

## Enthalpies of Formation of Cerium Zirconate: (Ce,Zr)O<sub>2</sub> Fluorite and Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> Pyrochlore

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Zirconium-doped ceria, Zr<sub>x</sub>Ce<sub>1-x</sub>O<sub>2</sub>, with the fluorite (*Fm3m*) structure has many technologically important applications due to its refractory nature and high oxygen ion conductivity. When doped with transition metals such as Co, Cu, Ni or Mo, Zr-doped CeO<sub>2</sub> acts as a catalyst for the reduction of SO<sub>2</sub> by CO.<sup>1</sup> Zirconium doping has the effect of stabilizing smaller CeO<sub>2</sub> crystallite sizes (<10 nm) and increases the material's resistance to sintering.<sup>1</sup> The result is a higher reactive surface area. Ceria reduces at high temperatures with significant reduction reported at >700°C. When the cerium is reduced, the zirconium and cerium order, forming the fluorite derivative pyrochlore (*Fd3m*) structure.<sup>2</sup> Pyrochlore-structured titanate materials comprise three of the four end-members of the ceramic proposed for plutonium immobilization.<sup>3</sup> The substitution of zirconium for titanium has been shown to dramatically increase the radiation-damage resistance of REE-pyrochlore.<sup>4,5</sup> During heavy ion bombardment, REE-zirconate pyrochlore transforms to fluorite and then resists amorphization.<sup>4,5</sup> Despite the relative importance of these materials, virtually no durability data, chemical or thermal, exists for zirconia-ceria solid solutions. Therefore, a thermochemical investigation of (Ce,Zr)O<sub>2</sub> fluorite and Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore is warranted.

High-temperature oxide melt solution calorimetry was used to measure drop solution enthalpies of the cerium zirconate samples plus their binary oxide components.

The samples were prepared at ORNL and kept under vacuum in glass vials and handled for calorimetry in an Ar-filled glove box to prevent hydration. Two solvents were used in this study, 3Na<sub>2</sub>O•4MoO<sub>3</sub>, at 976 K and 2PbO•B<sub>2</sub>O<sub>3</sub> at 1078 K. Drop solution enthalpies,  $\Delta H_{ds}$ , were measured by dropping pellets ( $\approx 5$  mg) of the powdered samples from room temperature into the solvent at calorimeter temperature. Oxygen was bubbled through the melt to aid in the dissolution of the pellets and to provide high oxygen fugacity that ensured the oxidation of Ce<sup>3+</sup> to Ce<sup>4+</sup>. The measured values of drop solution enthalpies were used in the appropriate thermodynamic cycles to calculate the enthalpies of formation from the oxides.

The drop solution enthalpy for Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> in sodium molybdate at 976 K,  $\Delta H_{ds}$  (kJ/mol) =  $-33.9 \pm 1.5$ . This value is more endothermic than a trend of other REE-zirconate pyrochlore data would predict. This suggests that despite our best handling efforts, the sample was hydrated. Steps to dehydrate the pyrochlore are underway and new calorimetric data will be presented.

$\Delta H_{f-ox}$  (kJ/mol), at 298 K for (Ce,Zr)O<sub>2</sub> was derived using data collected in both sodium molybdate and lead borate solvents giving  $+15.2 \pm 1.7$  and  $+18.6 \pm 1.7$ , respectively. The slightly higher  $\Delta H_{f-ox}$  derived from lead borate data may be a result of the greater dissolution difficulties of Ce-containing materials. (Ce,Zr)O<sub>2</sub> is unstable in enthalpy with respect to an assemblage of its binary oxides. This is consistent with observations of zirconia segregation from (Ce,Zr)O<sub>2</sub> after heat treatment at 1,000°C for one hour.<sup>1</sup>

## REFERENCES

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