

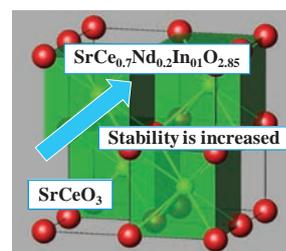
Thermochemical characteristics of strontium cerate doped by neodymium and indium oxides

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

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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The thermodynamic functions (formation enthalpy and stabilization energy) of $\text{SrCe}_{0.7}\text{Nd}_{0.2}\text{In}_{0.1}\text{O}_{2.85}$ were measured to demonstrate that strontium cerate doped by neodymium and indium oxides has higher stabilization energy than that of undoped strontium cerate. The result obtained can give advantage to apply this compound in comparison with SrCeO_3 .



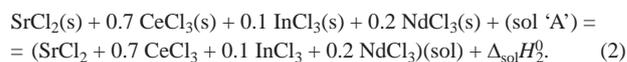
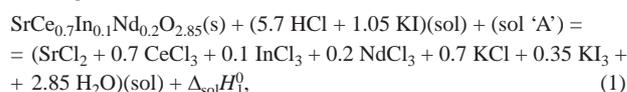
Keywords: doped strontium cerate, thermodynamic stability, formation enthalpy, stabilization energy, calorimetry.

Barium and strontium cerates with the general formula $\text{Sr}(\text{Ba})\text{Ce}_{1-x}\text{M}_x\text{O}_{3-y}$, where M is a Group III, V, or VI metal, are promising materials applied to alternative energetics.^{1–10} These compounds with cerium replaced by lanthanides exhibit high ionic conductivity at temperatures above 1000 K. It was found^{11–15} that co-doping of barium cerates by rare-earth elements and indium oxides leads to compounds having high ionic conductivity and thermodynamic stability. From practical point of view, the most promising composition is $\text{BaCe}_{0.7}\text{R}_{0.2}\text{In}_{0.1}\text{O}_{3-\delta}$ (R is a rare-earth element).

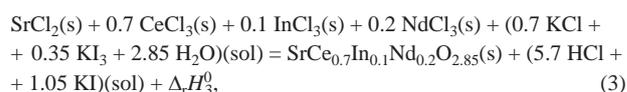
This study was aimed at the synthesis[†] of the new strontium cerate $\text{SrCe}_{0.7}\text{Nd}_{0.2}\text{In}_{0.1}\text{O}_{2.85}$ and the determination of its thermochemical properties using solution calorimetry.^{16–18} The thermochemical cycle was designed in such a way that the solution enthalpy of strontium cerate co-doped by neodymium and indium oxides was compared with the solution enthalpy of a mixture of strontium, cerium, neodymium, and indium chlorides ($\text{SrCl}_2 + 0.7 \text{CeCl}_3 + 0.2 \text{NdCl}_3 + 0.1 \text{InCl}_3$). Then, the standard formation enthalpy of $\text{SrCe}_{0.7}\text{Nd}_{0.2}\text{In}_{0.1}\text{O}_{2.85}$ was calculated. Calorimetric experiments

were carried out in hydrochloric acid with KI added to convert Ce^{4+} into Ce^{3+} (1 M HCl + 0.1 M KI, sol 'A').

The main reactions of the thermochemical cycle were the following:



On the basis of the measured solution enthalpies $\Delta_{\text{sol}}H_1^0$ and $\Delta_{\text{sol}}H_2^0$, the enthalpy of reaction (3) was calculated:



where $\Delta_{\text{sol}}H_3^0 = -\Delta_{\text{sol}}H_1^0 + \Delta_{\text{sol}}H_2^0$.

To perform the thermochemical cycle, we used the samples of $\text{SrCe}_{0.7}\text{In}_{0.1}\text{Nd}_{0.2}\text{O}_{2.85}$, SrCl_2 , CeCl_3 , InCl_3 , and NdCl_3 . The phase purity of $\text{SrCe}_{0.7}\text{In}_{0.1}\text{Nd}_{0.2}\text{O}_{2.85}$ was confirmed by X-ray powder diffraction analysis (Figure 1). The lattice parameters $a = 0.61229(3)$, $b = 0.85598(4)$ and $c = 0.59699(3)$ nm were determined using the FullProf.2k software; the compound has an orthorhombic structure, space group $Pnma$.

The solution enthalpies were measured at $T = 298.15 \pm 0.01$ K and a pressure of 100 ± 0.15 kPa in a solution calorimeter with an isothermal jacket, which was described elsewhere.^{16,17} Potassium chloride (KCl) was used to calibrate the calorimeter. The solution enthalpy of KCl was measured at 298.15 ± 0.01 K in water and the found value (17.561 ± 0.021 kJ mol⁻¹) is in a good agreement with a published one.¹⁹ The final molality of aqueous KCl was 0.109 mol kg⁻¹. Chemically pure potassium chloride was twice recrystallized from distilled water and dried at 773 K. In the calorimetric experiments, 0.04 g of $\text{SrCe}_{0.7}\text{Nd}_{0.2}\text{In}_{0.1}\text{O}_{2.85}$ and 0.06 g of a mixture of chlorides were dissolved (solvent volume, 250 ml).

[†] Strontium cerate co-doped by neodymium and indium oxides was synthesized by a solid state reaction from strontium carbonate, cerium(IV) oxide, and neodymium and indium oxides in a temperature range of 800–1300 K during several hours with final annealing at 1700 K for 40 h.

Detailed information on the preparation of anhydrous chlorides was reported previously.^{4,12} Anhydrous SrCl_2 was prepared by drying SrCl_2 (CERAC, >99.9%) at 500 K. Anhydrous CeCl_3 was prepared from CeCl_3 (CERAC, >99.9%) by vacuum sublimation (1143 K) at $<10^{-5}$ Pa. NdCl_3 was prepared from Nd_2O_3 (99.99%, Purathem, STREM Chemicals) dissolved in an excess of hydrochloric acid. Purified chlorine gas was bubbled through the solutions. InCl_3 was synthesized from Cl_2 and In. Chlorine gas was passed over indium at about 450 K. All manipulations with SrCl_2 , CeCl_3 , NdCl_3 and InCl_3 were performed in a dry box (pure Ar gas).

The phase purity was analyzed by X-ray diffraction (Shimadzu XRD-7000 diffractometer). Contents of strontium, cerium, neodymium and indium were determined by fluorescence analysis, flame photometry and spectrophotometry. The oxygen content was determined on a METAVAK-AK analyzer.

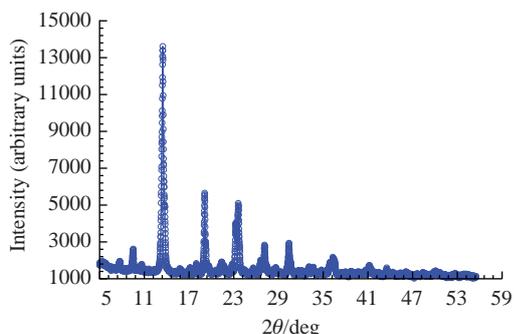
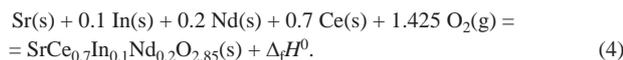


Figure 1 X-ray diffraction pattern for SrCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85} measured at 296.0 ± 0.1 K.

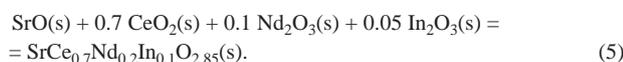
The measured solution enthalpies of SrCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85} and a mixture of SrCl₂ + 0.7 CeCl₃ + 0.2 NdCl₃ + 0.1 InCl₃ are $\Delta_{\text{sol}}H_1^0(298.15 \text{ K}) = -341.39 \pm 4.52 \text{ kJ mol}^{-1}$ ($n = 5$) and $\Delta_{\text{sol}}H_2^0 = -176.64 \pm 0.68 \text{ kJ mol}^{-1}$ ($n = 5$), respectively, where n is the number of experiments.

Using the enthalpies $\Delta_{\text{sol}}H_1^0$ and $\Delta_{\text{sol}}H_2^0$, we calculated the enthalpy of reaction (3): $\Delta_{\text{sol}}H_3^0 = -\Delta_{\text{sol}}H_1^0 + \Delta_{\text{sol}}H_2^0 = +164.75 \pm 4.57 \text{ kJ mol}^{-1}$.

On this basis and using published data^{20,21} on the formation enthalpies of SrCl₂(s), CeCl₃(s), InCl₃(s), NdCl₃(s), KCl(sol), KI₃(sol), H₂O(sol), HCl(sol), and KI(sol), we calculated the standard formation enthalpy $\Delta_f H^0(\text{SrCe}_{0.7}\text{Nd}_{0.2}\text{In}_{0.1}\text{O}_{2.85}, \text{ s}, 298.15 \text{ K}) = -1625.01 \pm 5.42 \text{ kJ mol}^{-1}$ for SrCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85} in accordance with the reaction



Then, we calculated the stabilization energy $\Delta_{\text{st}}H^0(298.15 \text{ K}) = -44.11 \pm 5.63 \text{ kJ mol}^{-1}$ for SrCeO₃ co-doped by Nd₂O₃ and In₂O₃ using the formula $\Delta_{\text{st}}H^0(\text{ABO}_3) = \Delta_f H^0(\text{ABO}_3) - [\Delta_f H^0(\text{AO}) + \Delta_f H^0(\text{BO}_2)]$ applied to the reaction



Cordfunke *et al.*²⁰ measured the standard formation enthalpy of undoped SrCeO₃, and we calculated a stabilization energy of $-6.17 \pm 3.04 \text{ kJ mol}^{-1}$ for undoped SrCeO₃ (298.15 K) on this basis. Thus, strontium cerate co-doped by neodymium and indium has a higher stabilization energy than that of undoped strontium cerate at room temperature.

We also calculated the stabilization energies $\Delta_{\text{st}}H^0(800 \text{ K}) = -38.30 \pm 5.63 \text{ kJ mol}^{-1}$ for SrCe_{0.7}In_{0.1}Nd_{0.2}O_{2.85} and $\Delta_{\text{st}}H^0(800 \text{ K}) = -1.33 \pm 3.04 \text{ kJ mol}^{-1}$ for SrCeO₃ at $T = 800 \text{ K}$ based on the experimental results and published data.²¹

Then, we compared the lattice parameters [$a = 0.61229(3)$, $b = 0.85598(4)$ and $c = 0.59699(3) \text{ nm}$] of SrCe_{0.7}Nd_{0.2}In_{0.1}O_{2.85} with the lattice parameters²² of undoped SrCeO₃ [$a = 0.61483(2)$,

$b = 0.85833(2)$ and $c = 0.60089(2) \text{ nm}$]. A decrease in lattice parameters¹² leads to an increase in the lattice energy and the thermodynamic stability of strontium cerate doped by neodymium and indium oxides in comparison with that of undoped strontium cerate.

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