15-35 nm.

LF-FSP provides easy access to many types of nanopowders with excellent control of phase purity and morphology. Furthermore, LF-FSP processing provides low-cost, easy and precise compositional (combinatorial) control to versatile nanomaterials in mixed-metal oxide systems using one-step processing. These nanopowders in turn offer potential access to a wide variety of materials for catalytic, mechanical, photonic and electrical applications.

The potential to make highly homogeneous ZTA nanopowders that offer relatively easy access to high strength monolithic ZTA components provides motivation

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for the work reported here. Additional motivation comes from the potential to create ZTA nanocomposites amenable to superplastic deformation [19]. Finally, the studies reported when combined with work on $[(CeO_2)_{1-x}-(ZrO_2)_x]_{1-y}(Al_2O_3)_y$ to be described elsewhere [20], suggest a potential for one step processing of the washcoats used in TWCs.

Unlike many of the nanopowders previously produced by LF-FSP processing by us and others [7-9, 24, 25], LF-FSP processing of materials along the $(ZrO_2)_x$ - $(Al_2O_3)_{1-x}$ tieline does not produce solid solutions but nanocomposites of each composition. As with other LF-FSP products, the resulting unaggregated nanopowders offer specific surface areas $(SSAs) \ge 45 \text{ m}^2/\text{g}$ without microporosity and although not yttria stabilized, the only zirconia phase observed is tetragonal over all compositions studied.

Experimental

Liquid-feed flame spray pyrolysis (LF-FSP)

LF-FSP, invented at the University of Michigan, has been described in more detail in published papers [12-18]. Briefly, alcohol (typically EtOH) solutions containing 1-10 wt % loading of ceramic as precursors, e.g. single-or mixed-metal alkoxides, carboxylates or β -diketonates are aerosolized with O₂ into a quartz chamber where it is ignited with methane pilot torches.

Initial combustion temperatures run 1500°-2000 °C, depending on the processing conditions, generating nanopowder "soot". Temperatures drop to 300-500 °C over 1.5 metre, equivalent to a 1000 °C quench in 100 ms leading to kinetic products and nanopowders that are largely unaggregated; although they are lightly agglomerated. "Shooting" rates can be 200 g/h when using wire-in-tube electrostatic precipitators operating at 10 kV. Typical powders are 15 to 100 nm APS with specific surface areas (SSAs) of 30 to 100 m²/g. When combinations of elements are used, the resulting nanopowders will have compositions identical to those of the precursor solutions. Since compositions of chemical solutions can be changed intentionally, potentially even during mixing just before aerosolization, it becomes possible to combinatorially produce mixed-metal oxide materials. Hence it becomes possible to rapidly optimize materials for given properties or for ease of processing.

Materials

- Alumatrane

 $N(CH_2CH_2O)_3Al$ prepared as described previously [21, 22] is used as the alumina source.

– Zirconium propionate

Zirconium carbonate $[2ZrO_2(CO_2)\cdot x(H_2O), 99\%, 150$ g, 0.34 mole] was reacted with excess propionic acid (500 ml, 6.80 mole) in a 1 l flask equipped with a still head and an addition funnel. N₂ was sparged directly through the solution (13.7 KPa pressure) as the solution

was heated at $120 \,^{\circ}\text{C}/2$ h with magnetic stirring to distill off ~150 ml of liquid (water and propionic acid). The ceramic loading of the resulting precursor was 11 wt% as determined by TGA.

XRD studies

As-prepared samples were characterized using a Rigaku Rotating Anode Goniometer. Powder samples were prepared by placing ≈ 100 mg in XRD sample holders (amorphous silica slides) for data collection. CuK α (λ = 1.54 Å) radiation with a Ni filter was used with a working voltage and current of 40 kV and 100 mA, respectively. Scans were continuous from 5-90° 20 with a step scan of 2° 20/minute in increments of 0.05° 20. Peak positions and relative intensities were characterized by comparison with PDF files of standard materials: ZrO₂ (PDF file 42-1164), δ -Al₂O₃ (PDF file 46-1131) Debye-Scherrer line broadening was used to calculate average particle sizes from the XRD powder patterns.

Thermal Gravimetric Analysis and Differential Thermal Analysis (TGA/DTA)

TGA-DTA was performed using a SDT 2960 Simultaneous Differential Thermal Analyzer (TA Instruments, Inc., New Castle, DE). The instrument was calibrated with gold supplied by Perkin-Elmer. Samples (70 mg) of asprepared powders were hand pressed in a 3 mm dual action die and placed inside Pt sample cups and heated at ramp rates of 10 K/minute from ambient temperature to 1400 °C. The reference material was a pellet of α alumina. A flow of synthetic air, 50 ml/minute, was maintained during all experiments.

Specific surface area (SSA).

SSA was measured on a Micromeritics ASAP 2000 sorption analyzer. Samples (200 mg) were degassed at 400 °C until the outgas rate was 5 mmHg/minute. Analyses was run at 77 K with N₂. SSAs were determined by the BET multipoint method using at least five data points. The average particle size was derived using the formula $\langle R \rangle = (3/\rho \times SSA)$ where $\langle R \rangle$ = average particle size, and ρ is the density of the material.

Scanning electron microscopy (SEM)

A field emission SEM (Phillips XL30FEG) was used to image powder morphologies. Powder samples were dispersed in distilled H₂O using an ultrasonic horn (Vibra-cell, Sonics and Materials, Inc., Newton, CT). A drop of the dispersed powder/water was placed on an aluminum SEM stub and allowed to dry for 4 h on a hot plate. Powders were sputter coated with 10-40 nm of Au-Pd to reduce charging effects. Operating voltage was between 15.0 and 30.0 kV.

Transmission electron microscopy (TEM)

An analytical high resolution TEM (Model 3011, JOEL, Osaka, Japan) was used to measure the particle

sizes and morphologies of as-prepared powders. Powder samples were prepared by dipping a holey carbon grid in a vial of emulsion with as-prepared powder. The specimen was held in a Gatan double tilt goniometer. An operating voltage of 300 kV was used.

FT-IR Spectra

Diffuse reflectance Fourier transform (DRIFT) spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer (Mattson Instruments, Inc., Madison, WI). Optical grade, random cuttings of KBr (International Crystal Laboratories, Garfield, NJ) were ground, with 1.0 wt % of the sample to be analyzed. For DRIFT analysis, samples were packed firmly and leveled off at the upper edge to provide a smooth surface. For transmission IR, 100 mg of each sample prepared for DRIFT analysis was pressed in a stainless steel double action die (12.75 mm diameter) at 100 MPa for 1 minute in a Carver Press (model 3912). Fresh backgrounds of pure KBr were done every 2 hour. The FTIR sample chamber was flushed continuously with N2 prior to data acquisition in the range 4000-400 cm⁻¹. Each run consisted of 128 scans with a resolution of $\pm 8 \text{ cm}^{-1}$.

Results and Discussion

In the following sections we begin by characterizing the zirconia precursor developed for LF-FSP processing. Thereafter we follow with sections on the production of selected nanopowders along the $(ZrO_2)_{1-x}(Al_2O_3)_x$ tieline, their phase behavior, particle morphologies, surface chemistries and thermal properties.

Precursor and precursor formation

We previously reported the characterization of alumatrane [N(CH₂CH₂O)₃Al] and its use as a precursor in LF-FSP for the synthesis of δ -alumina nanopowders [12, 16, 21, 22]. Here we report on the zirconium pre-



Fig. 1. TGA of $Zr(CH_3CH_2COO)_2(OH)_2$ ramped at 10 °C/min in synthetic air.

cursor, Zr(CH₃CH₂COO)₂(OH)₂, synthesized as discussed in the experimental section. This precursor has a thermal decomposition pattern similar to other metal carboxylate precursors studied previously [12-18].

Figure 1 shows a TGA trace for $Zr(CH_3CH_2COO)_2$ -(OH)₂. Initial mass losses (8%) are due to propionic acid of recrystallization. Thereafter, mass loss events are attributed to the decomposition of the propionate ligands as suggested in reactions (1)-(3) [12-18, 21, 22].

$$\begin{array}{l} Zr(CH_3CH_2COO)_2(OH)_2 \rightarrow \\ Zr(CH_3CH_2COO)(OH)_3+CH_3CH=C=O \qquad (1) \\ Calc. (Found) Mass Loss = 19.01\% (19\%) \end{array}$$

$$\begin{array}{l} Zr(CH_3CH_2COO)(OH)_3 \rightarrow Zr(OH)_4+CH_3CH=C=O \\ (2) \\ Calc. (Found) Mass Loss = 19.01\% (19\%) \end{array}$$

$$\begin{array}{l} Zr(OH)_4 \rightarrow ZrO_2+2H_2O \qquad (3) \\ Calc. (Found) Mass Loss = 12.22\% (12\%) \end{array}$$

Final ceramic yields [42% (ZrO₂)] are within experimental error of the calculated value (41.75%) from the decomposition of the precursor [Zr(CH₃CH₂COO)₂-(OH)₂] to oxide (ZrO₂) and are as expected based on previous studies [12-18, 21, 22].

Compositions of as-processed nanopowders

Eight different precursor compositions in the $(ZrO_2)_x$ - $(Al_2O_3)_{1-x}$ system were prepared by making simple mixtures of alumatrane and the propionate as detailed in the Experimental. Table 1 lists the compositions of the LF-FSP produced nanopowders. Compositions were confirmed by XRF. These nanopowders were analyzed by XRD, SEM, FT-IR and TGA-DTA as discussed in the following sections.

XRD powder pattern studies

Figure 2 provides XRD patterns for as-produced nanopowders along the $(ZrO_2)_x(Al_2O_3)_{1-x}$ tie-line (Table 1). In contrast to previous studies discussed above, we observe what appears to be complete phase separation as indicated by the presence of t-zirconia and δ -alumina in Samples 2-7, Table 1.

It is important to note that two excellent papers from

Table 1. Compositions of the $(ZrO_2)_x(Al_2O_3)_{1-x}$ nanopowders.

Sample	Mole % ZrO ₂	Wt % ZrO ₂	Mole % Al ₂ O ₃
1	2.4	3.0	96.8
2	4.1	5.0	94.9
3	4.6	5.6	94.3
4	5.9	7.1	92.8
5	8.4	10.0	90.0
6	13.6	16.0	93.9
7	49.7	54.5	45.4
8	79.4	82.4	17.6



Fig. 2. XRD powder patterns of $(ZrO_2)_x(Al_2O_3)_{1-x}$. 2.4 ZrA denotes 2.4 mole % ZrO₂ included in ZrO₂-Al₂O₃ binary system.

the Hahn and Winterer groups on low alumina content zirconias [23, 24], made by a process similar to LF-FSP have recently been published that corroborate our observations in this region of the tieline. Thus, their XRD studies of zirconia rich samples in $(ZrO_2)_x(Al_2O_3)_{1-x}$ at x=0.5 - 1.0 indicate that the tetragonal phase is dominant in the zirconia-rich region as seen for 49.7 ZrA and 79.4 ZrA with the minor phase being δ -alumina. They also briefly mention the formation of a transition alumina phase but did not characterize it.

Average particle size (APSs) and specific surface area (SSAs) from BET

The APSs for these materials were estimated from Debye-scherrer line broadening and their SSAs (Table 2). Both methods give very similar results. The average SSAs for the samples are 52 ± 5 m²/g, giving APS values of 15 ± 3 nm. Although the Hahn/Winterer studies [23, 24] show that particle sizes decrease with

Table 2. At 58 and 55As of as produced LT-TST samples.					
Sample	XRD line broadening Particle size (nm)	BET-derived Particle size (nm)	SSAs (m²/g)		
2.4ZrA	18 ± 1	14 ± 0.5	54 ± 0.5		
4.1ZrA	18 ± 1	13 ± 0.5	57 ± 0.5		
4.6ZrA	15 ± 1	13 ± 0.5	55 ± 0.5		
5.9ZrA	15 ± 1	13 ± 0.5	57 ± 0.5		
8.4ZrA	16 ± 1	14 ± 0.5	50 ± 0.5		
13.6ZrA	13 ± 1	15 ± 0.5	47 ± 0.5		
49.7ZrA	12 ± 1	11 ± 0.5	53 ± 0.5		
79.4ZrA	12 ± 1	11 ± 0.5	51 ± 0.5		

Table 2. APSs and SSAs of as produced LF-FSP samples.

increasing alumina contents, in the zirconia-rich region, we do not observe any such changes. This may be a consequence of the differences in method of processing or precursors used. Note that LF-FSP production is at rates of 100-300 g/h vs 3 g/h for CVS (chemical vapor synthesis) by Hahn/Winterer.

Scanning electron microscopy (SEM) studies

SEM was used to demonstrate powder uniformity. Figure 3 shows that SEM resolution is insufficient to reveal individual particles but does provide a view of the general particle population. These SEMs indicate that the particle populations produced here do not include any obvious micron size particles. Bell and Rodriguez [25] recently demonstrated that LF-FSP δ -Al₂O₃ nanopowders disperse perfectly in water without any apparent agglomeration or the presence of micron size particles [16, 25].

Transmission electron microscopy (TEM) studies of particle morphologies

TEM images were used to assess particle morphologies and sizes of as-prepared powders. Discussions of actual size/size distributions are not appropriate if based solely on TEM micrographs, unless combined with the XRD results. The Fig. 4 images are high-resolution



Fig. 3. SEM images of (a) 2.4 mole% ZrO_2 in Al_2O_3 . (b) 79.4 mole % ZrO_2 in Al_2O_3 .



Fig. 4. TEM micrographs of (a) 4.1 mole% ZrO₂ in Al₂O₃. (b) 49.7 mole % ZrO₂ in Al₂O₃. (c), (d) 79.4 mole % ZrO₂ in Al₂O₃.

TEM micrographs of $(ZrO_2)_x(Al_2O_3)_{1-x}$ nanopowders. The particle sizes here are typically below 30 nm in diameter with the vast majority < 20 nm.

In Fig. 4, clear lattice fringes show a high degree of crystallinity and strain, especially in the high zirconia content sample (49.7 mole % ZrO_2 in Al_2O_3 , 79.4 mole % ZrO_2 in Al_2O_3). The lattice fringes are multi-directional and strain directions are different and multi-faceted in single particles which is likely a consequence of particle formation during rapid quench from the gas phase.

The highest zirconia content sample (79.4 mole % ZrO_2 in Al_2O_3) images show the formation of coreshell materials. This corroborates the XRDs of Fig. 2 indicating phase segregation between t-zirconia and δ alumina. Since Al_2O_3 has a lower vaporization temperature (3000 °C) than ZrO_2 (5155 °C) in LF-FSP, ZrO_2 should condense and nucleate first from the gas phase followed by Al_2O_3 . We assume that t-zirconia nanoparticles form first during quenching, then alumina nucleates on the t-zirconia nanoparticles forming the observed core-shell nanopowders in single step.

In the low zirconia content sample (4.1 mole% ZrO_2 in Al_2O_3), the lattice fringes are uniform. Combined with XRD, the co-existence of t-zirconia and δ -alumina is easily observed in the high ZrO_2 content sample, while δ -alumina dominates the low ZrO₂ content samples.

FT-IR studies

Once particle morphologies were characterized, a detailed picture of particle surface chemistries and thermal behavior was developed. These studies began with FTIR examination of the particle surfaces per Fig. 5.

All of the materials exhibit weak OH absorptions in the 3700-3000 cm⁻¹ region, attributable to surface hydroxyls arising from both physi- (3500-3000 cm⁻¹) and chemi-sorbed (3500-3700 cm⁻¹) water [26]. These bands are associated with the 1-4% mass losses seen at 400 °C in the TGA studies below.

From 1800 to 1400 cm⁻¹, peaks attributable to surface confined CO₂ and carbonates are observed as expected and in accord with those seen for pure δ -Al₂O₃ [27]. Bands in the 1000-400 cm⁻¹ region correspond to tetrahedrally coordinated vAl-O at 810 cm⁻¹ and octahedrally coordinated vAl-O at 610 cm⁻¹ [28]. vZr-O stretching vibrations are found at 700 cm⁻¹ [29].

TGA-DTA studies

Figure 6a shows mass loss events for as-processed $(ZrO_2)_x(Al_2O_3)_{1-x}$ composition nanopowders. All powders exhibit 1-4 wt% mass losses up to ≈ 400 °C. Much of this, up to ≈ 350 °C, is attributed to evolution of both



Fig. 5. FTIR spectra of $(ZrO_2)_x(Al_2O_3)_{1-x}$. 2.4ZrA denotes 2.4 mole % ZrO₂.



Fig. 6. (a) TGA of as-processed $(ZrO_2)_x(Al_2O_3)_{1-x}$ ramped at 10 °C/min/air. (b) DTA of as-processed $(ZrO_2)_x(Al_2O_3)_{1-x}$ ramped at 10 °C/min/air.

physi- and chemisorbed water from particle surfaces. Mass losses between 350° and $400 \,^{\circ}$ C are attributed to decomposition of the carbonate species.

The δ to α alumina phase transformation is observed as exotherms above 1300 °C in the DTA (Fig. 6b). Coincidentally we also see slight mass gains in the TGA (Fig. 6a) simultaneously, except for the 79.4 mol % ZrO₂ sample. The most reasonable explanation for these mass gains is oxidation of some unknown Zr^{2+/3+} species. However their appearance, especially at relatively low ZrO₂ contents, requires some discussion.

From the literature, the solubility of zirconia in δ alumina is less than 0.03 wt% [30-34], and zirconia is essentially insoluble in α -alumina [33, 34]. We presume that some Zr^{2+/3+} ions are produced during LF-FSP and form solid solutions perhaps as a spinel phase (ZrAl₂O₄) or some unknown form (e.g. ZrAlO₃). Similar observations were made for Ti aluminate in previous studies [35, 36]. We presume that these Zr^{2+/3+} ions segregate out during the δ to α alumina transformation and oxidize to ZrO₂. The maximum mass gain of 0.2 wt% is assumed to be oxygen as these Zr ions oxidize to ZrO₂.

In Table 3, we estimate the possible maximum amounts of $Zr^{2+/3+}$ ions from the mass gains. Here we assume that the Zr species formed during LF-FSP are all either Zr^{2+} or Zr^{3+} ions without mixed states. We assume that the dissolved Zr^{3+} ions form coincident with oxygen vacancies. From this study, we find that the amount of dissolved zirconia (assuming ZrO/Zr_2O_3 stoichiometries) is greater than the solubility limit of zirconia in δ alumina reported in the literature [30-34].

As with many of our previous studies, LF-FSP materials generated by rapid quenching lead to novel kinetic products not expected based on traditional processing methods that typically drive formation through thermodynamic assaults on particle mixtures. Since traditional processing methods lead to thermodynamically rather than kinetically defined phase compositions, these materials may offer unique opportunities for catalyst and fuel cell

Table 3. Possible maximum portions of dissolved $\mathrm{Zr}^{2+/3+}$ ions in $\delta\text{-alumina}.$

Sample	Mass gain	Possible maximum Zr^{2+*} (mol $\pm 0.1\%$)	$\begin{array}{c} Possible \\ maximum \ Zr^{3+ \ \dagger} \\ (mol \pm 0.1\%) \end{array}$
2.4 ZrA	0.07 wt %	0.4	0.6
4.1 ZrA	0.09 wt%	0.5	0.7
4.6 ZrA	0.14 wt%	0.9	1.4
5.9 ZrA	0.2 wt%	1.2	1.8
8.4 ZrA	0.2 wt%	1.2	1.8
13.6 ZrA	0.2 wt%	1.2	1.8
49.7 ZrA	0.2 wt%	1.3	2.0

 *Assumes all reduced species are Zr^{2+} (ZrO). $^{\dagger}Assumes$ all reduced species are Zr^{3+} (Zr_2O_3)

applications.

 Zr^{3+} in Al₂O₃ may also offer utility in photonic applications. For example, Ti³⁺ in an α -alumina (Ti³⁺ doped sapphire) is widely-used as a laser material [37-39]. The amount of Ti³⁺ dissolved in sapphire (α -alumina) commercial lasers is usually 0.05~1.0 wt %. For a Ti³⁺ ion substitutionally incorporated in an Al³⁺ lattice site, the degenerate 3d¹ electron energy level is split under the influence of the local crystal field [40]. As a result, an optical transition arises leading to strong electronphonon coupling that broadens the optical transition vibronically. Excitation to upper levels is characterized by strong absorption in the blue-green, and a radiative relaxation to the lower level gives rise to the broad fluorescence band that extends from 600 to 1050 nm [40, 41].

Since we find similar amounts of Zr^{3+} (assumed) dissolved in δ -alumina from our TGA-DTA studies and Ti^{3+}/Zr^{3+} ions have same valence electron configuration ([Ar]3d¹ for Ti³⁺ and [Kr]4d¹ for Zr³⁺), we may expect photonic properties for our Zr³⁺ in Al₂O₃.

Finally, the identification of a method of forming core-shell nanoparticles suggests multiple opportunities for novel processing of ZTA materials for forming duplex structures and for superplastic deformation [42, 43]. We plan to test this approach in the near future.

Conclusions

LF-FSP provides access to mixed-metal oxide nanopowders with exceptional control of stoichiometry and phase purity. Here we have succeeded in preparing nanopowders of any composition in ZrO_2 -Al₂O₃ tieline with specific surface area of $\approx 50 \text{ m}^2/\text{g}$ at rates of 100-300 g/ h.

Furthermore we have demonstrated access to coreshell nanoparticles in the $(ZrO_2)_x(Al_2O_3)_{1-x}$ system that may offer novel potential for processing dense, defect free ZTA composite materials.

Since LF-FSP enables rapid quenching of the combustion species, it offers access to new, kinetic materials not accessible by other conventional processing method. Thus, we were able to observe what appears to be the presence of of $Zr^{2+/3+}$ ions in Zr-Al-O binary system. These nanopowders may offer utility in photonic applications anticipated based on Ti doped sapphire lasers.

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