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Energetic characteristics of barium cerates doped by yttrium, gadolinium and luthetium oxides

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ABSTRACT

For the first time solution enthalpies of $BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$, $BaCe_{0.8}Y_{0.1}Lu_{0.1}O_{2.9}$ and mixtures of $BaCl_2$ + $0.8CeCl_3$ + $0.1YCl_3$ + $0.1GdCl_3$, $BaCl_2$ + $0.8CeCl_3$ + $0.1YCl_3$ + $0.1LuCl_3$ in 1 mol dm^{-3} HCl with 0.1 mol dm^{-3} KI have been measured. On the basis of experimental data obtained and literature data the standard molar enthalpies of formation and stabilization energies were calculated. Using Born-Haber cycle the lattice energies were calculated. It was established that lattice energy was increased from $BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$ to $BaCe_{0.8}Y_{0.1}Lu_{0.1}O_{2.9}$. It correlates with decreasing of ion radius of rare earth element from gadolinium to lutetium. Increasing of lattice energy with decreasing of ion radius of rare earth element was explained with modified formula of Kapustinskii.

1. Introduction

Compounds on the basis of barium cerates have attracted considerable attention over the last two decades because of their important applications as perspective high temperature proton conductors (HTPCs) [1–10]. Barium cerates have lower energy activation for proton transportation in comparison with yttria-stabilized zirconia and trivalent-doped ceria. Besides being used as proton conductors, it has also found use as hydrogen separation membranes and hydrogen sensors. To improve the ionic conductivity and the sintering activity, a co-doping strategy is used. In particular, it was shown in paper [11] that the compounds $BaCe_{0.8}R_xY_{0.2-x}O_{3-d}$ are promising proton conductors with high conductivity and sufficient sintering activity for proton-conducting solid oxide fuel cells operating at reduced temperature. Authors [12] showed that barium cerates doped with Gd, Y, Sm, Nd exhibited relatively high electrical conductivity.

Thermodynamics of co-doped barium cerates is practically not studied, except for the pioneering papers of authors [13–16]. The goal of the present work is to perform thermochemical investigations of barium cerates co-doped with yttrium, gadolinium and lutetium. We plan to study how thermodynamic properties are changed with replacing of one lanthanide by another. Knowledge of direction of thermodynamic properties changing is very important to find the most perspective stable materials [17–19].

2. Experimental part

2.1. Synthesis and characterization of compounds

Compounds with general composition $BaCe_{0.8}Y_{0.1}R_{0.1}O_{2.9}$ ($BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$ and $BaCe_{0.8}Y_{0.1}Lu_{0.1}O_{2.9}$) were prepared by solid state reaction: $BaCO_3 + 0.5x\ (Y,R)_2O_3 + (1-x)CeO_2 = BaCe_{1-x}(Y,R)_xO_{3-x/2} + CO_2$. The following reagents were using for preparation: $BaCO_3$ (>99%, MERCK), CeO_2 (99.99%, Johnson Matthey GmbH, Alfa Products), Y_2O_3 (99.99%, ChemPur), Lu_2O_3 (99.99%, ChemPur), Gd_2O_3 (99.9%, Heraeus).

The technology of synthesis was the following. Starting reagents Y_2O_3, Gd_2O_3 and Lu_2O_3 were treated before synthesis at 1100 K up to constant weight. Then they were mixed in an agate mortar, ground in a planetary ball mill, pressed and heat treated in air at the temperature range of 1100–1700 K. Doped barium cerates were synthesized as individual phases in one cycle. X-ray analysis showed that all samples were single phase. XRD pattern is presented in Fig. 1. The samples have orthorhombic structure (Pnmc space group) and lattice parameters were the following for $BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$ – a = 0.88842 ± 3 nm, b = 0.61932 ± 5 nm, c = 0.61979 ± 5 nm; for $BaCe_{0.8}Y_{0.1}Lu_{0.1}O_{2.9}$ – a = 0.88325 ± 3 nm, b = 0.61628 ± 5 nm, c = 0.61350 ± 5 nm. Here the standard uncertainties are presented (for standard uncertainties the default level

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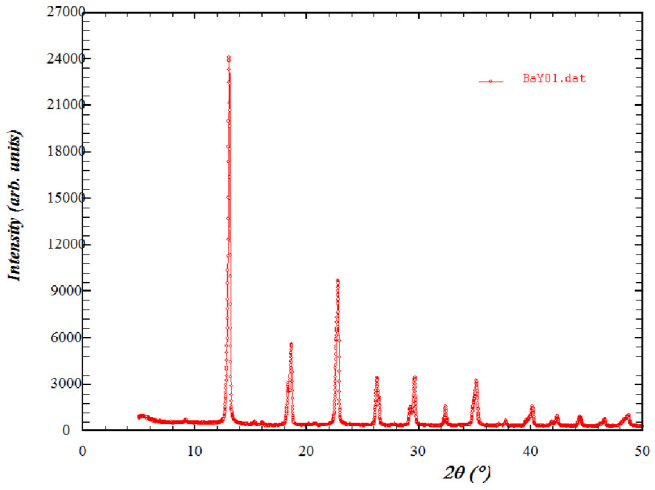

Fig. 1. XRD pattern for $BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$.

of confidence are 0.68) for cell parameters "a", "b", "c". The XDR patterns were measured at temperature 298 K. The number of formula units per lattice cell is Z = 4. The lattice parameters are in a good agreement with literature data [12].

The content of metals (Ba, Ce, Y, Gd, Lu) in compounds $BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$, $BaCe_{0.8}Y_{0.1}Lu_{0.1}O_{2.9}$, $BaCl_2$, $CeCl_3$, YCl_3, $GdCl_3$, $LuCl_3$ was analyzed with atomic absorption method. The oxygen content in $BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$, $BaCe_{0.8}Y_{0.1}Lu_{0.1}O_{2.9}$ was determined by reducing melting method. The results of chemical analysis are presented in Table 1. The results showed that phases with an accuracy of 1% are pure.

The phases $BaCl_2$, $CeCl_3$, YCl_3, $GdCl_3$, $LuCl_3$ were prepared as described in paper [13–16]. The results of characterization are presented in Table 1.

2.2. Thermochemical cycles

The solution calorimetry method was used to measure the thermochemical properties of $BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$ and $BaCe_{0.8}Y_{0.1}Lu_{0.1}O_{2.9}$. 1 mol dm^{-3} HCl with 0.1 mol dm^{-3} KI was used as a solvent for our thermochemical investigations. KI was added to transfer Ce^{+4} to Ce^{+3}. A mixture of $BaCl_2$, $CeCl_3$, YCl_3, RCl_3 ($GdCl_3$ or $LuCl_3$) was prepared in the ratio 1:0.8:0.1:0.1.

A thermochemical cycle was constructed in such a way that the enthalpy of solution for $BaCe_{0.8}Y_{0.1}R_{0.1}O_{2.9}$ (R = Gd, Lu) was compared with the solution enthalpy of the mixture: $BaCl_2 + 0.8CeCl_3 + 0.1YCl_3 + RCl_3$ (R = Gd, Lu).

The general scheme of the thermochemical cycle is presented below:

$$BaCe_{0.8}Y_{0.1}R_{0.1}O_{2.9}(s) + (5.8HCl + 1.2KI)(sol) = (BaCl_2 + 0.8CeCl_3 + 0.1YCl_3 + 0.1RCl_3 + 0.8KCl + 0.4KI_3 + 2.9H_2O)(sol) + \Delta_{sol}H^o_{1R} \quad (1)$$

$$BaCl_2(s) + 0.8CeCl_3(s) + 0.1YCl_3(s) + 0.1RCl_3(s) + (sol\ in\ "A") = (BaCl_2 + 0.8CeCl_3 + 0.1YCl_3 + 0.1RCl_3) + \Delta_{sol}H^o_{2R} \quad (2)$$

Here: solvent "A" stands for (1 mol dm^{-3} HCl with 0.1 mol dm^{-3} KI) aq.

By combining reactions of (1) and (2) one obtains:

$$BaCl_2(s) + 0.8CeCl_3(s) + 0.1YCl_3(s) + 0.1RCl_3(s) + (0.8KCl + 0.4KI_3 + 2.9H_2O)(sol) = BaCe_{0.8}Y_{0.1}R_{0.1}O_{2.9}(s) + (5.8HCl + 1.2KI)(sol) + \Delta_rH^o_{3R} \quad (3)$$

where: $\Delta_rH^o_{3R} = -\Delta_{sol}H^o_{1R} + \Delta_{sol}H^o_{2R}$.

2.3. Calorimetric technique

The solution calorimetry with an isothermal jacket [20,21] was used to measure solution enthalpies. Experimental temperature was T = 298.15 ± 0.01 K, pressure was 100 ± 0.15 kPa. The dissolution of KCl in water was performed to check the calorimeter operation. The obtained 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). Literature data are: 17.42 ± 0.02 kJ mol^{-1} [22]

The amount of $BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$ or $BaCe_{0.8}Y_{0.1}Lu_{0.1}O_{2.9}$ and mass of the chlorides mixture used in calorimetric experiments was about 0.04 and 0.06 g correspondently (volume of solvent 0.25 dm^{-3}).

3. Results and discussion

3.1. Formation enthalpy of $BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$

We measured the solution enthalpy of $BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$ and the solution enthalpy of a mixture of $BaCl_2 + 0.8CeCl_3 + 0.1YCl_3 + 0.1GdCl_3$ as follows: $\Delta_{sol}H^o_{1Gd} = -326.71 \pm 3.66$ kJ mol^{-1}, $\Delta_{sol}H^o_{2Gd} = -150.94 \pm 0.83$ kJ mol^{-1}. Everywhere in this paper the standard uncertainties (0.68 level of confidence) are reported. The data for solution enthalpies are presented in Tables 2 and 4.

Using solution enthalpies $\Delta_{sol}H^o_{1Gd}$ and $\Delta_{sol}H^o_{2Gd}$ we calculated the enthalpy of reaction:

Table 1
Characterization of chemical samples used in this study.

Chemical name	Chemical formula	Source	State	Mass fraction purity
Barium carbonate	$BaCO_3$	MERCK	Solid	>0.99*
Cerium oxide (IV)	CeO_2	ChemPur	Solid	>0.9999*
Yttrium oxide	Y_2O_3	ChemPur	Solid	>0.9999*
Gadolinium oxide	Gd_2O_3	Heraeus	Solid	>0.999*
Lutetium oxide	Lu_2O_3	ChemPur	Solid	>0.9999*
Barium chloride	$BaCl_2$	Synthesis	Solid	>0.99
Cerium chloride	$CeCl_3$	Synthesis	Solid	>0.99
Gadolinium chloride	$GdCl_3$	Synthesis	Solid	>0.99
Yttrium chloride	YCl_3	Synthesis	Solid	>0.99
Lutetium chloride	$LuCl_3$	Synthesis	Solid	>0.99
Barium cerate doped by Y and Gd	$BaCe_{0.8}Y_{0.1}Gd_{0.1}O_{2.9}$	Synthesis	Solid	>0.99
Barium cerate doped by Y and Lu	$BaCe_{0.8}Y_{0.1}Lu_{0.1}O_{2.9}$	Synthesis	Solid	>0.99

Atomic absorption method and reducing melting method were used for analysis; the standard uncertainty is 0.1–0.5%.
* The purities were taken from suppliers' certificates.