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ARTICLE

Oxygen content, crystal structure and chemical expansion of the double perovskites $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$

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Double perovskites $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x = 0 - 0.6$) were shown to have the tetragonal P4/mmm structure in air over complete temperature range investigated despite the oxygen content reaches the threshold value of 5.5 at temperature increasing from 850 °C for $x=0$ up to 1078 °C for $x=0.6$. However the P4/mmm–Pmmm structure transition was found to occur in $\text{PrBaCo}_2\text{O}_{6-\delta}$ under reducing conditions at temperature decreasing from 500 °C at $pO_2=10^{-3}$ atm down to 350 °C at $pO_2=10^{-4}$ atm. Lattice chemical expansion along a axis and contraction along c axis with decreasing oxygen content, $6-\delta$, were found to compensate each other completely in the double perovskites and, therefore, their volume chemical expansion becomes negligible. As a result the cell volume linearly increases with temperature contrary to simple cubic perovskites.

Introduction

Double perovskites $\text{AA}'\text{Co}_2\text{O}_5$, where A and A' are a rare earth element (RE) and Ba, respectively, have received great attention in past decade due to promising magnetic and transport properties at relatively low temperatures.¹⁻⁴ The double perovskite $\text{PrBaCo}_2\text{O}_{6-\delta}$ was recently found to exhibit the best performance as a cathode for IT SOFCs⁵⁻⁸ and an oxygen permeable dense ceramic membrane⁶. However, despite promising cathode behavior $\text{PrBaCo}_2\text{O}_{6-\delta}$ has too high thermal expansion coefficient (TEC).⁷ This obvious disadvantage seriously restricts its possible commercial application. Doping $\text{PrBaCo}_2\text{O}_{6-\delta}$ with other 3d- metal seems to be a possible way to solve the aforementioned problem. Indeed substitution of iron for cobalt was recently shown to decrease the TEC value of $\text{GdBaCo}_2\text{O}_{6-\delta}$.⁹

Change of the crystal structure parameters with temperature was studied in air for $\text{PrBaCo}_2\text{O}_{6-\delta}$ in Refs.^{5,9,10} However, reported results seem to be controversial. Structural transitions P4/mmm→Pmmm and Pmmm→P4/mmm at around 100 °C and 400 °C, respectively, were found for $\text{PrBaCo}_2\text{O}_{6-\delta}$ by Kim et al.⁹ whereas Chavez et al.⁵ reported only about Pmmm→P4/mmm transition in the temperature range between 350 and 400 °C. On the contrary, Zou et al.¹⁰ found that $\text{PrBaCo}_2\text{O}_{6-\delta}$ has tetragonal structure with space group (s.g.) P4/mmm from room temperature up to 900 °C in air. It was also shown that substitution of iron for cobalt in the double perovskite does not lead to change of the crystal structure of $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.4$) and one is tetragonal with s.g. P4/mmm irrespective of temperature.¹⁰

So far there are no data on a structure of the double perovskites $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ depending on oxygen nonstoichiometry except those reported for the undoped $\text{PrBaCo}_2\text{O}_{6-\delta}$.¹¹ Moreover there is a significant scattering in the reported values of oxygen content in $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ at given temperature and oxygen

partial pressure.^{1,9} For example, values of oxygen content, $6-\delta$, determined for $\text{PrBaCo}_2\text{O}_{6-\delta}$ at room temperature in air vary from 5.70¹ up to 5.89⁹.

Therefore the priority purposes of the present work were (i) to study the crystal structure of the double perovskites $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) as a function of temperature and oxygen content, (ii) to measure oxygen nonstoichiometry of $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ as a function of temperature, and (iii) to find a possible relation between a crystal structure and oxygen content for the double perovskites investigated.

Experimental

Powder samples of the nominal composition $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) were prepared by means of glycerol – nitrate method using Pr_6O_{11} , BaCO_3 , Co, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ as starting materials. All materials used had a purity of 99.99%.

Stoichiometric mixture of starting materials was dissolved in concentrated nitric acid (99.99% purity) and required volume of glycerol (99% purity) was added as a complexing agent and a fuel. Glycerol quantity was calculated according to full reduction of corresponding nitrates to molecular nitrogen N_2 . As prepared solutions were heated continuously at 100 °C till complete water evaporation and pyrolysis of the dried precursor. The resulting ash was subsequently calcined at 1100 °C for 10 hours to get the desired double perovskite powder.

The phase composition of the powder samples prepared accordingly was studied at room temperature by means of X-ray diffraction (XRD) with Equinox 3000 diffractometer (Inel, France) using Cu K_α radiation. XRD showed no indication for the presence of a second phase for as prepared compositions with $0 \leq x \leq 0.6$.

The crystal structure of the double perovskites $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x = 0 - 0.6$) was studied in the temperature range between 25

and 1100 °C in air and reducing atmospheres by means of “in situ” XRD with Cu K_{α} radiation using Equinox 3000 diffractometer (Inel, France) equipped with the high temperature camera HTK 16N (Anton Paar GmbH, Austria).

Oxygen nonstoichiometry, δ , as a function of temperature in air was studied by means of thermogravimetric (TG) technique using a STA409PC (Netzsch, Germany) microbalance. A sample was equilibrated first at the given oxygen partial pressure and temperature for 2 hours until a sample weight ceases to change. Temperature was then changed in steps within range between 25 to 1150 °C in both decreasing and increasing direction at the same pO_2 and the measurement procedure was repeated until equilibrium state was reached at each step. Absolute value of δ in $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) samples was determined by both direct reduction of corresponding double perovskites by hydrogen flux in the TG setup (TG/H₂) and iodometric titration of the samples slowly cooled to room temperature. Both methods are described in detail elsewhere.¹²

Results and discussion

XRD showed that as prepared and slowly (~100 °C/hour) cooled powder samples of the nominal composition $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ are single phases within the studied composition range $x=0-0.6$ (See Figure S1 in the ESI†). Their XRD patterns were indexed using the tetragonal P4/mmm space group (unit cell $a_c \times a_c \times 2a_c$, where a_c is the lattice parameter of the cubic cell) like it was done in Refs.^{1,10,11} Rietveld refined XRD pattern of $\text{PrBaCo}_2\text{O}_{6-\delta}$ is shown, as an example, in Fig. 1.

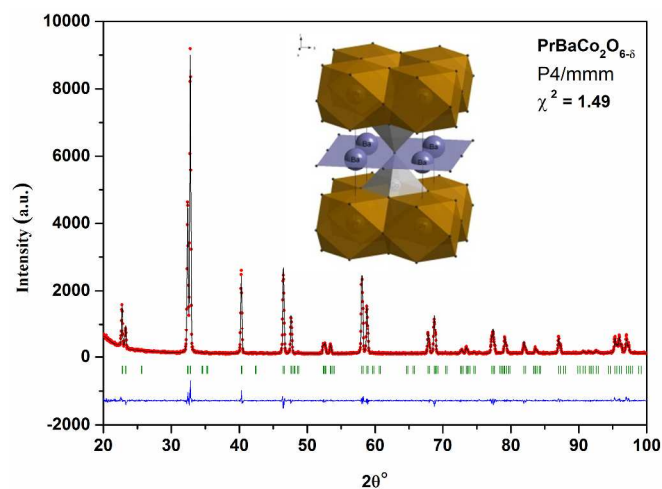


Fig. 1. Rietveld refined XRD pattern of slowly (~100 °C/hour) cooled double perovskite $\text{PrBaCo}_2\text{O}_{6-\delta}$ at room temperature in air: observed X-ray diffraction intensity (o) and calculated curve (line). The bottom curve is the difference of patterns, $y_{\text{obs}} - y_{\text{cal}}$, and the small bars indicate the angular positions of the allowed Bragg reflections. Inset: view of the $\text{PrBaCo}_2\text{O}_{6-\delta}$ crystal structure.

The refined lattice parameters of $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) are given in Fig. S2 in the ESI† as a function of iron content at room temperature in air. It is worth noting that cell parameter a for the Fe-doped double perovskites is very close to that of the undoped cobaltite $\text{PrBaCo}_2\text{O}_{6-\delta}$ within the composition range studied. In other words, it does not depend on the iron content in practical term whereas c parameter increases with iron

substitution. This result seems to be in good agreement with that reported earlier by J. Zou et al.¹⁰ X-ray diffraction patterns of $\text{PrBaCo}_2\text{O}_{6-\delta}$ sample obtained in the temperature range between 25 and 1000 °C in air are presented in Fig. 2. As follows the patterns do not show significant changes with temperature obviously indicating the P4/mmm structure at all temperatures investigated in full agreement with Ref.¹⁰ It is worth to note that aforementioned behavior was also found for all Fe-doped double perovskites studied in the present work.

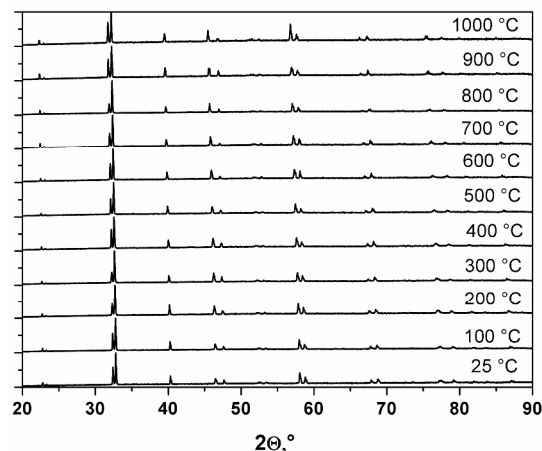


Fig. 2. “In situ” XRD patterns of $\text{PrBaCo}_2\text{O}_{6-\delta}$ in the temperature range between 25 and 1000 °C in air.

Differential scanning calorimetry (DSC) also did not show any heat effects for $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) over complete temperature range investigated. Thus DCS results obviously indicate in favor of lack of a first order phase transition for all double perovskites studied in the temperature range 25–1100 °C in air.

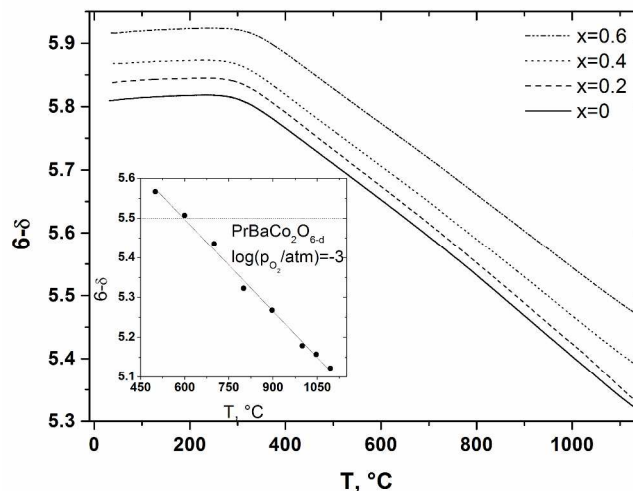


Fig. 3. Oxygen content of $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) as a function of temperature in air. Oxygen content of $\text{PrBaCo}_2\text{O}_{6-\delta}$ as a function of temperature at $pO_2=10^{-3}$ atm is given in the insertion.

Oxygen content in the double perovskites $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ measured by TG method is given in Fig. 3 as a function of temperature in air. As seen substitution of Fe for Co leads to

oxygen content increase in the oxide at a given temperature. Similar behavior was found earlier for $\text{GdBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ and $\text{NdBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ oxides.^{13,14}

Comparison of Figs. 2 and 3 shows that significant change of the oxygen content in $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) oxides with temperature in air have no influence on their crystal structure. The last result is of great interest since the double perovskites $\text{REBaCo}_2\text{O}_{6-\delta}$ are believed to have orthorhombic structure at the oxygen content about 5.5 due to oxygen vacancies ordering along b axis.¹⁻⁴ However, the oxygen content 5.5 in, for example, $\text{GdBaCo}_2\text{O}_{6-\delta}$ is reached at around 420 °C in air¹⁵, i.e. at significantly lower temperature as compared to 850-1080 °C for $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) oxides. Therefore, it is quite logical to suppose that $\text{P4}/\text{mmm} \rightarrow \text{Pmmm}$ phase transition in double perovskites is opposed by thermal disorder. Hence, we can expect oxygen vacancies ordering and corresponding $\text{P4}/\text{mmm} \rightarrow \text{Pmmm}$ transition in $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) if the oxygen content 5.5 could be reached at a temperature lower ca. 500 °C. Aforementioned assumption is completely supported by “in situ” XRD analysis performed for the double perovskites studied in gas atmospheres with reduced $p\text{O}_2$. As an example, variable temperature XRD data in 2θ range 45-48° obtained for $\text{PrBaCo}_2\text{O}_{6-\delta}$ at $p\text{O}_2=10^{-3}$ atm are shown in Fig. 4.

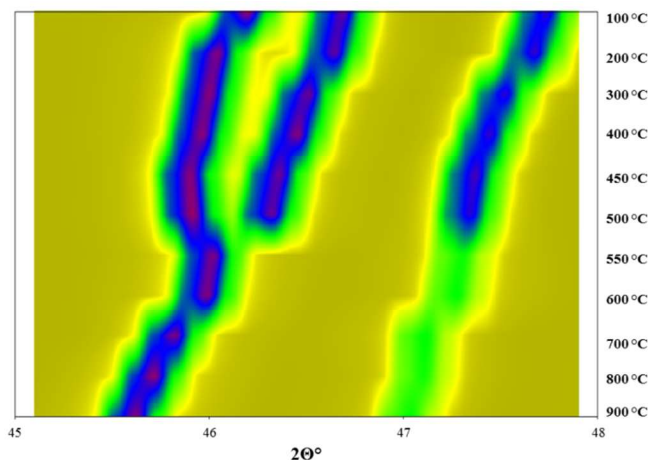


Fig. 4. Variable temperature XRD data in 2θ range 45-48° for $\text{PrBaCo}_2\text{O}_{6-\delta}$ at $p\text{O}_2=10^{-3}$ atm.

The phase transition from tetragonal structure $\text{P4}/\text{mmm}$ to orthorhombic Pmmm is clearly seen at around 500 °C, i.e. at the temperature corresponding to oxygen content 5.5 in $\text{PrBaCo}_2\text{O}_{6-\delta}$ at $p\text{O}_2=10^{-3}$ atm as seen in the insertion of Fig. 3. Moreover $\text{P4}/\text{mmm} \rightarrow \text{Pmmm}$ transition shifts to the temperature as low as 350 °C at $p\text{O}_2=10^{-4}$ atm (See Fig. S3 in the ESI†). It should be emphasized in addition that 350 °C at $p\text{O}_2=10^{-4}$ atm also corresponds to oxygen content 5.5 in $\text{PrBaCo}_2\text{O}_{6-\delta}$. Therefore, such significant lowering of temperature corresponding to the oxygen content 5.5 in $\text{REBaCo}_2\text{O}_{6-\delta}$ seems to enable the oxygen ordering in their lattice and, as a consequence, the structure transition.

The refined lattice parameters and cell volumes of the double perovskites $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) are given in Figs. S4 and S5 in the ESI† as a function of temperature in air. As an example such data are shown in Fig. 5 for $\text{PrBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{6-\delta}$ in comparison with those for the state-of-the-art SOFC cathode material $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\gamma}$ ¹⁶. As can be seen temperature dependence of the double perovskite cell parameters is nonlinear whereas cell volume linearly increases with temperature. Indeed, as seen in Fig. 5 a and c parameters

demonstrate gradual positive and negative deviation, respectively, from the linear trend of low temperature thermal lattice expansion. It should be emphasized that the onset of deviation from the linear trend for $\text{PrBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{6-\delta}$ cell parameters and one of oxygen release from its lattice (see Fig. 3) are quite consistent with each other. Indeed, Fig. 5 shows that the deviation starts at about 400 °C for $\text{PrBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{6-\delta}$ and this temperature completely corresponds to the onset of its lattice oxygen release as seen in Fig. 3. The onset of cell volume deviation from linear trend for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\gamma}$ (see Fig. 5) coincides completely with that of oxygen release by its lattice as well.¹⁶ Therefore, the deviation mentioned above can be attributed to the chemical lattice strain induced by oxygen vacancies formation since the thermal expansion is believed to be a linear function of temperature.¹⁷

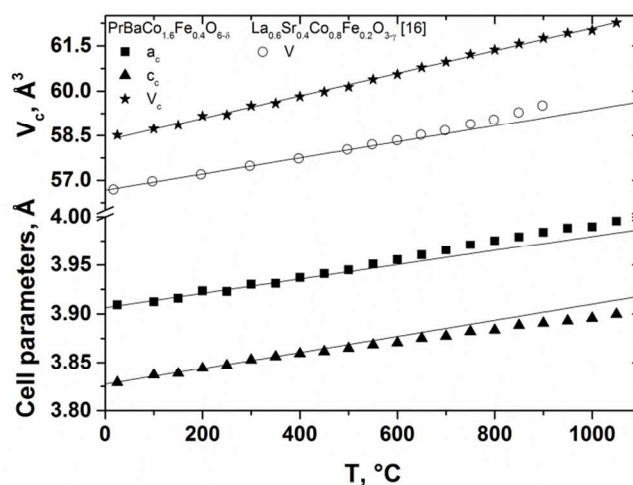


Fig. 5. Lattice parameters of $\text{PrBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{6-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\gamma}$ ¹⁶ as functions of temperature in air. Lines give the extrapolation of low temperature thermal expansion.

In order to estimate the chemical lattice strain mentioned above the values given by the linear trends observed for $\text{PrBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{6-\delta}$ cell parameters, $a(c)_{\text{expected}}$, and for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\gamma}$ cell volume, V_{expected} , at low temperatures (see Fig. 5) were subtracted from the measured values of cell parameters, $a(c)_{\text{measured}}$, and cell volume, V_{measured} , respectively. Chemical lattice strain normalized to room temperature can be given by the following equations

$$\varepsilon_a = \frac{a_{\text{measured}} - a_{\text{expected}}}{a_0}, \quad (1)$$

$$\varepsilon_c = \frac{c_{\text{measured}} - c_{\text{expected}}}{c_0}, \quad (2)$$

$$\varepsilon_V = \frac{V_{\text{measured}} - V_{\text{expected}}}{V_0}, \quad (3)$$

where a_0 , c_0 , V_0 – are lattice constants and cell volume at room temperature, respectively. ε_a , ε_c and ε_V are shown in Fig. 6 as a function of temperature. ε_a , ε_c and ε_V were also replotted in Fig. 7 as a function of oxygen content using data presented in Fig. 3. It is worth noting that positive chemical lattice strain along a axis and negative that along c axis calculated for $\text{PrBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{6-\delta}$ compensate each other and, as a result, its volume chemical expansion is negligible in practical term (see Figs. 6 and 7). What is why the $\text{PrBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{6-\delta}$ cell volume

itself linearly increases with temperature indicating only thermal expansion unlike $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\gamma}$ (see Fig. 5).

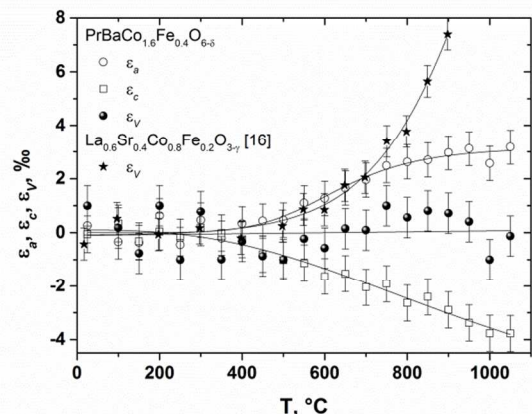


Fig. 6. Chemical lattice strain of $\text{PrBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{6-\delta}$ normalized as described in the text as a function of temperature in air in comparison with that for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\gamma}$.¹⁶ Curves are guide to eye only.

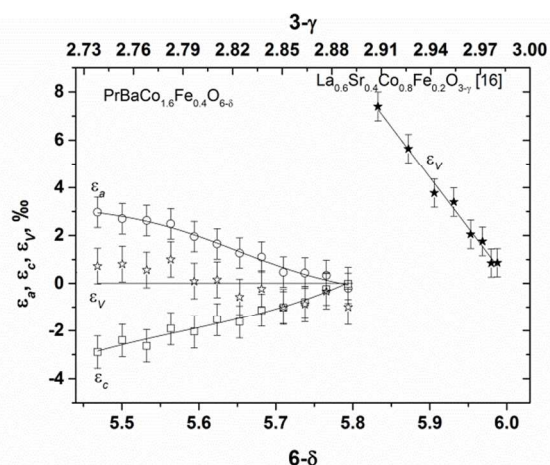


Fig. 7. Chemical lattice strain of $\text{PrBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{6-\delta}$ normalized as described in the text as a function of oxygen content in air in comparison with that of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\gamma}$.¹⁶ Curves are guide to eye only.

The tendency of the $\text{PrBaCo}_2\text{O}_{6-\delta}$ crystal lattice to expand along *a*-axis and to contract along *c* one while its oxygen content decreases is obviously seen in Fig. 8 where the cell parameters are plotted versus $p\text{O}_2$ at 900 °C.

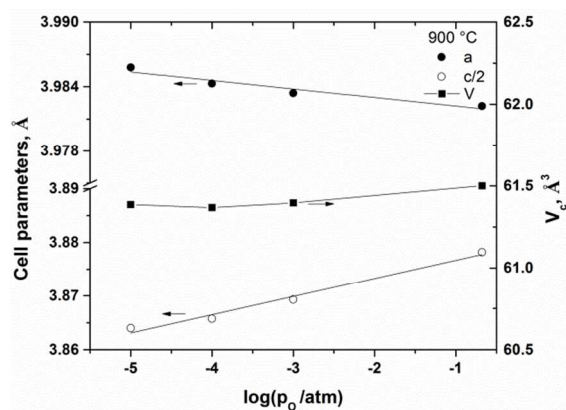


Fig. 8. Lattice parameters of $\text{PrBaCo}_2\text{O}_{6-\delta}$ versus $p\text{O}_2$ at 900 °C.

It is of interest to note that similar behavior was observed by Cox-Galhotra et al. for $\text{NdBaCo}_2\text{O}_{6-\delta}$ ¹⁸ and $\text{PrBaCo}_2\text{O}_{6-\delta}$ ¹⁹ and by Kharton et al.²⁰ who showed that opposite change of the $\text{La}_2\text{NiO}_{4\pm\delta}$ cell parameters with oxygen content cancels its total volume chemical expansion. On the basis of results obtained one can conclude that chemical expansion of layered perovskites such as $\text{PrBaCo}_{1-x}\text{Fe}_x\text{O}_{6-\delta}$ and $\text{La}_2\text{NiO}_{4\pm\delta}$ ²⁰ is anisotropic property unlike that of cubic perovskites such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\gamma}$. The latter is really isotropic property as it was shown early for perovskite oxides with pseudo cubic structure.^{21,22}

Conclusions

The crystal structure parameters were determined for the double perovskites $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) depending on temperature by means of “in situ” XRD in temperature range from 25 to 1100 °C in air and under reducing conditions ($p\text{O}_2=10^{-3}$ and 10^{-4} atm). All double perovskites studied were shown to have the tetragonal P4/mmm structure in air over complete temperature range investigated whereas “in situ” XRD data obtained at $p\text{O}_2=10^{-3}$ and 10^{-4} atm obviously indicate in favor of the P4/mmm–Pmmm structure transition for $\text{PrBaCo}_2\text{O}_{6-\delta}$ at temperature as low as 500 and 350 °C, respectively, when oxygen content in this oxide reaches threshold value of 5.5 according to TG data. Oxygen content was also found to reach the same value in air for all double perovskites studied at significantly higher temperatures as compared to 500 °C. Thus high temperature seems to suppress the oxygen vacancies ordering and, consequently, the structural transition P4/mmm–Pmmm is not observed in these double perovskites in air.

The crystal lattice of $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$ ($x=0-0.6$) was found to expand along *a* axis and simultaneously to contract along *c* axis when the oxygen content in the double perovskites decreases so their volume chemical expansion becomes negligible unlike in simple cubic perovskites.

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Notes and references

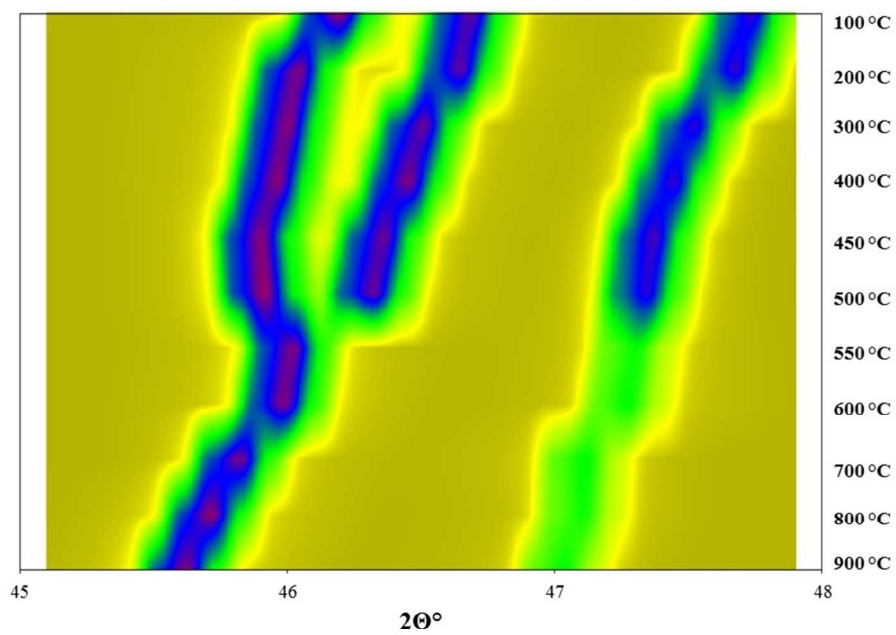
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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Variable temperature XRD data for $\text{PrBaCo}_2\text{O}_{6-\delta}$ at $p\text{O}_2=0.001$ atm
254x190mm (96 x 96 DPI)