BaCoO₂₊₆: A new highly oxygen deficient perovskite-related phase with unusual Co coordination obtained by high temperature reaction with short reaction times

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1. Experiment

1.1. Material synthesis

Conventional high temperature solid state synthesis was used for the synthesis. Precursor powders of BaCO₃ (99.99%) and Co₃O₄ (99.99%) were ball milled (with acetone) using vials and balls made of ZrO_2 at the rotation speed of 600 rpm followed by heating in the tube furnace up to 1000 °C for 1 hour with a heating and cooling rate of 2 °C per minute. The synthesis was carried in a Carbolite STF16180301 tube furnace equipped with an alumina tube (inner diameter of 50 mm) under an argon atmosphere (purity 99.996 %) with constant flow of 0.300 SLM (standard liter per minute). After this cycle, the steps were repeated once again to obtain the desired phase.

1.2. Diffraction experiments

X- ray diffraction (XRD) patterns of the compound were recorded on a Bruker D8 diffractometer using Bragg-Brentano geometry with a fine focusing X-ray tube with Cu K_{α 1}, radiation. A VANTEC detector (3° opening) and a variable divergence slit (4 mm) were used. The total scan time was set to 10 hours for the angular range between 5° and 130° 20 at a step size of 0.0075. This 10 hour room temperature XRD pattern must be recorded using an air tight sample holder to avoid water and CO₂ uptake. This holder causes increased background and reduced signal to noise ratio at the low angle range, which make the superstructure reflection at 10.75 ° 20 difficult to observe. However, this reflection, which is significant for the 2 x 2 x 1 superstructure, can be clearly observed for measurements taken without airtight conditions in shorter measurement times (see refinement provided in Fig. S5).

Time-of-flight (TOF) neutron powder diffraction (NPD) data were recorded on the high resolution diffractometer (HRPD) at the ISIS pulsed spallation source (Rutherford Appleton Laboratory, Didcot, U.K.). 2 g of powdered $BaCoO_{2+\delta}$ was loaded into 6-mm-diameter thin-walled cylindrical vanadium sample can under an inert atmosphere and sealed with indium wire. Data were collected at ambient temperature for 2 hr 40 m (120 μ Ah of integrated proton beam current) using the instrument's 30-130 ms time-of-flight window. The sample was then mounted in a Closed Cycle Refrigerator (CCR) and cooled to 10 K where data were collected for 2 hr (80 μ Ah) in the 30-130 ms TOF window. Raw

data were normalized to the incident spectrum and corrected for instrument efficiency using a V:Nb null-scattering standard with the Mantid suite of diffraction algorithms (<u>http://www.mantidproject.org/</u>).

The analysis of the nuclear structure of BaCoO_{2+δ} using both the NPD and XRD data was performed using the Rietveld method with the program TOPAS 5 (Bruker AXS, Karlsruhe, Germany) ¹. For the room temperature XRD data, the whole 2θ-range range was used, while for NPD, data collected from the highest resolution backscattering detector bank (bank 1, 158° > 2θ > 176°) as well as the high intensity bank (bank 2, 80° > 2θ > 100°) and the forward-scattering bank 3 (28° > 2θ > 32°) were used. For better depiction, the fit and measurement curves of the XRD pattern shown in Figure 1d in the manuscript were corrected by the refined background curve, which contains the high scattering contribution resulting from the air tight sample holder (see Fig. S5).

The instrumental intensity distribution for the X-ray data was determined empirically from a sort of fundamental parameters set ², using a reference scan of LaB₆ (NIST 660a), and the microstructural parameters were refined to adjust the peak shapes for the XRD data. Calibration of the instrumental contribution to the neutron powder diffraction pattern's peak positions and shapes was done using silicon and ceria standards. The lattice parameters were constrained to be the same for neutron and XRD data, and the same positional parameters were used and refined for both data sets. Independent thermal displacement parameters were refined for each type of atom for neutron data.

The overall oxygen content of the sample was constrained to a composition of BaCoO₂ to avoid correlation with thermal parameters being used. As it has been found previously by Kageyama et al.³, split sites for the iron or barium ions were found for the disordered structurally similar Ba_{0.8}Sr_{0.2}FeO₂. Therefore, we also examined the possibility of split sites for the ions individually, and only included them into the final refinement model, if substantial deviation from the ideal position was indicated.

The misfits in Bank 1 are due to the use of the cryostat to carry out the measurement at 10 K, which causes the appearance of additional sharper reflections. These reflections at 1.24 Å (overlapping with the reflections from BaCoO_{2+ δ}), 1.43 Å, 1.50 Å, 2.03 Å and 2.6 Å were not observed in the diffraction pattern recorded at room temperature, for which the

cryostat has not been used. Further, we ruled out the possibility of these reflections belonging to the title compound by testing various superstructure models within Pawley type refinements. This is also in agreement with the fact that the FWHM is significantly smaller than observed for the reflections belonging to $BaCoO_{2+\delta}$.

1.3. Simultaneous thermal analysis

Simultaneous thermal analysis combining thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted for $BaCoO_{2+\delta}$ on a Netzsch STA 449 F3 Jupiter thermal analyzer. The measurements were performed in the temperature range between 300 K to 973 K using a heating rate of 10 K min⁻¹. Thermal analysis was performed in corundum crucibles under an oxygen flow of 50 ml min⁻¹.

1.4. Impedance spectroscopy analysis

Alternating current electrochemical impedance spectroscopy measurements were carried out to record the conductivity of the BaCoO_{2+δ} pellet. The pellets were made by isotatically pressing the powders of BaCoO_{2+δ} at 700 kN. The pellet was placed inside the JANIS STVP-200-XG cryostat, which was operated under static helium atmosphere of 1 bar pressure. The pellet was investigated in the temperature range of 298 K to 338 K. Impedance measurements were recorded using a Solartron 1260 frequency response analyzer while applying an AC signal of 100 mV amplitude with frequency ranging from 1 MHz to 100 mHz. Fitting of the data was performed using the Z-view program 4 .

1.5. SQUID Magnetic Measurements

Magnetic characterization was performed with a Quantum Design MPMS. Powder samples were encapsulated in gelatin capsules and mounted in a straw. Zero-field cooled (ZFC) and field-cooled (FC) curves were measured from 5 to 300 K in the applied field $\mu_0H = 2$ T. All magnetization measurements were corrected by the diamagnetic contributions of the phases and of the gelatin capsule and straw used for sample mounting. Field-dependent measurements were performed at 5 K. The magnetic field was scanned from 2 to -2 T.

1.6. Energy Dispersive X-ray Spectroscopy

The energy dispersive spectroscopy (EDAX) analysis was carried out using Phillips XL30 FEG set up operating at 15 keV. An EDAX Genesis system was used and an energy resolution of about 140 eV was applied. The mapped area was of the order of 100 μ m² and the Ba to Co to Fe ratio was determined from the Ba L, Fe K and Co K lines. The samples were sputtered with approximately 10 nm of Au prior to the measurements.

1.7. Iodometric titration

The iodometric titrations were carried out to determine the oxidation state of the Co ions in BaCoO_{2+ δ}. 0.05 g of the compound was dissolved in 1M HCl solution and 1 g of Kl was added to the solution. Due to the presence of Co²⁺ ions no formation of I₂ could be observed. A few drops of starch solution were added as an indicator. The solution was titrated with sodium thiosulphate (Na₂S₂O₃).

1.8. Raman Spectroscopy

Raman spectra were recorded with a confocal micro-Raman spectrometer (Horiba HR 800, Horiba, Japan), using an Ar-ion laser with a wavelength of 514.5 nm. Spectra were recorded in a Raman shift range from 0 to 4000 cm⁻¹.

1.9. DFT Studies

The DFT calculations were carried out using the projector augmented wave method as implemented in the VASP code.⁵ The exchange-correlation potential is approximated in the generalized gradient approximation (GGA), as parameterized ⁶. The energy cutoff was taken to be 500 eV. For the Brillouin zone integration, the number of k-points Nk along each crystalline axis was determined by Nk×Latt~50, where Latt denotes the lattice constant in Angstrom. The structural optimizations were done with the lattice constants and atomic positions (tolerance for forces being 0.01 eV/Å) fully relaxed. To account for the local Coulomb correlations on the Co sites, GGA+U approximation in the rotational-invariant form⁷ was applied with the effective U-J = 4.2 eV. All the calculations have been performed assuming ferromagnetic (FM) configurations, where the antiferromagnetic (AFM) states will lower the energies further but cannot affect the energy difference between the structure models considered. For instance, for model#2, the G-AFM state is

about 0.063 eV per formula unit lower in energy than the FM state, confirming also the magnetic ground state (see the main text).

2. Results



Figure S1: EDAX spectra recorded for BaCoO₂₊₆ powders using 10 keV electron beam.



Figure S2: Raman spectra recorded for the BaCoO_{2+ δ} and BaCO₃ powders to show the absence of carbonate band around 1200 cm⁻¹ for BaCoO_{2+ δ}.

			u			0: 1d 4/mmm	2 2 2		O: 2e mmm.	2 % 0
			0: 1b 4/mmr	0 1/2		1b mm			0: 1d 4/mmm	72 72 72
						0: 4/m	0 0 1		0: 1b 4/mmm	0 72 72
0: 3 <i>d</i> 4/mm.m	0 0 %		2f m.			4j 2m	.75		0: 4n m2m.	x) <u>/</u> 2 x ~ 0.25
			O: mm	0		O: m.2	x x 0 ~ x		0: 4/ m2m.	x 0 0 x ~ 0.25
1a Sm			1a mm			Co: 1c 4/mmm	% % 0		Co: 2f mmm.	0 % 0
та Та	000		Co: 4/m	0 0 0		1a mm			Co: 1c 4/mmm	½ ½ 0
						Co: 4/m	5 5 5		Co: 1a 4/mmm	0
Ba: 1b m-3m	22 22 23		Ba: 1d 4/mmm	27 X X		Ba: 2e mmm.	0 7,2 2,4		Ba: 4 <i>k</i> m.2m	x x ½ x ~0.75
Cubic	Pm-3m (221) $a_1 = 4.00 \text{ Å}$ $a_2 = a_1$	$\begin{array}{c} 13 b_2 = b_1 \\ c_2 = c_1 \\ c_1 \\ c_2 = c_1 \end{array}$	P4/mmm (123)	$a_2 = 4.00 \text{ A}$ $b_2 = 4.00 \text{ A}$ $c_2 = 4.00 \text{ A}$	$\begin{array}{c} a_{3} = a_{2} - b_{2} \\ b_{3} = a_{2} + b_{2} \\ c_{3} = c_{2} \end{array}$	Tetragonal P4/mmm (123)	$a_3 = 5.66 \text{Å}$ $b_3 = 5.66 \text{Å}$ $c_3 = 4.00 \text{Å}$ $a_4 = a_3 - b_3$	$p_{4} = a_{3} + b_{3}$ $c_{4} = c_{3}$	Tetragonal P4/mmm (123)	$a_4 = 8.00 \text{ Å}$ $b_4 = 8.00 \text{ Å}$ $c_4 = 4.00 \text{ Å}$

Figure S3: Symmetry relationship for model 1, showing the similarity between the cubic aristotype perovskite structure and the tetragonal structure of perovskite-related $BaCoO_{2+\delta}$.

		0: 1c 4/mmm	% % 0		O: 2f mmm.	0 % 0		0: 4 <i>j</i> m.2m	x x 0 x ~ 0.25
0: 3c 4/mm.m	0 %	2e m.			4k :m	.75		0: 4o m2m.	x ½ X ~ 0.25
		 O	0 0 7		0: . <i>m</i> .2	x x x x x x x x x x x x x x x x x x x		0: 4m m2m.	x 0 ½ x ~ 0.25
Co: 1b m-3m	72 75 75	Co: 1d 41mmm	72 72 72		Co: 2e mmm.	0 1/2 1/2		Co: 4k m.2m	x x × 0.75
1a m		1a mr			Ba: 1c 4/mmm	2 ⁷ 22 0		Ba: 2f mmm.	0 72 0
Ba: <i>m</i> -3	000	Ba:	000		Ba: 1a 4/mmm	000		Ba: 1a Ba: 1c 4/mmm 4/mmm	0 % 0 % 0 0
Cubic	$Pm-3m (221) = 4.00 \text{Å}$ $a_1 = 4.00 \text{Å}$ $a_2 = a_1$ $a_2 = b_1$	$\mathbf{F}_{c_2}^{c_2} = c_1$ Tetragonal P4/mmm (123)	$a_2 = 4.00 \text{ A}$ $b_2 = 4.00 \text{ Å}$ $c_2 = 4.00 \text{ Å}$	$\begin{array}{c} a_3 = a_2 - b_2 \\ b_3 = a_2 + b_2 \\ c_3 = c_2 \\ c_3 = c_2 \\ \end{array}$	Tetragonal P4/mmm (123)	$a_3 = 5.66 \text{Å}$ $b_3 = 5.66 \text{Å}$ $c_3 = 4.00 \text{Å}$ $a_4 = a_3 - b_3$	$\begin{array}{c c} p_4 = a_3 + b_3 \\ c_4 = c_3 \\ \bullet \end{array}$	Tetragonal P4/mmm (123)	$a_4 = 8.00 \text{ Å}$ $b_4 = 8.00 \text{ Å}$ $c_4 = 4.00 \text{ Å}$

Figure S4: Symmetry relationship for model 1, showing the similarity between the cubic aristotype perovskite structure and the tetragonal structure of perovskite-related $BaCoO_{2+\delta}$.



Figure S5: Comparison of the X- ray diffraction patterns recorded for $BaCoO_{2+\delta}$ using within an air tight sample holder (red) and within a normal sample holder (black). Inset shows the zoomed view of the reflection at 10.74 ° which is best observed in the scan measured in the normal sample holder (see also experimental details provided in section 1. within this Supplementary Material) and more difficult to be seen in the sample measured in air tight conditions due to the higher signal to noise at lower 20 angles resulting from the plastic cover.





Figure S7: Rietveld refinement of X-ray diffraction pattern recorded after carrying out STA measurement.

Atom	Wyck	X	У	Z	Осс
Ва	4 <i>k</i>	0.75	=x	1/2	1
Co1	1 <i>a</i>	0	0	0	1
Co2	1c	1/2	1/2	0	1
Co3	2f	0	1/2	0	1
01	1 <i>b</i>	0	0	1/2	1
O2	1 <i>d</i>	1/2	1/2	1/2	1
O3	2e	0	1/2	1/2	1
04	4/	0.25	0	0	1
O5	4 <i>n</i>	0.25	1/2	0	1

Table S 1: Ideal positional parameters for a pseudocubic perovskite within model 1 (Co site splits), with space group P4/mmm with a ≈ 8 Å, $c \approx 4$ Å.

Atom	Wyck	X	У	Z	Осс	Beq
Ва	4 <i>k</i>	0.7593(3)	0.7593(3)	1/2	1	0.18(8)
Co1	1 <i>a</i>	0	0	0	1	
Co2	1c	1/2	1/2	0	1	0.06 (1)
Co3	4/	0	0.487(4)	0	0.5	-
01	1 <i>b</i>	0	0	1/2	0.4750(11)	
O2	1 <i>d</i>	1/2	1/2	1/2	0.2473(2)	-
O3	2e	0	1/2	1/2	0.2843(13)	1.15(5)
04	4/	0.2804(6)	0	0	1	-
O5	4 <i>n</i>	0.2675(12)	1/2	0	0.5585(12)	-
a(Å) (NPD)= 8.2064(4)		c(Å) (NPD)= 3.9113(3)		R _{wp} = 2.815		
GOF (NPD + XRD)		1.302	R _{Bragg} (%) = 1.571 (NPD Bank 1),1.387 (XRD)			

Table S2: Refined structural parameters for $BaCoO_{2+5}$ presented along with the unit cell parameters, GOF, R_{wp} values for coupled Rietveld refinement of NPD data recorded at 10 K and room temperature XRD. Standard deviations given are numerical standard deviations from the refinements and do not represent interval of trust.

Cation	Distance to anions (Å)	Cation	Distance to anions (Å)
Ba1	2.793(3) (O1 x 1)		1.908 (10) (O5 x 4)
	2.7985(15)(O4 x 4)		1.9555(1) (O2 x 2)
	2.899(2)(O5 x 4)	Co2	
	2.9034(1) (O3 x 2)		
	3.010 (3) (O2 x 1)		
Co1	1.9553(1) (O1 x 2)		1.91(3) (O4 x 1)
	2.301 (5) (O4 x 4)	603	1.9584 (16) (O3 x 2)
			2.198 (10) (O5 x 2)

Table S3: Refined bond distances between cations and anions for $BaCoO_{2+\delta}$ at 10K.

Atom	Wyck	X	У	Z	Осс
Ba1	1 <i>a</i>	0	0	0	1
Ba2	2f	1/2	0	0	1
Ba3	1c	1/2	1/2	0	1
Co1	4 <i>k</i>	0.75	=x	1/2	1
01	4 <i>j</i>	0.25	=x	0	1
O2	40	0.25	1/2	1/2	1
O3	4 <i>m</i>	0.25	0	1/2	1

Table S4: Ideal positional parameters for a pseudocubic perovskite within model 2 (Ba site splits), with space group P4/mmm with a ≈ 8 Å, $c \approx 4$ Å.

Atom	Wyck	X	У	Z	Осс	Beq
Ba1	1 <i>a</i>	0	0	0	1	
Ba2	2f	1/2	0	0	1	0.81(6)
Ba3	1c	1/2	1/2	0	1	
Co1a	4 <i>k</i>	0.320(10)	0.320(10)	1/2	0.136(4)	0 72(4)
Co1b	4 <i>k</i>	0.257(12)	0.257(12)	1/2	0.841(4)	0.72(4)
01	4 <i>j</i>	0.2557(8)	0.2557(8)	0	0.440(9)	
O2	40	0.2158(8)	1/2	1/2	0.885(11)	1.34(5)
O3	4 <i>m</i>	0.2302(12)	0	1/2	0.673(15)	
a(Å)(NPD) = 8.2058(4)			c(Å)(NPD)=	= 3.9101(2)	R _{wp} =	3.07
GOF (NPD + XRD) = 1.455			RBragg (%)	= 1.397 (NP	D Bank 1) ,1.	209 (XRD)

Table S5: Structural parameters for tetrahedral coordination of Co ion refined $BaCoO_{2+\delta}$ presented along with the unit cell parameters, GOF, R_{wp} values for coupled Rietveld refinement of NPD data recorded at 10 K and room temperature XRD. Standard deviations given are numerical standard deviations from the refinements and do not represent interval of trust.

model #1	-23.57 eV	
model #2	-23.80 eV	
model #3	-24.13 eV	

Table S6: Energies for different models as obtained via DFT+U modifications, given per BaCoO_{2+ δ} formula unit. Energies are given for FM configurations.

3. References

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