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# The origin of triple conductivity and water uptake in layered double perovskites: A case study on lanthanum-substituted $GdBaCo_2O_{6-\delta}$

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### ABSTRACT

Some layered double perovskite cobaltites have been shown recently to absorb water and exhibit increasing electrical conductivity in humid atmospheres. However, the assumptions that their crystal lattice is capable of proton uptake, and that these oxides really possess triple (oxide ion, protonic and electronic) conductivity, have already been brought into question. We investigated in detail the crystal structure and phase composition of various lanthanum-substituted GdBaCo<sub>2</sub>O<sub>6- $\delta}</sub> and came to several important conclusions. Firstly, in oxidative conditions (e.g. in air), the substitution of La for either only Gd or only Ba in GdBaCo<sub>2</sub>O<sub>6-<math>\delta}</sub> results in formation of multiphase materials. For example, BaCo<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-<math>\delta}</sub> exsolves from Gd<sub>1-x</sub>La<sub>x</sub>BaCo<sub>2</sub>O<sub>6-<math>\delta}</sub> due to the redistribution of La between Gd and Ba sites in Gd<sub>1</sub>-$ *x* $La<sub>x</sub>BaCo<sub>2</sub>O<sub>6-<math>\delta}</sub> lattice. Secondly, a single-phase double perovskite can be synthesized in air only by simultaneously substituting, within certain limits, both Gd and Ba in GdBaCo<sub>2</sub>O<sub>6-<math>\delta}</sub> with La. Finally, using Gd<sub>0.8</sub>La<sub>0.2</sub>Ba<sub>0.95</sub>La<sub>0.05</sub>Co<sub>2</sub>O<sub>6-<math>\delta}</sub> and BaCo<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3-<math>\delta}</sub> as examples, we demonstrated that while single-phase double perovskite does not hydrate, in the same conditions, the cubic perovskite BaCo<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3-<math>\delta}</sub> (BaCo<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-<math>\delta}$ </sub> is encountered in Gd<sub>1-x</sub>La<sub>x</sub>BaCo<sub>2</sub>O<sub>6- $\delta}</sub> as an impurity) absorbs significant amount of water. Thus, the water uptake by lanthanum-substituted GdBaCo<sub>2</sub>O<sub>6-<math>\delta}$  is most likely to occur due to the impurities, and not the main double perovskite phase.</sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub>

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### 1. Introduction

At least since the relatively recent discovery of fast oxide ion transport in A-site-ordered layered double perovskite cobaltites  $REBaCo_2O_{6-\delta}$  (RE = rare-earth element) [1], these oxides have been receiving constant attention as suitable materials for various electrochemical devices. High mixed oxide ion and electronic conductivity coupled with the catalytic activity towards the oxygen reduction reaction made  $REBaCo_2O_{6-\delta}$  look promising as cathodes for both oxide ion- and proton-conducting solid oxide fuel cells (O–SOFC and H–SOFC, respectively) [2–5]. The latter are generally considered to be better suited for practical applications due to lower operating temperatures and the absence of fuel contamination. In H–SOFC, the kinetics of the cathodic reaction can be greatly enhanced by "extending" the proton transfer into the cathode bulk,

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otherwise it proceeds only on the triple-phase boundary. In other words, it would be quite beneficial for the performance of H–SOFC if its cathode possessed triple (oxide ion, protonic and electronic) conductivity.

In this respect, the recent studies where possible proton conductivity in  $REBaCo_2O_{6-\delta}$  was pointed out, only reinforced the interest towards  $REBaCo_2O_{6-\delta}$  [6–10]. In particular, Grimaud et al. [6,7], using a combination of thermogravimetric analysis (TGA) and electrochemical studies, found out that  $PrBaCo_2O_{6-\delta}$  shows some proton conductivity and can be considered as a triple-conducting oxide. These conclusions are consistent with those of Goupil et al. [8], who interpreted their data on TGA coupled with mass spectrometry as evidence for the reversible hydration of  $REBaCo_2O_{6-\delta}$ (RE = Gd, Sm, Pr, Nd).

However, in the work of Goupil et al. [8], the amount of water in  $REBaCo_2O_{6-\delta}$  (RE = Gd, Sm, Pr, Nd) decreased upon cooling and reached zero at room temperature, whereas the opposite trend is expected of proton-conducting oxides. Moreover, the H<sub>2</sub>O signal measured by mass spectrometry during TGA experiments indicated







water condensation in the thermobalance [8]. And even if the experiments are free from the methodological errors, both the conductivity measurements and the TGA are, perhaps, necessary, but not sufficient to prove that a certain oxide phase possesses proton conductivity. The other factors, such as changes in structure or composition of a material, may be responsible for the observed conductivity or mass changes. For example, while some, though rather low, water content was detected in  $PrBaCo_2O_{6-\delta}$  with the aid of Karl Fischer titration [11] and TGA [9], X-ray diffraction (XRD) analysis performed on a hydrated  $PrBaCo_2O_{6-\delta}$  sample revealed the formation of a secondary phase, which decomposes during TGA experiments under dry atmosphere [6]. Later, secondary ion mass spectrometry (SIMS) studies showed that water in PrBaCo<sub>2</sub>O<sub>6- $\delta$ </sub> is likely to be present only in form of hydrated barium compound layer on the surface (the interior pore walls) of this double perovskite [5]. As for some other substituted REBaCo<sub>2</sub>O<sub>6- $\delta$ </sub>, the uptake of water by GdBaCo<sub>1.8</sub>Fe<sub>0.2</sub>O<sub>6- $\delta$ </sub>, NdBaCo<sub>2-x</sub>Mn<sub>x</sub>O<sub>6- $\delta$ </sub> (x = 0, 0.5) and  $La_{0.5}Ba_{0.5}CoO_{3-\delta}$  could not be clearly established from TGA [9], in situ high-temperature neutron powder diffraction [12] and SIMS [10] measurements, respectively.

Therefore, the water uptake capability of the bulk of  $REBaCo_2O_{6-\delta}$  double perovskites and the origins of proton conductivity in them still remain a moot point.

For this reason the present work is focused on  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$  double perovskites, at least one of which,  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$ , is, reportedly, a triple-conductive oxide [9,10]. Its protonation at temperature between 300 °C and 400 °C was confirmed by TGA [9] and SIMS [10]. At the same time, it was demonstrated that in the deuterated  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  the concentration of D decreases over the first  $\approx$  300 nm, possibly due to deuterium-containing species adsorbed on the surface of this material [10]. We suspected that, similarly to PrBaCo<sub>2</sub>O<sub>6- $\delta$ </sub> [5,6], the nature of proton conductivity in  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  may be not quite straightforward – and, indeed, our suspicions were confirmed by the phase composition studies on  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$ , the results of which are presented below.

### 2. Experimental

The powder samples of  $Gd_{1-x}La_xBa_{1-y}La_yCo_2O_{6-\delta}$  and  $Ba_{1-\nu}La_{\nu}Co_{1-x}Gd_{x}O_{3-\delta}$  were synthesized from high-purity La(N-O<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Gd<sub>2</sub>O<sub>3</sub>, BaCO<sub>3</sub> and Co precursors via a glycerol-nitrate route. Metallic cobalt was obtained by reducing Co<sub>3</sub>O<sub>4</sub> in hydrogen at 600 °C. Gadolinium oxide was pre-annealed at 1100 °C to decompose the gadolinium hydrates and carbonates. The exact amount of water in La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was estimated using TGA. Stoichiometric quantities of precursors were dissolved in concentrated HNO<sub>3</sub>, followed by addition of glycerol, which acted as a complexing agent and a fuel, and heated on a hot plate until the water evaporation and pyrolysis of the precursor mixture was complete. The resulting ash was calcined once at 900 °C and thrice at 1100 °C, with ca 10 h calcination dwell time and intermediate regrindings in an agate mortar. After the last annealing,  $Gd_{1-x}La_xBa_{1-y}La_yCo_2O_{6-\delta}$  samples were slowly (100 °C · h<sup>-1</sup>) cooled to room temperature, while those of  $Ba_{1-\nu}La_{\nu}Co_{1-x}Gd_{x}O_{3-\delta}$  – were quenched to room temperature, similarly to  $BaCo_{1-x}Y_{x}O_{3-\delta}$  [13]. The quenching experiments were carried out in an original setup described elsewhere [14].

The phase composition of all the samples prepared accordingly was investigated by means of room-temperature XRD. The XRD patterns were obtained with 7000S diffractometer (Shimadzu, Japan) using Cu K $\alpha$  radiation. In situ high-temperature XRD (HT XRD) experiments were implemented using Cu K $\alpha$  radiation on a DRON 6 diffractometer (JSC Bourevestnik, Russia) equipped with a high-temperature chamber HDK 1200 (Edmund Buehler GmbH, Germany). The scanning electron microscopy (SEM) and energydispersive X-ray (EDX) studies into the microstructure and the chemical composition of the samples were made on an AURIGA CrossBeam (FIB-SEM) Workstation (Carl Zeiss, Germany).

Thermogravimetric experiments were performed using a thermogravimetric setup based on CI Precision (UK) microbalance. Dry atmosphere in the thermobalance was obtained by passing the inlet gas through the zeolite-filled column, and the humid atmosphere was controlled by flowing the gas through a small Peltiercontrolled thermostat. The actual humidity during the TGA experiments was measured with factory-calibrated SHT31 (Sensirion, Switzerland) relative humidity sensors.

### 3. Results and discussion

#### 3.1. Phase composition and crystal structure of $Gd_{1-x}La_xBaCo_2O_{6-\delta}$

X-ray diffraction patterns of the as-prepared single-phase double perovskites with nominal compositions  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$  (x = 0.2-0.6) are shown in Fig. 1a. They were indexed using P4/mmm space group. It should be emphasized that, although the single-phase (at least as indicated by XRD) samples were obtained, it was rather hard to prepare them. The synthesis procedure employed quite often resulted in the two-phase powders, as verified by XRD analysis. This resembles the behavior of a solid solution with the chemical composition being very close to the solubility limit, where even a tiny variation of the conditions destabilizes such a solution, and the secondary phase exsolves. As will be described in detail below, even the samples that, according to XRD, can be regarded as single-phase, in fact, contain a small amount of impurities, whose composition strongly depends on the samples' history.

As for the  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$  samples with x > 0.6, as seen in Fig. 1a, the pattern of the as-prepared slowly cooled  $Gd_{0.2}La_{0.8}BaCo_2O_{6-\delta}$  (GL80BC SC in Fig. 1a) exhibits anomalous intensities of some diffraction lines, e.g., those at  $2\theta = 22.75^{\circ}$ ,  $32.55^{\circ}$ , 46.6° and 58°. It is known that the endpoint composition LaB $aCo_2O_{6-\delta}$  (Gd<sub>1-x</sub>La<sub>x</sub>BaCo<sub>2</sub>O<sub>6-\delta</sub> with x = 1.0) with a layered structure can be prepared only in a reducing atmosphere, and that it can be synthesized as a mixture of ordered (double perovskite) and disordered (cubic perovskite) phases, depending on T and  $p_{\Omega_2}$  [14]. For this reason, the XRD pattern of GL80BC SC was analyzed and refined as a two-phase mixture of ordered (P4/mmm) and disordered  $(Pm\overline{3}m)$  perovskites, and the fraction of the cubic (disordered) phase was found to be  $(42 \pm 1)$  wt %. In turn,  $Gd_{0.2}La_{0.8}BaCo_2O_{6-\delta}$  annealed for 24 h at 1100 °C and  $p_{O_2} = 10^{-3.0}$ atm and then quenched to room temperature (GL80BC Q in Fig. 1a), has double perovskite structure.

The refined lattice parameters and cell volume of double perovskites  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$  with x = 0.2-0.6 are shown in Fig. 1b as functions of lanthanum content at room temperature in air. The cell parameters are in good agreement with those reported previously for  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  [15]. The *a* parameter is almost independent of the lanthanum content, whereas the *c* parameter significantly increases with lanthanum substitution. For the sake of comparison, Fig. 1b also shows the lattice parameters and cell volume of undoped cobaltites GdBaCo\_2O\_{6-\delta} [16] and LaBaCo\_2O\_{6-\delta} [14]. As follows, the lattice volume monotonically increases with the lanthanum content because of the larger crystal ionic radius of La as compared to that of Gd [17].

In situ XRD patterns obtained in the temperature range (25-900) °C in air for the Gd<sub>0.8</sub>La<sub>0.2</sub>BaCo<sub>2</sub>O<sub>6- $\delta$ </sub> oxide are shown in Fig. 2a. As seen, the patterns do not show significant changes with temperature, indicating that a *P4/mmm* structure is retained at all



**Fig. 1.** (a) XRD pattern of  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$  (x = 0.2-0.8) samples slowly (100 °C·h<sup>-1</sup>) cooled from 1100 °C to room temperature in air, and quenched sample of  $Gd_{0.2}La_{0.8}BaCo_2O_{6-\delta}$  (GL80BC Q). (b) The refined lattice parameters and cell volume of  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$  as functions of lanthanum content at room temperature. Lines are guides to the eye only.



Fig. 2. (a) In situ HT XRD patterns of  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  in the temperature range between 25 °C and 900 °C in air (  $\bigvee$  – Pt sample holder). (b) The refined lattice parameters and cell volume of  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  vs temperature in air.

the temperatures investigated. The refined lattice parameters and the unit cell volume of  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  are presented in Fig. 2b as functions of temperature in air.

## 3.2. Exsolution of secondary phase from lanthanum-substituted GdBaCo\_2O\_{6-\delta}

As mentioned above, it is very difficult to reproducibly prepare the single-phase samples of Gd  $_{1-x}La_xBaCo_2O_{6-\delta}$  with x = 0.2-0.6. In fact, even seemingly single-phase, according to XRD, Gd<sub>0.8</sub>La<sub>0.2</sub>BaCo<sub>2</sub>O<sub>6- $\delta}$ </sub> samples were found to be dotted with the nanoparticles covering the grain surfaces of the main phase, as shown in Fig. 3a. Unfortunately, the very small size of the nanoparticles does not allow determining their chemical composition using EDX analysis. However, the presence of a secondary phase in the as-prepared  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$  samples with x = 0.2-0.6 can often be detected even by conventional XRD analysis. The reason why the secondary phase is not always discernible on the XRD pattern, while its nanoparticles seem to be always present, lies, most probably, in the size of these particles and their nature, as will be explained below.

Fig. 3b shows the XRD patterns of the as-prepared  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  (GL20BC 2ph), which contained peaks ( $\checkmark$ ) related to the secondary phase. Indexing these peaks can be performed within the cubic symmetry. After careful evaluation, we excluded undoped  $BaCoO_{3-\delta}$  from consideration as a possible



**Fig. 3.** (a) SEM micrograph of  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  slowly (100 °C ·h<sup>-1</sup>) cooled from 1100 °C to room temperature in air. (b) XRD patterns of two-phase  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  samples quenched from 1100 °C to room temperature in air ( $\mathbf{\nabla}$  – BaCo<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-\delta</sub> phase).

impurity because it is not cubic under the experimental conditions (in air) [18], and even if it were, its peak positions would not correspond to the XRD pattern of GL20BC 2ph. Nor do the peak positions of hexagonal  $BaCoO_{3-\delta}$  match those seen in Fig. 3b. In that our results do not support those of Vøllestad et al. [15], who claimed that hexagonal  $BaCoO_{3-\delta}$  is one of the products of  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  decomposition after stability test at 1.5 bar of water vapor and 600 °C. Note, however, that inconsistencies in the work of Vøllestad et al. [15] do not allow checking their assertions: two XRD patterns of partially decomposed Gd<sub>0.8</sub>La<sub>0.2</sub>BaCo<sub>2</sub>O<sub>6-δ</sub>, that presented for the sake of comparison with the XRD pattern of as-sintered sample and that used for the Rietveld refinement (see pages 3 and 4 in the Supplementary to Ref. [15]) differ significantly from each other, and both contain peaks that are hard to account for within the framework of the decomposition scheme proposed by Vøllestad et al. [15].

In fact, the positions of the impurity peaks in the GL20BC 2ph XRD pattern (see Fig. 3b) are almost identical to those of cubic BaCo<sub>0.75</sub>Y<sub>0.25</sub>O<sub>2.55</sub> perovskite (PDF-2 entry #00-057-0194). No information concerning the existence of Gd-substituted barium cobaltite, isostructural with BaCo<sub>0.75</sub>Y<sub>0.25</sub>O<sub>2.55</sub>, had been found in the literature. However, it is known that, in contrast to Nd [19] and larger *RE*, not only Y [13] but also Sm [19] and, possibly, other smaller *RE* can substitute Co ions in BaCoO<sub>3- $\delta$ </sub>. Thus, it seems likely that the impurity phase in Gd<sub>0.8</sub>La<sub>0.2</sub>BaCo<sub>2</sub>O<sub>6- $\delta$ </sub>, the amount of which was about 2 wt % according to Rietveld refinement, may have a composition represented by the general formula BaCo<sub>1-x</sub>Gd<sub>x</sub>O<sub>3- $\delta$ </sub>.

In order to support this assumption, we prepared the  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  oxide with 10 mol % excess of  $BaCo_{0.8}Gd_{0.2}O_{3-\delta}$  (GL20BC + BCG20). The XRD pattern of this material was found to correspond fairly well to that of the two-phase double perovskite  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  (GL20BC 2ph), except for increased intensities of the secondary phase diffraction lines ( $\mathbf{\nabla}$ ), as seen in Fig. 3b.

In addition, to exclude the possible substitution of La for Ba in  $BaCo_{1-x}Gd_xO_{3-\delta}$ , the Ba  $_{1-y}La_yCo_{0.8}Gd_{0.2}O_{3-\delta}$  samples with y = 0, 0.1 and x = 0.2 were prepared at 1100 °C in air. As a result, whereas a single-phase cubic perovskite  $BaCo_{0.8}Gd_{0.2}O_{3-\delta}$  (*Pm* $\overline{3}m$  space group) was obtained, even the sample with y = 0.1 already contained a mixture of  $BaCo_{1-x}Gd_xO_{3-\delta}$  and  $Ba_{3-x}La_xCo_2O_{8-\delta}$  ( $\mathbf{V}$ ), as seen in Fig. 4.

Furthermore, it was found that the intensity of the diffraction lines corresponding to  $BaCo_{1-x}Gd_xO_{3-\delta}$  in the XRD pattern of the two-phase sample GL20BC + BCG20 decreases significantly, and the width of the respective peaks – simultaneously increases after storage under ambient conditions, e.g., for 1 week at room



**Fig. 4.** XRD patterns of  $Ba_{1-y}La_yCo_{0.8}Gd_{0.2}O_{3-\delta}$  cobaltites prepared at 1100 °C in air followed by quenching to room temperature ( $\mathbf{\nabla} - Ba_{3-x}La_xCo_2O_{8-\delta}$  phase).

temperature with 30% relative humidity (see Fig. 3b). Such change in the intensities, being probably associated with the decomposition of BaCo<sub>1-x</sub>Gd<sub>x</sub>O<sub>3- $\delta$ </sub> in humid atmosphere [13], was also observed in two-phase Gd<sub>0.8</sub>La<sub>0.2</sub>BaCo<sub>2</sub>O<sub>6- $\delta$ </sub> (GL20BC 2ph). Therefore, it is most likely that Gd <sub>1-x</sub>La<sub>x</sub>BaCo<sub>2</sub>O<sub>6- $\delta$ </sub> oxides with x = 0.2-0.6, prepared in air, always contain BaCo<sub>1-x</sub>Gd<sub>x</sub>O<sub>3- $\delta$ </sub> cobaltite (or its decomposition products, depending on the synthesis route and storage conditions) even if no impurity phase is detected with XRD.

It should be noted that Rivas-Murias et al. [20] synthesized in air the GdBaCo<sub>2</sub>O<sub>6- $\delta$ </sub> sample with 50% of Gd replaced with Pr (Gd<sub>0.5</sub>Pr<sub>0.5</sub>BaCo<sub>2</sub>O<sub>6- $\delta$ </sub>), whose size is close to that of La. Interestingly, the XRD pattern of this sample clearly shows additional reflection at  $2\theta \cong 33.5^{\circ}$  (Cu K $\alpha$  radiation), which was not indexed in *P4/mmm* space group [20]. Moreover, the XRD patterns of double perovskites Pr<sub>0.5</sub>*R*<sub>0.5</sub>BaCo<sub>2</sub>O<sub>6- $\delta$ </sub>, prepared in air, also show this additional reflection in the case of *RE* = Eu–Dy [20] and Y [21], whereas the compounds with *RE* = Nd, Sm [20] were found to be single phase. Therefore, it can be expected that layered double perovskites with different A-site lanthanide cations in the rareearth layers can be prepared as single-phase samples in air only if these cations have close sizes.

It is noteworthy that a single-phase double perovskite  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  can be obtained by annealing two-phase  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  material (GL20BC 2ph) under reducing conditions, e.g.  $p_{O_2} = 10^{-5.3}$  atm at 1000 °C for 160 h as it follows from Fig. 5a. For the sake of comparison, the XRD pattern of two-phase  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  sample (GL20BC 2ph), calcined under less reducing conditions – 1000 °C and  $p_{O_2} = 10^{-3.2}$  atm for 160 h – is also given in Fig. 5a. If the secondary phase in GL20BC 2ph simply decomposed at  $p_{0_2} = 10^{-5.3}$  atm and 1000 °C, then some evidence of the products of its decomposition would be seen in the XRD pattern or the SEM micrograph. However, the XRD pattern and SEM micrograph of the as-annealed GL20BC 2ph sample, quenched to room temperature, showed no impurity phase peaks and the uniformity of the grain surfaces, as seen in Fig. 5a and 5b, respectively. Hence, it can be concluded that  $BaCo_{1-x}Gd_xO_{3-\delta}$ , being unstable under reducing conditions, should dissolve in  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$ bulk, making the material single phase. In air, accordingly, an exsolution of  $BaCo_{1-x}Gd_xO_{3-\delta}$  from  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  occurs.

We should briefly mention here that partial substitution of La for Ba in the GdBaCo<sub>2</sub>O<sub>6- $\delta$ </sub> double perovskite also leads to the formation of multiphase materials. Thus, the XRD patterns for the asprepared GdBa<sub>1-y</sub>La<sub>y</sub>Co<sub>2</sub>O<sub>6- $\delta$ </sub> with *y* = 0.05 and 0.1 contain peaks ( $\checkmark$ ) related to the Gd<sub>1-x</sub>La<sub>x</sub>CoO<sub>3- $\delta$ </sub> perovskite secondary phase, as seen in Fig. 6. Although Pietosa et al. [22] reported the successful preparation of NdBa<sub>1-y</sub>La<sub>y</sub>Co<sub>2</sub>O<sub>6- $\delta$ </sub> with a partial substitution of La for Ba (*y* = 0.06, 0.1), their findings should not be seen as contradicting ours: the stability of Nd-containing compounds may differ from that of Gd-containing ones. In addition, the authors [22] did not provide XRD patterns for these samples to corroborate their statement of the samples' phase purity.

### 3.3. A genuinely single-phase lanthanum-substituted GdBaCo<sub>2</sub>O<sub>6- $\delta$ </sub>

Logically, our next assumption was that if the cobaltite  $BaCo_{1-x}Gd_xO_{3-\delta}$  is formed as a result of exsolution from the  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$  lattice, then some deficit of Ba and Co cations in the latter may promote formation of a truly single-phase double perovskite. In order to check whether it is the case the  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  samples with 5 mol % and 10 mol % deficiency of  $BaCoO_{3-\delta}$  (GL20BC-5%BaCoO<sub>3</sub> and GL20BC-10%BaCoO<sub>3</sub>, respectively), i.e. with the simultaneous deficiency of Ba and Co cations, were prepared. Fig. 7 shows that GL20BC-5%BaCoO<sub>3</sub> can be successfully synthesized in air at 1100 °C as a single phase, as



**Fig. 5.** (a) XRD patterns of the samples obtained by annealing of two-phase  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  (GL20BC 2ph) at 1000 °C and different  $p_{O_2}$  for 160 h, followed by quenching to room temperature ( $\mathbf{\nabla} - BaCo_{1-x}Gd_xO_{3-\delta}$  phase). (b) SEM micrograph of the sample obtained by annealing of two-phase  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  (GL20BC 2ph) at 1000 °C and  $p_{O_2} = 10^{-5.3}$  atm for 160 h, followed by quenching to room temperature.



**Fig. 6.** XRD patterns of the double perovskites  $GdBa_{1-y}La_yCo_2O_{6-\delta}$  slowly (100 °C·h<sup>-1</sup>) cooled from 1100 °C to room temperature in air ( $\mathbf{\nabla} - Gd_{1-x}La_xCoO_{3-\delta}$  phase).



**Fig. 7.** XRD patterns of the  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  with simultaneous Ba and Co deficiency, prepared at 1100 °C in air followed by slow (100 °C·h<sup>-1</sup>) cooling to room temperature.

confirmed by XRD analysis of the slowly cooled sample. However, a larger deficiency leads to formation of Gd<sub>2</sub>O<sub>3</sub> impurity, as seen in the inset in Fig. 7.

Taking into account that high amount of cation vacancies in the double perovskite cobaltites is unlikely [23], the nominal

composition of the single-phase GL20BC-5%BaCoO<sub>3</sub> can be rewritten as  $Gd_{0.821}La_{0.179}Ba_{0.974}La_{0.026}Co_2O_{6-\delta}$ , assuming the possible redistribution of lanthanum between gadolinium and barium layers [15]. To sum up, the double perovskites  $Gd_{1-x}La_xBa_{1-y}La_yCo_2O_{6-\delta}$  can be prepared in air as a single phase only by simultaneous substitution of La for Gd and Ba. Consequently, the abovementioned exsolution of  $BaCo_{1-x}Gd_xO_{3-\delta}$  from  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  may be viewed as a result of the redistribution of La cations between rare-earth and barium sites.

Indeed, by trial and error we found that, for  $Gd_{1-x}La_xBa_{1-x}$  $_{\nu}\text{La}_{\nu}\text{Co}_{2}\text{O}_{6-\delta}$  with x = 0.2, the Gd<sub>0.8</sub>La<sub>0.2</sub>Ba<sub>0.95</sub>La<sub>0.05</sub>Co<sub>2</sub>O<sub>6-\delta</sub> double perovskite can be successfully and reproducibly synthesized in air at 1100 °C as a single-phase material. The corresponding XRD pattern and SEM micrograph of the slowly (100 °C·h<sup>-1</sup>) cooled sample showed no indication for the presence of a secondary phase, as seen in Fig. 8a and 8b, respectively. However, further increase in the lanthanum content in Ba-sublattice leads to formation of a mixture of  $Gd_{1-x}La_xBa_{1-y}La_yCo_2O_{6-\delta}$  double perovskite and the the  $Gd_{1-x}La_xCoO_{3-\delta}$  perovskite phase. Similar results were reported for the  $Gd_{0.8}La_{0.2}Ba_{1-y}La_yCo_2O_{6-\delta}$  samples with y = 0.2, 0.4 [15]: though Vøllestad et al. [15] did not focus on it specifically, the XRD patterns of these cobaltites also showed additional reflection at  $2\theta \approx 34^{\circ}$ , suggesting that these materials are not single phase. Thus, there is a narrow range of the possible ratios of lanthanum cations in Gd and Basublattices of  $Gd_{1-x}La_xBa_{1-y}La_yCo_2O_{6-\delta}$ , within which a single-phase double perovskite can be obtained.

In this regard, we would like to comment once again on the recent study of Vøllestad et al. [15], who found that the partial substitution of La for Ba in the double perovskite  $Gd_{0.8}La_{0.2}Ba_{1-\nu}La_{\nu}Co_{2}O_{6-\delta}$  increases its chemical stability in high water steam pressures. They reported that stability tests at 600 °C under 1.5 bar of steam for 72 h showed a separation of  $Gd_{0.8}La_{0.2}Ba_{1-y}La_yCo_2O_{6-\delta}$  with y = 0, 0.2, 0.4into two phases, whereas at y = 0.5 there was no sign of a second phase formation [15]. However, it seems that Vøllestad et al. [15] exaggerated the maximum possible amount of lanthanum in barium layers of  $Gd_{0.8}La_{0.2}Ba_{1-\nu}La_{\nu}Co_2O_{6-\delta}$ , at which the sample remains a single-phase double perovskite. As mentioned above, the unaccounted reflection at  $2\theta \approx 34^{\circ}$  in the XRD patterns of as-prepared  $Gd_{0.8}La_{0.2}Ba_{1-y}La_yCo_2O_{6-\delta}$  with y = 0.2, 0.4 casts doubt on the authors' [15] assertions about the phase purity of these oxides. What is more, the XRD pattern of as-prepared Gd<sub>0.8</sub>La<sub>0.2</sub>Ba<sub>0.5</sub>La<sub>0.5</sub>Co<sub>2</sub>O<sub>6-δ</sub> looks similar to that of cubic perovskite, and, probably, not exactly single phase at that, for several small diffuse peaks, e.g. at  $2\theta \approx 32.5^{\circ}$ 46.7°, 58.3° are clearly seen [15]. It is true that the XRD patterns of  $Gd_{0.8}La_{0.2}Ba_{0.5}La_{0.5}Co_2O_{6-\delta}$  before and after the pressurized water steam treatment, being close to each other, indicate the stabilization of the structure and phase composition of this material, as compared



**Fig. 8.** (a) XRD patterns of the double perovskites  $Gd_{0.8}La_{0.2}Ba_{1-y}La_yCo_2O_{6-\delta}$  prepared at 1100 °C in air followed by slow (100 °C·h<sup>-1</sup>) cooling to room temperature. (b) SEM micrograph of  $Gd_{0.8}La_{0.2}Ba_{0.95}La_{0.05}Co_2O_{6-\delta}$  prepared at 1100 °C in air followed by slow (100 °C·h<sup>-1</sup>) cooling to room temperature.

to  $Gd_{0.8}La_{0.2}Ba_{1-y}La_yCo_2O_{6-\delta}$  with  $y \le 0.4$ . Nonetheless, in case of  $Gd_{0.8}La_{0.2}Ba_{0.5}La_{0.5}Co_2O_{6-\delta}$ , it is not exactly the double perovskite structure that is stabilized.

### 3.4. The hydration of lanthanum-substituted GdBaCo<sub>2</sub>O<sub>6- $\delta$ </sub>

Fig. 9 presents the temperature dependences of the oxygen content in dry  $(p_{\rm H_2O} = 10^{-3.97})$ atm) synthetic air for  $Gd_{0.8}La_{0.2}Ba_{0.95}La_{0.05}Co_2O_{6-\delta}$  and  $BaCo_{0.8}Gd_{0.2}O_{3-\delta}$ , respectively. In contrast with the  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  material [9], for the singlephase double perovskite Gd<sub>0.8</sub>La<sub>0.2</sub>Ba<sub>0.95</sub>La<sub>0.05</sub>Co<sub>2</sub>O<sub>6-δ</sub> the difference between the weight change in humid ( $p_{H_2O} = 10^{-1.88}$  atm) and dry atmospheres of both synthetic air and nitrogen ( $p_{0_2} = 10^{-4.2}$ atm) is insignificant, as shown in the inset of Fig. 9a. Likewise, there is still no convincing evidence of water absorption in A-sublatticeundoped GdBaCo<sub>1.8</sub>Fe<sub>0.2</sub>O<sub>6- $\delta$ </sub> [9] and La<sub>0.5</sub>Ba<sub>0.5</sub>CoO<sub>3- $\delta$ </sub> [10] cobaltites. At the same time, the inset in Fig. 9b demonstrates significant weight increase in humid ( $p_{\rm H_2O} = 10^{-2.05}$  atm) synthetic air for the  $BaCo_{0.8}Gd_{0.2}O_{3-\delta}$  cubic perovskite. Hence, we can conclude that the protonation observed earlier in  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  [9,10] is due to the impurities, such as  $BaCo_{1-x}Gd_xO_{3-\delta}$ , that are always present in this material. Moreover, as compared to the other double perovskite cathodes without La-doping, Gd<sub>0.8</sub>La<sub>0.2</sub>BaCo<sub>2</sub>O<sub>6-δ</sub> cathode was shown earlier [9] to possess the lowest polarization resistance in contact with proton-conducting electrolyte. It may well be that the exsolution of  $BaCo_{1-x}Gd_xO_{3-\delta}$  cubic perovskite promotes the electrochemical activity of  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$ . Thus, a detailed study of water absorption and the possible proton conductivity in the cubic perovskites  $BaCo_{1-x}RE_xO_{3-\delta}$ , as well as the influence of their exsolution on the electrochemical properties of Gd  $_{1-x}$ La<sub>x</sub>BaCo<sub>2</sub>O<sub>6- $\delta$ </sub> oxides is of key importance for successful development of novel triple-conducting materials for practical applications. Such work is in progress now.

### 4. Conclusions

In this work, we investigated the crystal structure of double perovskites with nominal compositions  $Gd_{1-x}La_{x}BaCo_{2}O_{6-\delta}$ (x = 0.2 - 0.8). By sintering in air, it was possible to obtain the layered double perovskite structure (P4/mmm space group) for the samples with x up to 0.6. Annealed in air Gd  $_{1-x}La_xBaCo_2O_{6-\delta}$  with x = 0.8comprised a mixture of ordered (P4/mmm) and disordered ( $Pm\overline{3}m$ ) perovskite phases, which transformed into a double perovskite (P4/mmm) after annealing in mildly reducing conditions (1100 °C and  $p_{O_2} = 10^{-3.0}$  atm). The lattice volume of  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$ (x = 0.2 - 0.8) was shown to increase upon increasing lanthanum content x. In situ HT XRD demonstrated that Gd<sub>0.8</sub>La<sub>0.2</sub>BaCo<sub>2</sub>O<sub>6-δ</sub> sample possesses double perovskite structure (P4/mmm) in the temperature range of (25–900) °C with monotonically increasing unit cell parameters *a*. *c*. and unit cell volume.

Our subsequent study concerned the nature of a secondary phase, the nanoparticles of which were found by SEM to cover the surface of  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$ . Though it proved hard to pinpoint the actual composition of this impurity phase, most likely, it corresponds to the gadolinium-substituted barium cobaltite  $BaCo_{1-x}Gd_xO_{3-\delta}$ . The identification of  $BaCo_{1-x}Gd_xO_{3-\delta}$  as an impurity in  $Gd_{1-x}La_xBaCo_2O_{6-\delta}$  oxides is hampered by the instability of  $BaCo_{1-x}Gd_xO_{3-\delta}$  in ambient humid air; the intensity of its peaks



**Fig. 9.** Main plots – temperature dependences of the oxygen content in  $Gd_{0.8}La_{0.2}Ba_{0.95}La_{0.05}Co_2O_{6-\delta}$  (a) and  $BaCo_{0.8}Gd_{0.2}O_{3-\delta}$  (b) in dry ( $p_{H_2O} = 10^{-3.97}$  atm) synthetic air. Insets show relative weight differences between TGA curves in wet and dry atmospheres for  $Gd_{0.8}La_{0.2}Ba_{0.95}La_{0.05}Co_2O_{6-\delta}$  (a) and  $BaCo_{0.8}Gd_{0.2}O_{3-\delta}$ . (b) The solid lines and points represent the data obtained in dynamic and static mode, respectively.

on the XRD patterns depends strongly on the sintering conditions and decreases drastically even upon storage. In addition, genuinely single-phase double perovskites, which are stable in ambient air, cannot be produced by substitution of La for either just Gd or just Ba in GdBaCo<sub>2</sub>O<sub>6- $\delta$ </sub>. Only simultaneous replacement, within certain limits, of both Gd and Ba in GdBaCo<sub>2</sub>O<sub>6- $\delta$ </sub> with La can yield singlephase, according to both SEM and XRD, A-site ordered double perovskite. As an example of such Gd<sub>1-x</sub>La<sub>x</sub>Ba<sub>1-y</sub>La<sub>y</sub>Co<sub>2</sub>O<sub>6- $\delta$ </sub> oxide, Gd<sub>0.8</sub>La<sub>0.2</sub>Ba<sub>0.95</sub>La<sub>0.05</sub>Co<sub>2</sub>O<sub>6- $\delta$ </sub> was synthesized.

Finally, the hydration experiments demonstrated that, while truly single-phase layered Gd<sub>0.8</sub>La<sub>0.2</sub>Ba<sub>0.95</sub>La<sub>0.05</sub>Co<sub>2</sub>O<sub>6-\delta</sub> does not show any water uptake, the cubic perovskite  $BaCo_{0.8}Gd_{0.2}O_{3-\delta}$ significantly increases its weight in wet atmospheres. Our data indicate that, similarly to what was found recently about so-called triple conductivity in PrBaCo<sub>2</sub>O<sub>6- $\delta$ </sub> double perovskite [5,6], the water absorption by La-substituted GdBaCo<sub>2</sub>O<sub>6- $\delta$ </sub> is not due to the bulk double perovskite phase, but rather due to the impurities covering the surface of these materials. From the practical standpoint, it probably does not make much difference whether the superior electrochemical performance of a material, such as  $Gd_{0.8}La_{0.2}BaCo_2O_{6-\delta}$  [9], is because of the main phase or the secondary phase. However, in our opinion, the focus of the further development of better H-SOFC cathodes should be shifted to either investigating these impurity phases as possible triple conductors or studying the double-perovskite-based composite materials, where the beneficial properties of in situ exsolved secondary phase nanoparticles may complement those of the main phase.

### **CRediT** authorship contribution statement

**Dmitry Malyshkin:** Conceptualization, Investigation, Writing - original draft, Writing - review & editing, Funding acquisition. **Andrey Novikov:** Investigation. **Ivan Ivanov:** Investigation, Writing - original draft. **Vladimir Sereda:** Validation, Writing - original draft, Writing - review & editing. **Dmitry Tsvetkov:** Conceptualization, Project administration, Writing - original draft, Writing - original draft, Writing - neview & editing. **Andrey Zuev:** 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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