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On the thermodynamic stability of (Eu,Y)-doped barium cerate

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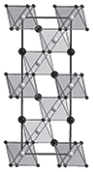
It has been experimentally established that the phase of $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ is thermodynamically stable in respect to decomposition into binary oxides.



$BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ is thermodynamically stable

The barium and strontium cerates substituted by rare-earth and other elements are good candidates for solid oxide fuel cell (SOFC) electrolytes.[1–10] A thermodynamic study of the systems should be performed to optimize the synthesis conditions of doped barium cerates.[5] Among materials of the general formula $BaCe_{1-x}R_xO_{3-d}$, compounds with R = Y, Gd possess the highest ionic conductivity.[3] However, the homogeneity field of the above compounds is limited to 20%.[4,7,10] Barium cerates doped by ZrO_2 have higher thermal stability but lower ionic conductivity.[3]

Barium cerates doped by rare earth elements are of fundamental interest to study thermodynamic characteristics of mixed oxides. It was found[10–12] that the doping of barium cerate with indium oxide results in the broadening of homogeneity range with growing thermodynamic stability. Barium cerates co-doped by indium and rare earth elements were synthesized.[11,12] However, the addition of indium decreased the conductivity of cerates. For this reason, we decided to use a strategy of co-doping by rare earth elements and yttrium. We synthesized and characterized the compound $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$. Its energetic characteristics (standard formation enthalpy, reaction enthalpy and stabilization enthalpy)[13] were obtained using solution calorimetry.

The main thermochemical reactions are the following:

$$BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}(s) + (5.7\,HCl + 1.05\,KI)(sol) + (sol\ in\ 'A') = (BaCl_2 + 0.7\,CeCl_3 + 0.1\,YCl_3 + 0.2\,EuCl_3 + 0.7\,KCl + 0.35\,KI_3 + 2.85\,H_2O)(sol) + \Delta_{sol}H_1^0 \quad (1)$$

$$BaCl_2(s) + 0.7\,CeCl_3(s) + 0.1\,YCl_3(s) + 0.2\,EuCl_3(s) + (sol\ in\ 'A') = (BaCl_2 + 0.7\,CeCl_3 + 0.1\,YCl_3 + 0.2\,EuCl_3)(sol) + \Delta_{sol}H_2^0 \quad (2)$$

Here, solvent 'A' stands for $(1\ M\ HCl\ with\ 0.1\ M\ KI)_{aq}$.

By combining the above reactions, we obtained

$$BaCl_2(s) + 0.7\,CeCl_3(s) + 0.1\,YCl_3(s) + 0.2\,EuCl_3(s) + (0.7\,KCl + 0.35\,KI_3 + 2.85\,H_2O)(sol) = BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}(s) + (5.7\,HCl + 1.05\,KI)(sol) + \Delta_rH_3^0, \quad (3)$$

where $\Delta_rH_3^0 = -\Delta_{sol}H_1^0 + \Delta_{sol}H_2^0$.

In order to perform this cycle, we used the following test samples: $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$, $BaCl_2$, $CeCl_3$, YCl_3 and $EuCl_3$.[†]

The phase purity and identity of $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ were confirmed by X-ray powder diffraction. Lattice parameters were calculated using the FullProff-2015 program. The sample had an orthorhombic structure (space group *Pnma*) with the lattice parameters $a = 0.883248$, $b = 0.621641$ and $c = 0.620963$ nm.

The solution enthalpies were determined in solution calorimetry with isothermal jacket as described in detail elsewhere.[13] The measured dissolution enthalpy of KCl was 17.41 ± 0.08 kJ mol^{-1} (the molality of the final solution was 0.028 mol kg^{-1}, T = = 298.15 K). The resulting dissolution heat of potassium chloride was compared with the published value.[12,13]

The amounts of $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ and the mixture of chlorides used in calorimetric experiments were about 0.04 and 0.06 g, respectively (the solvent volume was 0.25 dm^3).

The solution enthalpies were $\Delta_{sol}H_1^0 = -371.51 \pm 1.33$ kJ mol^{-1} ($n = 5$) for $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$, $\Delta_{sol}H_2^0 = -153.90 \pm 1.18$ kJ mol^{-1} ($n = 5$) for a mixture of $BaCl_2 + 0.7\,CeCl_3 + 0.1\,YCl_3 + 0.2\,EuCl_3$. The uncertainty was determined using the formula $\sigma = (\sum\sigma_i^2)^{1/2}$, where σ_i are the uncertainties in intermediate values.

The solution enthalpies $\Delta_{sol}H_1^0$ and $\Delta_{sol}H_2^0$ allowed us to calculate the enthalpy of reaction (3) $\Delta_rH_1^0 = -\Delta_{sol}H_1^0 + \Delta_{sol}H_2^0 = = 217.61 \pm 1.78$ kJ mol^{-1}.

[†] $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ was synthesized from barium carbonate (> 99%, Merck), cerium(IV) oxide (99.99%, Alfa Products), yttrium oxide (99.99%, ChemPur) and europium oxide (99.99%, Alfa Aesar), which were ground using a planetary mill (Fritsch pulverisette), pelletized and calcined at 1100–1700 K in a Carbolite furnace.

Anhydrous $BaCl_2$ was prepared by drying $BaCl_2$ (Cerac, 99.9%) in argon at about 500 K. $CeCl_3$ from Cerac (0.999) was purified by vacuum sublimation to remove a lanthanide oxychloride impurity. Y_2O_3 (99.99%, ChemPur) was dissolved in hydrochloric acid. Purified chlorine gas was bubbled through the solutions. Solution was evaporated. Further drying was accomplished by evaporating *in vacuo* at ~350 K until the remaining chloride crystals appeared. Final drying was accomplished by slow heating in a hydrogen chloride atmosphere to 600–700 K. The anhydrous europium chloride ($EuCl_3$) was prepared from $EuCl_3$ (Aldrich, 99.9%) at 723 K *in vacuo*. All manipulations were performed in a dry box (pure Ar gas).

X-ray powder diffraction was performed with a Stoe Stadi-P diffractometer (Mo radiation). An ARL Advant'XP sequential X-ray fluorescence spectrometer was also used to analyze the samples.

For the analysis of Ce, Eu, Y a spectrophotometric method was used. Ba was determined by flame photometry. The oxygen content was determined by reducing melting. Impurities were determined by mass spectrometry. The results showed that phases were pure with an accuracy of 1%.

Apparently, data on standard formation enthalpies for solid barium, cerium, yttrium and europium chlorides[14] are needed to calculate that of $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$(s) using enthalpy of reaction (3). In addition, data on the formation enthalpies of KCl(sol), KI_3(sol), H_2O(sol), HCl(sol) and KI(sol) are necessary.[14,15] Based on enthalpy of reaction (3) and literature data, the standard formation enthalpy for $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$(s) was calculated as follows:

$$Ba(s) + 0.1Y(s) + 0.2\,Eu(s) + 0.7\,Ce(s) + 1.425\,O_2(g) = \\ = BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}(s) + \Delta_f H^0 \quad (4)$$

Here, $\Delta_f H^0 = -1619.00 \pm 3.29$ kJ mol^{-1} is standard formation enthalpy of barium cerate doped by yttrium and europium oxides. It was of interest to determine the stabilization enthalpy ($\Delta_{st}H$) of obtained oxides according to the formula

$$\Delta_{st}H = \Delta_f H^0(BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}) - \Delta_f H^0(BaO) - \\ - 0.7\Delta_f H^0(CeO_2) - 0.05\Delta_f H^0(Y_2O_3) - 0.1\Delta_f H^0(Eu_2O_3) = \\ = -46.23 \pm 3.69 \text{ kJ mol}^{-1}.$$

Thus, the compound $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ is thermodynamically stable.

Then, we calculated the enthalpy of the reaction

$$BaCO_3 + 0.05Y_2O_3 + 0.1Eu_2O_3 + 0.7\,CeO_2 = \\ = BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85} + CO_2, \quad (5)$$

which was used to synthesize barium cerate co-doped by yttrium and europium oxides. The enthalpy of reaction (5) is 226.23 ± 3.69 kJ mol^{-1}. Using this value, we determined the synthesis temperature of 1303 K for $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ from the formula $\Delta G = \Delta H - T\Delta S$.

Using the Gibbs free energy from binary oxides for $BaCe_{0.8}Nd_{0.2}O_{2.9}$ and $BaCe_{0.8}Lu_{0.2}O_{2.9}$,[16] we estimated the Gibbs free energy of $BaCe_{0.8}Eu_{0.2}O_{2.9}$ $\Delta_{ox}G^0 = -39.2$ kJ mol^{-1} at 298.15 K. Comparing this value with $\Delta_{ox}G^0$ for $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ (–49.27 kJ mol^{-1}), we found that yttrium additives to $BaCe_{0.8}Eu_{0.2}O_{2.9}$ increased the thermodynamic stability.

Thus, we have synthesized $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ by a solid state reaction. For the first time, its solution enthalpy in 1 M HCl with 0.1 M KI and the solution enthalpy of a mixture of $BaCl_2$ + $0.7\,CeCl_3$ + $0.1YCl_3$ + $0.2\,EuCl_3$ have been measured. We have found that $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ is thermodynamically stable in respect to decomposition to binary oxides. The demonstrated increase in homogeneity field for $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ up to 30% is very important for applications of cerate compounds in fuel cells, selective membranes, electrocatalysis, *etc*. The obtained thermodynamic data for $BaCe_{0.7}Y_{0.1}Eu_{0.2}O_{2.85}$ give new insight into synthetic pathways to these technologically important materials.

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