Single Crystal Growth and Magnetic Properties of High Oxidation State Material Ba_2CoO_4

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This study reports on the physical properties of Ba_2CoO_4 single crystals grown in a high pressure mirror furnace at oxygen pressures of 20 bar. Direction dependent magnetic susceptibility measurements on the single crystals below $T_N \approx 25$ K reveal a spin direction which is parallel to the crystallographic *a*-axis. Therefore, the spin structure of Ba_2CoO_4 has been re-analyzed and a different magnetic structure with magnetic moments pointing mainly in *a*-direction is proposed which reconciles neutron, μ SR, and magnetic susceptibility measurements.

Cobalt oxide materials are known to be interesting because of a variety of fascinating properties such as superconductivity, magneto-resistance, thermoelectric power, the recent discovery of hour-glass magnetic excitation spectra as well as catalytic properties for clean energy conversion reaction including oxygen evolution (OER), hydrogen evolution reaction (HER), and applications in fuel cells and batteries.[1–15] The key aspect of Co ions that differs from other 3*d* transition metal (TM) ions is the spin state degree of freedom of the Co ions which can be in the low spin (LS), intermediate spin state (IS), or high spin (HS) state. The interplay of spin state, charge, and orbital degrees of freedom is responsible for its interesting properties. It was found more recently that the strong covalency of Co-oxygen bonds might be also relevant for lattice oxygen redox reactions. The Co-oxygen covalency is expected to increase with increasing Co valence from Co^{2+} to Co^{3+} and further to Co^{4+}. The spin state of Co^{3+} ions and its impact on electronic and magnetic properties in various materials are known for more than 60 years.[16,17] However, the Co^{4+} compounds are much less studied. One example is $SrCoO_3$ and also Sr_2CoO_4 where the tetravalent Co ions are in the IS state.[18–22] On the other hand Co^{4+}-ions in the LS state were found in $BaCoO_3$.[23–27] Finally, a Co^{4+} HS has been reported for Ba_2CoO_4 with tetrahedrally coordinated Co^{4+} ions.[28,29] However, so far the study of its electronic and magnetic properties was limited to studies on polycrystalline samples and very small single crystals.[28–30]

We have grown single crystals of Ba_2CoO_4 by the floating zone technique using a high pressure mirror furnace. These crystals were used to perform direction dependent magnetic susceptibility measurements which point to a different magnetic structure than indicated by an earlier neutron study. Here, we propose a new magnetic structure for Ba_2CoO_4 which is in aggreement with neutron, μ SR, and magnetic susceptibility data.

Experimental Details: Single crystals of Ba_2CoO_4 were grown by the traveling solvent floating zone method in a HKZ high pressure mirror furnace from *Scidre*. Feed and seed rods were prepared by high temperature solid state reaction. Therefore, appropriate amounts of $BaCO_3$ (99.997%, Alfa Aesar) and Co_3O_4 (99.997%, Alfa-Aesar), with Ba:Co molar ratio of 2:1, were ground together and sintered (two times for ≈1/2 and ≈1 day, respectively) at 1050 °C in air with intermediate grindings. Finally, a rod was pressed out of the powders and sintered for ≈12 h at 1060 °C in air. Then, Ba_2CoO_4 single crystals were grown in a high pressure mirror furnace at somewhat elevated oxygen pressures of ≈20 bar. Suitable growth conditions could be reached only with a slow growth rate of ≈3 mm/h (with feed and seed rods being inversely rotated). The crystal structure was determined by means of powder and single crystal X-ray diffraction (XRD) using a Bruker powder X-ray diffractometer with Cu-K_α radiation and a Bruker D8 Venture single crystal diffractometer using Mo-K_α radiation. The analysis of the XRD data has been performed with the Jana2006 and Fullprof program packages.[31–33] The magnetic properties of our samples were studied using a SQUID magnetometer (MPMS3 SQUID VSM, Quantum Design Inc.). Because Ba_2CoO_4 is hygroscopic we prepared the samples for the measurements of the magnetic susceptibility mainly in an argon-filled glovebox with the level of O_2 and H_2O being around 1 ppm. Finally, the exposure time in air was reduced to less than 10 min before mounting samples into the SQUID-VSM or PPMS devices. Using an incident neutron wavelength of 2.41 Å neutron scattering experiments have been performed at the D20 diffractometer at the ILL in Grenoble, France.

Results and Discussion: Parts of our Ba_2CoO_4 single crystal were crushed to powder and analyzed by means of powder X-ray diffraction, see **Figure 1**. These measurements indicate that our

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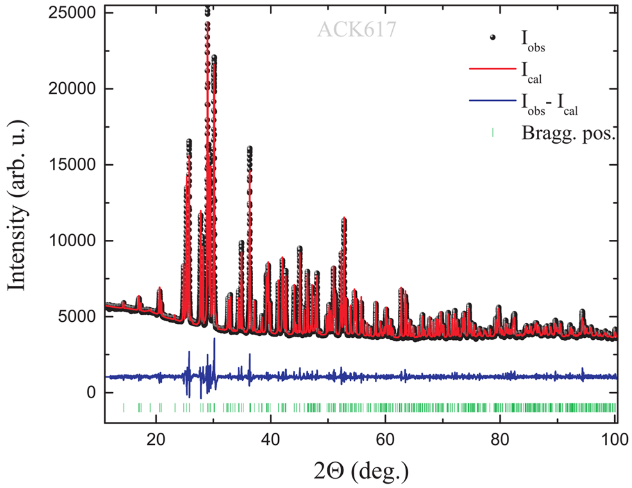

Figure 1. Room temperature powder XRD (PXRD) pattern of our Ba_2CoO_4 crystals grown at $p_{O_2} = 20$ bar (black dots). Red and blue solid lines are fits obtained by Le Bail fits and the difference between observed and calculated intensities, respectively. Vertical bars at the bottom show the calculated positions of Bragg peaks.

single crystals are free from impurities. The lattice parameters obtained from the refinement with space group $P2_1/n$ are listed in **Table 1**. Subsequent single crystal X-ray diffraction experiments have been performed and the observed X-ray scattering intensities within the $(0KL)$, $(H0L)$, and $(HK0)$ planes of reciprocal space are shown in **Figure 2**a–c. The structural information obtained within a crystal structure refinement is listed in Table 1. Our results are consistent with literature values.[28,29] In Ba_2CoO_4 the Co-ions are tetrahedrally surrounded by the oxygen ions and the CoO_4 tetrahedra are separated by the Ba ions, that is, the Ba ions are octahedrally coordinated by the CoO_4 tetrahedra. The typical Co—O bond lengths within the CoO_4 tetrahedra are of the order of 1.8 Å, which is shorter than the ones in $BaCoO_3$ with the same valence state of Co^{4+}, but with an octahedral coordination – the latter ones amount to ≈1.9 Å.[20,21]

The magnetic susceptibility $\chi(T)$ and magnetization $M(H)$ of Ba_2CoO_4 are shown in **Figure 3** for H parallel to the a, b, and c axis (black, red, and blue symbols). $\chi(T)$ exhibits a broad peak around 25 K which is associated with the emergence of antiferromagnetic correlations,[28] see Figure 3a. Below 25 K the magnetic susceptibility is almost constant for $H\|c$ and for $H\|b$ whereas a strong decrease toward zero can be observed with decreasing temperature for $H\|a$. This observation indicates an anti-ferromagnetic structure with moments pointing in a-direction. However, a different magnetic structure was derived from neutron scattering experiments,[29] which reported magnetic moments of 3.08 μ_B per Co ion in c-direction and 0.91 μ_B in b-direction within a noncollinear antiferromagnetic structure with propagation vector $\mathbf{k} = (1/2\ 0\ 1/2)$.[29] Also μSR experiments provide conflictive results and indicate magnetic moments within the ab-plane.[34]

Table 1. Room-temperature structure of Ba_2CoO_4 (grown at 20 bar oxygen pressure) obtained by means of single crystal XRD on a twined single crystal.

Formula	Ba_2CoO_4		
Space group	$P2_1/n$ (No.14)		
a (Å)	5.91916(13)		
b (Å)	7.62832(18)		
c (Å)	10.42286(27)		
β (°)	91.270(1)		
Atomic coordinates			
Atom	x	y	z
Ba1	0.75481(7)	0.85082(4)	0.08216(3)
Ba2	0.24244(7)	0.49187(3)	0.19006(3)
Co1	0.74767(13)	0.27562(8)	0.07983(6)
O1	0.7621(8)	0.5079(5)	0.0821(4)
O2	0.5105(7)	0.1992(6)	0.1646(5)
O3	1.0009(7)	0.1790(6)	0.1445(4)
O4	0.7184(7)	0.1860(5)	0.9197(4)
Atom	U_{11}	U_{22}	U_{33}
Ba1	0.01735(15)	0.00570(12)	0.01545(15)
Ba2	0.01660(14)	0.00447(11)	0.00702(12)
Co1	0.0109(3)	0.0034(2)	0.0068(3)
O1	0.035(2)	0.0065(15)	0.019(2)
O2	0.020(2)	0.019(2)	0.034(2)
O3	0.0137(18)	0.0157(19)	0.025(2)
O4	0.027(2)	0.0111(16)	0.0104(17)
Atom	U_{12}	U_{13}	U_{23}
Ba1	–0.00028(12)	0.00009(13)	–0.00150(10)
Ba2	–0.00019(11)	–0.00033(11)	0.00018(10)
Co1	0.0000(2)	0.0002(3)	–0.0001(2)
O1	0.0020(18)	–0.001(2)	0.0000(15)
O2	0.0019(17)	0.0128(18)	0.0137(19)
O3	–0.0009(16)	–0.0037(16)	0.0076(17)
O4	0.0005(16)	–0.0036(16)	–0.0012(14)
Co–O distances			
Atoms	Distance (Å)		
Co1–O1	1.774(4)		
Co1–O2	1.774(5)		
Co1–O3	1.789(4)		
Co1–O4	1.808(4)		

12457 reflections have been collected up to $2\Theta_{max} = 79°$ with an internal R-value of 4.38% and a redundancy of 4.72. The R-values and goodness of fit amount to $R = 3.94\%$, $R_w = 6.65\%$ and GOF = 1.48. The refined volume fractions of the two monoclinic twin domains amount to 91.4(4)% and 8.6(4)%, respectively. The corresponding lattice parameters were determined from powder X-ray diffraction measurements on pulverized single crystals ($\chi^2 = 2.91$).

In order to reconcile the neutron measurements with our direction dependent susceptibility and μSR measurements we re-analyzed the magnetic structure of Ba_2CoO_4 and performed powder neutron diffraction measurements at the D20 diffractometer ($\lambda = 2.41$ Å). We propose a different magnetic structure for Ba_2CoO_4 which is, finally, in agreement with neutron scattering experiments, $\chi(T)$ results as well as with μSR measurements.[34] We also indexed all magnetic reflections with

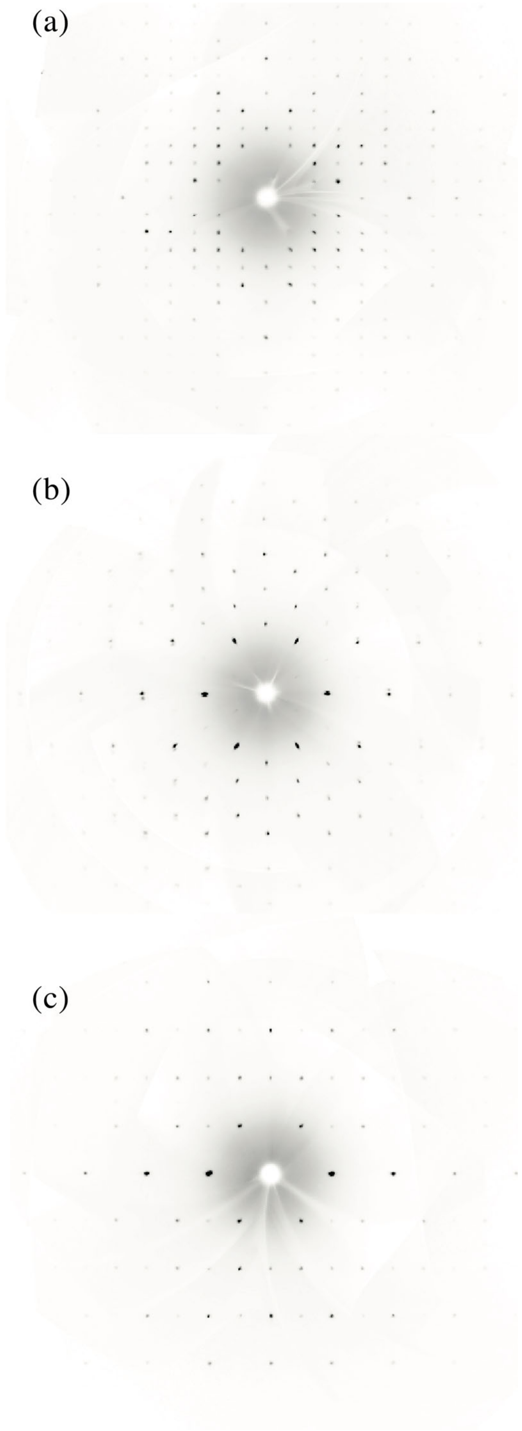

Figure 2. Intensities within the (a) (0*KL*), (b) (*H*0*L*), and (c) (*HK*0) planes of reciprocal space measured in single crystal X-ray diffraction measurements of our Ba_2CoO_4 single crystal grown at 20 bar oxygen pressure.

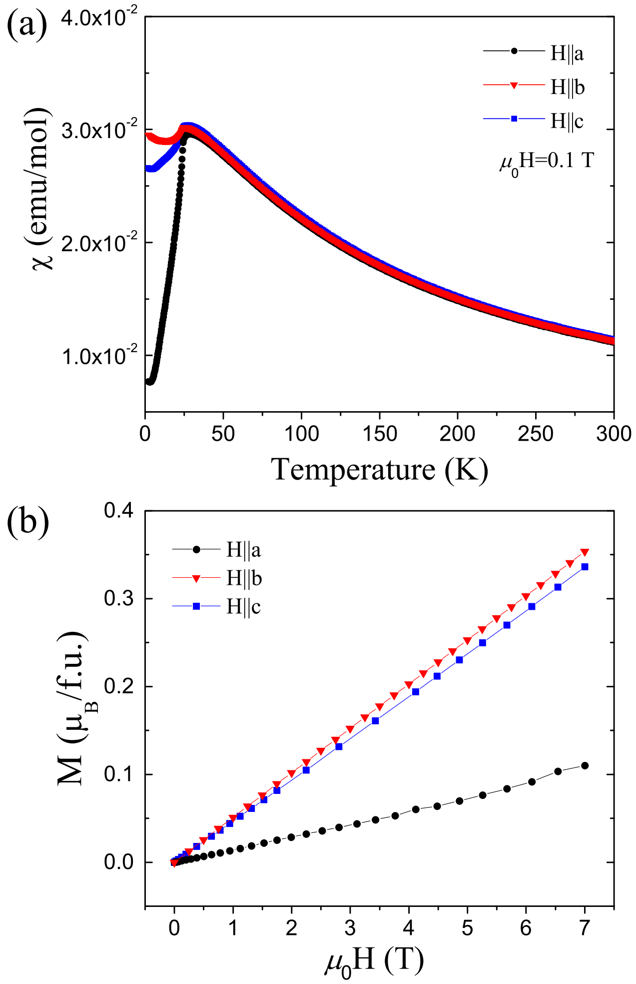

Figure 3. (a) Temperature dependence of the (ZFC) magnetic susceptibility of Ba_2CoO_4 measured for all crystallographic directions *H*||*a*, *H*||*b*, and *H*||*c*. (b) Magnetization of Ba_2CoO_4 at 2K.

a propagation vector $\mathbf{k} = (1/2\ 0\ 1/2)$. The magnetic symmetry analysis for space group $P2_1/n$ and the Co^{4+} ions at the 4*e* site yields irreducible representations with the basis vectors that are summarized in **Table 2**. The magnetic structure can be described by IR Γ_4 with magnetic moments pointing mainly in *a*-direction, thus, being consistent with our direction-dependent magnetic susceptibility measurements. The refinement of the magnetic structure (magnetic *R*-factor ≈21.0%) yields a moment size of ≈3.5(1) μ_B/Co which is only tilted by roughly 21(1)° (24(2)°) away from the *a*- toward the *b*- (*c*-) direction. The components of the ordered magnetic moment along the *a*-, *b*-, and *c*-direction amount to 2.97(5) μ_B/Co, −1.13(5) μ_B/Co, and −1.30(9) μ_B/Co, respectively. The magnetic structure is shown in the inset of **Figure 4**.

In Ref. [29] a refinement with same magnetic symmetry but with the *a*-component of the magnetic moment being fixed to zero has been performed. Such a refinement leads to somewhat larger magnetic *R*-values (22.8% compared to 21.0%) and is also conflictive with our orientation dependant magnetic susceptibility measurements.

Conclusion: We have grown sizeable single crystals of Ba_2CoO_4 in a high pressure floating zone furnace. Our direction dependent magnetic susceptibility measurements on our single crystals reveal a spin direction which is basically parallel to the crystallographic *a*-axis within the anti-ferromagnetic state. Hence, we re-analyzed the magnetic structure of Ba_2CoO_4 by

Table 2. Nonzero IRs together with basis vectors ψ_v for Co atoms in Ba_2CoO_4 with space group $P2_1/n$ and $\mathbf{k} = (1/2\ 0\ 1/2)$ obtained from representational analysis.

IRs	ψ_v	Co1	Co2	Co3	Co4
Γ_1	ψ_1	(1 0 0)	(−1 0 0)	(1 0 0)	(−1 0 0)
	ψ_2	(0 1 0)	(0 1 0)	(0 1 0)	(0 1 0)
	ψ_3	(0 0 1)	(0 0 −1)	(0 0 1)	(0 0 −1)
Γ_2	ψ_1	(1 0 0)	(−1 0 0)	(−1 0 0)	(1 0 0)
	ψ_2	(0 1 0)	(0 1 0)	(0 −1 0)	(0 −1 0)
	ψ_3	(0 0 1)	(0 0 −1)	(0 0 −1)	(0 0 1)
Γ_3	ψ_1	(1 0 0)	(1 0 0)	(1 0 0)	(1 0 0)
	ψ_2	(0 1 0)	(0 −1 0)	(0 1 0)	(0 −1 0)
	ψ_3	(0 0 1)	(0 0 1)	(0 0 1)	(0 0 1)
Γ_4	ψ_1	(1 0 0)	(1 0 0)	(−1 0 0)	(−1 0 0)
	ψ_2	(0 1 0)	(0 −1 0)	(0 −1 0)	(0 1 0)
	ψ_3	(0 0 1)	(0 0 1)	(0 0 −1)	(0 0 −1)

The atoms are defined as Co1: (0.7477 0.2756 0.0798); Co2: (−0.2477 0.7756 0.4202); Co3: (−0.7477 −0.2756 −0.0798); Co4: (1.2477 0.2244 0.5798).

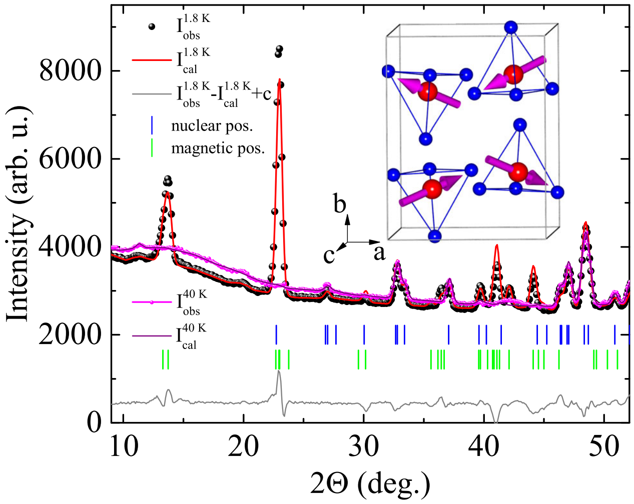

Figure 4. Fit of the (magnetic) neutron scattering intensities at 1.8 K with our new proposed spin structure of Ba_2CoO_4. Red/blue spheres denote Co/O ions. The blue polyhedra indicate the CoO_4 tetrahedra. The magenta arrows indicate the spin directions within this magnetic structure. The corresponding components along the *a*-, *b*-, and *c*-direction amount to 2.97(5) μ_B/Co, −1.13(5) μ_B/Co, and −1.30(9) μ_B/Co, respectively. The comparison with the 40 K data reveals the magnetic peaks that appear below T_N.

means of powder neutron diffraction and propose a magnetic structure with magnetic moments mainly pointing in *a*-direction that reconciles neutron, μSR, and susceptibility measurements.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cobaltate, high oxidation state material, magnetism, spin structure

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