BaCoO₂+ δ

Waidha, Aamir; Zhang, Hongbin ; Lepple, Maren ; dasgupta, supratik; lambert, alff; Slater, Peter; fortes, dominic; Clemens, Oliver

DOI:

[10.1039/C8CC09532A](https://doi.org/10.1039/C8CC09532A)

License:

None: All rights reserved

Document Version

Peer reviewed version

Citation for published version (Harvard):

Waidha, A, Zhang, H, Lepple, M, dasgupta, S, lambert, A, Slater, P, fortes, D & Clemens, O 2019, 'BaCoO₂+ δ : A new highly oxygen deficient perovskite-related phase with unusual Co coordination obtained by high temperature reaction with short reaction times', *Chemical Communications*, vol. 55, no. 20, pp. 2920-2923. <https://doi.org/10.1039/C8CC09532A>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

Checked for eligibility 13/02/2019

Published in Chemical Communications

<https://pubs.rsc.org/en/journals/journalissues/cc#!recentarticles&adv>

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. I. Waidha, H. Zhang, M. Lepple, S. Dasgupta, A. Lambert, P. Slater, A. D. Fortes and O. Clemens, *Chem. Commun.*, 2019, DOI: 10.1039/C8CC09532A.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Journal Name

COMMUNICATION

BaCoO_{2+δ}: A new highly oxygen deficient perovskite-related phase with unusual Co coordination obtained by high temperature reaction with short reaction times

Aamir Iqbal Waidha,^a Hongbin Zhang,^b Maren Lepple,^c Supratik Dasgupta,^d Lambert Alff,^d Peter Slater,^e A.D. Fortes,^f and Oliver Clemens^{*a,g}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A new highly oxygen deficient metastable modification of perovskite-related BaCoO_{2+δ} (δ ~ 0.01 – 0.02) has been prepared using high temperature reactions with short heating times. This defect rich compound has at least partially square planar coordination of the Co²⁺ ions, a highly unusual coordination environment for Co. Low temperature neutron powder diffraction showed a G-type antiferromagnetic ordering, confirmed by SQUID magnetic measurements, which indicate a high Néel temperature of 220 K. This work shows how novel defective phases can be synthesized by exploiting short reaction times in solid state synthesis, thus offering an alternative route for new materials synthesis.

Perovskite-type or perovskite-related ABX_{3-y} compounds are interesting candidates for a wide range of applications in the field of electronics ¹, solid oxide fuel ² and solar cells ³. In particular, cobalt based perovskites ACoO_{3-y} have drawn a lot of attention due to their interesting electronic, magnetic and catalytic properties ^{4, 5}. For the latter, especially such compounds with a Co-sublattice, which can be derived from the cubic aristotype structure (i. e. from a close cubic packed (*ccp*) arrangement of AX₃ layers with Co occupying ¼ of octahedral voids), were reported to be of most interest. Within such an atomic arrangement, the structure is highly flexible and can

tolerate large amounts of anion vacancies, ABX_{3-y} ⁶⁻⁸, with values of y up to 1 being known, from which a high mobility of oxygen ions originates.

For non-stoichiometric BaCoO_{3-y} perovskite-related oxides, a broad structural variety of compounds has been found depending on the detailed value of y. Those were summarized by Raveau et al.⁵ as well as by Mentré et al.⁹ with hexagonal modifications known for oxygen rich systems (2H, 5H, 12H). For large values of y, the most oxygen deficient cubic perovskite phase BaCoO_{2.22}⁹ as well as trigonal BaCoO₂¹⁰ are known, where the structure of the latter was reported as an ordering variant (*P*3₁21) of the cubic aristotype structure with only tetrahedral coordination of the Co ions.

Apart from the thermodynamically stable modifications, highly anion deficient metastable compounds have been previously prepared almost entirely via hydride based reductions ^{7, 8}. Such reactions are time consuming multi step procedures which require additional washing steps to obtain a phase pure sample. In contrast, direct synthesis of such metastable ABO₂ type perovskite-related phases has not been reported so far.

In this article, we report for the first time the preparation of a highly oxygen deficient tetragonal modification of BaCoO_{2+δ} synthesized using a simple route, involving high temperature solid state synthesis with considerably short reaction times (twice at 1000 °C for 1 h using heating / cooling rates of 2 °C/min) of high energy ball milled powders of BaCO₃ and Co₃O₄ under pure argon atmosphere. The synthesis conditions show a very narrow sweet spot. Changing the conditions slightly (temperature, flow of argon, heating time, etc.) results either in the formation of the trigonal BaCoO₂ modification, or cubic BaCoO_{2.22}, or melting of the sample.

The composition of the sample was determined from a combination of iodometric titration and energy dispersive X-ray spectroscopy (EDAX, Figure S1 in ESI) ^{9, 11}. The average oxidation state of Co was determined to be Co^{+2.03(2)} with a 1:1 ratio of Ba:Co. This results in an overall composition of the sample close to BaCoO_{2+δ} with δ ~ 0.01 – 0.02. Since carbonate has been previously reported to be stabilized on the B site within the

^a Technische Universität Darmstadt, Institut für Materialwissenschaft, Fachgebiet Materialdesign durch Synthese, Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany.

^b Institute of Materials Science, TU Darmstadt, 64287 Darmstadt, Germany

^c Technische Universität Darmstadt, Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Alarich-Weiss-Straße 12, 64287 Darmstadt, Germany.

^d Technische Universität Darmstadt, Institut für Materialwissenschaft, Fachgebiet Dünne Schichten, Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany

^e University of Birmingham, School of Chemistry, Edgbaston, Birmingham B15 2TT, UK

^f ISIS Facility, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0QX, United Kingdom

^g Karlsruher Institut für Technologie, Institut für Nanotechnologie, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein Leopoldshafen, Germany

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Figure 1: Coupled Rietveld refinement of the neutron diffraction data recorded at 10 K and room temperature X-ray diffraction patterns of $\text{BaCoO}_{2.6}$ using model#1 (see text).

perovskite structure, the presence of this species was further ruled out by the use of Raman spectroscopy¹² (Figure S2 in ESI). The structure and phase composition of the obtained powder was studied via a combined Rietveld analysis of X-ray and neutron powder diffraction data. All of the reflections could be indexed with a $2 \times 2 \times 1$ tetragonally distorted superstructure of the cubic perovskite aristotype (Figure 1) with $a = 8.2201(15)$ Å and $c = 3.9181(7)$ Å, additionally, 8.8(3) wt-% of trigonal BaCoO_2 and $\sim 3.1(3)$ wt-% of CoO were identified as impurity phases. Among the maximum subgroups of $Pm\text{-}3m$ with those lattice parameter restrictions, only $P4/mmm$ (and its *translationengleiche* subgroups, Figure S3 and S4 in ESI for structural relationship), allow for the (1 0 0) superstructure reflection observed at $10.74^\circ(2\theta)$ (Figure S5 in ESI) in the XRD pattern.

This tetragonal distortion is unusual, since it implies a c/a ratio smaller than 0.5 ($c_{\text{prim}}/a_{\text{prim}} < 1$), which is often found for compounds with (partial) square planar coordination of the transition metal. Remarkably, only $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{FeO}_2$ was previously reported to crystallize in such a $2 \times 2 \times 1$ primitive superstructure by Kageyama et al.⁶, with the B-site cation being located at three independent crystallographic sites ($\text{Ba} @ 4k$; $\text{Co} @ 1a, 1c, 2f$). For this compound, square planar, but also 6-fold coordination of Fe^{2+} and coordination numbers lower than four would have to result from the structural model suggested, originating from an only partial ordering of the anion vacancies, confirmed by Mössbauer spectroscopy. A structural similarity between the phase prepared here to this Fe-based phase is chemically plausible regarding the overall anion content and because barium ferrates / cobaltates are known for their

structural similarity^{11,13}. However, no tetrahedral coordination is possible from the ideal site symmetries of the Co sites ($2x 4/mmm$, $1x mmm$). This is surprising with respect to the tetrahedral coordination found for the previously known modification of BaCoO_2 ¹⁰.

Therefore, we also investigated a second structural setting within the same space group, which differs by distribution of the Ba and Co ion on the different crystallographic sites ($\text{Ba} @ 1a, 1c, 2f$; $\text{Co} @ 4k$). In this structural setting, a tetrahedral coordination of Co is allowed from its site symmetry ($m2m$). Both, the model suggested by Kageyama et al.⁶ (model#1) as well as the alternative model (model#2) were used for the analysis of the neutron (ambient and 10 K) and X-ray diffraction data (see Table S1 and S4 for the starting and Table S2 and S5 for the refined structural models). Both models result in a good description of the diffraction data, with model#1 resulting in the best goodness of fit / R_{wp} values. Remarkably, no full ordering of oxygen vacancies was found for both models, and this implies that at least some of the Co^{2+} ions must be present in a square planar coordination or in a coordination with even lower coordination numbers (Figure 2a and b).

Subsequently, we attempted to refine the structure within the tetragonal *translationengleiche* subgroups of $P4/mmm$, which allow for further tilting of the polyhedra. However, such models do not result in a significant improvement of fit with respect to the additional parameters and do not result in an increase of localization of the oxygen ions and anion vacancies. Furthermore, model#2 does not become favourable over model#1. We also would like to emphasize, that the data showed no indication for further symmetry lowering, e. g. from

Figure 2: Structural representation of BaCoO_{2+δ}. (a) model#1, (b) model#2. Oxygen sites are depicted to indicate their fractional occupancy. For model#2, a split site model was used to refine the position of the Co ion, and most plausible polyhedra are indicated for the different possible coordination scenarios. (c) G-type AFM structure found for the magnetic moments ($C_{\text{magnetic}} = 2 \times C_{\text{nuclear}}$).

the appearance of superstructure reflections or splitting of the reflections, and using structures within lower symmetry crystal systems did not result in an improved fit.

To the best of our knowledge, a planar coordination of Co²⁺ has not been observed so far in anion deficient perovskite structures⁹, although it can be found, e. g., in Sr₂CoO₂Cu₂S₂¹⁴. To obtain a deeper understanding on the role of coordination geometry around Co on the stability of a phase with ideal composition BaCoO₂, we carried out DFT based calculations on fully ordered models #1 and #2, with square planar and tetrahedral coordination of the Co ions, respectively, as well as on the trigonal modification (model #3). The values are summarized in Table S6, showing model #1 to be the least favourable setting and the trigonal modification to be energetically most favourable ($E(\#3) < E(\#2) < E(\#1)$, with differences of $\Delta(E(\#3)-E(\#1)) \sim -0.5$ eV and $\Delta(E(\#3)-E(\#2)) \sim -0.25$ eV). Therefore, the disorder generated by the small amount of additional oxygen δ (which are too costly to be calculated) must influence the overall structural stability, making the disordered tetragonal modification more favourable.

A magnetic phase transition was found to occur at a temperature of approximately 220 K, indicating antiferromagnetic (AFM) ordering (see Figure 3a; the magnetic properties are unknown for the trigonal phase of BaCoO₂; CoO

Figure 3: (a) Susceptibility vs temperature curve (black) and inverse susceptibility curve (red) for BaCoO_{2+δ} measured at the field of 2 Tesla. (b) M vs H curve for BaCoO₂ measured at 5 K.

orders AFM below ~ 290 K^{9,15}). This is also in agreement with the presence of only a small residual ferromagnetic moment in the magnetisation curve recorded at 5 K (Figure 3b). To determine the magnetic structure of BaCoO_{2+δ}, neutron diffraction data at 10 K were recorded. At this temperature, additional reflections appear as compared to the room temperature data. A part of them arise from the AFM ordering of CoO, and can be described with the magnetic structure of this phase as described previously¹⁵. The other reflections originate from the magnetic ordering of BaCoO_{2+δ} and can be indexed based on a magnetic k -vector of $[0\ 0\ \frac{1}{2}]$. We tested all models within the maximum magnetic subgroups of $P4/mmm$, and found that the magnetic scattering can be best described by the presence of anti-ferromagnetic (AFM) G-type order with the magnetic moment of $2.55(2) \mu_B$ being aligned along the c -axis. This ordering corresponds to the magnetic symmetries $P4/mcc$ (124.360) for model#1 or Pc_2/mmc (131.444) for model#2 respectively, see Figure 2c. The refined magnetic moment is in agreement with what would be expected for high-spin Co²⁺ ($3.7 \mu_B$), taking into account that the magnetic moment obtained from neutron diffraction is reduced by covalent contributions. We also studied the conductivity of the sample by means of electrochemical impedance spectroscopy (Figure 4). The conductivity is of the order 10^{-8} S cm⁻¹ at 298 K, which is significantly lower by ~ 3 -4 orders of magnitude as compared to, e. g., BaCoO_{1.80}(OH)_{0.86} with Co in a mixed valent +2/+3 oxidation state. The slope of the Arrhenius plot corresponds to an activation energy of $0.30(1)$ eV, and no blocking behaviour could be observed at low frequencies. Both suggest mainly electronic conductivity of the sample. The relatively low conductivity can be understood from the presence of mainly divalent Co²⁺, and the similarity of activation energy to mixed valent BaCoO_{1.80}(OH)_{0.86}¹¹ indicates a similar conduction

Figure 4: (a) Nyquist and (b) Arrhenius plot for temperature dependent total electrical conductivity of $\text{BaCoO}_{2+\delta}$ sample.

mechanism by electron hopping due to the presence of Co^{3+} . We also found that the sample is highly sensitive towards re-oxidation by means of simultaneous thermal analysis (STA) (Figure S6 in ESI) in pure oxygen. The onset of mass increase due to oxygen uptake upon heating at ~ 425 K is in agreement with the exothermic peak in the DSC profile which is due to the oxygen uptake forming a compound of composition of $\text{BaCoO}_{2.40}$ at this point. XRD measurements showed that the sample is then composed of a cubic perovskite phase (as reported, e. g., for $\text{BaCoO}_{2.22}$ ⁹) plus a further unknown phase. This is similar to what was observed previously for the dehydration of $\text{BaCoO}_{1.80}(\text{OH})_{0.86}$ ¹¹. On further heating, the mass increase continues up to a temperature of approximately 900 K leading to formation of $\text{BaCoO}_{2.66(2)}$, and this oxygen uptake is then accompanied by a complete structural transformation to the 2H modification, see Figure S7 in ESI.

Conclusions

In summary, a new highly oxygen deficient metastable perovskite-related phase of barium cobaltate with composition of $\text{BaCoO}_{2+\delta}$ ($\delta \sim 0.01$ – 0.02) is reported in this article. The compound was found to show strong structural similarity to the previously reported Fe based system $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{FeO}_2$ ⁶, with unusual coordination for Co^{2+} (which is at least partially square planar) and G-type AFM ordering below 220 K. It is surprising that such a highly oxygen deficient metastable phase could be formed, although the structure of the thermodynamically most stable modification of BaCoO_2 can also be derived from the cubic perovskite structure (i. e., shows a nearly identical Ba/Co sublattice). Therefore, the incorporation of small amounts of additional oxygen δ via short reaction times and fine-tuned Ar gas flow, in combination with the milling-

based activation of the precursors powders, are likely to be key to its formation. Thus, the findings presented here highlight the potential impact of small deviations of anion composition on anion ordering within a given cation lattice, and show how control of synthesis parameters can be exploited to produce new defective phases, thus offering an additional avenue for chemists to exploit in the quest for new materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was funded by the German Research Foundation (DFG) within CL551/2-1. We gratefully acknowledge awarding of beam time from the STFC (DOI: 10.5286/ISIS.E.87849379).

Notes and references

1. M. L. Medarde, *J. Phys. : Condens. Matter*, 1997, **9**, 1679–1707.
2. S. J. Skinner, *Int. J. Inorg. Mater.*, 2001, **3**, 113–121.
3. M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643–647.
4. G. Chen, W. Zhou, D. Guan, J. Sunarso, Y. Zhu, X. Hu, W. Zhang and Z. Shao, *Sci. Adv.*, 2017, **3**, e1603206.
5. B. Raveau and M. Seikh, *Cobalt Oxides: From Crystal Chemistry to Physics*, Wiley VCH, 2012.
6. T. Yamamoto, Y. Kobayashi, N. Hayashi, C. Tassel, T. Saito, S. Yamanaka, M. Takano, K. Ohoyama, Y. Shimakawa, K. Yoshimura and H. Kageyama, *J. Am. Chem. Soc.*, 2012, **134**, 11444–11454.
7. C. Tassel, J. M. Pruneda, N. Hayashi, T. Watanabe, A. Kitada, Y. Tsujimoto, H. Kageyama, K. Yoshimura, M. Takano, M. Nishi, K. Ohoyama, M. Mizumaki, N. Kawamura, J. Iniguez and E. Canadell, *J. Am. Chem. Soc.*, 2009, **131**, 221–229.
8. Y. Tsujimoto, C. Tassel, N. Hayashi, T. Watanabe, H. Kageyama, K. Yoshimura, M. Takano, M. Ceretti, C. Ritter and W. Paulus, *Nature*, 2007, **450**, 1062–1065.
9. O. Mentre, M. Iorgulescu, M. Huve, H. Kabbour, N. Renaut, S. Daviero-Minaud, S. Colis and P. Roussel, *Dalton Trans.*, 2015, **44**, 10728–10737.
10. U. Spitsbergen, *Acta Crystal.*, 1960, **13**, 197–198.
11. A. I. Waidha, M. Lepple, K. Wissel, A. Benes, S. Wollstadt, P. R. Slater, A. D. Fortes and O. Clemens, *Dalton Trans.*, 2018, **47**, 11136–11145.
12. J. Deakin, I. Trussov, A. Gibbs, E. Kendrick and P. R. Slater, *Dalton Trans.*, 2018, **47**, 12901–12906.
13. P. L. Knochel, P. J. Keenan, C. Loho, C. Reitz, R. Witte, K. S. Knight, A. J. Wright, H. Hahn, P. R. Slater and O. Clemens, *J. Mater. Chem. A*, 2016, **4**, 3415–3430.
14. C. F. Smura, D. R. Parker, M. Zbiri, M. R. Johnson, Z. A. Gal and S. J. Clarke, *J. Am. Chem. Soc.*, 2011, **133**, 2691–2705.
15. K. Tomiyasu, T. Inami and N. Ikeda, *Phys. Rev. B*, 2004, **70**.

A pinch of oxygen: Incorporation of small additional oxygen introduces partly square planar coordination into $\text{BaCoO}_{2+\delta}$. [View Article Online](#)
DOI: 10.1039/C8CC09532A