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Short communication

# Thermodynamic stability and hydration enthalpy of strontium cerate doped with yttrium

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**Abstract**

The standard molar enthalpy of formation of $SrY_{0.05}Ce_{0.95}O_{2.975}$ has been derived by combining the enthalpy of solution in 1 M HCl + 0.1 KI with auxiliary literature data, $\Delta_f H^\circ$ ($SrY_{0.05}Ce_{0.95}O_{2.975}$, s, 298.15 K) = −1720.4 ± 3.4 kJ/mol. The formation enthalpy of $SrY_{0.05}Ce_{0.95}O_{2.975}$ from the mixture of binary oxides is $\Delta_{ox}H^\circ$ (298.15 K) = −45.9 ± 3.4 kJ/mol and the enthalpy of reaction of $SrY_{0.05}Ce_{0.95}O_{2.975}$ with water forming $Sr(OH)_2$, $CeO_2$, and $Y_2O_3$ is $\Delta_r H^\circ$ (298.15 K) = −85.5 ± 3.4 kJ/mol. Our data and the entropies of different substances show that $SrY_{0.05}Ce_{0.95}O_{2.975}$ is thermodynamically stable with respect to a mixture of SrO, $Y_2O_3$, $CeO_2$ and that the reaction of $SrY_{0.05}Ce_{0.95}O_{2.975}$ with water is thermodynamically favourable.

*Keywords:* Calorimetry; Thermodynamic stability; Hydration enthalpy

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## 1. Introduction

Proton conductors based on alkaline-earth (barium or strontium) cerates are of considerable interest for application in hydrogen sensors, electrocatalytic reactors, steam electrolyzers, and as electrolytes in fuel cells [1]. The substituted solid solutions based on the perovskite oxides $MCeO_3$ (M = Ba, Sr), in which RE replaces Ce, is a typical example of this class of materials. The general formula is written as $BaCe_{1-x}RE_xO_{3-x/2}$, where RE is a rare earth element.

Solid oxide fuel cells typically operate at 1273 K [1,2]. There is considerable emphasis on moving to lower temperature of operation in the next generation of fuel cells. Doped barium cerates achieve this target around 873 K. Operation at lower temperature potentially offers reduced materials and process costs and increased thermodynamic efficiency, provided the necessary solid electrolyte and electrodes can be developed. A highly attractive alternative may be to use proton conducting electrolytes such as the perovskite $BaCeO_3$ (or $SrCeO_3$) instead of doped zirconium oxide to provide good ionic conductivity in the temperature range of 773–1023 K. In order to use these alternative electrolytes systems, it is necessary to perform detailed physico-chemical study of employed compounds. There are no data on thermodynamics of $SrCe_{1-x}Y_xO_{3-x/2}$ solid solutions in literature.

The objective of this work was to measure formation enthalpy of $SrCe_{1-x}Y_xO_{3-x/2}$ and to study the thermodynamic stability and hydration enthalpy.

## 2. Experimental

$SrY_{0.05}Ce_{0.95}O_{2.975}$(s) was prepared by solid state synthesis by heating stoichiometric amounts of dried $CeO_2$(s), $SrCO_3$(s), $Y_2O_3$(s) (Cerac, mass fractions of compounds are more than 0.9999). Stoichiometric mixtures were mixed and milled in a planetary mill with agate balls during 12 h with intermediate regrinding. Then the powders were pressed into pellets with a diameter of 10 mm and calcinated at 1273 K during 70 h. X-ray analysis showed that these conditions were not sufficient to prepare phase pure $SrCe_{0.95}Y_{0.05}O_{2.975}$. The samples consisted of a mixture of $CeO_2$ and $SrCe_{0.95}Y_{0.05}O_{2.975}$. Therefore after regrinding a second sintering was carried out at 1573 K during 17 h. A final sintering at 1773 K during 40 h resulted in a phase pure $SrCe_{0.95}Y_{0.05}O_{2.975}$ sample. The compound was

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Table 1
Reaction scheme to obtain the standard molar enthalpy of formation of $SrY_{0.05}Ce_{0.95}O_{2.975}$ at 298.15 K

| No. | Reaction | $\Delta_{sol}H^\circ_m$ ($kJ\,mol^{-1}$) | Ref. |
|---|---|---|---|
| 1 | $SrY_{0.05}Ce_{0.95}O_{2.975}(s) + (5.95\ HCl + 0.95\ KI)_{sol} = (SrCl_2 + 0.05YCl_3 + 0.95CeCl_3 + 0.95KCl + 0.475I_2 + 2.975\ H_2O)_{(sol)}$ | −323.9 ± 3.1 | This work |
| 2 | $SrCl_2(s) + 0.05YCl_3(s) + 0.95CeCl_3(s) + \text{solution } 1 = (SrCl_2(s) + 0.05YCl_3(s) + 0.95CeCl_3)_{(sol)}$ | −181.32 ± 0.55 | [7] |
| 3 | $2.975H_2(g) + 1.4875O_2(g) + \text{solution } 1 = 2.975H_2O_{(sol)}$ | −850.37 ± 0.13 | [8] |
| 4 | $0.95KI(s) + \text{solution } 1 = 0.95KI_{(sol)}$ | +19.79 ± 0.33 | [7] |
| 5 | $0.95K(s) + 0.475I_2(s) = 0.95KI_{(sol)}$ | −312.69 ± 0.13 | [9] |
| 6 | $0.475I_2(s) + \text{solution } 1 = 0.475I_{2(sol)}$ | +2.65 ± 0.48 | [7] |
| 7 | $0.95KCl(s) + \text{solution } 1 = 0.95KCl_{(sol)}$ | +17.11 ± 0.05 | [9] |
| 8 | $0.95K(s) + 0.475Cl_2(g) = 0.95KCl(s)$ | −414.64 ± 0.12 | [9] |
| 9 | $2.975H_2(g) + 2.975Cl_2(g) + \text{solution } 1 = 5.95HCl_{(sol)}$ | −977.94 ± 0.06 | [8] |
| 10 | $Sr(s) + Cl_2(g) = SrCl_2(s)$ | −832.43 ± 0.85 | [10] |
| 11 | $0.95Ce(s) + 1.425Cl_2(g) = 0.95CeCl_3(s)$ | −1007.51 ± 0.50 | [11] |
| 12 | $0.05Y(s) + 0.075Cl_2(g) = 0.05YCl_3(s)$ | −48.68 ± 0.15 | [11] |
| 13 | $Sr(s) + 0.05Y(s) + 0.95Ce(s) + 1.4875O_2(g) = SrY_{0.05}Ce_{0.95}O_{2.975}(s)$ | −1720.45 ± 3.36 | This work |

Solution 1 is a solution of 1 M HCl with 0.1 M KI; s: solid; g: gas; $\Delta_{sol}H^\circ_m$: the molar enthalpy of solution.

characterized by X-ray powder diffraction and chemical analysis [3]. According to the results of the analyses, the compound was found to be single phase with an accuracy of about 1%.

Solution calorimetry was performed in a calorimeter described elsewhere [4,5]. The volume of the calorimetric vessel was 200 ml. The reproducibility of the heat equivalent of the calorimeter with an automatic calibration system was 0.03%. To check the precision of the calorimeter, dissolution of a standard substance, potassium chloride, was performed. The obtained dissolution heat of KC1 (17.529 + 0.009 kJ/mol) was found to be in a good agreement with the value recommended in the literature (17.524 + 0.007 kJ/mol) [6]. The amounts of substances used were 0.05–0.1 g.

Thermodynamic cycles were designed in such a way that it was possible to determine the formation enthalpy of $SrY_{0.05}Ce_{0.95}O_{2.975}$ on the basis of measured and literature reference data [7–11]. A solution of 1 M HCl with 0.1 M KI was the solvent. KI was added to account for the reduction of $Ce^{4+}$ to $Ce^{3+}$. The thermochemical cycle, from which the enthalpy of formation of $SrY_{0.05}Ce_{0.95}O_{2.975}$ was derived, was given in Table 1.

## 3. Results

The dissolution enthalpy of $SrY_{0.05}Ce_{0.95}O_{2.975}$ in 1 M HCl with 0.1 M KI, $\Delta_{sol}H^\circ$ ($SrY_{0.05}Ce_{0.95}O_{2.975}$, 298.15 K) = −323.9 ± 3.1 kJ/mol is the average of six calorimetric experiments. Errors were calculated for the 95% confidence interval using the Student's coefficient.

Other solution enthalpies, which were necessary to calculate the enthalpy of formation of $SrY_{0.05}Ce_{0.95}O_3$, were taken from literature references (Table 1).

After combining all reactions, we obtain: $\Delta_f H^\circ$ ($SrY_{0.05}Ce_{0.95}O_{2.975}$, s, 298.15 K) = −1720.45 ± 3.36 kJ/mol.

On the basis of formation enthalpy of $SrY_{0.05}Ce_{0.95}O_{2.975}$ obtained by us and literature data for formation enthalpies of SrO (−591.0 kJ/mol), $CeO_2$ (−1090.4 kJ/mol), $Y_2O_3$ (−1905.0 kJ/mol) [12], we calculated the enthalpies of formation of $SrY_{0.05}Ce_{0.95}O_{2.975}$ from binary oxides

$$SrO(s) + 0.95CeO_2(s) + 0.025Y_2O_3(s) = SrCe_{0.95}Y_{0.05}O_{2.975}(s)$$

$$\Delta_{ox}H^\circ(298.15\,K) = -45.9 \pm 3.4\,kJ/mol$$

These data and entropies of all the substances employed in above reactions allow us to conclude that the formation of $SrCe_{0.95}Y_{0.05}O_{2.975}$ from the oxides is thermodynamically favourable at room temperature.

Using our experimental data for $\Delta_f H^\circ$ ($SrCe_{0.95}Y_{0.05}O_{2.975}$, s), literature data for $\Delta_f H^\circ$($CeO_2$, s), $\Delta_f H^\circ$($Y_2O_3$, s), and formation enthalpies for $Sr(OH)_2$ (−964.3 kJ/mol), $H_2O$ (−241.9 kJ/mol) [12], it is possible to obtain the hydration enthalpy of $SrCe_{0.95}Y_{0.05}O_3$.

$$SrY_{0.05}Ce_{0.95}O_{2.975}(s) + H_2O(g) = Sr(OH)_2(s) + 0.95CeO_2(s) + 0.025Y_2O_3(s)$$

$$\Delta_r H^\circ(298.15\,K) = -85.5 \pm 3.4\,kJ/mol$$

The value of enthalpy of the above reaction and literature data on the entropies of $SrY_{0.05}Ce_{0.95}O_{2.975}(s)$, $H_2O(g)$, $Sr(OH)_2(s)$, $CeO_2(s)$, $Y_2O_3(s)$ allow us to conclude that the reaction of $SrY_{0.05}Ce_{0.95}O_{2.975}(s)$ with water is thermodynamically favourable. The hydration enthalpy is a very important value for the understanding of fundamental aspects of the application of electrolytes in fuel cells [1]. The high value of hydration obtained by us allows one to assume that $SrY_{0.05}Ce_{0.95}O_{2.975}$ will have high transport properties.

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