# Supporting Information

The XRD pattern of $Gd_2Zr_2O_7$ powder samples is presented in Fig. S1. Only cubic phase (*Fd3m* symmetry, PDF card 04-012-8000) was detected by XRD analysis in the heat treated sample.

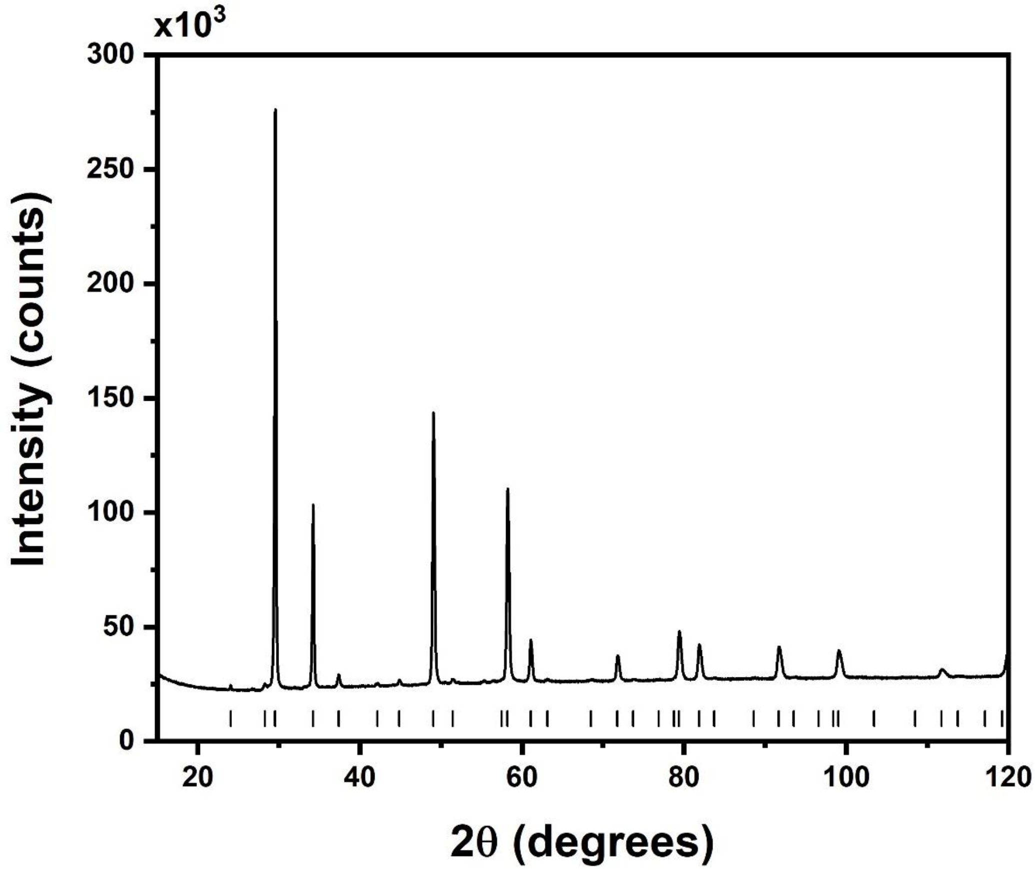


**Fig. S1** - X-ray diffraction pattern of $Gd_2Zr_2O_7$ powder sample powder sample. Tick marks below the patterns show the positions of allowed reflections.

Chemical composition of the $Gd_2Zr_2O_7$ powder sample is given in Table S1 was confirmed to be the same within the analytical uncertainties as the nominal composition (66.7 mol% $ZrO_2$ and 33.3 mol% $Gd_2O_3$).

| **Coating Material** | **Oxide content (mol%)*** | |
|---|---|---|
| | **$ZrO_2$** | **$Gd_2O_3$** |
| $Gd_2Zr_2O_7$ | 66.8(1) | 33.2(1) |

*Uncertainties of the contents are given in parentheses.

The thermochemical cycles used in the calculation of the enthalpies of formation of the coating materials shown in Table 6 are given below. Enthalpies of drop solution were taken from Table 3.

<u>$\Delta H°_{f,ox}$ of 7YSZ from drop solution calorimetry:</u>

| | Reaction | Enthalpy (kJ/mol) |
|---|---|---|
| 1 | xYSZ (25 °C) → $xY_2O_3$ + (1-x)$ZrO_2$ (1450 °C, CMAS) | 93.77 ± 1.96 |
| 2 | $Y_2O_3$ (25 °C, cubic) → $Y_2O_3$ (1450 °C, CMAS) | 169.35 ± 6.32 |
| 3 | $ZrO_2$ (25 °C, monoclinic) → $ZrO_2$ (1450 °C, CMAS) | 99.09 ± 2.63 |
| 4 | $xY_2O_3$ (25 °C) + (1-x)$ZrO_2$ (25 °C, monoclinic) → xYSZ (25 °C, cubic) | |

$$\Delta H_{f,ox} = \Delta H_4 = -\Delta H_1 + x\Delta H_2 + (1-x)\Delta H_3$$

$\Delta H_{f,ox}$ (7YSZ) = $\Delta H_4$ = (-93.77 ± 1.96) + 0.12*(0.5*169.35 ± 6.32) + 0.88*(99.09 ± 2.63) kJ/mol

$\Delta H_{f,ox}$ (7YSZ) = 3.59 ± 3.06 kJ/mol

$\Delta H°_{f,ox}$ of 7YSZ from previous study[36]:

$\Delta H°_{f,ox}$ (7YSZ, tetragonal) = $\Delta H°_{f,ox}$ (7YSZ, cubic) + $\Delta H°(7YSZ)_{cubic \rightarrow tetragonal}$

$\Delta H°_{f,ox}$ (7YSZ, tetragonal) ≈ $\Delta H°_{f,ox}$ (7YSZ, cubic) + $\Delta H°(ZrO_2)_{cubic \rightarrow tetragonal}$

$\Delta H°_{f,ox}$ (7YSZ, tetragonal) ≈ (1.37 ± 0.7) + (3.4 ± 3.1) kJ/mol

$\Delta H°_{f,ox}$ (7YSZ, tetragonal) ≈ 4.77 kJ/mol ± 3.18 kJ/mol

$\Delta H^\circ_{f,ox}$ of 31YSZ from drop solution calorimetry:

| | Reaction | Enthalpy (kJ/mol) |
|---|---|---|
| 1 | xYSZ (25 °C) → $xY_2O_3$ + (1-x)$ZrO_2$ (1450 °C, CMAS) | 91.29 ± 5.18 |
| 2 | $Y_2O_3$ (25 °C, cubic) → $Y_2O_3$ (1450 °C, CMAS) | 169.35 ± 6.32 |
| 3 | $ZrO_2$ (25 °C, monoclinic) → $ZrO_2$ (1450 °C, CMAS) | 99.09 ± 2.63 |
| 4 | $xY_2O_3$ (25 °C) + (1-x)$ZrO_2$ (25 °C, monoclinic) → xYSZ (25 °C, cubic) | |

$$\Delta H_{f,ox} = \Delta H_4 = -\Delta H_1 + x\Delta H_2 + (1-x)\Delta H_3$$

$\Delta H_{f,ox}$ (31YSZ) = $\Delta H_4$ = (-91.29 ± 5.18) + 0.12*(0.5*169.35 ± 6.32) + 0.88*(99.09 ± 2.63) kJ/mol

$\Delta H^\circ_{f,ox}$ (31YSZ) = 1.02 ± 5.86 kJ/mol

$\Delta H^\circ_{f,ox}$ of $Y_2Si_2O_7$ from drop solution calorimetry:

| | Reaction | Enthalpy (kJ/mol) |
|---|---|---|
| 1 | $SiO_2$ (25 °C, quartz) → $SiO_2$ (1450 °C, CMAS) | 87.17 ± 4.02 |
| 2 | $Y_2O_3$ (25 °C, cubic) → $Y_2O_3$ (1450 °C, CMAS) | 169.35 ± 6.32 |
| 3 | $Y_2Si_2O_7$ (25 °C, crystal) → $Y_2O_3$ (1450 °C, CMAS) + 2$SiO_2$ (1450 °C, CMAS) | 453.94 ± 10.57 |
| 4 | $Y_2O_3$ (25 °C, cubic) + 2$SiO_2$ (25 °C, α-quartz) → $Y_2Si_2O_7$ (25 °C, crystal) | |

$$\Delta H^\circ_{f,ox} = \Delta H_4 = -\Delta H_3 + \Delta H_2 + 2\Delta H_1$$

$\Delta H^\circ_{f,ox}$ ($Y_2Si_2O_7$) = (-453.94 ± 10.57) + (169.35 ± 6.32) + 2 * (87.17 ± 4.02)

$\Delta H^\circ_{f,ox}$ ($Y_2Si_2O_7$) = -110.25 ± 14.71 kJ/mol

$\Delta H^\circ_{f,ox}$ of $Gd_2Zr_2O_7$ from drop solution calorimetry:

| | Reaction | Enthalpy (kJ/mol) |
|---|---|---|
| 1 | $Gd_2Zr_2O_7$ (25 °C) → $Gd_2Zr_2O_7$ (1450 °C, CMAS) | 357.07 ± 6.08 |
| 2 | $Gd_2O_3$ (25 °C, cubic) → $Gd_2O_3$ (1450 °C, CMAS) | 120.41 ± 5.84 |
| 3 | $ZrO_2$ (25 °C, monoclinic) → $ZrO_2$ (1450 °C, CMAS) | 99.09 ± 2.63 |
| 4 | $Gd_2O_3$ (25 °C, cubic) + $2ZrO_2$ (25 °C, monoclinic) → $Gd_2Zr_2O_7$ (25 °C) | |

$$\Delta H^\circ_{f,ox} = \Delta H_4 = -\Delta H_1 + \Delta H_2 + 2\Delta H_3$$

$$\Delta H^\circ_{f,ox} = (-357.07 \pm 6.08) + (120.41 \pm 5.84) + (2 * 99.09 \pm 2.63) \text{ kJ/mol}$$

$$\Delta H^\circ_{f,ox} = -38.48 \pm 9.93 \text{ kJ/mol}$$

$\Delta H^\circ_{f,ox}$ of 16RESZ from drop solution calorimetry:

| | Reaction | Enthalpy (kJ/mol) |
|---|---|---|
| 1 | $ZrO_2$ (25 °C, monoclinic) → $ZrO_2$ (1450 °C, CMAS) | 99.09 ± 2.63 |
| 2 | $Y_2O_3$ (25 °C, cubic) → $Y_2O_3$ (1450 °C, CMAS) | 169.35 ± 6.32 |
| 3 | $Gd_2O_3$ (25 °C, cubic) → $Gd_2O_3$ (1450 °C, CMAS) | 120.41 ± 5.84 |
| 4 | $Yb_2O_3$ (25 °C, cubic) → $Yb_2O_3$ (1450 °C, CMAS) | 190.03 ± 9.63 |
| 5 | 16RESZ (25 °C, cubic) → 16RESZ (1450 °C, CMAS) | 94.28 ± 2.65 |
| 6 | $xZrO_2 + yY_2O_3 + zGd_2O_3 + wYb_2O_3$ (all 25 °C) → 16RESZ (25 °C, cubic) | |

$$\Delta H^\circ_{f,ox} \text{ (16RESZ)} = \Delta H_6 = - \Delta H_5 + w\Delta H_4 + z\Delta H_3 + y\Delta H_2 + x\Delta H_1$$

$$\Delta H^\circ_{f,ox} \text{ (16RESZ)} = -(94.28 \pm 2.65) + 0.5 * [0.045 * (190.03 \pm 9.63) + 0.056 * (120.41 \pm 5.84) + 0.172 * (169.35 \pm 6.32) + 0.73 * (99.09 \pm 2.63)$$

$$\Delta H^\circ_{f,ox} = 18.20 \pm 3.47 \text{ kJ/mol}$$