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Influence of doping with indium and neodymium on energy characteristics of barium cerate

Nata I. Matskevich,* Anna N. Semerikova, Mariya Yu. Matskevich and Olga I. Anyfrieva

A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. E-mail: nata.matskevich@yandex.ru

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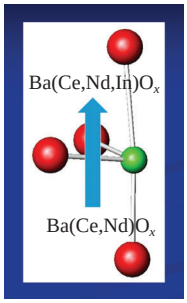
A new compound with the composition $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ has been synthesized. The influence of doping with indium and neodymium on the energy characteristics of barium cerate, necessary to improve the range of devices, has been studied. It has been found that the lattice enthalpy of $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ is greater than the lattice enthalpy of $BaCe_{0.8}Nd_{0.2}O_{2.9}$ and $BaCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85}$, which allows us to consider the investigated compound as a promising representative of solid-state compounds for various applications.



Keywords: doped barium cerate, co-doping with indium and neodymium, enthalpy of solution, standard enthalpy of formation, lattice enthalpy, Born–Haber cycle, solid-state reaction, predictive thermodynamics.

As is known, compounds based on cerates and zirconates of alkaline earth elements are widely used as catalysts, inorganic pigments and also as electrolytes in fuel cells.[1–13] These compounds are also widely studied as they are waste products generated during the operation of nuclear reactors. Cerates change their functional properties when cerium is partially replaced by other elements, in particular, rare earth elements. The study of the effect of doping on the functional properties and stability of compounds, especially their thermodynamic stability, is one of the urgent tasks of materials science. In 2021, the authors[12] who studied the effect of co-doping with Y and Nd and segregation of Nd on the stability and transport of protons in $BaCeO_3$ concluded that $BaCeO_3$ and $BaZrO_3$ have broad prospects for application as proton-conducting electrolytes at intermediate temperatures. The authors predict that segregation of neodymium at grain boundaries may be favorable for proton transfer between grains. In addition, they report[12] that the $BaCe_{0.8}Y_{0.15}Nd_{0.05}O_{3-\delta}$ electrolyte has the highest electrical conductivity among the materials tested, demonstrating the importance of studying co-doping of compounds. The effect of co-doping is practically not studied at present. Indium, which has an ionic radius close to that of yttrium, can be considered one of the most promising co-dopants.[14–18]

As mentioned in the classic work,[11] the optimization of all relevant material properties, including stability, seems to be an attractive way to develop new materials for specific applications. The strategy is promising, mainly when the interdependencies of the relevant properties can be expressed in terms of the same structural, thermodynamic and dynamic parameters.[11] Thermodynamics is essential for compound preparation technology. It allows, in particular, by optimizing the synthesis conditions to establish the directions of changes in stability and degradation when changing the composition. It should be noted that for the management of cerates present in nuclear waste, it is necessary to have information on cerates with isotopes. The properties of cerates with isotopes are complicated to measure directly because isotopes are expensive and controlled; after measurements, the isotopes must be removed from the solution. The study of the dependences of thermodynamic properties, which makes it possible to predict the properties of unstudied compounds, makes it possible to evaluate the properties of compounds with isotopes.

Partial displacement of cerium with indium in barium cerates has been reported[3,14–18] to increase stability, making indium an ideal dopant for modifying the functional properties of barium cerate. Indium can be incorporated into barium cerate at the level of 80%. However, doping barium cerate with a large amount of indium leads to a decrease in conductivity. In this regard, to increase stability and maintain conductivity, a co-doping strategy is used, which has hardly been studied. Nevertheless, cerates doped with indium and rare-earth elements were obtained,[3,14–18] and compounds of the composition $BaCe_{0.8}Nd_{0.2}O_{2.9}$ and $BaCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85}$ were studied.[3,19] Here, we investigate the composition of barium cerate doped with 10% neodymium and 10% indium. Since it was reported[12] that barium cerate doped with 20% trivalent ions (yttrium and neodymium) has the best conductivity, we also decided to investigate barium cerate partially doped with 20% trivalent ions (indium and neodymium). Indium has been used as a promising dopant.

This work aims to synthesize a new barium cerate doped with 10% neodymium and 10% indium, determine its standard enthalpy of formation and lattice enthalpy and compare the thermodynamic properties of the compound under study with the properties of $BaCe_{0.8}Nd_{0.2}O_{2.9}$ and $BaCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85}$ obtained by us earlier. This work is part of a series of our research on predictive thermodynamics, which is of fundamental and applied importance. We develop thermodynamics of low doping, which allows predicting the direction of changes in stability and thermodynamic properties of uninvestigated compounds based on the obtained dependences of thermodynamic properties on

content. The latter is important regardless of the class of compounds under study.

A new barium cerate with the composition $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ was synthesized by the solid-state reaction method. We used reaction calorimetry to determine the enthalpy of solution of barium cerate doped with 10% neodymium and 10% indium ($BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$). Then, proceeding from the enthalpy of solution of $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ and the enthalpy of solution of the mixture of chlorides ($BaCl_2$ + 0.8 $CeCl_3$ + 0.1 $NdCl_3$ + 0.1 $InCl_3$), together with the literature data, the standard enthalpy of formation and lattice enthalpy were calculated for $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$. The design of the calorimeter and the experimental procedure have been described in detail earlier.[20–22]

The calorimetric cycle was designed to determine the standard enthalpy of formation for $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$. In this cycle, the enthalpy of solution of $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ is compared with the enthalpy of solution of a mixture of chlorides. The solvent was 1 M HCl with the addition of 0.1 M KI. Potassium iodide was added to convert Ce^{4+} to Ce^{3+}.

The main thermochemical reactions for determining the standard enthalpy of formation for $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ are presented below:

$$BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}(s) + (5.8\,HCl + 1.2\,KI)(sol) + (sol\ 'A') = $$
$$= (BaCl_2 + 0.8\,CeCl_3 + 0.1\,InCl_3 + 0.1\,NdCl_3 + 0.8\,KCl + \quad (1)$$
$$+ 0.4\,KI_3 + 2.9\,H_2O)(sol) + \Delta_{sol}H_1^0,$$

$$BaCl_2(s) + 0.8\,CeCl_3(s) + 0.1\,InCl_3(s) + 0.1\,NdCl_3(s) + (sol\ 'A') = $$
$$= (BaCl_2 + 0.8\,CeCl_3 + 0.1\,InCl_3 + 0.1\,NdCl_3)(sol) + \Delta_{sol}H_2^0, \quad (2)$$

where sol 'A' is 1 M HCl + 0.1 M KI.

To implement the thermochemical cycle, we needed the following compounds: $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$, $BaCl_2$, $CeCl_3$, $InCl_3$ and $NdCl_3$. The synthesis of $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ is described in the experimental section,† and its phase purity was confirmed by powder X-ray diffraction analysis (Figure 1). We found the compound to be an individual phase.

The lattice parameters of $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ (space group *Pnma*) obtained in this work were a = 0.6191(2), b = 0.8739(2) and c = 0.6193(2) nm. We compared the lattice parameters of $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ with those of the $BaCe_{0.8}Nd_{0.2}O_{2.9}$ compound obtained by us earlier.[19] The lattice parameters of the latter were[19] a = 0.6222(2), b = 0.8791(2) and c = 0.6224(2) nm. As can be seen, the lattice parameters of barium cerate doped with indium and neodymium are less than those of barium cerate doped only with neodymium, which is due to a decrease in the ionic radius when going from neodymium to indium. For comparison, the lattice parameters for pure $BaCeO_3$ were a = 0.6227(2), b = 0.8791(2) and c = 0.6252(2) nm.

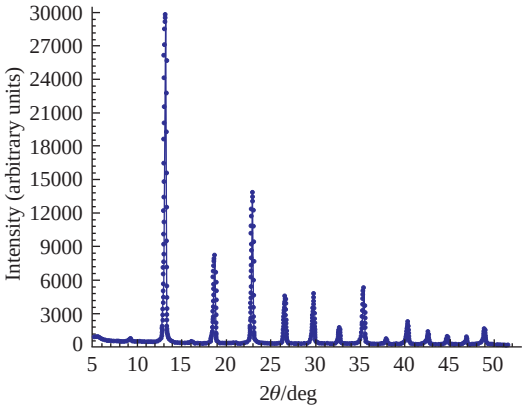


Figure 1 X-ray diffraction pattern for $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$.

To obtain the enthalpy of solution for $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$(s) and the enthalpy of solution for a mixture of chlorides [$BaCl_2$(s) + 0.8 $CeCl_3$(s) + 0.1 $InCl_3$(s) + 0.1 $NdCl_3$(s)], six parallel calorimetric experiments were performed for each of the two parameters and their average values were calculated. Then, based on the measured enthalpies of solution $\Delta_{sol}H_1^0$ and $\Delta_{sol}H_2^0$, the enthalpy of reaction (3) can be obtained as follows:

$$BaCl_2(s) + 0.8\,CeCl_3(s) + 0.1\,InCl_3(s) + 0.1\,NdCl_3(s) +$$
$$+ (0.8\,KCl + 0.4\,KI_3 + 2.9\,H_2O)(sol) = \quad (3)$$
$$= BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}(s) + (5.8\,HCl + 1.2\,KI)(sol) + \Delta_rH^0{}_3,$$

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

The enthalpies of solution were measured in a solution calorimeter with an isothermal jacket at a temperature T = 298.15 ± 0.01 K and a pressure of 100 ± 0.15 kPa. A sealed ampoule with the sample was placed in a calorimeter. After the calorimeter reached the regular thermal regime, the ampoule was broken and washed. The temperature rise was measured. After the dissolution experiment, a calibration experiment was carried out by introducing a known power into the calorimeter. The power was calculated based on the measured values of voltage, current and time. Potassium chloride (KCl) was used to calibrate the calorimeter. The enthalpy of solution of KCl was measured at a temperature of 298.15 ± 0.01 K. The resulting enthalpy of solution of potassium chloride in water (17.561 ± 0.021 kJ mol^{-1}) is in good agreement with a published one.[23] The final molality of aqueous KCl was 0.109 mol kg^{-1}. In the calorimetric experiments, 0.04 g of $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ and 0.06 g of the mixture of chlorides were dissolved in a solvent volume of 250 ml.

The measured enthalpies of solution for $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$ and the mixture $BaCl_2$(s) + 0.8 $CeCl_3$(s) + 0.1$InCl_3$(s) + + 0.1 $NdCl_3$(s) are $\Delta_{sol}H_1^0$ (298.15 K) = –372.08 ± 5.24 kJ mol^{-1} (n = 6) and $\Delta_{sol}H_2^0$ = –137.53 ± 0.61 kJ mol^{-1} (n = 6), respectively. Hereinafter, the enthalpies of solution are given with expanded uncertainties for a confidence level of 95%.

Using the enthalpies of solution $\Delta_{sol}H_1^0$ and $\Delta_{sol}H_2^0$, we calculated the enthalpy of reaction (3): $\Delta_rH_3^0 = -\Delta_{sol}H_1^0 + \Delta_{sol}H_2^0 =$ = +234.55 ± 5.28 kJ mol^{-1}.

Based on the measured enthalpy of reaction (3) and published data[24,25] on the enthalpies of formation for $BaCl_2$(s), $CeCl_3$(s), $InCl_3$(s), $NdCl_3$(s), KCl(sol), KI_3(sol), H_2O(sol), HCl(sol) and KI(sol), we calculated the standard enthalpy of formation Δ_fH^0($BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$, s, 298.15 K) = = –1588.34 ± 5.75 kJ mol^{-1} for $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$ in accordance with the reaction

† Barium cerate co-doped with neodymium and indium oxides ($BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$) was synthesized by a solid-state reaction from barium carbonate, cerium(IV) oxide and oxides of neodymium and indium. The mixture of starting components was ground in a planetary mill, pressed into pellets and heated in the temperature range 800–1300 K for several hours with final annealing at 1300 K for 30 h. Anhydrous $BaCl_2$, $CeCl_3$ and $NdCl_3$ were obtained by purification of the respective commercial reagents (CERAC, >99.9 wt%) as described previously.[19] $InCl_3$ was synthesized from Cl_2 and In according to a known procedure.[3] Chlorine gas was passed over indium at a temperature of about 450 K. All manipulations with $BaCl_2$, $CeCl_3$, $NdCl_3$ and $InCl_3$ were carried out in a dry box (pure Ar gas).

The phase purity of $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$ was determined by X-ray diffraction analysis on a Shimadzu XRD-7000 diffractometer with Cu Kα1 radiation at a temperature of 296.0 ± 0.1 K. The lattice parameters a = 0.6191(2), b = 0.8739(2) and c = 0.6193(2) nm were determined using the FULLPROF program; the compound has an orthorhombic structure, space group *Pnma*. The content of barium, cerium, neodymium and indium was determined by fluorescence analysis with an accuracy of about 0.2% to establish that the compound formula is $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$.

$$Ba(s) + 0.8\,Ce(s) + 0.1\,In(s) + 0.1\,Nd(s) + 1.45\,O_2(g) = \quad (4)$$
$$= BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}(s) + \Delta_f H^0_4.$$

Then it was interesting to calculate the lattice enthalpy of the investigated compound $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$ and compare it with those of other barium cerates. The lattice enthalpy was calculated according to the Born–Haber cycle, which includes reaction (4) and reactions (5)–(9), presented below:

$$Ba^{2+}(g) = Ba(s) + \Delta_r H^0_5, \quad (5)$$
$$0.8\,Ce^{4+}(g) = 0.8\,Ce(s) + 0.8\,\Delta_r H^0_6, \quad (6)$$
$$0.1\,Nd^{3+}(g) = 0.1\,Nd^{3+}(s) + 0.1\,\Delta_r H^0_7, \quad (7)$$
$$0.1\,In^{3+}(g) = 0.1\,In^{3+}(s) + 0.1\,\Delta_r H^0_8, \quad (8)$$
$$2.9\,O^{2-}(g) = 1.45\,O_2(g) + 2.9\,\Delta_r H^0_9. \quad (9)$$

Based on reactions (4)–(9), we calculated the lattice enthalpy $\Delta_{lat}H^0(BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9},\ 298.15K) = -12770 \pm 20$ kJ mol^{-1} for compound $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$ according to the following equation:

$$Ba^{2+}(g) + 0.8\,Ce^{4+}(g) + 0.1\,Nd^{3+}(g) + 0.1\,In^{3+}(g) + 2.9\,O^{2-}(g) =$$
$$= BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}(s) + \Delta_{lat}H^0_{10}, \quad (10)$$

where $\Delta_{lat}H^0_{10} = \Delta_f H^0_4 + \Delta_r H^0_5 + 0.8\,\Delta_r H^0_6 + 0.1\,\Delta_r H^0_7 + 0.1\,\Delta_r H^0_8 + + 2.9\,\Delta_r H^0_9$.

Previously, we synthesized the compounds $BaCe_{0.8}Nd_{0.2}O_{2.9}$ and $BaCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85}$ and measured their standard enthalpies of formation.[3,19] Using these values in the Born–Haber cycle, we calculated the lattice enthalpies $\Delta_{lat}H^0(BaCe_{0.8}Nd_{0.2}O_{2.9},\ 298.15\ K) = -12690 \pm 20$ kJ mol^{-1} for $BaCe_{0.8}Nd_{0.2}O_{2.9}$ and $\Delta_{lat}H^0(BaCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85}, 298.15\ K) = = -12410 \pm 20$ kJ mol^{-1} for $BaCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85}$.

As can be seen, the lattice enthalpy of the studied compound $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$ is higher in absolute value than those of $BaCe_{0.8}Nd_{0.2}O_{2.9}$ and $BaCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85}$. Thus, the studied compound $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$ is more stable and promising for various applications.

In summary, we synthesized a new compound of the composition $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$ by a solid-state reaction of barium carbonate, neodymium oxide, CeO_2 and indium oxide. The compound crystallizes in an orthorhombic system (space group *Pnma*). The enthalpy of solution of $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$ in 1 M HCl with 0.1 M KI, as well as the enthalpy of solution of the mixture $BaCl_2 + 0.8\,CeCl_3 + 0.1\,InCl_3 + 0.1\,NdCl_3$, have been measured for the first time. Based on the data obtained, the standard enthalpy of formation and lattice enthalpy were calculated for $BaCe_{0.8}In_{0.1}Nd_{0.1}O_{2.9}$. It was found that the lattice enthalpy of $BaCe_{0.8}Nd_{0.1}In_{0.1}O_{2.9}$ is higher than those of $BaCe_{0.8}Nd_{0.2}O_{2.9}$ and $BaCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85}$, which allows us to consider the compound under study as a promising representative of solid-state compounds for various applications.

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