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ENTHALPY OF FORMATION OF $BaCe_{0.9}In_{0.1}O_{3-\delta}$(s)

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Enthalpy of formation of the perovskite-related oxide $BaCe_{0.9}In_{0.1}O_{2.95}$ has been determined at 298.15 K by solution calorimetry. Solution enthalpies of barium cerate doped with indium and mixture of $BaCl_2$, $CeCl_3$, $InCl_3$ in ratio 1:0.9:0.1 have been measured in 1 M HCl with 0.1 M KI. The standard formation enthalpy of $BaCe_{0.9}In_{0.1}O_{2.95}$ has been calculated as -1611.7 ± 2.6 kJ mol^{-1}. Room-temperature stability of this compound has been assessed in terms of parent binary oxides. The formation enthalpy of barium cerate doped by indium from the mixture of binary oxides is $\Delta_{ox}H^0(298.15\ K)= -36.2\pm3.4$ kJ mol^{-1}.

Keywords: *$BaCeO_3$-based perovskite, solution calorimetry, thermodynamic stability*

Introduction

$BaCeO_3$-based perovskites are potential candidates for application in mid-temperature solid oxide fuel cells and electrocatalysis because of their high proton conduction [1–5]. It is generally accepted that proton conduction is induced through the substitution of trivalent dopant ions on the cerium site. Solid solutions typically form over the range $BaCe_{1-x}M_xO_{3-x/2}$, $0<x<0.2$, with $M=Y^{3+}$, Yb^{3+}, Gd^{3+}, Sm^{3+}, Nd^{3+}, etc. [6]. As it has been recently shown (luminescent and IR absorption studies) [7], doping of cerates by M^{3+} stabilizes the valence state +4 of Ce. The thermodynamic stability is one of the important facts for application [1]. The stability of cerium-based perovskites depends on not only thermal conditions but also on the nature of B-site doped ion [1]. It has been suggested that stability increases when the dopant ion is small and does not exhibit strong base properties. Sufficient research of this has not been carried out.

In the following, for the first time we report the standard formation enthalpy of $BaCe_{0.9}In_{0.1}O_{3-\delta}$ determined by solution calorimetry and calculated enthalpies for the reactions including this compound. Indium is not a rare earth metal but can form solid solutions on the basis of $BaCeO_3$ [8]. The compound has high conducting properties and can be considered as a prospective solid electrolyte. There are no thermodynamic data for compounds in the Ba–Ce–In–O system, in particular, for $BaCe_{1-x}In_xO_{3-\delta}$.

Thermodynamic properties linked to structural data have been used to develop systematic structure-stability relationships in perovskite type oxides.

Experimental

Materials and methods

Sample preparation

Sample of overall composition $BaCe_{1-x}In_xO_{3-\delta}$ was prepared by solid-state reaction [9]. Appropriate quantities of $BaCO_3$, CeO_2 and In_2O_3 powders (CERAC, TM incorporated, USA, 99.9%) were mixed and milled in a planetary mill for 12 h. The powder was then pressed into pellets (P=3000 kg cm^{-2}) and calcined at 1100 K for 16 h. Following this, calcinations were performed in air at 1300 K for 5 h, 1400 K for 10 h, 1700 K for 24 h with intermediate regrinding.

Anhydrous $BaCl_2$ was prepared by drying $BaCl_2$ (CERAC, TM incorporated, USA, 99.9%) in argon at about 500 K. $CeCl_3$ was also purchased from CERAC (mass fraction is more than 0.999) and purified by vacuum sublimation in order to remove the lanthanide oxychloride impurities. For this purpose $CeCl_3$ was sublimated above the melting temperature (1143 K) in a vacuum better than 10^{-5} Pa. $InCl_3$ was synthesized from Cl_2 and In. Chlorine gas was passed over indium at temperature about 450 K. All manipulations with $CeCl_3$, $BaCl_2$ and $InCl_3$ were performed in a dry box (pure Ar gas).

X-ray powder diffraction was performed at room temperature (STADI-P diffractometer; CuK_α radiation). The samples were found to be single phases. An orthorhombic $BaCe_{0.9}In_{0.1}O_{3-\delta}$ (space group Pnma) was prepared [8, 9]. Refined cell parameters: a=0.6196(3) Å, b=0.8749(3) Å, c=0.6219(2) Å. All compounds were also characterized by chemical analysis [10]. The content of barium was determined by

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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
$InCl_3$	In, 51.94±0.03	In, 51.91
$BaCe_{0.9}In_{0.1}O_{2.95}$	Ba, 42.61±0.03; Ce, 39.10±0.03; In, 3.58±0.01	Ba, 42.63; Ce, 39.15; In, 3.56

Table 2 The data of dissolution enthalpies of $BaCe_{0.9}In_{0.1}O_{2.95}$ (1 M HCl with 0.1 M KI) at 298.15 K

m/g	Heat/J	$\Delta_{sol}H_1^0$ for single experiments/kJ mol^{-1}	The mean value with error margin/kJ mol^{-1}
0.07465	83.580	–360.65	
0.07412	82.340	–357.84	
0.07494	83.935	–360.78	
0.07511	83.983	–360.17	
0.07478	83.129	–358.08	
0.07415	82.366	–357.81	–359.22±1.52

photometric method in the flame of nitrogen dioxide-acetylene. The content of cerium and indium was determined by spectrophotometry. The stoichiometric coefficient of oxygen was determined by iodometric titration according to method described in paper [11] with accuracy better than ±0.03. Results of chemical analysis are presented in Table 1.

Calorimetric technique

Calorimetry experiments were conducted in our laboratory in an automatic calorimeter with isothermal shield of our own design and construction. Detailed description of construction, procedure of performing experiments and checking calorimeter are presented in paper [12]. The measurement procedure has been also extensively described in literature in detail [13]. The calorimeter had the reaction vessel (volume of 200 mL), the computer-controller platinum thermometer and the Matlab program written at our laboratory. The program allows one to measure and record the temperature of 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 temperature drift less than 0.0003°C for 10 h. Dissolution of potassium chloride in water was performed to check the precision of the calorimeter. The obtained dissolution heat of KCl was 17.41±0.04 kJ mol^{-1} (the molality of the final solution was 0.028 mol kg^{-1}). The certified values are: 17.42±0.02 kJ mol^{-1}) [14], 17.47±0.07 kJ mol^{-1} [15].

1 M HCl with 0.1 KI was chosen as a solvent. A mixture of $BaCl_2$, $CeCl_3$, $InCl_3$ was prepared in ratio 1:0.9:0.1. The molar concentration of $CeCl_3$ was the same as in paper [16].

The amount of $BaCe_{0.9}In_{0.1}O_{2.95}$ was chosen in such a way to have concentration of I_2 and KI as authors [16] used (about 0.08 g). Typical curve of calorimetric experiment is presented in Fig. 1.

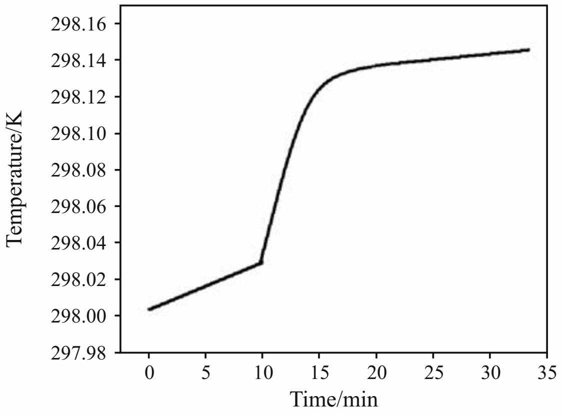

Fig. 1 Curve of calorimetric experiment

Results and discussion

Calorimetric investigation

In most cases three solvents are used for dissolution of compounds on the basis of alkaline earth and rare earth elements: HCl, $HClO_4$, HF. We have chosen 1 M hydrochloric acid. KI was added to reduce Ce^{4+} to Ce^{3+}. This solvent was also used by Morss and Menz [17] for determination of the enthalpy of formation of $BaCeO_3$ and by Goudiakas *et al.* [18] for $BaCeO_3$ and $SrCeO_3$. 1 M HCl is the most suitable solvent for solution calorimeters [19]. We measured

Table 3 Reaction scheme to determine the standard molar enthalpy of formation of $BaCe_{0.9}In_{0.1}O_{2.95}$ at the temperature 298.15 K

Reaction	$\Delta_{sol}H^0_m$/kJ	Ref.
1. $BaCe_{0.9}In_{0.1}O_{2.95}(s)+(5.9HCl+0.9KI)sol=(BaCl_2+0.9CeCl_3+0.1KCl+0.45I_2+2.95H_2O)$ (sol)	–359.22±1.52	This work
2. $BaCl_2(s)+0.9CeCl_3(s)+0.1InCl_3(s)=(2BaCl_2+0.9CeCl_3+0.1InCl_3)$ (sol)	–137.41±0.59	This work
3. $2.95H_2(g)+1.475O_2(g)=2.95H_2O(sol)$	–843.23±0.13	[16]
4. 0.9KI(s)+ solution 1=0.9KI(sol)	+18.75±0.32	[16]
5. $0.9K(s)+0.45I_2(s)=0.9KI(sol)$	–296.24±0.13	[16]
6.$0.45I_2(s)$+solution 1=$0.45I_2(sol)$	+2.51±0.46	[16]
7. 0.9KCl(s)+solution 1=0.9KCl(sol)	+16.21±0.05	[16]
8. $0.9K(s)+0.45Cl_2(g)=0.9KCl(s)$	–392.81±0.12	[16]
9. $2.95H_2(g)+2.95Cl_2(g)$+solution 1=5.9HCl(sol)	–969.72±0.06	[16]
10. $Ba(s)+Cl_2(g)=BaCl_2(s)$	–855.15±1.73	[16]
11. $0.9Ce(s)+1.35Cl_2(g)=0.9CeCl_3(s)$	–954.49±0.48	[16]
12. $0.1In(s)+0.15Cl_2(g)=0.1InCl_3(s)$	–53.72±0.84	[14]
13. $Ba+0.1In+0.9Ce+1.475O_2=BaCe_{0.9}In_{0.1}O_{2.95}$	–1611.66±2.64	This work

the dissolution enthalpy of $BaCe_{0.9}In_{0.1}O_{2.95}$ and the dissolution enthalpy of mixture $BaCl_2+CeCl_3+0.1InCl_3$ in this solvent, as these measurements were not previously done. The dissolution enthalpy of barium cerate doped with indium in 1 M HCl with 0.1 M KI, $\Delta_{sol}H^0(BaCe_{0.9}In_{0.1}O_{2.95}$, 298.15 K)= –359.22±1.52 kJ mol^{-1} is the average of six calorimetric experiments (Table 2). The dissolution enthalpy of mixture $BaCl_2(s)+0.9CeCl_3(s)+0.1InCl_3(s)$ in 1 M HCl with 0.1 M KI, $\Delta_{sol}H^0$ (298.15 K)= –137.41±0.59 kJ mol^{-1} is the average of five calorimetric experiments. Errors were calculated for the 95% confidence interval using the Students coefficient.

The thermochemical cycle from which the enthalpy of formation of $BaCe_{0.9}In_{0.1}O_{2.95}(s)$ derived is given in Table 3.

The cycle was completed with the auxiliary values for the molar enthalpies of formation of H_2O(aq), HCl(aq), $BaCl_2$, $CeCl_3$, KCl and $InCl_3$ and others. The values were taken from [14, 16].

After combining all reactions (1)–(12) we obtain

$$\Delta_r H^0_{13} = -\Delta_{sol} H^0_1 + \Delta_{sol} H^0_2 + \Delta_{sol} H^0_3 - \Delta_{sol} H^0_4 - \Delta_{sol} H^0_5 + \Delta_{sol} H^0_6 + \Delta_{sol} H^0_7 + \Delta_{sol} H^0_8 - \Delta_{sol} H^0_9 + \Delta_{sol} H^0_{10} + \Delta_{sol} H^0_{11} + \Delta_{sol} H^0_{12}$$

where $\Delta_f H^0$ ($BaCe_{0.9}In_{0.1}O_{2.95}$(s), 298.15 K)= –1611.7±2.6 kJ mol^{-1}.

From the standard enthalpy of formation, it is possible to calculate the enthalpy of formation of this complex oxide with respect to the parent binary oxides

$$BaO(s)+0.9CeO_2(s)+0.05In_2O_3(s)= BaCe_{0.9}In_{0.1}O_{2.95}(s)$$

$$\Delta_{ox}H^0(BaCe_{0.9}In_{0.1}O_{2.95}(s), 298.15\ K)= -36.2\pm3.4\ kJ\ mol^{-1}$$

For these calculations we have used $\Delta_f H^0$ (BaO(s), 298.15 K), $\Delta_f H^0$ (CeO_2(s), 298.15 K), $\Delta_f H^0$ (In_2O_3(s) 298.15 K) taken from [14].

The same value for $BaCeO_3$ calculated from data of paper [13] is $\Delta_{ox}H^0$ (298.15 K)= –51.6±2.5 kJ mol^{-1}.

Since entropy changes for solid-state reactions are very small, the enthalpies of these reactions may be used to argue that these complex oxides are more stable than the parent binary oxides and that barium cerate doped with indium is less stable than undoped $BaCeO_3$.

Conclusions

The standard molar enthalpy of formation of $BaCe_{0.9}In_{0.1}O_{2.95}$ obtained in the present study by solution calorimetry was measured for the first time. It was established that barium cerate doped with indium is thermodynamically stable at room temperature with respect to decomposition to the constituent binary oxides but less stable than undoped $BaCeO_3$.

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