

Preparation, Stability and Thermodynamic Properties of Nd- and Lu-Doped BaCeO₃ Proton-Conducting Ceramics

Nata I. Matskevich,^[a] Thomas Wolf,^[b] Mariya Yu. Matskevich,^{*[a]} and Tatiana I. Chupakhina^[c]

Keywords: Ceramics / Rare earths / Calorimetry / Thermodynamics / Solid-state reactions

The preparation of BaCeO₃ doped by neodymium and lutetium oxides (BaCe_{0.8}Nd_{0.2}O_{2.9}, BaCe_{0.8}Lu_{0.2}O_{2.9}) has been performed by solid-state reactions of BaCO₃ and CeO₂ with Nd₂O₃ and Lu₂O₃, respectively. The compound BaCe_{0.8}Lu_{0.2}O_{2.9} has been synthesized for the first time. The X-ray measurements have showed that BaCe_{0.8}RE_{0.2}O_{2.9} (RE = Nd, Lu) has an orthorhombic structure (space group *Pnma*). The standard formation enthalpies of BaCe_{0.8}RE_{0.2}O_{2.9} have been determined from solution calorimetry by combining the solution enthalpies of BaCe_{0.8}RE_{0.2}O_{2.9}, a BaCl₂ + 0.8CeCl₃ + 0.2RECl₃ mixture in 1 M HCl with 0.1 M KI at 298.15 K and

literature data. It has been determined that both of the above-mentioned complex oxides are thermodynamically stable with regard to their decomposition into binary oxides at room temperature. It has been established that BaCe_{0.8}Nd_{0.2}O_{2.9} and BaCe_{0.8}Lu_{0.2}O_{2.9} react with water, Al₂O₃ and ZrO₂ at ambient temperatures. It has also been shown that the reactions with Al₂O₃, ZrO₂ and water for BaCe_{0.8}Nd_{0.2}O_{2.9} are more thermodynamically favoured than those for BaCe_{0.8}Lu_{0.2}O_{2.9}.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2009)

Introduction

At present the interest in perovskite-type solid solutions based on alkaline earth cerates is large.^[1–10] Rare-earth-doped barium cerates with high protonic conductivity have a wide range of technological applications in fuel cells, sensors, batteries, electro catalysis devices, etc. The investigation of proton conductivity in perovskite ceramics started more than 20 years ago. A number of reports were published with regard to the conduction of BaCeO₃-based oxides. Neodymium-doped barium cerates are believed to be the most conductive electrolytes.

However, there is still a lack of studies on other properties of these materials. In particular, the thermodynamics of BaCe_{1-x}RE_xO_{3-δ} compounds has been little studied. The stabilities of these phases, in particular thermodynamic stability, are interesting and important^[1] in order to underpin further practical applications. The thermodynamic stability of complex oxides may have an impact on the mechanical stability of the microstructure of corresponding ceramics.

Thermodynamics may be useful in other aspects as well. In some cases it is possible to see the direction in which functional properties change on the basis of correlations between thermodynamic and conductivity properties. However, there are no thermodynamic values for compounds in the systems BaO–CeO₂–RE₂O₃. There are only formation enthalpies, heat capacities and entropies for BaCeO₃, measured by authors.^[6–9] Thermodynamic properties linked to structural characteristics have been used to develop systematic structure-stability relationships for solid solutions of BaCe_{1-x}RE_xO_{3-δ}.

This paper is part of our wide investigations devoted to the synthesis and study of the thermodynamics of compounds in the BaO–CeO₂–RE₂O₃ systems. The aim is to prepare known and unknown doped BaCeO₃ to investigate the thermochemistry of BaCe_{1-x}Nd_xO_{3-δ} and BaCe_{1-x}Lu_xO_{3-δ} solid solutions and to compare the stability and thermodynamic values of these compounds.

Results and Discussion

In the present study we report on the preparation of BaCeO₃ doped by neodymium and lutetium oxides (BaCe_{0.8}Nd_{0.2}O_{2.9}, BaCe_{0.8}Lu_{0.2}O_{2.9}) and their thermochemical properties. The compound BaCe_{0.8}Lu_{0.2}O_{2.9} has been synthesized for the first time.

Previously, we used the expensive technique from Karlsruhe Research Center that enables one to prepare different complex oxides of high quality.^[11–13]

[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Science, Lavrentiev Prospect, 3, Novosibirsk, 630090, Russia
Fax: +7-383-3306449
E-mail: nata@che.nsk.su

[b] Karlsruhe Research Center GmbH, Institute of Solid State Physics, Hermann-von-Helmholtz-Platz 1, Karlsruhe, 76334, Germany

[c] Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Science, Pervomaiskaya Street, 91, Ekaterinburg, Russia

Phase purity and identity of $\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$ and $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$ were confirmed by X-ray powder diffraction (XRD) using a STADI-P, Stoe diffractometer, Germany, $\text{Cu-K}\alpha_1$ and ARL ADVANT'XP sequential X-ray Fluorescence Spectrometer. The samples were shown to be phase-pure ceramics with an orthorhombic structure (space group $Pnma$). The refined cell parameters obtained for $\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$ are $a = 6.222(2) \text{ \AA}$, $b = 8.791(1) \text{ \AA}$ and $c = 6.224(2) \text{ \AA}$ and for $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$ are $a = 6.181(2) \text{ \AA}$, $b = 8.855(1) \text{ \AA}$ and $c = 6.183(2) \text{ \AA}$. The powder pattern and cell parameters of $\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$ agree well with the patterns known for this phase from the literature.^[14,15] The powder X-ray diffraction pattern of barium cerate doped by lutetium oxide is presented in Figure 1.

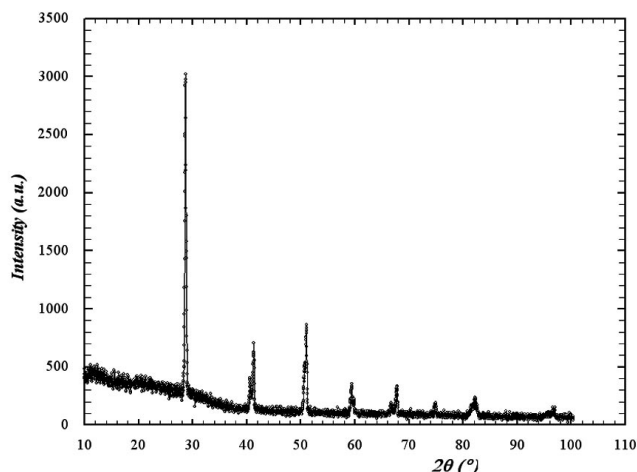


Figure 1. Powder X-ray diffractogram of $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$.

All compounds were also characterized by chemical analysis.^[16,17] Analytical results are presented in Table 1. For the analysis of Nd, Ce and Lu a spectrophotometric method (spectrophotometer SF-46) was used. Ba was determined by flame photometry (air-acetylene, Hitachi Z-8000). The content of impurities was determined by spectral methods (mass-spectrometer "Element", Finnigan Mat, Germany). The analyses indicated that impurities of Ho, Dy, Eu, Yb, La, Tm, Er, Pr, Sm, Te, Ca, Mg, Mn, Pb and Ag metals were present at the level of 10^{-3} – 10^{-4} at.%. The oxygen contents were determined by iodometric titrations using $0.01 \text{ M Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ according to the method described in the literature.^[18] The results of the chemical analysis for $\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$ and $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$ allow us to conclude that these phases have the following compositions: $\text{BaCe}_{0.81 \pm 0.03}\text{Nd}_{0.19 \pm 0.02}\text{O}_{2.92 \pm 0.03}$, $\text{BaCe}_{0.78 \pm 0.03}\text{Lu}_{0.18 \pm 0.02}\text{O}_{2.89 \pm 0.03}$.

Table 1. Analytical results.

Compound	Found (%)	Calculated (%)
CeCl_3	Ce, 56.81 ± 0.04	Ce, 56.85
BaCl_2	Ba, 65.93 ± 0.05	Ba, 65.95
NdCl_3	Nd, 57.52 ± 0.05	Nd, 57.56
LuCl_3	Lu, 61.13 ± 0.07	Lu, 61.19%

The solution calorimetric experiments were carried out in an automatic calorimeter with an isothermal jacket. The calorimeter consists of a Dewar vessel with a brass cover ($V = 200 \text{ mL}$). The platinum resistance thermometer, calibration heater, cooler, mixer and device to break the ampoules were mounted on the lid of the Dewar vessel. The construction of the solution calorimeter and the experimental procedure are described elsewhere.^[12,17] The resistance of the platinum resistance thermometer was measured with a high precision voltmeter Solartron 7061. The voltmeter was connected to the computer through an interface and the program was written in Matlab^[19] at our laboratory. The program allows one to measure and record the temperature of the vessel, calibrate the instrument with precise injections of electrical energy and calculate calorimeter constants and enthalpies. The calorimetric vessel was maintained at 298.15 K with a temperature drift of less than $0.0003 \text{ }^\circ\text{C}$ for 10 h. Dissolution of potassium chloride in water was performed to calibrate the calorimeter. The obtained dissolution heat of KCl was $17.41 \pm 0.08 \text{ kJ mol}^{-1}$ (the molality of the final solution was $0.028 \text{ mol kg}^{-1}$, $T = 298.15 \text{ K}$). The literature data are: $17.42 \pm 0.02 \text{ kJ mol}^{-1}$,^[20] $17.47 \pm 0.07 \text{ kJ mol}^{-1}$.^[21]

The amount of substance used ($\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$, $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$) was about 0.08 g for each compound. All compounds were stored in a dry box to prevent interaction with moisture or CO_2 .

In general, three techniques are used to determine the enthalpy of formation at 298.15 K of metal cerates: solution calorimetry, e.m.f. measurements and mass spectrometric Knudsen cell measurements.^[6–9] In our paper we used solution calorimetry as an investigation method. HCl (1 M) along with KI (0.1 M) was chosen as the solvent. KI was added to reduce Ce^{+4} to Ce^{+3} .

$\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$

The derivation of the enthalpy of formation of $\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$ was done by using the following scheme of thermochemical reactions (Table 2). The principal scheme is based on the dissolution of barium cerate doped by neodymium oxide as well as the mixture of barium chloride, cerium chloride and neodymium chloride in hydrochloric acid [$\text{HCl}(\text{sol})$] with KI. The molar concentration of metal chlorides was the same as in the literature.^[6] A mixture of BaCl_2 , CeCl_3 and NdCl_3 was prepared in a ratio of 1:0.8:0.2.

$\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$

In order to determine the formation enthalpy of barium cerate doped by lutetium oxide we chose a thermochemical cycle in which we dissolved $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$ and a mixture of BaCl_2 , CeCl_3 and LuCl_3 . A detailed scheme of the thermochemical reactions for $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$ is given below (Table 3). The solvent was the same as that used for $\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$, namely 1 M HCl with 0.1 M KI . A mixture

Table 2. Thermochemical cycle for the determination of the enthalpy of formation of BaCe_{0.8}Nd_{0.2}O_{2.9}.^[a]

Reactions	$\Delta_{\text{sol}}H_m^\circ$ [kJ]	Ref.
BaCe _{0.8} Nd _{0.2} O _{2.9} (s) + (5.8HCl + 1.2KI)(sol) = (BaCl ₂ + 0.8CeCl ₃ + 0.2NdCl ₃ + 0.8KCl + 0.4KI ₃ + 2.9H ₂ O)(sol) (1)	−385.89 ± 3.34	this work
BaCl ₂ (s) + 0.8CeCl ₃ (s) + 0.2NdCl ₃ (s) + (solution 1) = (BaCl ₂ + 0.8CeCl ₃ + 0.2NdCl ₃)(sol) (2)	−144.26 ± 0.61	this work
2.9H ₂ (g) + 1.45O ₂ (g) + (solution 1) = 2.9H ₂ O(sol) (3)	−828.94 ± 0.13	[6]
1.2KI(s) + (solution 1) = 1.2KI(sol) (4)	+25.00 ± 0.53	[6]
1.2 K(s) + 0.6I ₂ (s) = 1.2KI(s) (5)	−394.98 ± 0.21	[6]
0.4 K(s) + 0.6I ₂ (s) + (solution 1) = 0.4KI ₃ (sol) (6)	−121.10 ± 0.14	[6]
0.8KCl(s) + (solution 1) = 0.8KCl(sol) (7)	+14.41 ± 0.05	[6]
0.8 K(s) + 0.4Cl ₂ (g) = 0.8KCl(s) (8)	−349.17 ± 0.13	[6]
2.9H ₂ (g) + 2.9Cl ₂ (g) + (solution 1) = 5.8HCl(sol) (9)	−953.29 ± 0.06	[6]
Ba(s) + Cl ₂ (g) = BaCl ₂ (s) (10)	−855.15 ± 1.73	[6]
0.8Ce(s) + 1.2Cl ₂ (g) = 0.8CeCl ₃ (s) (11)	−848.43 ± 0.53	[6]
0.2Nd(s) + 0.3Cl ₂ (g) = 0.2NdCl ₃ (s) (12)	−208.11 ± 1.26	[20]
Ba(s) + 0.2Nd(s) + 0.8Ce(s) + 1.45O ₂ (g) = BaCe _{0.8} Nd _{0.2} O _{2.9} (s) (13)	−1631.59 ± 4.10	this work

[a] Solution 1 is a 1 M solution of HCl with 0.1 M KI.

Table 3. Thermochemical cycle for the determination of the enthalpy of formation of BaCe_{0.8}Lu_{0.2}O_{2.9}.^[a]

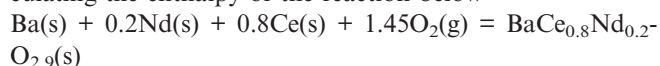
Reactions	$\Delta_{\text{sol}}H_m^\circ$ [kJ]	Ref.
BaCe _{0.8} Lu _{0.2} O _{2.9} (s) + (5.8HCl + 1.2KI)(sol) = (BaCl ₂ + 0.8CeCl ₃ + 0.2LuCl ₃ + 0.8KCl + 0.4KI ₃ + 2.9H ₂ O)(sol) (14)	−358.40 ± 3.71	this work
BaCl ₂ (s) + 0.8CeCl ₃ (s) + 0.2LuCl ₃ (s) + (solution 1) = (BaCl ₂ + 0.8CeCl ₃ + 0.2NdCl ₃)(sol) (15)	−156.98 ± 0.61	this work
2.9H ₂ (g) + 1.45O ₂ (g) + (solution 1) = 2.9H ₂ O(sol) (16)	−828.94 ± 0.13	[6]
1.2KI(s) + (solution 1) = 1.2KI(sol) (17)	+25.00 ± 0.53	[6]
1.2 K(s) + 0.6I ₂ (s) = 1.2KI(s) (18)	−394.98 ± 0.21	[6]
0.4 K(s) + 0.6I ₂ (s) = 0.4KI ₃ (sol) (19)	−121.10 ± 0.14	[6]
0.8KCl(s) + (solution 1) = 0.8KCl(sol) (20)	+14.41 ± 0.05	[6]
0.8 K(s) + 0.4Cl ₂ (g) = 0.8KCl(s) (21)	−349.17 ± 0.13	[6]
2.9H ₂ (g) + 2.9Cl ₂ (g) + (solution 1) = 5.8HCl(sol) (22)	−953.29 ± 0.06	[6]
Ba(s) + Cl ₂ (g) = BaCl ₂ (s) (23)	−855.15 ± 1.73	[6]
0.8Ce(s) + 1.2Cl ₂ (g) = 0.8CeCl ₃ (s) (24)	−848.43 ± 0.53	[6]
0.2Lu(s) + 0.3Cl ₂ (g) = 0.2LuCl ₃ (s) (25)	−197.42 ± 0.50	[20]
Ba(s) + 0.2Lu(s) + 0.8Ce(s) + 1.45O ₂ (g) = BaCe _{0.8} Lu _{0.2} O _{2.9} (s) (26)	−1661.11 ± 4.25	this work

[a] Solution 1 is a 1 M solution of HCl with 0.1 M KI.

of BaCl₂, CeCl₃ and LuCl₃ was prepared in a ratio of 1:0.8:0.2.

The measured enthalpies of solution of BaCe_{0.8}Nd_{0.2}O_{2.9} and BaCl₂ + 0.8CeCl₃ + 0.2NdCl₃ were determined as: $\Delta_{\text{sol}}H_1^\circ(298.15 \text{ K}) = -385.89 \pm 3.34 \text{ kJ mol}^{-1}$ ($n = 5$), $\Delta_{\text{sol}}H_2^\circ(298.15 \text{ K}) = -144.26 \pm 0.61 \text{ kJ mol}^{-1}$ ($n = 6$). Errors were calculated for the 95% confidence interval using standard procedures for the treatment of the experimental data.^[12,15,17]

The measured enthalpies of dissolution were used for calculating the enthalpy of the reaction below



according to the equation

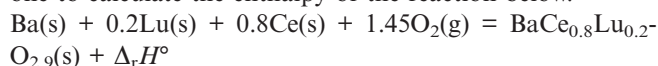
$$\Delta_r H_{13}^\circ = -\Delta_{\text{sol}}H_1^\circ + \Delta_{\text{sol}}H_2^\circ + \Delta_{\text{sol}}H_3^\circ - \Delta_{\text{sol}}H_4^\circ - \Delta_{\text{sol}}H_5^\circ + \Delta_{\text{sol}}H_6^\circ + \Delta_{\text{sol}}H_7^\circ + \Delta_{\text{sol}}H_8^\circ - \Delta_{\text{sol}}H_9^\circ + \Delta_{\text{sol}}H_{10}^\circ + \Delta_{\text{sol}}H_{11}^\circ + \Delta_{\text{sol}}H_{12}^\circ$$

Here, $\Delta_r H_{13}^\circ = \Delta_f H^\circ(\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}, \text{s}, 298.15 \text{ K}) = -1631.59 \pm 4.10 \text{ kJ mol}^{-1}$ is the standard formation enthalpy of barium cerate doped by neodymium oxide.

To calculate this value we used experimental data measured by us and literature data for the formation enthalpies

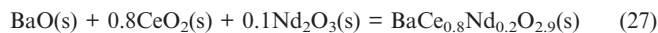
of different compounds and processes taken from ref.^[6,20] and presented in Table 2.

The derivation of the enthalpy of formation of BaCe_{0.8}Lu_{0.2}O_{2.9} from the solution calorimetric data was done using the dissolution enthalpies of barium cerate doped by lutetium oxide and the BaCl₂ + 0.8CeCl₃ + 0.2LuCl₃ mixture in hydrochloric acid with potassium iodide. The solution enthalpies of reactions (14)–(15), namely $\Delta_{\text{sol}}H_{14}^\circ(298.15 \text{ K}) = -358.40 \pm 3.71 \text{ kJ mol}^{-1}$ ($n = 5$), $\Delta_{\text{sol}}H_{15}^\circ(298.15 \text{ K}) = -156.98 \pm 0.61 \text{ kJ mol}^{-1}$ ($n = 6$), allow one to calculate the enthalpy of the reaction below.

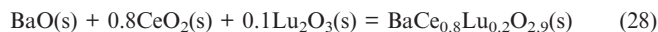


$\Delta_r H^\circ(298.15 \text{ K}) = \Delta_f H^\circ(\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}, \text{s}, 298.15 \text{ K}) = -1661.11 \pm 4.25 \text{ kJ mol}^{-1}$ is the standard formation enthalpy of BaCe_{0.8}Lu_{0.2}O_{2.9} calculated taking into account the scheme presented in Table 3. The standard formation enthalpy is the enthalpy at $P = 1 \text{ atm}$, $T = 298.15 \text{ K}$.

Literature data for the formation enthalpies of BaO, CeO₂, Nd₂O₃ and Lu₂O₃ taken from ref.^[20] were used to calculate the enthalpies of formation of BaCe_{0.8}Lu_{0.2}O_{2.9} and BaCe_{0.8}Nd_{0.2}O_{2.9} from binary oxides as following:



$$\Delta_{\text{ox}}H^\circ(298.15 \text{ K}) = -30.44 \pm 4.83 \text{ kJ mol}^{-1}$$



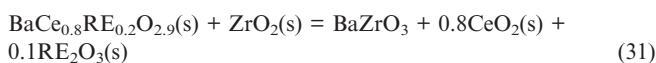
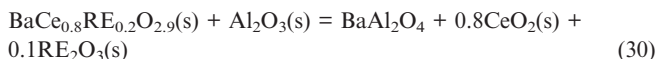
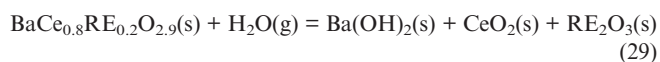
$$\Delta_{\text{ox}}H^\circ(298.15 \text{ K}) = -52.97 \pm 5.01 \text{ kJ mol}^{-1}$$

In order to understand whether the $\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$ or $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$ phases are stable or unstable with regard to decomposition to $\text{BaO} + 0.8\text{CeO}_2 + 0.1\text{Nd}_2\text{O}_3$ or $\text{BaO(s)} + 0.8\text{CeO}_2 + 0.1\text{Lu}_2\text{O}_3$ mixtures it is necessary to know the Gibbs energies ($\Delta G = \Delta H - T\Delta S$). There are no entropy values for the $\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$ and $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$ phases in the literature. These values were estimated using entropies of Nd_2O_3 , Lu_2O_3 , BaCeO_3 , CeO_2 taken from ref.[6,22] Using the formation enthalpies of reactions (27) and (28), the Gibbs energies for the processes (27) and (28) were estimated as: $\Delta_{\text{ox}}G^\circ(298.15 \text{ K}) = -33.48 \pm 4.83 \text{ kJ mol}^{-1}$ and $\Delta_{\text{ox}}G^\circ(298.15 \text{ K}) = -52.97 \pm 5.01 \text{ kJ mol}^{-1}$.

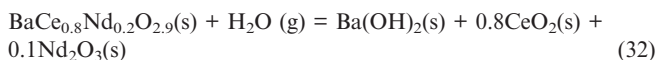
As can be seen, both of the above-mentioned complex oxides are thermodynamically stable with regard to their decomposition into binary oxides at room temperature. It is not an obvious result for this class of compounds because there is a discussion about the thermodynamic stability of BaCeO_3 .^[6–9] There is a paper that claims that BaCeO_3 is unstable with regard to its decomposition into BaO and CeO_2 .^[7] It is interesting to mention that usually the enthalpy of formation of complex oxides from binary oxides is close to zero [for example, $\Delta_{\text{ox}}H(298.15 \text{ K}, \text{CdSiO}_3) = -6.28 \text{ kJ mol}^{-1}$]. In our case we have values at the level -30 – 50 kJ mol^{-1} , which are higher than the usual values for complex oxides but lower than formation enthalpies from binary oxides for HTSC materials [$\Delta_{\text{ox}}H$ for $\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ phase (RE = rare earth element) is about -200 kJ mol^{-1}]. In accordance with increasing Gibbs energies one therefore observes an increasing stability in the order BaCeO_3 doped by neodymium oxide to BaCeO_3 doped by lutetium oxide. Hence, barium cerate doped by lutetium oxide is more thermodynamically stable than BaCeO_3 doped by neodymium oxide.

As some researchers have pointed out, a concern for BaCeO_3 is its stability in the external atmosphere.^[3,23,24] The compound reacts with water vapour to decompose into barium hydrate and cerium oxide according to the reaction: $\text{BaCeO}_3 + \text{H}_2\text{O} = \text{Ba(OH)}_2 + \text{CeO}_2$.^[24] It is also known that when pellets of BaCeO_3 were sintered in alumina or zirconia containers, XRD patterns of the contact substrates showed that BaAl_2O_4 was formed on the alumina and BaZrO_3 was formed on the zirconia. It was thus concluded that BaCeO_3 reacts with Al_2O_3 or ZrO_2 and decomposes through the following reactions: $\text{BaCeO}_3 + \text{Al}_2\text{O}_3 = \text{BaAl}_2\text{O}_4 + \text{CeO}_2$ and $\text{BaCeO}_3 + \text{ZrO}_2 = \text{BaZrO}_3 + \text{CeO}_2$.^[24]

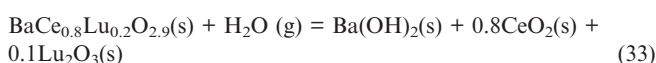
With regard to this it was interesting to discover that $\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$ and $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$ react with water vapour, Al_2O_3 or ZrO_2 . For this reason we considered the following reactions:



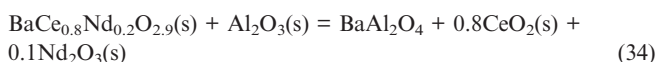
The possibility of the interaction was estimated using our experimental data, formation enthalpies of the solid phases, namely $\text{CeO}_2\text{(s)}$, $\text{Nd}_2\text{O}_3\text{(s)}$, $\text{Lu}_2\text{O}_3\text{(s)}$, $\text{Ba(OH)}_2\text{(s)}$, BaAl_2O_4 , BaZrO_3 , and the formation enthalpy of the gas phase $\text{H}_2\text{O(g)}$ taken from ref.^[20,23] The calculated heats of reactions (32)–(37) are:



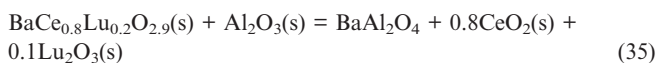
$$\Delta_r H^\circ(298.15 \text{ K}) = -122.11 \pm 4.83 \text{ kJ mol}^{-1}$$



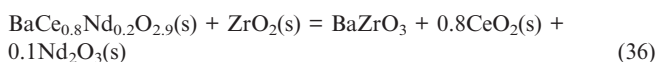
$$\Delta_r H^\circ(298.15 \text{ K}) = -99.58 \pm 5.01 \text{ kJ mol}^{-1}$$



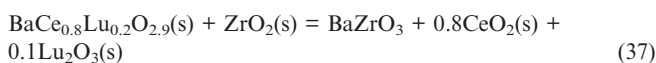
$$\Delta_r H^\circ(298.15 \text{ K}) = -74.26 \pm 4.83 \text{ kJ mol}^{-1}$$



$$\Delta_r H^\circ(298.15 \text{ K}) = -51.63 \pm 5.02 \text{ kJ mol}^{-1}$$



$$\Delta_r H^\circ(298.15 \text{ K}) = -68.26 \pm 4.42 \text{ kJ mol}^{-1}$$



$$\Delta_r H^\circ(298.15 \text{ K}) = -45.63 \pm 4.62 \text{ kJ mol}^{-1}$$

It is necessary to note that the direction of any chemical transformation is determined by the sign of the Gibbs energy $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Below we will calculate the Gibbs energies for reactions (32)–(37). As it was mentioned earlier the values of the entropies of $\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$ and $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$, which were absent in the literature, were estimated using entropies of Nd_2O_3 , Lu_2O_3 , BaCeO_3 and CeO_2 taken from ref.[6,22] The Gibbs energies for processes (32)–(37) were calculated as

$$\Delta_r G^\circ(298.15 \text{ K}) = -73.32 \pm 4.83 \text{ kJ mol}^{-1} \text{ [for (32)]},$$

$$\Delta_r G^\circ(298.15 \text{ K}) = -50.79 \pm 5.01 \text{ kJ mol}^{-1} \text{ [for (33)]},$$

$$\Delta_r G^\circ(298.15 \text{ K}) = -72.37 \pm 4.83 \text{ kJ mol}^{-1} \text{ [for (34)]},$$

$$\Delta_r G^\circ(298.15 \text{ K}) = -49.74 \pm 5.02 \text{ kJ mol}^{-1} \text{ [for (35)]},$$

$$\Delta_r G^\circ(298.15 \text{ K}) = -65.91 \pm 4.42 \text{ kJ mol}^{-1} \text{ [for (36)]},$$

$$\Delta_r G^\circ(298.15 \text{ K}) = -43.26 \pm 4.62 \text{ kJ mol}^{-1} \text{ [for (37)]}.$$

Taking into account the Gibbs energies of reactions (32)–(37) it is possible to say that both complex oxides ($\text{BaCe}_{0.8}\text{Nd}_{0.2}\text{O}_{2.9}$, $\text{BaCe}_{0.8}\text{Lu}_{0.2}\text{O}_{2.9}$) react with water, Al_2O_3 and ZrO_2 at ambient temperature. Usually the zirconia crucibles are preferable for the synthesis of barium cerates, however, they are more expensive than the alumina crucibles. The enthalpies of the reactions of $\text{BaCe}_{0.8}\text{RE}_{0.2}\text{O}_{2.9}$

(RE = Nd, Lu) with ZrO₂ and Al₂O₃ are practically the same, so it is unnecessary to use the expensive ZrO₂ crucibles. It should also be noted that the reactions with Al₂O₃, ZrO₂ or water for BaCe_{0.8}Nd_{0.2}O_{2.9} are more thermodynamically favoured than those for BaCe_{0.8}Lu_{0.2}O_{2.9}.

There is also a second type of reaction for the doped-BaCeO₃ with water. It can be written as follows.



Unfortunately there is no thermodynamic data for BaCe_{0.8}RE_{0.2}O_{2.9-x}(OH)_{2x} in the literature. For this reason we can not estimate the Gibbs energies for processes (38).

Conclusions

In this paper, for the first time we have synthesized the compound BaCe_{0.8}Lu_{0.2}O_{2.9} by a solid-state reaction. We also prepared BaCeO₃ doped by neodymium oxide (BaCe_{0.8}Nd_{0.2}O_{2.9}) and determined its structure parameters, which are in good agreement with the literature data. Both compounds have an orthorhombic structure (space group *Pnma*). We also measured the standard formation enthalpies of BaCe_{0.8}Nd_{0.2}O_{2.9} and BaCe_{0.8}Lu_{0.2}O_{2.9} by solution calorimetry in 1 M HCl with 0.1 M KI. We determined the stability of Nd- and Lu-doped barium cerates with regard to mixtures of binary oxides, and the enthalpies and Gibbs energies of the interaction with alumina, zirconia and water. On the basis of these data we established that both of the above-mentioned complex oxides are thermodynamically stable with regard to their decomposition into binary oxides at room temperature. BaCe_{0.8}Nd_{0.2}O_{2.9} and BaCe_{0.8}Lu_{0.2}O_{2.9} react with water vapour, Al₂O₃ and ZrO₂ at room temperature and the reactions for BaCe_{0.8}Nd_{0.2}O_{2.9} are more thermodynamically favoured than those for BaCe_{0.8}Lu_{0.2}O_{2.9}.

Experimental Section

Polycrystalline samples of BaCe_{0.8}Nd_{0.2}O_{2.9} and BaCe_{0.8}Lu_{0.2}O_{2.9} were prepared by solid-state synthesis from barium carbonate, cerium dioxide and neodymium or lutetium oxide. All starting materials were annealed at high temperatures before undergoing the solid-state reactions. Nd₂O₃ (99.99%, Purathem, STREM Chemicals, USA), Lu₂O₃ (99.999%, Chempur, Chem. Pur Feinchemikalien und Forschungsbedarf GmbH, Karlsruhe) and CeO₂ (99.9%, Vetron GmbH, Karlsruhe) were annealed at 1023 K in air for 10 h. BaCO₃ (CERAC, TM incorporated, 99.999% pure, USA) was annealed at 650 K in air for 4 h.

Stoichiometric amounts of BaCO₃, CeO₂, Nd₂O₃ or Lu₂O₃ were mixed by ball milling in an agate container with agate balls using a planetary mill (FRITSCH pulverisette) for 72 h. The ground materials were palletized using a 10-mm-diameter die and fired at 1300 K for 70 h, 1400 K for 10 h and 1700 K for 24 h using a CARBOLITE furnace.

Anhydrous BaCl₂ was prepared by drying BaCl₂ (CERAC, TM incorporated, USA, 99.9%) in argon at about 500 K. CeCl₃ was also purchased from CERAC (mass fraction is more than 0.999) and purified by vacuum sublimation in order to remove the lantha-

nide oxychloride impurities. For this purpose CeCl₃ was sublimated above the melting temperature (1143 K) in a vacuum at more than 10⁻⁵ Pa. NdCl₃ and LuCl₃ were prepared from Nd₂O₃ and Lu₂O₃ (99.99%, Purathem, STREM Chemicals, Newburyport, USA) and Lu (99.999%, Chempur, Chem. Pur Feinchemikalien und Forschungsbedarf GmbH, Karlsruhe) were dissolved in an excess of hydrochloric acid. Purified chlorine gas was bubbled through the solutions. Each solution was then evaporated. Further drying was accomplished by evaporation under vacuum at about 350 K until the remaining chloride crystals appeared in composition. Final drying was accomplished by slow heating, in a hydrogen chloride atmosphere, to a final temperature of 600 to 700 K. All manipulations with CeCl₃, BaCl₂, NdCl₃ and LuCl₃ were performed in a dry box (pure Ar gas).

Acknowledgments

This work is supported by the Deutsche Forschungsgemeinschaft (DFG) (grant LO 250/24-1), the Forschungszentrum Karlsruhe and the Program of Fundamental Investigation of the Siberian Branch of the Russian Academy of Sciences.

- [1] A. Selmi, G. Corbel, S. Kojikian, V. Voronkova, E. Khartanova, P. Lacorre, *Eur. J. Inorg. Chem.* **2008**, 11, 1813–1821.
- [2] M. L. Martinez-Sarrion, L. Mestres, M. Herraiz, O. Maqueda, A. Bakkali, N. Fernandez, *Eur. J. Inorg. Chem.* **2002**, 7, 1794–1800.
- [3] K. D. Kreuer, S. J. Paddison, E. Spohr, M. Schuster, *Chem. Rev.* **2004**, 104, 4637–4678.
- [4] T. Norby, M. Wideroe, R. Glockner, Y. Larring, *Dalton Trans.* **2004**, 19, 3012–3018.
- [5] A. I. Ruiz, M. L. Lopez, M. L. Veiga, C. Pico, *Eur. J. Inorg. Chem.* **2000**, 4, 659–664.
- [6] E. H. P. Cordfunke, A. S. Booi, M. E. Huntelaar, *J. Chem. Thermodyn.* **1998**, 30, 437–447.
- [7] C. W. Tanner, A. V. Virkar, *J. Electrochem. Soc.* **1996**, 143, 1386–1389.
- [8] J. Goudiakas, R. G. Haire, J. Fuger, *J. Chem. Thermodyn.* **1990**, 22, 577–587.
- [9] V. A. Levitskii, S. L. Sorokina, Yu. Ya. Skolis, M. L. Kovba, *Inorg. Mater.* **1986**, 21, 1190–1193.
- [10] M. L. Martinez-Sarrion, L. Mestres, M. Herraiz, O. Maqueda, N. Fernandez, M. F. Garcia, *Eur. J. Inorg. Chem.* **2003**, 13, 2458–2462.
- [11] Th. Zeiske, R. Sonntag, D. Hohlwein, N. H. Andersen, Th. Wolf, *Nature* **1991**, 353, 542–544.
- [12] N. I. Matskevich, Th. Wolf, Yu. I. Pochivalov, *Inorg. Chem.* **2008**, 47, 2581–2584.
- [13] N. I. Matskevich, Th. Wolf, *Thermochim. Acta* **2008**, 467, 113–116.
- [14] X. T. Su, Q. Z. Yan, X. H. Ma, W. F. Zhang, C. C. Ge, *Solid State Ionics* **2006**, 177, 1041–1045.
- [15] R. C. T. Slade, N. Singh, *J. Mater. Chem.* **1991**, 1, 441–445.
- [16] L. P. Kozeeva, M. Yu. Kamenova, N. V. Podberezhskaya, D. Yu. Naumov, N. F. Beizel, U. Hyon Paek, V. E. Fedorov, *J. Ceram. Pros. Res.* **2002**, 3, 123–127.
- [17] N. I. Matskevich, C. Greaves, *Thermochim. Acta* **2007**, 459, 125–126.
- [18] A. I. Nazzari, V. Y. Lee, E. M. Engler, R. D. Jacowitz, Y. Tokura, J. B. Torrance, *Physica C* **1988**, 153–155, 1367–1368.
- [19] J. H. Mathews, K. D. Fink, *Numerical Methods Using MATLAB*, 3rd ed., Prentice Hall, **2001**, p. 720.
- [20] V. P. Glushko, *Termicheskie Konstanty Veshchestv* (Thermal Constants of Substances), VINITI, Moscow, **1965–1982**, issued 1–10.

- [21] C. Gunter, R. Pfestorf, M. Rother, J. Seidel, R. Zimmermann, G. Wolf, V. Schroder, *J. Therm. Anal. Calorim.* **1988**, 33, 359–363.
- [22] V. P. Glushko, Termicheskie Konstanty Veshchestv (Thermal Constants of Substances), VINITI, Moscow, **1965–1982**, issued 1–10.
- [23] T. Matsui, *Thermochim. Acta* **1995**, 253, 155–165.
- [24] E. Chen, O. T. Sorensen, G. Meng, D. Peng, *J. Mater. Chem.* **1997**, 7, 481–485.

Received: June 12, 2008

Published Online: March 10, 2009