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Synthesis and thermodynamic functions of barium cerate co-doped with erbium and indium

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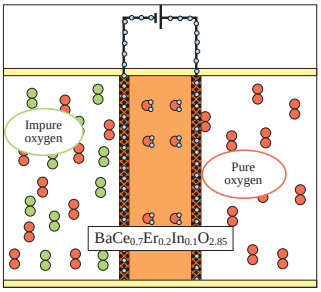
The new compound $BaCe_{0.7}Er_{0.2}In_{0.1}O_{2.85}$ was synthesized as a representative of promising class of solid state ionic conductors. Thermodynamic functions needed to improve and extend devices portfolio with a special emphasis on the heat capacity and phase transition have been revealed. It has been experimentally established that there is no phase transition for $BaCe_{0.7}Er_{0.2}In_{0.1}O_{2.85}$ in the temperature range of 191–695 K, which can give advantage to the practical application of this compound in comparison with materials possessing the phase transitions.



Compounds based on alkaline earth cerates are widely investigated due to a variety of their unique functional properties.[1–10] For example, barium cerates doped with rare-earth elements can be used as a trap in nuclear reactors.[11] Moreover, barium cerate is the decomposition product of uranium and plutonium.[12] Strontium and barium cerates possessing high ionic conductivity at high temperatures are promising materials for fuel cells, in electro catalysis, as gas separation membranes, *etc*. To expand and optimize technologies for the application of cerate materials, detailed physical and chemical investigations are needed. In particular, it is necessary to perform a thermodynamic study to predict decay products of uranium and plutonium, which are formed at various temperatures.

It was previously demonstrated[13,14] that the addition of indium to barium cerate extends the homogeneity field up to 80%. However, the ionic conductivity of barium cerate doped with indium is decreased as compared to barium cerates doped with rare-earth elements.[15] Some works[16,17] reported on a co-doping strategy (doping with two or more elements) to increase the ionic conductivity and stability of barium cerate. For this purpose, barium cerates doped with indium, yttrium and other rare-earth elements were synthesized, and the homogeneity field was expanded up to 30%.[16,17]

Phase transitions of barium cerate doped with indium and rare-earth elements were also explored.[18,19] It was noted that $BaCe_{0.7}Ho_{0.2}In_{0.1}O_{2.85}$ and $BaCe_{0.8}Gd_{0.1}Y_{0.1}O_{2.9}$ exhibited a second-order phase transition at the temperature above 500 K. However, it is not clear how the enthalpy and temperature of phase transition depends on replacing one rare-earth element by another. It is better to deal with compounds without phase transition in terms of practical applications.

The present work was aimed at the synthesis and investigation of thermodynamic properties of $BaCe_{0.7}Er_{0.2}In_{0.1}O_{2.85}$ **1** in the temperature range of 191–695 K. Polycrystalline sample of compound **1** was prepared by solid-state reaction from $BaCO_3$, CeO_2, Er_2O_3, and In_2O_3.[†] Heat capacity of phase **1** was studied by the differential scanning calorimetry (DSC) to reveal whether there are any phase transitions in this compound.[‡]

Figure 1 shows the acquired heat capacity data. A consideration of the heat capacity curve revealed the absence of any anomalies within the interval of measurements. The specific heat in the temperature range of 191–695 K varies smoothly.

[†] Before synthesis, Er_2O_3 and In_2O_3 were calcined at 900 K up to constant weight to remove water and CO_2. A stoichiometric mixture of $BaCO_3$ (Cerac Inc., 99.999% pure), CeO_2 (99.99%, Johnson Matthey GmbH, Alfa Products), Er_2O_3 (99.99%, Ventron), and In_2O_3 (99.99%, Reacton) was ball-milled (agate balls) for several hours. Afterward, the procedure of ball-milling was repeated on the powder before it was pressed into pellets (diameter of 1 cm). The pellets were placed in an alumina crucible and sintered in ambient laboratory air in the temperature range of 1300–1700 K.

The resultant powder was identified as pure compound **1** by X-ray diffraction (XRD) analysis using STADI-P STOE powder X-ray diffractometer with Mo radiation. According to XRD, the sample was single phase with orthorhombic structure. Cell parameters were: a = 0.87728(6), b = = 0.61729(5) and c = 0.61745(5) nm.

The compound was also characterized by flame photometric, spectrophotometric and reducing melting methods for the maintenance of Ba, Ce, Er, In, O. The spectrophotometer SF-46 and spectrometer iCE 3000 were used for analysis. The oxygen content was determined by reducing melting method in a helium flow on a METAVAK-AK analyzer.

Experimental data for the elemental composition were: Ba, 42.09 ± 0.06; Ce, 30.03 ± 0.09; Er, 10.31 ± 0.05; In, 3.55 ± 0.03; O, 14.06 ± 0.08. Calculated data for content of elements were: Ba, 42.13; Ce, 30.09; Er, 10.26; In, 3.52; O, 13.99. According to the results of analysis, the investigated compound **1** corresponds to $BaCe_{0.7}Er_{0.2}In_{0.1}O_{2.85}$ within the accuracy < 1%.

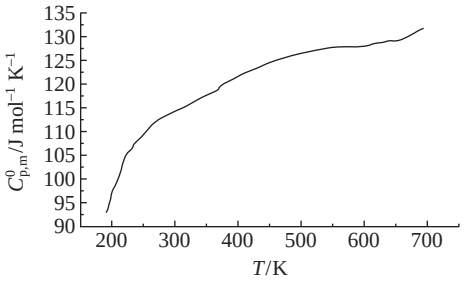


Figure 1 Experimental heat capacities for $BaCe_{0.7}Er_{0.2}In_{0.1}O_{2.85}$.

Therefore, the observed fact of absence of any phase transitions caused by co-doping of barium cerate with erbium and indium is of interest.

The heat capacity data was fitted using a suite of polynomials. We used a special program for the fitting, which allows one to determine the sum of squares of deviations.[18,19] A polynomial with a minimal sum of squares of deviations to describe the heat capacity in the temperature range of 191–584 K was the following:

$$C^0_{p,m}(T) = 111.67 + 0.031366\,T - 1.6777\times10^8/T^3 \quad (1)$$
$$(\text{J mol}^{-1}\text{ K}^{-1})$$

The scatter of heat capacity experimental data *vs.* the approximating curve did not exceed 1.5%.

The heat capacity of compound **1** in the temperature range of 584–695 K is well described by a polynomial, which has the following minimal sum of squares of deviations:

$$C^0_{p,m}(T) = -1101.7 + 5.9387\,T - 9.5715\times10^{-3}\,T^2 + 5.1510\times10^{-6}\,T^3\ (\text{J mol}^{-1}\text{ K}^{-1}) \quad (2)$$

The deviation uncertainty of experimental heat capacity values from the smoothed values was less than 0.3%.

Before fitting the heat capacity data by polynomials, we divided the data into the three temperature ranges, where the values vary absolutely smoothly: 191–565, 565–584 and 584–695 K. Each part of data was fitted by one polynomial. The first two temperature ranges were then combined, and the data was fitted only by two polynomials, *viz.*, polynomials in the temperature ranges (i) 191–584 K and (ii) 584–695 K. It was observed that the sum of squares of deviations was the minimal one when the heat capacity data were described by two polynomials, as compared to the case of the data described with three polynomials.

Taking into account the smoothed values of heat capacity, the entropy and enthalpy increments were calculated as follows: $H^0_m(T) - H^0_m(298.15) = -2.8655\times10^4 + 74.584\,T + 8.6120\times10^{-2}\,T^2 - 4.5629\times10^{-5}\,T^3$ (J mol^{-1}) and $S^0_m(T) = -27.491 + 0.7419\,T - 7.5347\times10^{-4}\,T^2 + 3.4837\times10^{-7}\,T^3$ (J K^{-1} mol^{-1}).

The heat capacity under standard conditions was calculated as 114.7 J K^{-1} mol^{-1} and within 5% agreed with that (108.4 J K^{-1} mol^{-1}) estimated as the sum of $BaCeO_3$, Er_2O_3 and In_2O_3 heat capacities taken from ref. 20. These values were used to estimate the heat capacity of compound **1** since such an approach gives better results than just using the heat capacity of simple oxides.

DSC data measured in the temperature range of 191–695 K allow one to calculate only entropies increments $S(T) - S(298.15)$. Thus, to calculate $S(T)$, it is necessary to know the entropy value at 298.15 K. We have estimated the entropy of compound **1** for the standard conditions as a sum of simple oxides entropies: 136.1 J K^{-1} mol^{-1} (at T = 298.15 K). The entropies of oxides (BaO, CeO_2, Er_2O_3, and In_2O_3) were taken from ref. 20.

It is of note that a smeared phase transition of second order was found for compound $BaCe_{0.7}Ho_{0.2}In_{0.1}O_{2.85}$,[18] while there was no phase transition in the case of compound **1**. A second-order phase transition is related to some structural changes during this process. The structures of both $BaCe_{0.7}Ho_{0.2}In_{0.1}O_{2.85}$ and compound **1** at room temperatures are the orthorhombic ones. Meanwhile, the lattice enthalpy is increased going from $BaCe_{0.7}Ho_{0.2}In_{0.1}O_{2.85}$ to compound **1**, which can be explained by the modified Kapustinsky rule.[21] This means that the lattice becomes more stable going from $BaCe_{0.7}Ho_{0.2}In_{0.1}O_{2.85}$ to compound **1**, which may be the reason of phase transition absence.

In conclusion, the development of novel materials is necessary to realize new device concepts and to improve and extend devices portfolio. In this work, we have estimated the thermodynamic characteristics of new material $BaCe_{0.7}Er_{0.2}In_{0.1}O_{2.85}$, in particular, measured the heat capacity and checked the presence or absence of phase transition in the average range of temperatures. Our results demonstrating the absence of any phase transitions in the temperature range of 191–695 K for $BaCe_{0.7}Er_{0.2}In_{0.1}O_{2.85}$ can provide advantage to this compound in comparison with materials possessing the phase transitions, and make it promising for the practical applications.

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‡ DSC measurements were performed using a DSC 404 F1 automated experimental setup (NETZSCH). Four sets of experiments (up and down) were carried out in two different temperature ranges: (i) 191–374 and (ii) 322–700 K. Heat flow as a function of temperature was measured from 191 to 695 K at a heating rate of 6 K min^{-1} under an Ar flow of 20 ml min^{-1}. The $BaCe_{0.7}Er_{0.2}In_{0.1}O_{2.85}$ **1** sample mass was 127.44 mg (molar mass is 325.95 g mol^{-1}). Al_2O_3 was used as the standard to calculate the heat capacities of compound **1**. The detailed conditions of measurements were reported in our previous works.[18,19] The estimated accuracy of heat capacity was 1–3% with the highest error at a high temperature.

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