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Redox energetics and enthalpy increments of $GdBaCo_2O_{6-\delta}$

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ABSTRACT

The enthalpy increments for the $GdBaCo_2O_{6-\delta}$ double perovskite were determined by means of drop calorimetry in air in the temperature range between 365.4 K and 1272.4 K. The heats of orthorhombic I→orthorhombic II phase transition at 347.2 K and orthorhombic II \rightarrow tetragonal transition at 745.8 K are equal to (2.95 \pm 0.07) kJ-mol⁻¹ and (2.40 ± 0.09) kJ-mol⁻¹, respectively, as measured with differential scanning calorimetry for GdBaCo₂O_{6.8}. These calorimetric data were used to determine the heat capacity of GdBaCo₂O_{6.8} and the hightemperature 'chemical' contribution to the enthalpy increments, caused by the oxygen exchange. The differentiation of the 'chemical' contribution with respect to oxygen nonstoichiometry yielded the partial molar enthalpy of oxygen in the GdBaCo₂O_{6.8}, which agrees well with the previously reported results. The enthalpy increment data of nonstoichiometric oxides have proven itself as a valuable source of redox energetics information.

1. Introduction

Complex oxides $RBaCo_2O_{6-\delta}$ (R = rare-earth metal) with double perovskite structure have received great attention as promising materials for oxygen permeable membranes and cathodes of solid oxide fuel cells (SOFCs). However, most of the studies on these materials are focused on their crystal structure [1,2], phase behavior [3-5], mass and charge transfer [6,7] and evaluation of their electrochemical performance in SOFCs [8]. At the same time, there is still lack of information on the key thermodynamic properties of double perovskites. The heat capacity was studied only at low temperatures for the selected RBaCo₂O_{6- δ} with R = Y, Gd, Pr and $\delta = 0.5$ [5,9–11], and the results obtained were presented only in graphical form, which seriously restricts their value as a source of thermodynamic data. As for the hightemperature thermodynamic properties of RBaCo2O6-8 double perovskites, they have not been reported so far. However, the knowledge of the oxide materials' thermodynamics is of key significance for understanding physical and chemical properties of solids, as well as for assessment of both the materials' stability under particular environmental conditions and the chemical compatibility with other components of SOFCs.

Further, it has to be emphasized that high-temperature properties of strongly nonstoichiometric oxides, such as double perovskite cobaltites, depend not only on temperature (T), but also on oxygen nonstoichiometry (δ), which varies with *T* and oxygen partial pressure () in

the surrounding atmosphere [12]. For example, the oxygen content in $PrBaCo_2O_{6-\delta}$ decreases from 5.77 to 5.3 during heating in air from 298 K to 1273 K [13], which may lead to the heat capacity change of up to almost 1.5R, under the assumption of classical Dulong-Petit limit of 3R for the heat capacity per each atom. Therefore, when using hightemperature calorimetric techniques, one has to take into account the variation in the sample's chemical composition during the course of the measurements. In a typical drop calorimetry experiment, which is performed at constant oxygen activity, the enthalpy increment measured on dropping the sample from room temperature to high temperature in the absence of phase transitions can be represented as

$$\Delta_{298}^T H^{\bigcirc} = \int_{298}^T C_p^{\delta_1} dT - \int_{\delta_1}^{\delta_2} \overline{H}_0^T d\delta$$
⁽¹⁾

where $C_p^{\delta_1}$ – isobaric heat capacity of the sample with constant chemical composition, δ_1 ; \overline{H}_0^T – partial molar enthalpy of oxygen in the sample at the temperature *T*. Therefore, the first term in the right-hand side of Eq. (1) represents the enthalpy of heating the sample with certain composition (δ_1) from 298 K to *T*, whereas the second one is the enthalpy of oxide reduction from initial (δ_1) to equilibrium (δ_2) composition at temperature T, according to the following reaction:

$$RBaCo_2O_{6-\delta_1} = RBaCo_2O_{6-\delta_2} + \frac{\delta_2 - \delta_1}{2}O_2$$
(2)

On the one hand, the heat capacity calculations are somewhat more

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complicated for strongly nonstoichiometric oxides than for stoichiometric materials. On the other hand, the enthalpy increments may be an important source of thermodynamic information on both heat capacity and redox energetics of nonstoichiometric oxides. However, for this information to be of use, both terms in Eq. (1) must be determined, which requires additional measurements. The oxygen content in the oxide sample should be studied under the conditions similar to those employed during the drop calorimetry experiment. Some assumptions on the temperature dependence of the heat capacity and partial molar enthalpy of oxygen in the oxide are also required [14]. As a consequence, as will be shown in this work, the sample's heat capacity and the partial molar enthalpy of oxygen can be extracted from the measured enthalpy increments.

Thus, the present study was aimed at: (i) measuring enthalpy increments for $GdBaCo_2O_{6-\delta}$ double perovskite; (ii) calculating its heat capacity and partial molar enthalpy of oxygen; and (iii) calculating enthalpy increments and isobaric heat capacities of $GdBaCo_2O_{6-\delta}$ double perovskite with arbitrary oxygen content.

2. Experimental

Powder sample of GdBaCoO₆₋₈ double perovskite was synthesized by means of glycerol-nitrate technique using Co, Gd₂O₃ and BaCO₃ as the precursors. Metallic Co was obtained by reduction of Co₃O₄ (purity 99.99 wt %) in H₂ atmosphere at 873 K. Gd₂O₃ and BaCO₃ were preliminary calcined to remove the adsorbed H₂O and CO₂ at 1373 K and 873 K, respectively. The purity and the suppliers of the materials used are listed in Table 1. The details of the synthesis procedure were described elsewhere [7]. The as-obtained powder sample was finally calcined at 1373 K for 30 h and slowly (100 K·h⁻¹) cooled to room temperature in air. Phase composition of the sample was controlled by X-ray diffraction (XRD) in Cu Ka radiation using XRD-7000 diffractometer (Shimadzu, Japan). XRD showed no indication for the presence of a second phase in the as-prepared sample of GdBaCo₂O₆₋₈. Its average chemical composition was first determined using ICP spectrometry (ICAP 6500 DUO) and atomic absorption spectrometry (Solaar M6, Thermo Scientific), and then local compositions were probed by scanning electron microscopy (SEM) coupled with energydispersive spectrometry (EDX) using an AURIGA CrossBeam (FIB-SEM) Workstation (Carl Zeiss SMT). The nominal cation stoichiometry of the as-prepared sample and a homogeneous distribution of the elements were confirmed. The overall level of impurities was found to be less than 0.1 wt %.

For the drop calorimetry measurements, the as-obtained singlephase powder of the double perovskite was axially pressed into a rectangular bar of $30 \times 4 \times 4$ mm³. The green sample bar was sintered at 1473 K for 12 h in air and slowly (100 K·h⁻¹) cooled to room temperature. The relative density of the ceramic sample prepared accordingly was found to be 80 %.

Variation of the oxygen content in the GdBaCo₂O₆₋₈ was measured in air as a function of temperature in the range (298–1273) K by thermogravimetric method (TG) using STA 409 PC thermobalance (Netzsch GmbH, Germany). Heating and cooling rates were 100 K·h⁻¹.

The absolute value of δ in GdBaCo₂O_{6- δ} was determined by two independent techniques: direct reduction of the oxide in hydrogen flux in the TG setup (TG/H₂) and redox titration. TG/H₂ was carried out at

1373 K, and Gd₂O₃, BaO and metallic Co were found to be the final products [15]. As a result, in the as-prepared and slowly cooled (100 K·h⁻¹) in air ceramic sample of GdBaCo₂O₆₋₈, the oxygen content was found to be equal to 5.515 \pm 0.005 (expanded uncertainty with 0.95 level of confidence).

Enthalpy increments were determined by high-temperature dropcalorimetry using MHTC 96 calorimeter (Setaram, France). Small, (20–30) mg, ceramic pieces of GdBaCo₂O_{5.515} were dropped from the autosampler at room temperature ($T_{\rm low}$) to the calorimetric cell, preheated to the desired temperature $T_{\rm high}$ in the range of (373–1323) K. In each experiment, the sample pieces were dropped alternately with the pieces of synthetic sapphire standard (NIST SRM720) for calibration of the calorimeter sensitivity. All the drop calorimetry measurements were performed in ambient air, $\log(p_{O_2}/p^{\bigcirc}) = -0.67 \pm 0.02$ (expanded uncertainty with 0.95 level of confidence, $p^{\bigcirc} = 101325$ Pa), with average atmospheric pressure (101.5 \pm 0.5) kPa (expanded uncertainty with 0.95 level of confidence).

Phase transitions in $GdBaCo_2O_{6-\delta}$ in the temperature range from room temperature to 873 K were studied by differential scanning calorimetry (DSC) in the original DSC setup described elsewhere [16]. Two platinum crucibles, one of which empty and another one containing around 0.700 g of GdBaCo₂O_{5.515} powder, were used for measurements. The DSC measurements were carried out with heating rate 2 K·min^{-1} in 50 ml·min⁻¹ flow of dry air $(\log(p_{\text{H}>0}/p^{\circ}) \le -3.5,$ $p^{\circ} = 101325 \text{ Pa}$). The inlet air was dried by passing it through the column with pre-annealed zeolites. The DSC experiment was repeated, at least, 3 times. The temperature corresponding to the onset of each DSC-peak was assumed to represent the temperature of the phase transition. The temperature and heat sensitivity of the DSC setup was calibrated in scanning mode with the heating rate of 2 K·min^{-1} using melting points and heats of fusion of standard high purity (99.99 wt %) metals, and the sensitivity coefficient obtained was used to calculate the phase transition enthalpies.

3. Results and discussion

3.1. Sample characterization

XRD pattern of the as-prepared slowly cooled GdBaCo₂O_{5.515} sample at (298 ± 2) K (expanded uncertainty with 0.95 level of confidence) is shown in Fig. 1. The pattern was indexed using the tetragonal *Pmmm* space group. The lattice constants *a*, *b* and *c*, refined using Le Bail procedure, are equal to (3.910 ± 0.004) Å (expanded uncertainty with 0.95 level of confidence), (7.750 ± 0.001) Å (expanded uncertainty with 0.95 level of confidence) and (7.532 ± 0.003) Å (expanded uncertainty with 0.95 level of confidence), respectively. The calculated density of the GdBaCo₂O_{5.515} sample equals (7.285 ± 0.008) g·cm⁻³ (expanded uncertainty with 0.95 level of confidence).

3.2. Drop calorimetry measurements

The results of the drop calorimetry measurements for $GdBaCo_2O_{6-8}$ sample are summarized in Fig. 2 and Table 2.

As has been mentioned above, the starting oxygen content in the GdBaCo₂O₆₋₈ sample before the drop was $(6 - \delta_0) = 5.515$. The final

Table 1

Chemical compounds used in the present work.

Chemical name	Source	Mass fraction purity	Analysis method
BaCO ₃	Lanhit	> 0.9999	-
Gd_2O_3	Lanhit	> 0.9999	-
Co ₃ O ₄	MCP Hek GmbH	> 0.9999	-
Со	synthesis	> 0.999	XRD
GdBaCo ₂ O ₆₋₈	synthesis	> 0.99	XRD, ICP and AAS spectrometry, SEM EDX



Fig. 1. XRD pattern of the as-prepared double perovskite $GdBaCo_2O_{5.515}$. Red circles represent the experimental data and the solid black curve is the calculated profile. A difference curve is plotted at the bottom of the pattern. Vertical green lines represent the position of the allowed Bragg reflections (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Fig. 2. Enthalpy increments and oxygen content in GdBaCo₂O₆₋₈ as a function of temperature in air. Black points represent enthalpy increments, dashed black line – their low-temperature linear trend. The oxygen content in the sample at room temperature equals 5.515; the final (equilibrium) oxygen content at each temperature studied is shown by red triangles. The inset shows the variation of the oxygen content in GdBaCo₂O₆₋₈ across the orthorhombic to tetragonal phase transition (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

oxygen content, 6 – δ , as measured in a separate TG experiment, when the sample is equilibrated in air at high temperature under the conditions similar to those inside the calorimeter, is plotted in Fig. 2. As seen, it is constant at the three lowest temperatures. As a result, the enthalpy increments measured at these temperatures correspond only to the sample heating. At higher temperatures, the final oxygen content increasingly deviates from that at room temperature; hence, the contribution of the reduction process to the measured enthalpy increment also increases, as evidenced by the steeper slope of the enthalpy vs. T curve. Furthermore, it is well known that $GdBaCo_2O_{6-\delta}$ with oxygen content close to 5.5 exhibit two phase transitions at about (330-360) K [5,17] and 750 K [18]. During the first one, at lower temperature, the symmetry of the lattice remains orthorhombic with Pmmm space group. During the second transition, the symmetry of the lattice increases from orthorhombic to tetragonal with P4/mmm space group. The enthalpies, ΔH_{tr}^{\bigcirc} , and temperatures, T_{tr} , of these phase transitions, which should be also taken into account when analyzing the measured enthalpy increments, were determined by DSC and are given in Table 3. The example DSC-curve is shown in Fig. 3.

Table 2 The drop calorimetry results for GdBaCo₂O₆₋₈.

T _{low} / K ^a	T _{high} / K ^a	Enthalpy increment, $\Delta_{T \text{low}}^{T \text{high}} H^{\bigcirc} / k J \cdot \text{mol}^{-1}$	$U(\Delta_{T_{low}}^{T_{high}}H^{\bigcirc}) / kJ \cdot mol^{-1b}$	Final oxygen nonstoichiometry δ in GdBaCo ₂ O ₆₋₈ ^c
298.15	1272.4	286.9	3.8	0.933
	1172.7	258.9	4.2	0.888
	1072.7	224.8	2.4	0.821
	974.1	197.2	1.8	0.737
	873.7	162.7	2.4	0.652
	773.0	130.4	1.5	0.575
	674.0	99.8	1.2	0.507
	572.6	71.9	1.0	0.485
	470.6	46.1	0.6	0.485
	365.4	19.0	0.1	0.485

^a The standard uncertainties *u* are $u(T_{\rm how}) = u(T_{\rm high}) = 0.02$ K, ambient pressure is (101.5 ± 0.5) kPa (expanded uncertainty with 0.95 level of confidence).

^b The values of the expanded uncertainties $U_c = ku_c$ are determined from a combined standard uncertainty u_c and a coverage factor k = 2 (level of confidence ≈ 95 %).

^c The values of the expanded uncertainties of nonstoichiometry measurements, $U_c = ku_c$, are determined from a combined standard uncertainty u_c and a coverage factor k = 2 (level of confidence ≈ 95 %) as 0.005.

Let us now discuss the low temperature interval where $GdBaCo_2O_{6-8}$ sample possesses constant oxygen content equal to 5.515. In this temperature range, the enthalpy increments are determined by the heat capacity of the sample with constant chemical composition and the enthalpy of the first phase transition:

$$\Delta_{298}^{T} H^{\bigcirc} = \int_{298}^{347.2} C_{p(1)}^{\delta_{1}} dT + \int_{347.2}^{T} C_{p(2)}^{\delta_{1}} dT + \Delta H_{tr,1}^{\bigcirc}$$
(3)

where $C_{p(1)}^{\delta_1}$ – the heat capacity of the 'orthorhombic I' phase, $C_{p(2)}^{\delta_1}$ – the heat capacity of the 'orthorhombic II' phase, and $\Delta H_{tr,1}^{\odot}$ – the enthalpy of 'orthorhombic I-→orthorhombic II' transition (see Table 3). Since all the drop calorimetry measurements were carried out at temperatures higher than the temperature of the first phase transition (T > 347.2 K), differentiation of Eq. (3) with respect to temperature allows estimation of the heat capacity of the GdBaCo₂O_{5.515} in the 'orthorhombic II' state. As seen in Fig. 2, all three measured increments in the low temperature range closely follow linear trend with respect to T. Therefore, it is not surprising that numerical differentiation leads to almost the same values of $C_{p(2)}^{\delta_1}$ irrespective of temperature. The average $C_{p(2)}^{\delta_1}$ obtained in this way equals (251.7 ± 6.7) J·mol⁻¹K⁻¹ (expanded uncertainty with 0.95 level of confidence) in the temperature range (365.4–572.6) K.

In the high-temperature range, where the second phase transition and the sample reduction should be taken into account as well, the enthalpy increments can be represented as follows:

$$\Delta_{298}^{T} H^{\bigcirc} = \int_{298}^{347.2} C_{p(1)}^{\delta_{1}} dT + \Delta H_{tr,1}^{\bigcirc} + \int_{347.2}^{745.8} C_{p(2)}^{\delta_{1}} dT + \Delta H_{tr,2}^{\bigcirc} + \int_{745.8}^{T} C_{p(3)}^{\delta_{1}} dT - \int_{\delta_{1}}^{\delta_{2}} \overline{H}_{O}^{T} d\delta$$
(4)

where $C_{p(3)}^{\delta_1}$ – heat capacity of the 'tetragonal' phase, and $\Delta H_{tr,2}^{\circ}$ – the enthalpy of 'orthorhombic II->tetragonal' phase transformation (see Table 3). Eq. (4) can be rearranged in the following way:

$$\Delta_{298}^{T} H^{\bigcirc} = \Delta_{298}^{347.2} H_{1,\delta_{1}}^{\bigcirc} + \Delta H_{\mathrm{tr},1}^{\bigcirc} + \Delta_{347.2}^{745.8} H_{2,\delta_{1}}^{\bigcirc} + \Delta H_{\mathrm{tr},2}^{\bigcirc} + \Delta_{745.8}^{T} H_{3,\delta_{1}}^{\bigcirc} \\ - \int_{\delta_{1}}^{\delta_{2}} H_{0}^{T} d\delta$$
(5)

Table 3

Enthalpies and temperatures of the phase transitions in GdBaCo₂O_{5.515}.

Phase transition ^a	T _{tr} ∕ K	$U(T_{\rm tr}) \neq {\rm K}^{\rm b}$	Transition enthalpy, $\Delta H_{tr}^{O} / kJ \cdot mol^{-1}$	$U(\Delta H_{ m tr}^{ m O}) / m kJ \cdot m mol^{-1a}$
1. orthorhombic I→orthorhombic II	347.2	0.4	2.95	0.07
orthorhombic II→tetragonal	745.8	0.1	2.40	0.09

^a Ambient pressure is (101.5 \pm 0.5) kPa (expanded uncertainty with 0.95 level of confidence).

^b Expanded uncertainty $U_c = ku_c$ determined from a combined standard uncertainty u_c and a coverage factor k = 2 (level of confidence ≈ 95 %).



Fig. 3. DSC curve of GdBaCo_2O_{5.515} (heating rate $2\,{\rm K\cdot min}^{-1})$ in air. 1 and 2 – phase transitions.

where $\Delta_{298}^{347.2} H_{1,\delta_1}^{\circ}$ – enthalpy increment between 298 K and 347.2 K for 'orthorhombic I' phase, $\Delta_{347.2}^{745.8} H_{2,\delta_1}^{\circ}$ – enthalpy increment between 347.2 K and 745.8 K for 'orthorhombic II' phase and $\Delta_{745.8}^{T} H_{3,\delta_1}^{\circ}$ – enthalpy increment for 'tetragonal' phase. Note that all the mentioned phases have the same chemical composition and, therefore, their heat capacities should be close to each other. Assuming that the low-temperature linear trend of the enthalpy increment vs. *T* can be extrapolated to the high-temperature range, the 'chemical' part of the increment, represented in Eq. (5) by the integral of the partial molar enthalpy of oxygen in GdBaCo₂O₆₋₈, can be estimated as a difference between the measured and extrapolated values of the increments, taking into account the enthalpy of the second phase transition:

$$\Delta_{\delta_1}^{\delta_2} H_{\text{chem}}^{\bigcirc} = -\int_{\delta_1}^{\delta_2} \overline{H}_0^T d\delta = \Delta_{298}^T H^{\bigcirc} - (a+bT) - \Delta H_{\text{tr},2}^{\bigcirc}$$
(6)

where $\Delta_{\delta_1}^{\delta_2} H_{\text{chem}}^{\mathbb{O}}$ is a 'chemical' part of the enthalpy increment, (a + bT)is a low temperature linear trend of the enthalpy increment vs. T, a and b – constants. Numerical differentiation of the as-calculated $\Delta_{\delta_1}^{\delta_2} H_{chem}^{\bigcirc}$ with respect to the oxygen content, with the assumption that temperature does not influence the $\Delta_{\delta_1}^{\delta_2} H_{chem}^{O}$, allows estimating the partial molar enthalpy of oxygen in the $GdBaCo_2O_{6-\delta}$ as a function of the oxygen content. The result of such calculations is shown in Fig. 4 in comparison with the data available in literature [19,20]. Although, as a consequence of the differentiation procedure, the error margins for the as-estimated partial molar enthalpy are large, the agreement between the different data sets in Fig. 4 seems to be good. As seen, the partial molar enthalpy of oxygen in GdBaCo_2O_{6-\delta} is almost constant in the δ range from 0.9 to 0.6, whereas it becomes more positive at lower δ . This increase in \overline{H}_0 indicates some stabilization of oxygen vacancies, most probably, due to their ordering, which finally results in the 'tetragonal→orthorhombic II' phase transition [5]. This example shows how enthalpy increments of strongly nonstoichiometric phases may be the valuable source of information about not only their redox energetics but also the ordering phenomena and the reasons behind the phase transitions.



Fig. 4. Relative partial molar enthalpy of oxygen in GdBaCo₂O_{6- δ} as a function of nonstoichiometry index δ .



Fig. 5. Heat capacity of $GdBaCo_2O_{5.515}$, obtained in the present work, in comparison with the literature data.

Fig. 5, where the heat capacity of the GdBaCo₂O_{5.515}, calculated from the slope of the low-temperature enthalpy increment trend vs. *T*, is compared with that reported in literature [9,10], demonstrates good agreement between different data sets.

Finally, let us discuss the possibilities of calculating the enthalpy increments and constant pressure heat capacities of the oxide samples with arbitrary oxygen content. The following processes can be considered:

$$GdBaCo_2O_{6-\delta_1}(298 \text{ K}) \to GdBaCo_2O_{6-\delta_1}(T), \ \Delta H^{\bigcirc}$$
$$= \Delta_{298}^T H^{\bigcirc}(GdBaCo_2O_{6-\delta_1}) \tag{7}$$

$$GdBaCo_2O_{6-\delta_2}(298 \text{ K}) \rightarrow GdBaCo_2O_{6-\delta_2}(T), \ \Delta H^{\bigcirc}$$
$$= \Delta_{298}^T H^{\bigcirc}(GdBaCo_2O_{6-\delta_2})$$
(8)

$$GdBaCo_2O_{6-\delta_1}(298 \text{ K}) + \frac{\Delta\delta}{2}O_2(298 \text{ K}) \rightarrow GdBaCo_2O_{6-\delta_2}(298 \text{ K}), \ \Delta H^{\bigcirc}$$
$$= \Delta_{298} H_{ox}^{\bigcirc}$$
(9)

$$GdBaCo_2O_{6-\delta_1}(T) + \frac{\Delta\delta}{2}O_2(T) \to GdBaCo_2O_{6-\delta_2}(T), \ \Delta H^{\bigcirc} = \Delta_T H_{ox}^{\bigcirc}$$
(10)

They represent the heating of the unoxidized (Eq. (7)) and oxidized (Eq. (8)) samples, and the oxidation of GdBaCo₂O_{6- δ_1} at temperatures 298 K (Eq. (9)) and *T* (Eq. (10)), respectively. The heats of these processes are the enthalpy increments of unoxidized $(\Delta_{298}^{T}H^{\bigcirc}(\text{GdBaCo}_2O_{6-\delta_1}))$ and oxidized $(\Delta_{298}^{T}H^{\bigcirc}(\text{GdBaCo}_2O_{6-\delta_2}))$ samples, and the oxidation enthalpies at two temperatures, 298 K ($\Delta_{298} H_{\text{ox}}^{\bigcirc}$) and *T* ($\Delta_{T} H_{\text{ox}}^{\bigcirc}$), respectively.

To calculate $\Delta_{298}^T H^{O}$ (GdBaCo₂O_{6- δ_2}), the enthalpy increment of gaseous oxygen is required:

$$O_2(298 \text{ K}) \to O_2(T), \ \Delta H^{\bigcirc} = \Delta_{298}^T H^{\bigcirc}(O_2)$$
 (11)

Combining Eqs. (7),(9 – 11) allows obtaining the following expression for the heat effect of Eq. (8), i.e. the enthalpy increment of $GdBaCo_2O_{6-\delta_7}$ with arbitrary oxygen content:

$$\Delta_{298}^{T} H^{\bigcirc}(\text{GdBaCo}_{2}\text{O}_{6-\delta_{2}}) = \Delta_{T} H_{\text{ox}}^{\bigcirc} - \Delta_{298} H_{\text{ox}}^{\bigcirc} + \Delta_{298}^{T} H^{\bigcirc}(\text{GdBaCo}_{2}\text{O}_{6-\delta_{1}})$$
$$+ \frac{\Delta\delta}{2} \cdot \Delta_{298}^{T} H^{\bigcirc}(\text{O}_{2})$$
(12)

or, if $\Delta_{298} H_{ox}^{\bigcirc} = \Delta_T H_{ox}^{\bigcirc}$:

$$\Delta_{298}^T H^{\bigcirc}(\text{GdBaCo}_2\text{O}_{6-\delta_2}) = \Delta_{298}^T H^{\bigcirc}(\text{GdBaCo}_2\text{O}_{6-\delta_1}) + \frac{\Delta\delta}{2} \bullet \Delta_{298}^T H^{\bigcirc}(\text{O}_2)$$
(13)

Therefore, if the oxidation enthalpy is assumed to be temperatureindependent, the heat capacity of oxidized sample is a sum of the heat capacities of unoxidized sample and gaseous oxygen:

$$C_{p}(GdBaCo_{2}O_{6-\delta_{2}}) = C_{p}(GdBaCo_{2}O_{6-\delta_{1}}) + \frac{\Delta\delta}{2} \cdot C_{p}(O_{2})$$
(14)

Eqs. (13) and (14) allow calculating enthalpy increments and heat capacities of the oxide samples with arbitrary oxygen content provided that there are experimental data for the sample with some particular composition.

4. Conclusions

The enthalpy increments for the double perovskite GdBaCo2O6-8 were measured by drop calorimetry in air in the temperature range of (365.4-1272.4) K. While in the low-temperature range the sample possesses constant chemical composition and the increments increase linearly with temperature, at high temperatures they are significantly affected by the redox processes. This 'chemical' enthalpy contribution, caused by the changing oxygen content in the double perovskite, was estimated by subtracting from the high-temperature increments their low-temperature trend, assuming it holds at higher temperatures for the sample with constant composition. The phase transitions that occur in the temperature range in question had to be taken into account as well. Numerical differentiation of the resultant 'chemical' contribution led to the partial molar enthalpy of oxygen in the GdBaCo₂O_{6- δ_1} which was found to coincide well with the previously reported results. Therefore, enthalpy increments of the strongly nonstoichiometric phases may indeed be the valuable source of information on their red-ox energetics. The possibilities to calculate enthalpy increments and constant pressure heat capacities of the oxide samples with arbitrary oxygen content were also discussed. As a result, assuming temperature independence of the oxidation enthalpy, the simple equations useful for practical calculations were derived.

CRediT authorship contribution statement

D.S Tsvetkov: Project administration, Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Funding acquisition. **A.L Sednev-Lugovets:** Investigation, Writing original draft. **V.V Sereda:** Formal analysis, Writing - original draft, Writing - review & editing. **D.A Malyshkin:** Validation, Writing - original draft, Writing - review & editing. **I.L Ivanov:** Investigation, Writing - original draft. **A.Yu Zuev:** Data curation, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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